

Development of improved Cu-based electrocatalysts for the electroreduction of CO₂

Cátia Sofia Ribeiro Azenha

Dissertation presented for obtaining the degree of
Doctor in Chemical and Biological Engineering
by the
University of Porto

Supervisor: Adélio Miguel Magalhães Mendes, Full Professor



**Department of Chemical Engineering,
Faculty of Engineering, University of Porto**

2022

This thesis was financially supported by Foundation for Science and Technology (FCT) through the PhD grant SFRH/BD/128768/2017, and by projects: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); (ii) “SunStorage - Harvesting and storage of solar energy”, with reference POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through Operational Programme for Competitiveness and Internationalization (COMPETE 2020 - Programme for Competitiveness and Internationalization (OPCI), and by national funds, through FCT; and, (iii) “PorphSol - Taylor made porphyrinoids for emerging efficient solar energy devices”, with reference POCI-01-0145-FEDER-030357, funded by FEDER funds through COMPETE2020 - Programme for Competitiveness and Internationalization (OPCI) and by national funds (PIDDAC) through FCT/MCTES.



Cátia Sofia Ribeiro Azenha

LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Acknowledgments

I am grateful to the Portuguese Foundation for Science and Technology (FCT) for my PhD grant (SFRH/BD/128768/2017) and for the projects POCI-01-0145-FEDER-016387 (SunStorage) and POCI-01-0145-FEDER-030357 (PorphSol). I would also like to acknowledge LEPABE/ALiCE, DEQ and FEUP for providing me all the conditions to develop my work.

I would like to express my sincere gratitude to my supervisor, Professor Adélio Mendes, for his wisdom, guidance, and continuous support throughout my PhD. For always finding time for me in his busy schedule, for all the transmitted knowledge and optimism, without which this thesis would not be possible. Thank you for giving me the opportunity to work in such an interesting field and in this research group, full of fantastic people.

A special thanks to Doctor Cecilia Mateos-Pedrero, my co-supervisor during the first half of this thesis, for teaching me so much about catalysis, for her guidance and critical insights that were fundamental in the development of my work. But, most of all, for always encouraged me to pursue my dream.

I gratefully acknowledge Professor Angel Irabien and Professor Manuel Alvarez-Guerra for accepting me into their research group at Cantabria University and providing the facilities and materials needed during three profitable months. Thanks to all members of the research group for welcoming me and promptly helping me every time I needed it.

My thankful words also go to all my lab mates for contributing to a productive yet fun working environment. In particular, I would like to thank Mafalda Pereira for the support and for being there with kind words and a smile since day 1, when I submitted my grant proposal to FCT.

I am very thankful to all my friends for their support, affection, and all the good moments that we have been living together.

I am grateful to Juncal and her family for making me feel at home during the three amazing months I spent in Santander.

A very special thanks to Jeffrey Capitão for all the encouragement, all the laughs and tears shared, for helping me get through the difficult moments, and for showing me that there is always a solution for each problem.

Last but not least, I would like to express my warm gratitude to my lovely family for their endless support throughout this journey. Thank you for always being present in the most important moments of my life. Especially, I would like to express my heartfelt gratitude to my parents for the values you have taught me that make me who I am today. Without your support, none of this would have been possible.

To all who have been part of this tireless journey and I may have forgotten, my sincere gratitude!

To my family

Preface

The present work was developed at the Laboratory for Process Engineering, Environmental, Biotechnology and Energy (LEPABE) and at the Associate Laboratory in Chemical Engineering (ALiCE) facilities in the Chemical Engineering Department of the Faculty of Engineering of the University of Porto (FEUP), between 2018 and 2022, under the FCT (Foundation for Science and Technology) grant SFRH/BD/128768/2017. The work was supervised by Professor Adélio Mendes from LEPABE/ALiCE-FEUP.

Part of this thesis was also performed at the Department of Chemical and Biomolecular Engineering of the School of Industrial Engineering and Telecommunications (ETSIIT), University of Cantabria, Spain, under the supervision of Professor Manuel Alvarez-Guerra.

This thesis presents six chapters: one introduction chapter, four scientific articles, each representing one independent chapter, and a final chapter with the general conclusions and perspectives for future work.

Contents

Abstract	xiii
Sumário	xv
Figure captions	xvii
Table captions.....	xxvii

Chapter 1

Introduction

1.1 Motivation.....	3
1.2 CO ₂ mitigation strategies	4
1.3 Electrochemical reduction of CO ₂ (ERCO ₂).....	7
1.3.1 Characterization parameters of the ERCO ₂ process	11
1.3.2 Desired products.....	14
1.4 Catalysts for CO ₂ reduction	17
1.4.1 Catalyst engineering	19
1.5 ERCO ₂ mechanisms on copper surfaces.....	30
1.6 Objectives and outline of this work	34
Nomenclature	36
References	38

Chapter 2

Influence of Synthesis Time on the Properties of Bimetallic CuZn Oxide Catalysts for CO₂ Electrochemical Reduction

2.1 Abstract.....	59
-------------------	----

2.2	Introduction.....	60
2.3	Experimental.....	62
2.3.1	Catalyst synthesis	62
2.3.2	Electrode preparation.....	62
2.3.3	Material characterization	63
2.3.4	Electrochemical measurements	65
2.3.5	CO ₂ electrochemical reduction and product analysis	66
2.4	Results and discussion	67
2.4.1	Physicochemical properties of the developed catalysts.....	67
2.4.2	Electrochemical CO ₂ reduction	77
2.5	Conclusions.....	87
	Acknowledgments	88
	Nomenclature	89
	References	91

Chapter 3

Tuning the Selectivity of Cu₂O/ZnO Catalyst for CO₂ Electrochemical Reduction

3.1	Abstract.....	103
3.2	Introduction.....	104
3.3	Experimental.....	106
3.3.1	Catalyst synthesis	106
3.3.2	Electrode preparation.....	107
3.3.3	Conditioning/post-synthesis treatments.....	107
3.3.4	Electrochemical measurements	108

3.3.5	CO ₂ reduction electrolysis and product analysis	109
3.3.6	Physicochemical characterization.....	109
3.4	Results and discussion	110
3.4.1	Physicochemical properties of the as-prepared CuZn catalyst	110
3.4.2	Influence of the conditioning on the physicochemical properties	115
3.4.3	Influence of the conditioning on the electrochemical activity.....	120
3.4.4	Influence of the physicochemical properties on the electrocatalytic activity.....	127
3.4.5	Cu ₂ O-ZnO synergy	132
3.5	Conclusions.....	142
	Acknowledgments	142
	Nomenclature	144
	References	146

Chapter 4

Enhancement of the Electrochemical Reduction of CO₂ to Methanol and Suppression of H₂ Evolution Over CuO Nanowires

4.1	Abstract.....	157
4.2	Introduction.....	158
4.3	Experimental.....	159
4.3.1	Electrode preparation.....	159
4.3.2	Physicochemical characterization.....	160
4.3.3	Electrochemical measurements	161
4.3.4	CO ₂ reduction electrolysis and product analysis	162
4.3.5	Filter-press tests.....	162

4.4	Results and discussion	164
4.4.1	Electrode characterization	164
4.4.2	Electrochemical performance and stability	168
4.4.3	Electrochemical CO ₂ reduction	173
4.4.4	Understanding the superior performance of CuO NWs	175
4.4.5	CO ₂ reduction in a gas-phase GDE configuration	179
4.5	Conclusions.....	181
	Acknowledgments	182
	Nomenclature	183
	References	185

Chapter 5

Binary Copper-Bismuth Catalysts for the Electrochemical Reduction of CO₂: Study on Surface Properties and Catalytic Activity

5.1	Abstract.....	195
5.2	Introduction.....	196
5.3	Experimental.....	198
5.3.1	Electrode preparation.....	198
5.3.2	Electrochemical measurements	199
5.3.3	Physicochemical characterization.....	200
5.4	Results and discussion	201
5.4.1	Physicochemical properties of the catalysts	201
5.4.2	ERCO ₂ activity	208
5.4.3	CO ₂ and CO adsorption behavior	213
5.4.4	CO ₂ coordination	218

5.5 Conclusions.....	223
Acknowledgments	224
Nomenclature	225
References	227

Chapter 6

General Conclusions and Outlook

6.1 Conclusions.....	239
6.2 Outlook	241

Appendix A

Supplementary Figures and Tables

A.1 Supplementary figures and tables to Chapter 2	245
A.2 Supplementary figures and tables to Chapter 3	255
A.3 Supplementary figures and tables to Chapter 4	272
A.4 Supplementary figures and tables to Chapter 5	280

Abstract

Beginning with the industrial revolution in the late 18th century, the increasing use of fossil fuels has escalated the concentration of atmospheric carbon dioxide (CO₂). It is widely recognized that CO₂ emissions are the primary driver of global climate change. As a result, the Earth is about 1.1 °C warmer than in the 1800s, owing to the 48 % increase of CO₂ concentration in the atmosphere caused by industrial activities, which are the foundation of our modern civilization. To avoid the severe effects of climate change, it is urgent to reduce CO₂ emissions and adopt more sustainable industrial practices. According to the Intergovernmental Panel on Climate Change (IPCC), limiting global warming to 1.5 °C, as set by the Paris Agreement, implies reaching net-zero CO₂ emissions globally by 2050.

In this context of environmental concerns and the need for energy transition, the electrochemical reduction of CO₂ (ERCO₂) to value-added chemicals and fuels offers a potential platform for harvesting and storing CO₂ in renewable energy vectors and chemical feedstock. However, significant challenges prevent the widespread use of this technology, including (i) low energy efficiency and sluggish kinetics, (ii) low selectivity for the target product, (iii) the presence of the competing hydrogen evolution reaction (HER), and (iv) low catalyst stability over extended operating periods. Thus, a major challenge for implementing the ERCO₂ is the development of high-efficient ERCO₂ catalysts. To achieve this goal is fundamental to understand the relationship between the structure and activity of the catalysts and the reaction mechanism.

Copper has been pointed out as one of the best-promising materials for ERCO₂ catalysts. Thus, the present work targets the development of high-performing Cu-based ERCO₂ catalysts. With this aim, two different classes of catalysts were explored: the traditional powder-based and self-supported.

Considering the powder-based catalysts, this work evaluated the influence of the synthesis conditions and post-synthesis treatments on the physicochemical and electrochemical characteristics of the developed materials. It provides evidence of the strong influence of the synthesis method, particularly the synthesis time, on the

physicochemical properties of the resulting material, which governs catalytic activity. Moreover, this work highlights the importance of post-synthesis procedures for improving the ER CO_2 selectivity. In particular, it is proposed that the CO/H_2 production ratio (syngas composition) can be controlled through the application of *in situ* treatments. So far, this fine-tuning has been mainly achieved by controlling the catalyst properties during the synthesis stage.

The catalyst morphology was also studied when working with self-supported catalysts. The direct growth of the active material (CuO nanowires) on a conductive substrate (commercial copper foam) allowed the precise tuning of the catalyst morphology. This unique nanowire structure lowers the CO_2 activation barrier and enhances the electron transfer, increasing the reaction kinetics. Infrared spectroscopy experiments were performed to identify the species formed on the catalyst surface after CO_2 adsorption. The results suggest that the coordination of the formed species is mainly controlled by the Lewis acidity and basicity of the catalyst surface. In particular, it is proposed that a bidentate carbonate is preferably formed in the presence of strong Lewis acid and base sites. This bidentate species is suggested as a key intermediate for the selective ER CO_2 to propane, which is reported for the first time in this work.

Sumário

Com início na revolução industrial do final do século XVIII, a utilização crescente de combustíveis fósseis resultou no aumento excessivo da concentração de dióxido de carbono (CO_2) na atmosfera. É amplamente reconhecido que as emissões de CO_2 são o principal motor das alterações climáticas. Como consequência, a Terra está cerca de $1.1\text{ }^\circ\text{C}$ mais quente do que em 1800, devido ao aumento de 48 % na concentração atmosférica de CO_2 resultante das atividades industriais, a base da nossa civilização moderna. Para evitar os graves efeitos das alterações climáticas é urgente reduzir as emissões de CO_2 e adotar práticas industriais mais sustentáveis. Segundo o Painel Intergovernamental sobre Mudanças Climáticas (IPCC), limitar o aquecimento global a $1.5\text{ }^\circ\text{C}$, conforme estabelecido pelo Acordo de Paris, implica atingir zero emissões líquidas ("net-zero") de CO_2 a nível mundial até 2050.

Neste contexto de preocupações ambientais e da necessidade de uma transição energética, a redução eletroquímica de CO_2 (ERCO_2), para produção de produtos químicos e combustíveis de valor acrescentado, oferece uma potencial plataforma para a captura e armazenamento de CO_2 em vetores de energia renovável e produtos químicos. Contudo, desafios substanciais impedem a utilização em grande escala desta tecnologia, incluindo (i) baixa eficiência energética e cinética lenta, (ii) baixa seletividade para o produto alvo, (iii) presença da reação concorrente de evolução do hidrogénio (HER), e (iv) baixa estabilidade do catalisador durante longos períodos de operação. Por conseguinte, um grande desafio para a implementação da ERCO_2 é o desenvolvimento de catalisadores de elevada eficiência. Para se atingir este objetivo é fundamental compreender a relação entre a estrutura e a atividade dos catalisadores e o mecanismo da reação.

O cobre é considerado um dos materiais mais promissores para uso como catalisador para a ERCO_2 . Assim, o presente trabalho visa o desenvolvimento de catalisadores de alto desempenho baseados em cobre. Com este objetivo, foram exploradas duas classes de catalisadores: os tradicionais em pó e os auto-suportados.

Considerando os catalisadores em pó, este trabalho avaliou a influência das condições de síntese e tratamentos pós-síntese nas características físico-químicas e eletroquímicas dos materiais desenvolvidos. Este trabalho fornece provas da forte influência dos métodos de síntese, particularmente o tempo de síntese, sobre as propriedades físico-químicas do material produzido que, por sua vez, controlam a atividade catalítica. Além disso, este trabalho sublinha a importância dos procedimentos pós-síntese para melhorar a seletividade da ER CO_2 . Em particular, propõe-se que o rácio CO/H_2 (composição do gás de síntese) pode ser controlado através da aplicação de tratamentos *in situ*. Até agora, este ajuste fino foi conseguido principalmente através do controlo das propriedades do catalisador durante a fase de síntese.

A morfologia dos catalisadores também foi estudada quando se trabalhou com catalisadores auto-suportados. O crescimento do material ativo (nanofios de CuO) diretamente sobre um substrato condutor (espuma de cobre comercial) permitiu o controlo preciso da morfologia do catalisador. Esta estrutura singular com nanofios diminui a barreira de ativação do CO_2 e melhora a transferência de eletrões, aumentando a cinética da reação. A espectroscopia de infravermelho foi usada para identificar as espécies formadas na superfície do catalisador após a adsorção do CO_2 . Os resultados sugerem que a coordenação das espécies formadas é principalmente controlada pela acidez e basicidade de Lewis da superfície do catalisador. Em particular, propõe-se que carbonatos bidentados sejam preferencialmente formados na presença de centros ácidos e básicos fortes. Esta espécie bidentada é sugerida como intermediário de reação chave para a ER CO_2 seletiva ao propano, que é reportada pela primeira vez neste trabalho.

Figure captions

Figure 1.1. Different strategies for reducing CO ₂ emissions, including decarbonization, afforestation, carbon capture and sequestration (CCS), and carbon capture and utilization (CCU).....	5
Figure 1.2. ERCO ₂ coupled with renewable energy sources can enable a CO ₂ -free energy cycle, in which CO ₂ is sustainably converted to fuels and chemicals.	8
Figure 1.3. Illustration of the ERCO ₂ process and some possible products generated in an electrochemical cell.....	9
Figure 1.4. Economic analysis of ERCO ₂ products. The values shown are an average of several economic studies reported in the literature [11,21,57–59].	16
Figure 1.5. Reaction mechanism of ERCO ₂ on metal electrodes in aqueous solutions, according to the work of Hori <i>et al.</i> [67]. Adapted from [40,70].....	18
Figure 1.6. Influence of different length scales involved in the performance of ERCO ₂ catalysts, adapted from [31,57].	22
Figure 1.7. Possible ERCO ₂ mechanisms on copper-based catalysts, adapted from [12]. The different colors of the arrows identify the various reaction pathways proposed in the literature: — Hori <i>et al.</i> [67]; — Peterson <i>et al.</i> [129] and Kuhl <i>et al.</i> [140]; — Kortlever <i>et al.</i> [142]; — Cheng <i>et al.</i> [132]; — Feaster <i>et al.</i> [126] and Liu <i>et al.</i> [143]; and, — Chernyshova <i>et al.</i> [124].....	33
Figure 2.1. Synthesis of bimetallic CuZn oxide catalysts.....	62
Figure 2.2. Conventional three-electrode electrochemical cell.	65
Figure 2.3. Experimental set-up for the ERCO ₂ tests.	67
Figure 2.4. SEM images of (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.....	68
Figure 2.5. XRD pattern of the developed catalysts.	69

Figure 2.6. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of CuZn_5, CuZn_15, and CuZn_25.	70
Figure 2.7. Correlation between the BET-specific surface area and pore volume with the double-layer capacitance of the electrodes.	71
Figure 2.8. (a) H ₂ -TPR profile of CuZn_5, CuZn_15 and CuZn_25. (b) H ₂ -TPR profile of Cu and Zn single element catalysts synthesized according to the same procedure used to prepare the CuZn bimetallic catalysts within 15 h of synthesis.	72
Figure 2.9. (a) Cu 2p _{3/2} and (b) Zn 2p _{3/2} XPS spectra of the CuZn catalysts.	74
Figure 2.10. Proposed formation mechanism of two-shelled hollow spheres <i>via</i> a simple one-pot solvothermal route. The mechanism involves three main stages: (1) nucleation, (2) crystal growth and formation of the core-shell microspheres, and (3) Ostwald ripening.	76
Figure 2.11. (a, c) Low and (b, d) high magnification SEM images of (a, b) copper and (c, d) zinc monometallic samples.	77
Figure 2.12. IR-corrected LSV polarization curves at cathodic potentials in N ₂ (dashed lines) and CO ₂ -saturated (full lines) 0.1 M KHCO ₃ for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25. Scan rate, 20 mV s ⁻¹	78
Figure 2.13. Chronoamperometric curves at various potentials for CO ₂ reduction in CO ₂ -saturated 0.1 M KHCO ₃ for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.	79
Figure 2.14. (a) Total current density and faradaic efficiency over (b) CuZn_5, (c) CuZn_15, and (d) CuZn_25 at different applied potentials.	80
Figure 2.15. IR-corrected cyclic voltammograms of CuZn_5, CuZn_15, and CuZn_25 in N ₂ -purged 0.1 M KHCO ₃ solution. Scan rate, 50 mV s ⁻¹	83
Figure 2.16. CO-TPD profile of CuZn_5, CuZn_15, and CuZn_25.	84

Figure 2.17. Work function of the developed CuZn catalysts and Cu single element catalyst.	85
Figure 2.18. SEM images of the electrodes prepared with the developed catalysts, (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25, before and after the ERCO ₂ reaction at -1.4 V.	86
Figure 3.1. Experimental procedure for the evaluation of the different conditioning approaches: <i>in situ</i> – blue arrows, and <i>ex situ</i> – red arrows.	108
Figure 3.2. XRD pattern of the CuZn catalyst, as-prepared and after electrode production.....	110
Figure 3.3. (a) Cu 2p _{3/2} and (b) Zn 2p _{3/2} XPS spectra of the CuZn catalyst and Cu and Zn single-element samples.	111
Figure 3.4. (a) TEM image of the as-prepared CuZn catalyst power, (b) representative HAADF-STEM image, and (c-d) energy dispersive X-ray spectroscopy maps of (c) O, (d) Cu, (e) Zn, and (f) superposition of Cu and Zn.	113
Figure 3.5. H ₂ -TPR profile of CuZn, and Cu and Zn single-element catalysts.	114
Figure 3.6. SEM images of (a) CuZn_240, (b) CuZn_300, (c) CuZn_AS, and (d) CuZn_CS.	115
Figure 3.7. XRD patterns of the CuZn catalyst before and after (a) <i>ex situ</i> and (b) <i>in situ</i> conditioning.	117
Figure 3.8. O 1s XPS spectra of (a) CuZn, (b) CuZn_AS and (c) CuZn_CS.	119
Figure 3.9. IR-corrected LSV at cathodic potentials in N ₂ (dashed lines) and CO ₂ -saturated (full lines) 0.1 M KHCO ₃ for (a) CuZn catalyst as-prepared (reference sample) and after conditioning: (b) CuZn_240, (c) CuZn_300, (d) CuZn_AS, and (e) CuZn_CS. Scan rate, 20 mV s ⁻¹	121

Figure 3.10. (a) Total current density and faradaic efficiency over (b) CuZn, (c) CuZn_240, (d) CuZn_300, (e) CuZn_AS, and (f) CuZn_CS at different applied potentials.....	123
Figure 3.11. (a) Total current density and faradaic efficiency over (b) Cu and (c) Zn single-element catalysts at different applied potentials.	126
Figure 3.12. Faradaic efficiency over (a) Cu and (b) Cu_AS at different applied potentials.	129
Figure 3.13. Nyquist plots, with fitting curves (dashed lines), of CuZn, CuZn_AS, and CuZn_CS in CO ₂ -saturated 0.1 M KHCO ₃ with a frequency from 1 MHz to 100 mHz and 10 mV of amplitude.	130
Figure 3.14. CO ₂ -TPD profiles for CuZn, CuZn_AS and CuZn_CS.	132
Figure 3.15. H ₂ -TPR profile of the CuZn catalyst prepared by a physical mixture of Cu and Zn single-element powders; profiles of Cu and Zn samples are also shown for comparison purposes.	133
Figure 3.16. SEM micrographs and EDS mapping pictures of the CuZn catalyst prepared by a physical mixture of Cu and Zn single-element powders.	133
Figure 3.17. Faradaic efficiency over (a) Zn and (b) Zn_AS at different applied potentials.	134
Figure 3.18. (a) Total current density and faradaic efficiency over (b) CuZn _{mix} , and (c) CuZn _{mix} _AS at different applied potentials.....	135
Figure 3.19. Comparison between the FE values obtained for (a, b) CuZn and (c, d) CuZn _{mix} , (a, c) before and (b, d) after <i>in situ</i> anodic conditioning.....	136
Figure 3.20. Schematic showing the proposed reaction mechanism on the surface of (a) CuZn _{mix} and (b) CuZn.....	138
Figure 3.21. IR-corrected CVs in N ₂ -saturated 0.1 M KHCO ₃ , (a) starting from the anodic scan (AS) and (b) starting from the cathodic scan (CS).	139

Figure 4.1. Experimental procedure used to prepare the CuO NWs electrodes.	160
Figure 4.2. (a) Disassembled filter-press cell and (b) working principle of the filter-press cell for continuous CO ₂ electrolysis.	163
Figure 4.3. Digital photographs of (a) Cu foam, (b) Cu(OH) ₂ NWs, and (c) CuO NWs.	164
Figure 4.4. SEM image of (a) Cu foam, (b, c) low- and high-magnification of Cu(OH) ₂ NWs, and (d) CuO NWs.	165
Figure 4.5. XRD pattern of the developed electrodes.	166
Figure 4.6. (a-c) Cu 2p _{3/2} XPS and (d-f) Cu Auger LMM spectra for (a, d) Cu foam, (b, e) Cu(OH) ₂ NWs, and (c, f) CuO NWs.	167
Figure 4.7. IR-corrected LSV curves at cathodic potentials in N ₂ (dashed lines) and CO ₂ -saturated (full lines) 0.1 M KHCO ₃ for (a) Cu foam, (b) Cu(OH) ₂ NWs, and (c) CuO NWs. Scan rate, 20 mV s ⁻¹	169
Figure 4.8. (a) Cu 2p _{3/2} XPS and (b) Cu Auger LMM spectra of CuO NWs after ERCO ₂	170
Figure 4.9. (a) Dependence of the total current density over time for the CuO NWs sample, with and without the TiO ₂ protection layer, recorded at -1.2 V. SEM image of the CuO NWs electrode without the TiO ₂ layer (b) before and (c) after 2 h of electrolysis.	171
Figure 4.10. (a) Area-specific resistance vs. compression pressure for Cu foam and CuO NWs with and without TiO ₂ , at multiple applied current densities. (b) Faradaic efficiency over CuO NWs with and without TiO ₂ at -1.2 V.	172
Figure 4.11. (a) Total current density and faradaic efficiency over (b) Cu foam, (c) Cu(OH) ₂ NWs, and (d) CuO NWs at different applied potentials.	174

Figure 4.12. (a) Tafel plots of the CO ₂ reduction partial current density. (b) IR-corrected single oxidative LSV scans at 50 mV s ⁻¹ in N ₂ -saturated 0.1 M NaOH.	176
Figure 4.13. Nyquist plots, with fitting curves (dashed lines), of the prepared electrodes in CO ₂ -saturated 0.1 M KHCO ₃ with a frequency from 1 MHz to 10 mHz, and 10 mV amplitude at (a) -0.8 V and (b) -1.2 V.	177
Figure 4.14. (a) Faradaic efficiencies and (b) production yield for Cu foam and CuO NWs, working on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell, working at a current density of -45 mA cm ⁻²	180
Figure 5.1. Experimental procedure used for the electrocatalysts preparation.	198
Figure 5.2. Experimental setup.	199
Figure 5.3. (a-c) Low and (d-i) high-magnification SEM images with elemental mapping of Cu and Bi for (a, d, g) #5C, (b, e, h) #20C, and (c, f, i) #50C.	202
Figure 5.4. XRD pattern of the developed catalysts.	203
Figure 5.5. (a) Bi 4f, and (b) Cu 2p _{3/2} spectra of the developed catalysts.	205
Figure 5.6. O 1s XPS spectra of the developed catalysts.	207
Figure 5.7. (a, c) Faradaic efficiencies and (b, d) production yield for the developed catalysts. Tests were performed on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell at a current density of -45 mA cm ⁻² . (a, b) Catholyte A: 0.1 M KHCO ₃ ; (c, d) catholyte B: 0.45 M KHCO ₃ + 0.5 M KCl.	209
Figure 5.8. (a) Faradaic efficiency and (b) production yield for catalyst #20C, working on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell, at a current density of -45 mA cm ⁻² or -90 mA cm ⁻² . An aqueous solution of 0.45 M KHCO ₃ + 0.5 M KCl was used as catholyte (catholyte B).	210

Figure 5.9. Relative ratio and strength of the CO ₂ adsorption sites (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B. The error bar relates to the standard deviation of three independent reads.	214
Figure 5.10. Representative CO ₂ desorption pattern obtained (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B.	217
Figure 5.11. Representative CO desorption pattern obtained (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B.	218
Figure 5.12. Infrared spectra collected over catalysts (a) #5C, (b) #20C, and (c) #50C, as prepared, after CO ₂ adsorption, and during the stepwise CO ₂ desorption at 150 °C, 250 °C, 350 °C, and 450 °C.	219
Figure A.1. SEM-EDX analysis of CuZn_5. Accelerating voltage of 10 kV.	245
Figure A.2. SEM-EDX analysis of CuZn_15. Accelerating voltage of 10 kV.	246
Figure A.3. SEM-EDX analysis of CuZn_25. Accelerating voltage of 10 kV.	247
Figure A.4. SEM-EDX analysis of the electrodes produced with the CuZn catalysts: (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25. Accelerating voltage of 15 kV.	248
Figure A.5. Cyclic voltammograms in the non-faradaic region of (a) CuZn_5, (b) CuZn_15, (c) CuZn_25 and (d) polycrystalline Cu foil.	249
Figure A.6. Double-layer capacitance of the electrodes prepared with the developed CuZn catalysts.	250
Figure A.7. Cu Auger LMM spectra for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.	251
Figure A.8. XRD pattern of the gas diffusion layer (GDL, Sigracet 35BC, SGL Group) used for electrode preparation.	255
Figure A.9. XPS survey spectra of (a) Cu, (b) Zn, and (c) CuZn samples.	256

Figure A.10. Cyclic voltammograms of (a) CuZn, (b) CuZn_240, (c) CuZn_300, (d) CuZn_AS, and (e) CuZn_CS, obtained for a non-faradaic potential range.....	257
Figure A.11. Double-layer capacitance of the CuZn electrodes.....	258
Figure A.12. Chronoamperometric curves at various potentials for CO ₂ reduction in CO ₂ -saturated 0.1 M KHCO ₃ for (a) CuZn, (b) CuZn_240, (c) CuZn_300, (d) CuZn_AS, and (e) CuZn_CS.....	259
Figure A.13. IR-corrected CVs in N ₂ -saturated 0.1 M KHCO ₃ , starting with the anodic scan (AS), for (a) Cu and (b) Zn single-element catalysts.....	260
Figure A.14. Cu 2p _{3/2} XPS spectra of CuZn, CuZn_AS and CuZn_CS.	260
Figure A.15. LSV curves at cathodic potentials in N ₂ (dashed lines) and CO ₂ -saturated (full lines) 0.1 M KHCO ₃ for (a) Cu(OH) ₂ NWs and (b) CuO NWs. Scan rate, 20 mV s ⁻¹ ..	272
Figure A.16. Double-layer capacitance of the developed electrodes and polycrystalline copper foil.....	272
Figure A.17. SEM-EDS elemental mapping of Cu and Ti for CuO NWs electrode after TiO ₂ deposition by ALD.	273
Figure A.18. (a) SEM image of the CuO NWs electrode coated with a protective TiO ₂ layer after 2 h electrolysis; and (b) CO ₂ -TPD-MS profile of CuO NWs electrode with (green curve) and without TiO ₂ (blue curve).....	273
Figure A.19. Chronoamperometric curves at various potentials for CO ₂ reduction in CO ₂ -saturated 0.1 M KHCO ₃ for (a) Cu foam, (b) CuO(OH) ₂ NWs, and (c) CuO NWs.	274
Figure A.20. Comparison between CO ₂ and CO desorption profile obtained for catalyst #50C, after electrolysis with catholyte A. CO ₂ and CO-TPD experiments were performed under the same operating conditions (<i>e.g.</i> , attenuation, adsorbate flow rate, heating ramp, catalyst mass).	280

Figure A.21. Comparison of CO₂ desorption pattern obtained with catholyte A and catholyte B for catalysts (a) #5C, (b) #20C, and (c) #50C. 281

Figure A.22. Comparison of CO desorption pattern obtained with catholyte A and catholyte B for catalysts (a) #5C, (b) #20C, and (c) #50C. 281

Table captions

Table 1.1. Standard electrode potentials (E^0) for ERCO ₂ half-reactions under standard conditions; pH 7, 25 °C and 1 atm [1,12,45].	10
Table 1.2. Quality of CO ₂ from various sources with estimated capture cost, according to Grim <i>et al.</i> [21].	14
Table 1.3. ERCO ₂ efficiency using metal-based catalysts, from selected literature. Results are ordered according to the total current density obtained (reverse order).	28
Table 2.1. Average crystallite size estimated from XRD data using the Scherrer equation.	70
Table 2.2. Textural and electrical properties of the developed catalysts.	71
Table 2.3. Zn 2p _{3/2} , Cu 2p _{3/2} , Cu and Zn LMM, and modified Auger parameter values for the developed CuZn catalysts. Curve-fitting parameters.	74
Table 3.1. Zn 2p _{3/2} , Cu 2p _{3/2} , Cu LMM, Zn LMM, and modified Auger parameter values for the as-prepared catalysts. Curve-fitting parameters.	112
Table 3.2. Physicochemical and electrical properties of the electrodes, before and after conditioning.	117
Table 3.3. Zn 2p _{3/2} , Cu 2p _{3/2} , Cu and Zn LMM, and modified Auger parameter values for the catalysts after conditioning. Curve-fitting parameters.	118
Table 3.4. O 1s values for the as-prepared catalyst and after conditioning. Curve-fitting parameters.	120
Table 3.5. Physicochemical properties of the monometallic Cu electrode, before and after <i>in situ</i> conditioning (anodic scan).	129
Table 3.6. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -0.8 V.	131

Table 3.7. Summary of cyclic voltammetry results obtained for CuZn_AS and CuZn_CS.....	140
Table 3.8. Influence of the different post-synthesis treatments on the physicochemical structure of the catalysts and electrochemical behavior. A structure-activity relationship is also presented.	141
Table 4.1. Cu 2p _{3/2} , Cu Auger LMM, and modified Auger parameter values for the electrodes. Curve-fitting parameters.	166
Table 4.2. Capacitance values and surface roughness factors of the developed electrodes.....	169
Table 4.3. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -0.8 V.	178
Table 4.4. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -1.2 V.	179
Table 5.1. Results of XRD analysis.....	204
Table 5.2. Bi 4f _{7/2} , Cu 2p _{3/2} , Cu LMM, and modified Auger parameter values for the prepared electrodes.....	206
Table 5.3. Surface atomic ratio determined by XPS.....	208
Table 5.4. Details of the ERCO ₂ testing.	212
Table 5.5. Summary of the IR absorption frequencies (cm ⁻¹) for the various adsorbed CO ₂ species.	222
Table A.1. ERCO ₂ results for CuZn_5 electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	252
Table A.2. ERCO ₂ results for CuZn_15 electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	253

Table A.3. ERCO ₂ results for CuZn ₂₅ electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	254
Table A.4. ERCO ₂ results for CuZn electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	261
Table A.5. ERCO ₂ results for CuZn ₂₄₀ electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	262
Table A.6. ERCO ₂ results for CuZn ₃₀₀ electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	263
Table A.7. ERCO ₂ results for CuZn _{AS} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	264
Table A.8. ERCO ₂ results for CuZn _{CS} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	265
Table A.9. ERCO ₂ results for Cu electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	266
Table A.10. ERCO ₂ results for Cu _{AS} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	267
Table A.11. ERCO ₂ results for Zn electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	268
Table A.12. ERCO ₂ results for Zn _{AS} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	269
Table A.13. ERCO ₂ results for CuZn _{mix} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	270
Table A.14. ERCO ₂ results for CuZn _{mix} _{AS} electrode. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	271
Table A.15. Cell voltage (V), measured between the working and counter electrodes, for each catalyst and applied cathodic potential.....	275

Table A.16. Cell energy efficiency (EE) for CO ₂ reduction to methanol.	275
Table A.17. ERCO ₂ results for Cu foam. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	276
Table A.18. ERCO ₂ results for Cu(OH) ₂ NWs. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	277
Table A.19. ERCO ₂ results for CuO NWs. Tests were performed using step-potential electrolysis in CO ₂ -saturated 0.5 M KHCO ₃	278
Table A.20. Faradaic efficiency and production rate of the ERCO ₂ products determined using the filter-press cell, working at a current density of -45 mA cm ⁻²	279
Table A.21. Faradaic efficiency and production rate of the ERCO ₂ products determined using the filter-press cell, working at a current density of -45 mA cm ⁻² , using catholyte A: 0.1 M KHCO ₃	282
Table A.22. Faradaic efficiency and production rate of the ERCO ₂ products determined using the filter-press cell, working at a current density of -45 mA cm ⁻² , using catholyte B: 0.45 M KHCO ₃ + 0.5 M KCl.	283

CHAPTER 1

Introduction

Introduction

1.1 Motivation

Since the industrial revolution, fossil fuels, including base oil, coal, and natural gas, have become the dominant energy feedstock. Unfortunately, its tremendous burning rate led to a dramatic buildup of greenhouse gases in the atmosphere (*e.g.*, CO₂ and CH₄) [1]. As a result, the current atmospheric CO₂ level has exceeded 413 ppm (October 2021) [2] and is forecast to increase to 540-970 ppm by 2100, according to the Intergovernmental Panel on Climate Change (IPCC) [3]. The rising global CO₂ concentration is a serious environmental threat that is considered one of the major causes of global warming and, thus, climate change [4–6].

As of December 2015, 195 member states of the United Nations Framework Convention on Climate Change (UNFCCC) acknowledged that climate change represents an urgent and potentially irreversible threat to human life [7]. Moreover, climate change jeopardizes the achievement of several Sustainable Development Goals (SDGs) set by the United Nations on the 2030 Agenda. Rising temperature leads to the loss of species and ecosystems, reducing agricultural and fishing yields, thus, contributing to food insecurity and affecting livelihoods (SDGs 1, 2, 14, and 15). Extreme weather and climate events can increase health risks, damage infrastructures, and lead to water scarcity (SDGs 1, 3, 6, 9, and 11). Inevitably, these threats are interrelated with conflict and stability issues (SDG 16) [8]. Finally, there is ample evidence that people living near or below the poverty line are particularly vulnerable to climate change impacts, reinforcing or worsening existing inequalities (SDG 10) [8,9].

On the other hand, energy is essential for satisfying primary needs and sustaining comfortable and improved living standards [10]. As living standards continue to increase worldwide, especially in emerging economies, access to affordable and reliable energy

sources will be essential to maintain the pace of technological and societal progress [11]. Like biological metabolism, whose core is the ability to convert carbon between different oxidation states, the human's collective *industrial metabolism* relies on the oxidation of carbon, consisting of our energy infrastructure and chemical industry. In biological metabolism, CO₂ reduction through photosynthesis balances the oxidation of carbon in cellular respiration. However, carbon reduction is a missing piece of human industrial metabolism, misbalancing the natural carbon cycle [12]. Immediate changes to established manufacturing methods are then required to achieve the 2050 carbon neutrality goal set by the IPCC [13]. Thereby, creating a global-scale sustainable energy system for the future, while preserving our environment, is one of the most crucial challenges of our time [14].

Driven by the Kyoto protocol (1997), the Paris Agreement (2015), and, more recently, the Glasgow Climate Pact (2021), the global community has imposed mitigation actions to all countries. In particular, the European Union (EU) expects to achieve at least a 55 % reduction in CO₂ emissions by 2030 (compared to 1990) to be on track to reach the target of climate neutrality by 2050 [15]. Only this great effort will ensure that the internationally agreed goal to limit atmospheric warming below 2 °C is achieved [16,17]. Reducing and removing that much CO₂ will require a broad portfolio of solutions deployed at a massive scale, which can be grouped into three main categories: decarbonization, carbon sequestration, and carbon recycling [12], **Figure 1.1**.

1.2 CO₂ mitigation strategies

Noteworthy progress is currently being made in decarbonization, namely in the energy and industry sectors. For instance, electricity from renewable sources is increasing in volume and decreasing in price, and private investment in renewable energy is outpacing investment in fossil fuels [11,12,18]. However, the actual fraction of energy that can be used from those renewable sources is limited owing to their intermittent nature unless approaches for large-scale energy storage become available [11,19]. In contrast to

decarbonization, carbon sequestration is a strategy that accepts some continuous net production of CO_2 but aims to prevent its release into the atmosphere. Unfortunately, most currently operating carbon capture and sequestration (CCS) facilities are designed to aid in the extraction of additional fossil fuels through enhanced oil recovery (EOR) [20]. Accordingly, one of the main challenges of CCS is the lack of viable business. In the absence of political or economic incentives, the high costs of capture and purification make this technology economically unviable without EOR [12,21]. In turn, the limitations to the full implementation of decarbonization and CCS can be overcome by carbon recycling. CO_2 recycling can enable the storage of renewable electricity from intermittent sources in a dense and versatile form, provide a renewable carbon feedstock for chemical industries, and add value to CO_2 captured at industrial point sources or directly from the air (DAC) [14,21,22].

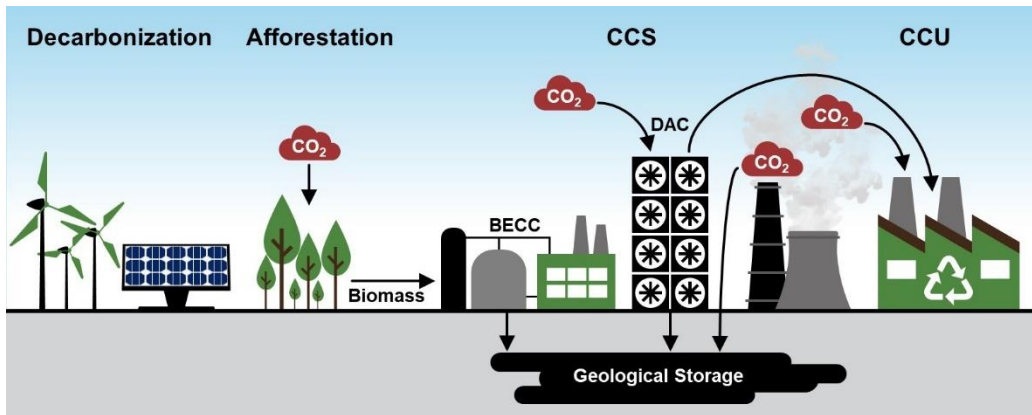
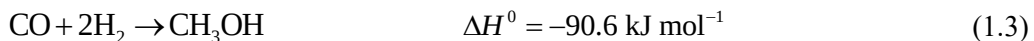
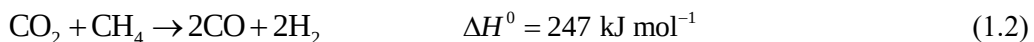
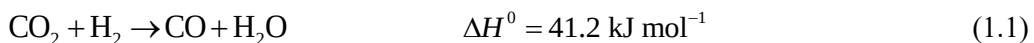


Figure 1.1. Different strategies for reducing CO_2 emissions, including decarbonization, afforestation, carbon capture and sequestration (CCS), and carbon capture and utilization (CCU).

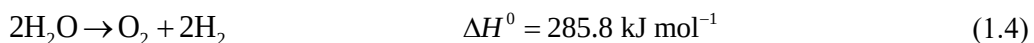
Natural photosynthesis by plants and other phototrophs can fixate a large amount of the globally emitted carbon. So, this is an obvious carbon recycling strategy, however limited by the amount of land required [12]. Another potential strategy is biomass energy with carbon capture and storage (BECCS). BECCS involves the production of energy through biomass burning, coupled with the capture and storage of the resulting CO_2 in

geological reservoirs [23]. Nevertheless, the large-scale implementation of BECCS requires extensive land, water, and nutrient usage, raising concerns about environmental and biodiversity impacts. Moreover, limitations to the amount of developed geologic storage sites constitute a challenge for BECCS upscaling from its current demonstration phase [24,25].

Carbon capture and utilization (CCU) is an important CO₂ mitigation strategy to support and complement CCS objectives. It represents various pathways that use CO₂ as a feedstock for producing value-added commodities [22]. In the traditional chemical industry, thermally activated processes can be used for CO₂ recycling with H₂ as reductant agent [12]. For instance, CO₂ can be reduced to CO by the reverse water gas shift reaction (RWGS, Equation (1.1)); if an excess of H₂ is used and the water is condensed out, syngas is obtained. Syngas can also be obtained through CO₂ dry reforming with hydrocarbons (*e.g.*, methane, Equation (1.2)). Among other applications, syngas is a precursor for methanol synthesis, a well-known commercial process that typically employs Cu-Zn oxides as catalyst (Equation (1.3)). The same catalytic system can be applied when CO₂ is present in the feed stream. If so, the traditional approach consists of a two-step process (with intermediate water removal), the first to catalyze the RWGS followed by CO reduction to methanol, CAMERE process [12,26].



However, all of the above processes operate at high pressure and temperature. For instance, *ca.* 100 bar and 250 °C are the typical conditions for methanol synthesis (the mildest reaction presented) [12]. Moreover, for achieving a sustainable process without additional CO₂ emissions, water is the only suitable source of H₂, which must be produced via water splitting coupled with renewable energy (Equation (1.4)) [27].



As an alternative to conventional chemical processes, the electrochemical reduction of CO₂ (ERCO₂) presents several advantages [1,28,29]. Namely: (i) it combines the electrochemical water splitting and subsequent CO₂ reduction into a single electrochemical process [12]; (ii) can operate at mild conditions of temperature and pressure (usually at ambient conditions) [12,29,30]; (iii) enables the production of compounds that are not easily obtained by thermally driven processes (*e.g.*, C₂₊ alcohols) [12,26]; (iv) can use green chemicals as electrolytes and electricity from renewable energy sources (wind, solar and hydro), thus not contributing to new CO₂ emissions [28–30]; (v) the integration with renewable electricity from intermittent energy sources helps to stabilize the electric grid, and enables the storage of energy in chemical products [21,31]; (vi) products and conversion rates can be tuned by using different catalysts and applying various potentials [28,29]; and, (vii) the electrolyzer and electrolysis process can be developed based on already existing technologies, *e.g.*, water electrolyzers, proton-exchange membrane fuel cell (PEMFC), and solid oxide fuel cells (SOFC) [28]. These features, mainly the simplicity and near-ambient operation conditions, make the ERCO₂ more suitable for decentralization than its thermal counterparts, reducing transportation-related impacts and costs [32]. In addition, the ERCO₂ can be designed to enable relatively quick adjustment of production; this way, it may be possible to match the overproduction of electricity from intermittent renewable sources or to operate on-demand at the point of usage [12,33].

1.3 Electrochemical reduction of CO₂ (ERCO₂)

ERCO₂ represents a viable alternative to help close the anthropogenic carbon cycle and convert intermittent electricity from renewable and clean energy sources to chemical energy in the form of fuels and chemical feedstock [21,34,35]. At the industrial scale, this technology can enable the transition from a linear to a circular carbon economy and somewhat relieve our dependency on fossil fuels, **Figure 1.2** [1,21].

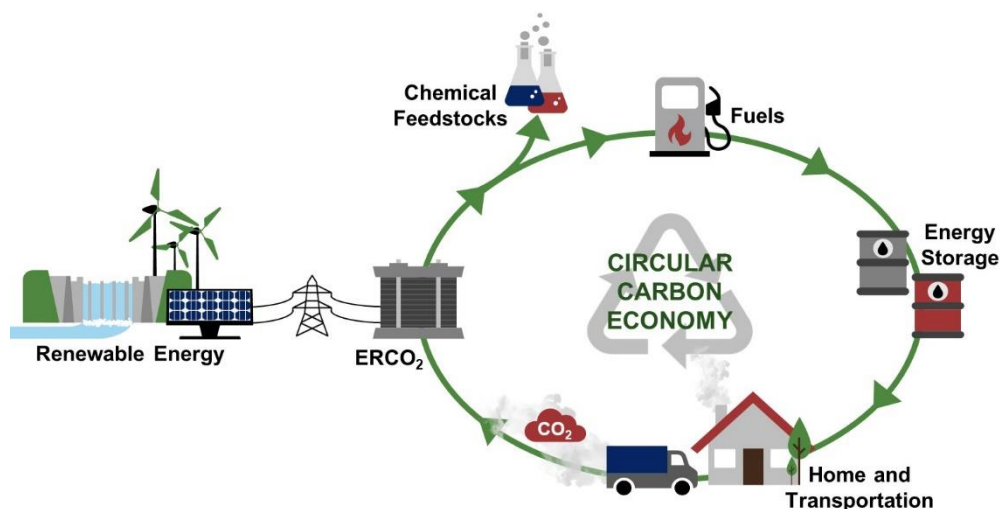


Figure 1.2. ERCO₂ coupled with renewable energy sources can enable a CO₂-free energy cycle, in which CO₂ is sustainably converted to fuels and chemicals.

The CO₂ reduction using electrochemical methods was first proposed by Royer in 1870, after observing formic acid synthesis from CO₂ on a Zn electrode [36]. However, it is not yet commercially available due to great technological challenges. In particular, the low energy efficiency and sluggish kinetics, even at high applied potential, are drawbacks faced during the process [37,38]. Moreover, the ERCO₂ is a complex multi-electron reaction involving many different surface-bond reaction intermediates and a large number of possible end products, including carbon monoxide, formic acid, formaldehyde, methane, methanol, and C₂₊ hydrocarbons and alcohols, **Figure 1.3** [39].

During the ERCO₂ process, electrical energy is provided to set up a potential between two electrodes (anode and cathode), which enables the reduction of CO₂. Comparable to PEM water electrolyzers, water is converted to protons at the anode side by the oxygen evolution reaction (OER) [34]. The resulting protons cross the membrane, and the electrons flow through the outer circuit, reaching the cathode. At the cathode, and depending on the pH of the medium, the electrons can combine with protons (acidic) or water (alkaline) to produce hydrogen (HER, hydrogen evolution reaction), or it combines with CO₂ forming the different ERCO₂ products, **Figure 1.3** [37]. Many of

these products require a large number of protons and electrons to be transferred and possibly proceed through different intermediates as well [14]. Moreover, since the equilibrium potentials for most of the CO₂ reduction half-reactions are comparable to that of HER, H₂ is the major side-product in aqueous electrolytes, **Table 1.1** [14,40]. **Table 1.1** also shows that the thermodynamic potential of the various CO₂ products is only slightly different, explaining why reducing CO₂ to the target product with good selectivity is quite challenging [40].

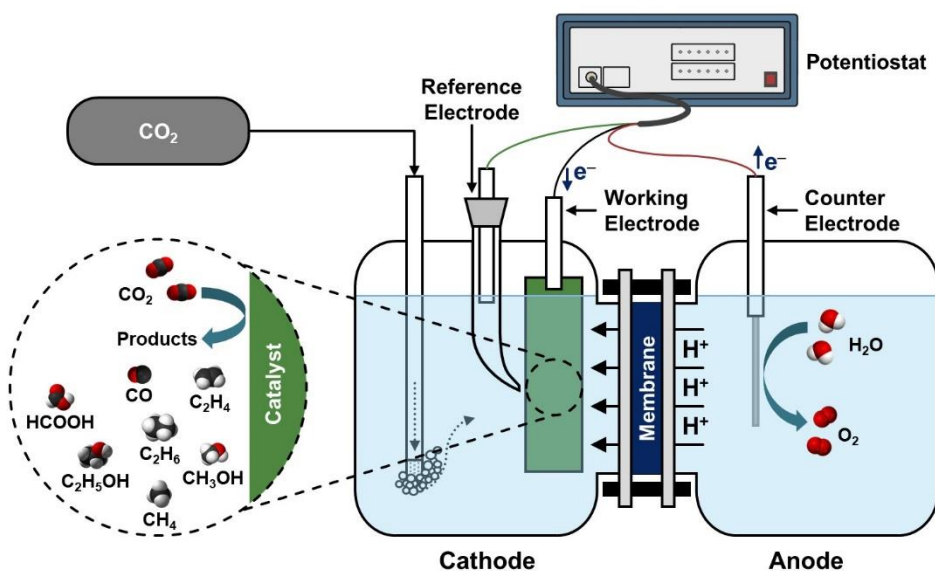


Figure 1.3. Illustration of the ERCO₂ process and some possible products generated in an electrochemical cell.

Typically, three major stages can be considered in ERCO₂: (i) chemical adsorption of CO₂ on the catalyst surface; (ii) electron transfer and/or proton migration to cleave C–O bonds and/or form C–H bonds; and, (iii) configuration rearrangement of products to desorb them from the catalyst surface and diffuse into the electrolyte [40,41]. Throughout the first stage, it is commonly accepted that a single electron is transferred to the CO₂ molecule to form the key intermediate CO₂^{•−}. The formation of this radical anion is generally considered as the critical step during the activation of CO₂ [40,42].

The large reorganizational energy ($-1.9 \text{ V}_{\text{RHE}}$, **Table 1.1**) required for transforming linear CO_2 to bent $\text{CO}_2^{\bullet-}$ imposes a high overpotential and slow reaction rates [21,43,44].

Table 1.1. Standard electrode potentials (E^0) for ERCO_2 half-reactions under standard conditions; pH 7, 25 °C and 1 atm [1,12,45].

Equation	$E^0 \text{ (V}_{\text{RHE}})$	Product
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.42	Hydrogen (HER)
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	0.82	Oxygen (OER)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53	Carbon monoxide
$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CO} + 2\text{OH}^-$	-0.52	
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61	Formic acid/Formate
$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HCOO}^- + \text{OH}^-$	-0.43	
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48	Formaldehyde
$\text{CO}_2 + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{HCHO} + 4\text{OH}^-$	-0.89	
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38	Methanol
$\text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + 6\text{OH}^-$	-0.81	
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24	Methane
$\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{CH}_4 + 8\text{OH}^-$	-0.25	
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-0.32	Ethanol
$2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^-$	-0.33	
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.33	Ethylene
$2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	-0.34	
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\bullet-}$	-1.9	

As mentioned, considerable challenges still prevent the large-scale implementation of the ERCO_2 technology. CO_2 is the most oxidized form of carbon (oxidation state + 4), and a highly stable molecule due to its linear and centrosymmetric molecular structure (the energy required to dissociate a $\text{C}=\text{O}$ bond in CO_2 is *ca.* 800 kJ mol^{-1}) [12,21]. Thus, its conversion is an energy-intensive process that usually requires harsh reaction conditions [1]. Other drawbacks of ERCO_2 include the production of H_2 as a by-product (from the parasitic HER reaction), low selectivity toward the target products, and low

reaction rates [14,40]. The identified limitations can only be overcome by developing efficient ER CO_2 catalysts. A viable catalyst must be capable of lowering the CO_2 reduction overpotential and controlling the reaction pathways toward a specific product with maximum activity [46]. Therefore, current ER CO_2 research hotspots include developing suitable catalysts and understanding the relationship between catalyst structure and activity [1].

1.3.1 Characterization parameters of the ER CO_2 process

Electrochemical processes are commonly evaluated based on at least three metrics: faradaic efficiency, current density, and overpotential [21]. However, other figures of merit such as onset potential, energy efficiency, and Tafel slope are also commonly considered [40].

Faradaic efficiency (FE): The FE is defined as the fraction of electrons consumed for forming a given product and can be simply calculated by Equation (1.5).

$$\eta_{\text{FE}} = \frac{z n F}{q} \quad (1.5)$$

In this equation, z represents the number of electrons exchanged (*e.g.*, 2 for ER CO_2 to CO), n is the number of moles of product produced, F refers to the Faraday constant (96 485 C mol⁻¹), and q represents the total charge passed [40,47].

Current density: The overall current density for CO_2 reduction is typically calculated by dividing the current by the geometric surface area of the working electrode, *i.e.*, electron flux per unit area (mA cm⁻²). As a measure of the reaction rate, this parameter is critical for practical applications. Maximizing the current density is essential for reducing the reactor size and capital cost, especially in systems with low selectivity.

The partial current density for a specific product can be calculated by multiplying the corresponding FE by the overall current density [21,40]. Besides the geometric area, the current density can be normalized by the electrochemically active surface area (ECSA), which provides more accuracy when comparing catalysts. However, caution is needed since, in some cases, the entire surface area of the electrode is not catalytically active, *e.g.*, nanoparticles supported on an inert support, like Toray paper [48].

The ECSA of a catalyst can be estimated by measuring the double-layer capacitance of the electrode-electrolyte interface. Cyclic voltammograms are acquired in the non-faradaic region of the voltammogram at multiple scan rates, and the slope of the current density *vs.* scan rate provides the capacitance value [49]. The measured capacitance can be compared to that of a smooth planar surface to obtain a relative roughness factor of the catalyst [48].

Product formation rate (k): The product formation rate is defined as the amount of product produced per unit of cathode area and time. This metric can be calculated according to Equation (1.6).

$$k = \frac{n}{A t} \quad (1.6)$$

In this equation, A is the cathode geometric surface area, and t represents the duration of each experiment [50,51].

Onset potential: The onset potential refers to the applied voltage *vs.* the reference electrode, under which the desired product is yielded at a detectable amount [40].

Activation overpotential (η): In practice, the potential observed experimentally is greater than the thermodynamically determined value (**Table 1.1**) due to internal resistances related to mass transfer, ohmic resistances, and activation barriers [21]. Thus,

the difference between the experimental potential (E) and the equilibrium potential (E_{eq}) is defined as overpotential and can be calculated according to Equation (1.7) [40,51,52].

$$\eta = E - E_{eq} \quad (1.7)$$

The equilibrium potential under reaction conditions is related to the standard potential (E^0) via the Nernst equation, Equation (1.8).

$$E_{eq} = E^0 - \frac{R}{z} \frac{T}{F} \ln Q \quad (1.8)$$

In this equation, R stands for the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature, and Q represents the reaction quotient ($Q = [\text{X}]_{\text{out}}/[\text{X}]_{\text{in}}$) [53].

Energy efficiency (EE): The EE defines the overall energy utilization toward the desired product and is determined according to Equation (1.9) [40,52].

$$\eta_{EE} = \frac{\eta_{FE} \Delta E^0}{\text{Cell voltage}} \quad (1.9)$$

In this equation, ΔE^0 represents the difference between the standard half-reaction potential for OER (anode) and the equilibrium potential for ER CO_2 under reaction conditions (cathode).

Tafel slope: The Tafel plot, which correlates the overpotential with the logarithm of the current density, is a useful metric to evaluate the performance of catalysts. In general, a smaller Tafel slope indicates better catalytic performance. For the ER CO_2 , the Tafel slope is very useful for investigating the reaction mechanism [40]. A Tafel slope of 118 mV dec^{-1} suggests that the rate-determining step for CO_2 reduction is the generation of the $\text{CO}_2^{\cdot-}$ key intermediate by the initial one-electron transfer step [54,55]. On the other hand, a slope of 59 mV dec^{-1} indicates a fast initial electron transfer before a later rate-limiting chemical step (*e.g.*, protonation of $\text{CO}_2^{\cdot-}$) [4,56].

1.3.2 Desired products

Currently, only carbon monoxide and formic acid can be produced from the ER CO_2 with high yield and faradaic efficiency close to 100 %. On the other hand, long-chain hydrocarbons have a larger market scale and higher energy density but are obtained from the ER CO_2 with lower selectivity (*e.g.*, 30 % for propanol) [13,57]. Thus, the industrial implementation of ER CO_2 depends on a series of factors, including not only market size and product price, but also capital costs (CO_2 electrolyzer) and operational costs (CO_2 source, electricity, and product separation) [11,21].

CO_2 sources range from the near-infinite atmospheric supply at *ca.* 413 ppm (October 2021) to concentrated streams released from biorefineries and ammonia synthesis plants, **Table 1.2**. Sources with the most concentrated streams require the least intensive cleanup processing and have the lowest capture cost, *ca.* €0.02 kg^{-1} CO_2 . In comparison, DAC is currently the most expensive pathway for CO_2 capture, with an estimated price ranging from *ca.* €0.35 kg^{-1} to €0.88 kg^{-1} CO_2 . However, it is the only approach capable of capturing CO_2 emitted from non-point sources, such as transportation, which accounts for approximately 40 % of total CO_2 emissions [21].

Table 1.2. Quality of CO_2 from various sources with estimated capture cost, according to Grim *et al.* [21].

Source	CO_2 concentration (%)	Common impurities	Capture cost (€ per ton)
Ethanol fermentation	99	$\text{C}_2\text{H}_5\text{OH}$, CH_3OH , H_2S , H_2O , $\text{C}_2\text{H}_6\text{S}$	17.6 – 21.1
Ammonia synthesis	> 95	NH_3 , H_2 , CO , H_2O	21.1 – 22.0
Natural gas wells	90 – 100	N_2 , CH_4 , C_2H_6 , C_3H_8 , trace HCs	17.6 – 19.4
Coal-fired flue gas	10 – 12	NO_x , SO_x , CO , O , N , Hg , As , Se	40.5 – 85.4
Gas-fired flue gas	3 – 6	NO_x , SO_x , CO , O , N , Hg , As , Se	37.8 – 78.3
Atmospheric CO_2	413 ppm	N_2 , O_2	352 – 880

The production cost of five different ER CO_2 products (CO, formate/formic acid, methanol, methane, and ethylene) was estimated by Durst *et al.*, using the H_2 production from alkaline water electrolysis as a benchmark [58]. This work assumed an electricity cost of $\text{€}0.04 \text{ kWh}^{-1}$, operating current density of *ca.* 0.2 A cm^{-2} , and energy conversion efficiency of *ca.* 40 % (roughly half of the efficiency of an alkaline water electrolyzer). According to the obtained results, CO production is economically attractive, with an estimated price ranging from $\text{€}0.24 \text{ kg}^{-1}$ to $\text{€}0.48 \text{ kg}^{-1}$, well below the current market price of $\text{€}0.57 \text{ kg}^{-1}$. Moreover, the global market for CO is large (annual production of 150 Mt [21,59]) since, in combination with H_2 (syngas) serves as an important chemical precursor for several industrial processes (*e.g.*, Fischer-Tropsch). Besides CO, formic acid was identified as an interesting product, with an estimated production cost 2 to 4-times lower than the current market price ($\text{€}0.30 \text{ kg}^{-1}$ vs. $\text{€}0.70 - \text{€}1.1 \text{ kg}^{-1}$). However, the market for formic acid is much smaller compared to the global demand for CO/syngas [58]. Formic acid is a feedstock for producing fuels, solvents, plastic monomers, and food-grade protein. In addition, it is widely used as a preservative and antibacterial agent in livestock feed [21,60].

Jin *et al.* also estimated that the minimum cost for converting CO_2 to CO and formic acid is $\text{€}0.11 \text{ kg}^{-1}$ and $\text{€}0.07 \text{ kg}^{-1}$, respectively. The authors also considered the cost of product separation, which is higher for formic acid (*ca.* $\text{€}0.05 \text{ kg}^{-1}$ vs. $\text{€}0.01 \text{ kg}^{-1}$ for CO) [57]. In addition to being economically attractive products, Grim *et al.* identified CO and formic acid as the top near-term targets for the efficient conversion of electrical energy to chemical energy in seasonal or off-peak energy storage applications [21].

More recently, Bushuyev *et al.* identified ethylene glycol and propanol as economically attractive targets. This analysis assumed an electrolyzer cost of $\text{€}440 \text{ kW}^{-1}$, an energy conversion efficiency of 60 %, FE of 90 %, electricity cost of $\text{€}0.02 \text{ kWh}^{-1}$ (expected to be achievable using renewable sources [12]), and CO_2 capture cost of $\text{€}0.03 \text{ kg}^{-1}$ [11].

Figure 1.4 summarizes several techno-economic analyses reported in the literature, which are unanimous in suggesting that the electrocatalytic conversion of CO_2 to CO and formic acid are the most accessible approaches, representing deployable entry points for the ER CO_2 on an industrial scale [21,57]. Furthermore, considering the market

demand (values of 2018) for ERCO₂ products, the conversion of CO₂ could offset up to 22 % of the 36 GT CO₂ emitted annually. Compared to the 0.1 % reduction of the total global emissions provided by CSS, a commercially available technology, these values show the tremendous potential of the ERCO₂ [21]. Indeed, ERCO₂-based technologies are close to commercialization, with startups and established companies such as Opus-12, Mitsui Chemicals, Carbon Recycling International, Dioxide Materials, and Carbon Electrocatalytic Recycling Toronto taking the lead [11,61]. Moreover, since the electricity cost is the main expense of the ERCO₂ process (*ca.* 58 % of total costs [59]), this technology becomes more attractive as the price of renewable energy continues to decrease, approaching €0.02 kWh⁻¹ [11].

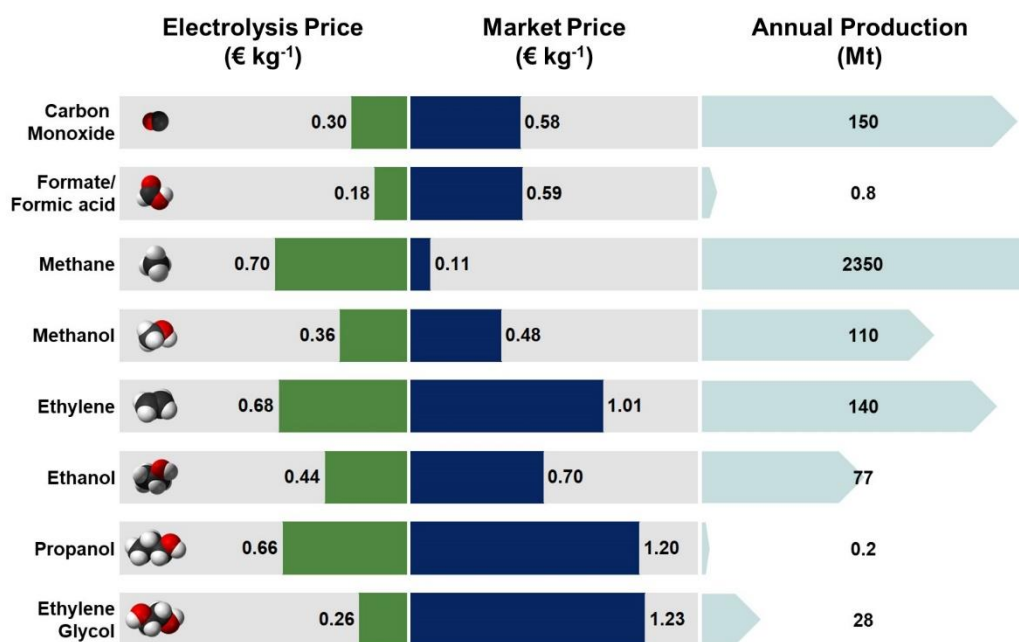


Figure 1.4. Economic analysis of ERCO₂ products. The values shown are an average of several economic studies reported in the literature [11,21,57–59].

On the other hand, the economic studies reported in the literature usually consider current densities as high as 0.2 A cm⁻². However, systems that report commercially relevant values, *i.e.*, FE for target product > 90 %, current density > 200 mA cm⁻², cell

voltage < 1.8 V, and stability > 1000 h are almost inexistent [13,57]. Moreover, ER CO_2 to C_{2+} products face many challenges with an anticipated long timeline for development. In particular, it involves multiple single-step reactions that further exacerbate the sluggish kinetics and lead to high overpotentials [21,57]. Since the catalyst is at the heart of a catalytic reaction, the search for more efficient catalysts must be at the forefront of ER CO_2 development. At the technical design level, further improvement of the electrolyzers is necessary, whose development is still at an early stage and is outside the scope of the present work [57].

1.4 Catalysts for CO_2 reduction

As previously discussed, the ER CO_2 represents one promising approach for reducing anthropogenic CO_2 emissions and developing a sustainable energy system [62–65]. However, the energy conversion and current density of current ER CO_2 systems are limited by the lack of efficient catalysts [63,66]. Therefore, over the past decades, different materials capable of electrochemically reducing CO_2 in aqueous environment have been identified. Unfortunately, none of the reported catalysts is efficient and stable enough for practical use [38,65]. The various materials explored as ER CO_2 catalysts include metals, metal oxides, metal disulfides, carbon-based materials, and molecular catalysts [40]. Among them, the most commonly studied are transition metal elements and their associated compounds, such as metal complexes. These metals have vacant orbitals and active d electrons, which are believed to energetically facilitate the bonding between the metal and CO_2 for adduct formation and, later, the desorption of the reduction products [38].

Between the 80-90s, Hori *et al.* conducted a comprehensive pioneer survey of various metals for CO_2 reduction in aqueous electrolytes (mainly 0.1 M KHCO_3) [67,68]. As a result, the different metals were categorized into four groups based on their product distribution: (i) Cu, the only metal capable of reducing CO_2 to hydrocarbons (or oxygenated hydrocarbons) at significant rates; (ii) Au, Ag, Zn, Pd and Ga, from which

CO is the major product; (iii) Pb, Hg, In, Sn, Cd, Tl, and Bi, primarily producing formate; and, (iv) Ni, Fe, Pt and Ti, where HER is almost exclusively observed [27,66]. The different reduction products are associated with the tendency to bind various reaction intermediates on the metal surface, following the Sabatier principle, **Figure 1.5** [40,69].

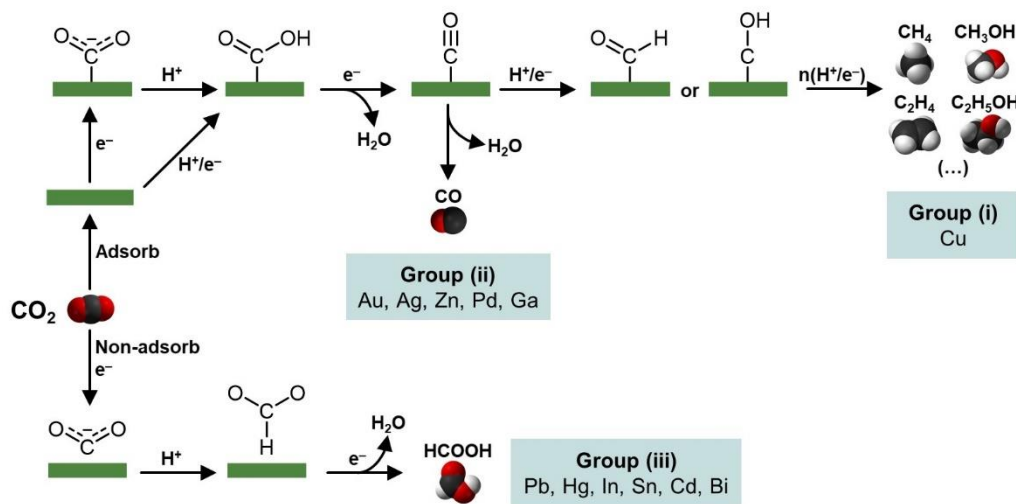


Figure 1.5. Reaction mechanism of ER-CO₂ on metal electrodes in aqueous solutions, according to the work of Hori *et al.* [67]. Adapted from [40,70].

CO₂ reduction ability of the metals in groups (i) and (ii) is attributed to the stabilization of *CO₂⁻ and/or *COOH (* denotes a surface adsorption site) on their surfaces, which are then reduced to *CO. In particular, the obtained *CO intermediate is weakly bound to the surface of metals from group (ii); thus, it readily desorbs from the surface and emerges as the predominant reaction product. Cu is the only metal belonging to group (i), and it has the capacity to bind and convert *CO to higher value-added products through *COH or *CHO intermediates [40,66]. The formate production of group (iii) metals is believed to occur via hydration of non-adsorbing CO₂⁻ since metals in this group can hardly bind the CO₂⁻ intermediate. Group (iv) metals are thought to bind too strongly to the *CO intermediate, preventing its further reduction and thus resulting in H₂ evolution from the interstitial sites among adsorbed CO [27,66]. Another study, performed using 0.05 M KHCO₃ as electrolyte, found that C, Al, Si, V, Cr, Mn, Fe, Co,

Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, and Ir are mostly inactive materials for CO₂ reduction [27]. However, in the cited work, structurally simple catalysts were used (*e.g.*, metal sheet). Later studies highlighted that controlling the catalyst morphology [71–74], crystallite size [75–77], electronic properties [78–80], and/or facet orientation [81] are effective catalyst engineering strategies for improving the ERCO₂ efficiency [30].

1.4.1 Catalyst engineering

Catalyst engineering was identified as an effective strategy to improve the performance of ERCO₂ catalysts. Through catalyst engineering, it is possible to modulate the chemical state, surface structure, atomic arrangements, and electronic properties, thus, creating different/new catalytic active sites [30]. As a result, the CO₂ activation energy can be lowered to enhance the reaction activity, and the binding energy of key reaction intermediates can be tuned to improve the selectivity [35]. Recent developments toward structural engineering of metal-based catalysts, focusing on copper, are discussed below, including particle size, morphology, defects, composition, and facets (**Figure 1.6**).

Size

Particle size is considered one essential criterion in controlling the activity of a catalyst, which leads to several possible effects, mainly related to a significant increase in the surface to bulk atom ratio as the size decreases [43,82]. As the size of a particle decreases, the curvature of its surface becomes larger and the average coordination of the surface atoms is lowered, increasing the population of undercoordinated sites. The higher occurrence of undercoordinated sites results in a perturbed electronic structure, which usually increases the catalyst reactivity [12,82]. Moreover, for transition metals, reducing the coordination number increases the binding energy of intermediate reaction species (*e.g.*, CO) [83,84].

Reske *et al.* studied the influence of Cu particle size and reported that the overall current density dramatically increases for Cu particles below 5 nm. More interestingly, the

particle size strongly impacts the product selectivity; hydrocarbon formation is suppressed for < 5 nm Cu particles while CO and H₂ production is enhanced [75]. According to the authors, a drastic increase in undercoordinated atoms is observed below 5 nm. These strong binding sites accelerate the HER and CO₂ reduction to CO. However, the lower surface mobility of *CO prevents its further reduction, explaining why small particles have low hydrocarbon selectivity and produce more H₂.

Similar conclusions were presented by Jeon *et al.*, who studied the size-dependent activity and selectivity of Zn nanoparticles (NPs). In their work, Zn NPs ranging from 3 nm to 5 nm showed the highest activity and selectivity for CO production, while those larger than 5 nm exhibited bulk-like catalytic properties. Moreover, a drastic increase in H₂ production was observed for particles smaller than 3 nm, which was associated with increased content of undercoordinated sites [85].

Zhu *et al.* studied Au NPs as catalysts. Among monodisperse 4 nm, 6 nm, 8 nm, and 10 nm NPs tested, the 8 nm Au NPs showed maximum efficiency for CO production. The authors found that 8 nm particles were small enough to provide a near-optimum number of edge sites, favoring CO production. On the other hand, the number of corner sites, mainly responsible for H₂ evolution, was minimized [86].

In general, a size-controlling strategy can help design more efficient CO₂ reduction catalysts [82]. However, according to a recent study, small Au NPs are unstable and grow in diameter over time under typical electrolysis conditions [87]. Cu surface segregation and possibly sintering were also observed for CuCo NPs [88]. Thus, additional studies focusing on solving the problem of size-instability are needed [82].

Morphology

The morphology of the catalyst is another crucial parameter that attracted scientific interest [89]. This phenomenon can be explained by the fact that catalysts with specific shapes can predominantly expose their reactive sites and increase the specific surface

area, improving the ER CO_2 performance [43]. Thus, the production of electrodes with nanostructured surfaces is a path for better efficiency and selectivity [49,62].

According to Tang *et al.*, roughened Cu electrodes exhibit better catalytic performance for ER CO_2 than their smooth counterparts due to two different effects: higher current density and improved faradaic selectivity toward hydrocarbons. The increased current density is explained by the higher surface area of the roughened sample, providing more active sites for both CO_2 conversion and hydrogen evolution. In turn, the improvement in selectivity for hydrocarbons is explained by the significantly higher abundance of undercoordinated sites on roughened surfaces, such as steps, edges, and defects, which appear to be more active toward CO_2 reduction [74].

Li and Kanan observed that CO and formic acid production is enhanced for Cu_2O rods compared to polycrystalline Cu. According to the Tafel data, Cu_2O rods facilitate the formation of the $\text{CO}_2^{\cdot-}$ intermediate while suppressing the hydrogen evolution [90]. Polyhedron Cu_2O particles were also identified as a selective material for ethylene and ethanol production. The higher selectivity toward C_2 compounds is attributed to the optimized density of steps and edges in this structure. Moreover, it was demonstrated that the FE for C_2 products can be tuned by varying the thickness of the Cu_2O overlayers [91]. Aside from polyhedron particles, a cubic nanostructure was reported to favor strongly multicarbon product formation, particularly ethylene. The enhanced ethylene production can be associated with increased exposure of the (100) facet of copper and/or higher local pH vs. bulk pH during the reaction [92]. The higher pH near roughened surfaces can be ascribed to the higher OH^- generation rate per geometric electrode area [93]. Sen *et al.* reported that copper foams provide high surface roughness, hierarchical porosity, and confinement of reactive species, resulting in enhanced production of formic acid [94]. The authors, however, did not study how changes in pore diameter and pore depth affect product distribution.

Morphology control can also change the surrounding environment of the catalysts. As previously mentioned, it can impact the local pH. Furthermore, morphology can affect the local electric field. Literature reports that structures with high curvature (*e.g.*, needle-like shapes) produce higher local electric fields, which can concentrate

electrolyte cations like K^+ [95]. In turn, the presence of electrolyte cations results in an increased concentration of CO_2 close to the active surface. Moreover, K^+ helps the stabilization of reaction intermediates as CO_2^* , lowering the thermodynamic barrier for CO_2 activation. As a result, the $ERCO_2$ is promoted, and the competitive HER process is suppressed [96]. For this reason, Cu nanowires (NWs) were recently identified as advanced catalysts for CO_2 [49,62] and CO [97] electroreduction. Especially for $ERCO_2$, this type of catalyst requires an overpotential as low as 300 mV to reach a total current density of -1 mA cm^{-2} and enables the production of CO with high FE [62].

Overall, the ultimate goal of morphology control is to expose more active sites or change the reaction environment around the catalyst to improve the reaction activity [82].

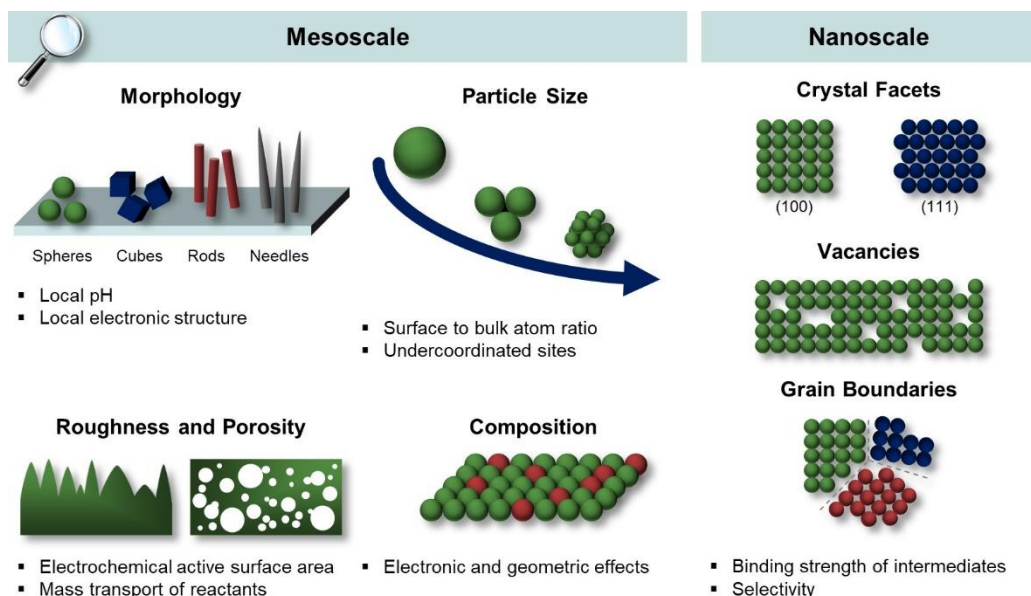


Figure 1.6. Influence of different length scales involved in the performance of $ERCO_2$ catalysts, adapted from [31,57].

Defects

The imperfection of crystals offers the opportunity to tune properties, which otherwise would be determined only by composition and crystal structure. Defects exist widely in

bulk and nanomaterials and can be classified into different types, including pores, vacancies, and grain boundaries [98].

Zhang and co-workers reported that nanodefected Cu nanosheets, with 2-14 nm pore defects, have much higher activity and selectivity toward ethylene production than smooth Cu nanosheets. It was proposed that the defective Cu structure provides more accessible active sites than the smooth counterpart. Furthermore, the nanoscale defects favor the adsorption and confinement of the reaction intermediates and OH^- , which synergistically promote the C–C coupling for ethylene formation [99].

As discussed, the first electron transfer to CO_2 is usually considered the critical step during CO_2 activation. Thus, it is of significant importance the development of approaches to facilitate CO_2 activation. An efficient strategy is the introduction of oxygen vacancies into the catalysts, as proposed by Geng *et al.* [42]. In their work, a mechanistic study revealed that introducing oxygen vacancies into ZnO nanosheets increases the CO_2 binding strength and facilitates CO_2 activation, resulting in enhanced CO production. Following the same trend, Devi *et al.* introduced controlled concentrations of oxygen vacancy defects in $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites for an efficient and selective CO_2 -to-CO conversion. The defect-rich samples have a higher surface area, suggesting the presence of more active sites for CO_2 adsorption. Density functional theory (DFT) calculations revealed that the CO_2 activation barrier decreased as the concentration of defects increased [100].

Kanan and co-workers demonstrated that the grain boundaries on the catalyst surface are highly active sites for ERCO_2 [101,102]. In particular, the authors showed that the CO_2 reduction activity increases with the increased density of grain boundaries, while no direct correlation with the HER activity was observed [102]. DFT simulations on Au NPs revealed that the grain boundary can effectively stabilize key reaction intermediates (*e.g.*, COOH) and thus improve the CO_2 -to-CO conversion efficiency in this type of catalyst [103]. Recently Woldu *et al.* reported a simple method to induce grain boundaries in Au films via O_2 plasma treatment. The grain boundary enrichment resulted in improved ERCO_2 performance and lowered the overpotential [104]. For copper-based catalysts, grain boundary defects were associated with enhanced

selectivity for CO₂ reduction toward multicarbon products, mainly ethylene and ethanol. In this case, *in situ* infrared spectroscopy analysis and DFT simulations revealed that the existence of grain boundaries on metallic copper enhances the adsorption of CO (key reaction intermediate), promoting the C–C coupling reactions and thus hydrocarbons formation [105].

In short, defect control has attracted widespread interest in modulating the catalytic performance of materials since it can create active sites and mass transfer channels. Furthermore, it can change the coordination number, geometric environment, and electronic structures [30].

Composition

Multicomponent systems offer numerous opportunities to precisely modulate the surface chemistry and tune the stabilization degree of key intermediates [43,66]. Accordingly, composition control is widely used to modulate the catalytic performance of catalysts by regulating the element species, element ratio, and chemical state [30]. In particular, the performance of bimetallic systems is primarily determined by two important factors: electronic and geometric effects [80]. Electronic effects refer to changes in the electronic structure of the host material caused by the addition of another element, which alters the binding strength of intermediate adsorbates on the surface according to the *d*-band model [12,106]. Geometric effects refer to a change in the atomic arrangement of active sites, which alters the way adsorbates interact with the surface and each other, allowing the catalyst to deviate from the scaling relation [12,80].

Literature reports that combining other metal elements with Cu significantly improves the ERCO₂ performance of Cu-based catalysts. To date, several elements with intrinsic ERCO₂ activity have been identified as promising candidates, including Au, Ag, Pd, Ga, Sn, Pb, Bi, Zn, Pt, and Ni [30,107]. For instance, Higgins *et al.* studied the ERCO₂ performance of a series of CuAg thin films with controllable compositions, ranging from Cu-rich to Ag-rich phases. As expected, pure Cu catalysts exhibited high activity and selectivity toward the formation of hydrocarbons and alcohols, whereas pure Ag

catalysts favored the generation of CO. In turn, the CuAg thin films showed significantly higher activity and selectivity toward liquid carbonyl products, such as acetaldehyde and acetate. Suppressed activity and selectivity for hydrocarbons and H₂ formation were also demonstrated for CuAg versus Cu, whose degree of suppression increased with increasing nominal Ag composition. The simultaneous inhibition of HER and hydrogenation of oxygenated intermediates is most likely due to a decreased surface binding energy of oxygen-containing and *H species over CuAg surfaces [108].

In addition, incorporating Cu with other metal elements (*e.g.*, Zn and Au) can also change the binding states of *CO species, promoting the formation of C₂ products. Jeon *et al.* found that introducing Zn dopants to Cu can tune the selectivity of the CO₂ reduction toward methane. By adjusting the concentration of Zn, a drastic increase in methane selectivity was achieved for Zn contents from 10 % to 50 % (molar ratio), which was accompanied by a suppression of H₂ production [109]. A two-site mechanism can explain the obtained results. In detail, Cu or Zn sites first reduce CO₂ molecules to CO, and then the weakly adsorbed CO on Zn sites desorbs and migrates to near Cu sites, where CO is further reduced [110]. Interestingly, the authors also reported that when a CuZn alloy is formed, the Cu sites lose the ability to hydrogenate adsorbed CO, favoring CO production. This behavior is due to a decrease in the CO binding strength caused by a shift in the *d*-band center of Cu after forming an alloy [109]. Likewise, Zhang *et al.* demonstrated that CuAu and CuAg catalysts outperform pure Cu in terms of CH₄ selectivity and, at the same time, inhibit the HER activity. DFT calculations support the two-site mechanism previously mentioned by suggesting that the abundant CO produced on the Ag or Au surfaces can migrate to surface Cu. Moreover, through operando spectroscopic observations, the authors demonstrated that CO produced on Ag sites can migrate to stronger binding sites on the catalyst surface for further reduction. Thus, for the first time, the CO spillover phenomenon was experimentally demonstrated [111].

Besides Cu-bimetallic systems, other multicomponent catalysts were proposed. For instance, He *et al.* suggested that combining In, which weakly binds H₂ or CO, with transition metals that show stronger M–CO bonding interaction would suppress HER and promote CO formation. Different M_xIn_{1-x} alloys (M = Fe, Co, Ni, Cu, and Zn) were

tested, and Cu-In exhibited the highest CO production within a broad copper ratio region from 50 % to 80 %. Fe-In, Co-In, and Ni-In also showed high CO production when indium was the main component of the alloy [112]. Toreli *et al.* identified Ni_xGa_y alloys as promising systems to convert CO_2 to C_2 hydrocarbons. Compared to polycrystalline Cu foil, Ni_xGa_y showed lower ER CO_2 onset potential. The authors reported that the interaction of Ni_xGa_y phase with CO is stronger than Cu, which allows the further reduction of chemisorbed CO at low applied potential [113].

Bimetallic materials enable access to catalytic properties that monometallic catalysts cannot replicate. Additionally, it offers the possibility of designing catalysts based solely on earth-abundant elements with high efficiency for CO_2 reduction under mild overpotential, which is typically achieved using precious metals [114].

Facet

Facet control usually refers to tailoring the exposed facets of catalysts, which is also quite effective in modulating the catalytic performance toward various chemical reactions. Typically, the exposed crystal facets of catalysts can be tuned by controlling the nucleation rate or using capping agents, like polyvinylpyrrolidone (PVP) [30].

During the first fundamental studies of CO_2 reduction, Hori *et al.* discovered that the Cu(111) facet favors the CO_2 conversion to methane, while the Cu(100) facet is more selective for ethylene production [115]. Following this initial work, it was gradually accepted that Cu(111) favors the formation of C_1 products (*e.g.*, formate and methane), and Cu(100) promote C_2 compounds (*e.g.*, ethylene). At the same time, other high-index facets, such as Cu(110), facilitate the generation of more complex C_2 products (*e.g.*, acetic acid) [116].

During the growth of nanocrystals, the facets with higher surface energies usually grow more quickly; however, they are unstable and eventually disappear due to the reduction of the total surface energy of crystals [117]. For this reason, Wang *et al.* reported a simple chemical etching procedure to create high-energy facets on Pd@Cu nanocrystals.

Selenium dissolved in tri-*n*-octylphosphine (TOP) served as the oxidant for etching. The etched catalysts with enriched high-energy facets, *i.e.*, Cu(110), showed significantly enhanced activity toward CO₂ reduction. Thus, the authors suggested that forming high-energy facets on the catalyst surface is a promising technique for boosting their catalytic activity. Furthermore, according to cited work, Cu(110) is more stable and selective toward methane, ethylene, ethane, and propane than Cu(100) [118].

In conclusion, tremendous efforts have been made in recent years to develop and improve the performance of metal catalysts for ERCO₂, with various strategies adopted and reported in the literature [89], as summarized in **Table 1.3**. Even so, the search for high-performing catalysts is far from complete [39,119]. The improvement of catalyst design also requires a deep understanding of the reaction mechanism, whose investigation is still inconclusive [40]. In particular, more attention should be placed on elucidating the chemical adsorption/desorption steps, breakage/reconstruction of C=O bonds, rate-determining factors, and competition of reaction pathways [39]. Finally, the combination of experimental results with instrumental characterization should also be used to explore favorable catalyst structures and chemical properties [39,40].

Table 1.3. ER CO_2 efficiency using metal-based catalysts, from selected literature. Results are ordered according to the total current density obtained (reverse order). The current density was noted without a minus sign here.

Catalyst	Applied Potential (V_{RHE})	Electrolyte	Membrane ^a	Main Product(s) ($\eta_{\text{FE}}\%$)	$J_{\text{total}}^{\text{b}}$ (mA cm^{-2})	Stability	Ref./Date
Cu NPs (roughened)	-1.10	0.1 M KClO_4	PEM	C_2H_4 (36 %); CO (35 %); H_2 (30 %)	N/A ^c	15 min	[74]/2012
Cu nanofoam	-0.90	0.1 M KHCO_3	PEM	H_2 (55 %); HCOOH (37 %)	N/A	N/A	[94]/2014
$\text{CuO}/\text{In}_2\text{O}_3$	-0.90	0.5 M KHCO_3	PEM	CO (85 %)	N/A	N/A	[100]/2019
Cu polycrystalline	-0.50	0.5 M NaHCO_3	AEM	H_2 (90 %)	0.45	1-2 h	[90]/2012
Cu NWs	-0.60	0.1 M KHCO_3	PEM	CO (50 %); HCOOH (30 %); H_2 (26 %)	0.6	90 min	[49]/2015
Cu NWs	-0.40	0.1 M KHCO_3	AEM	CO (60 %); H_2 (23 %)	0.7	55 min	[62]/2015
Cu_2O rods	-0.50	0.5 M NaHCO_3	AEM	CO (40 %); HCOO^- (33 %); H_2 (27 %)	1.68	1-2 h	[90]/2012
Au film	-0.65	0.1 M KHCO_3	AEM	CO (89 %)	1.9	160 min	[104]/2021
Pd nanosheets	-0.60	0.1 M KHCO_3	PEM	CO (95 %)	3	8 h	[120]/2018
$\text{Cu}_{75}\text{In}_{25}$	-0.70	0.5 M NaHCO_3	AEM	CO (80 %); H_2 (20 %)	3.5	5 h	[112]/2017
CuZn alloy	-1.10	0.1 M KHCO_3	AEM	H_2 (48 %); C_2H_4 (33 %)	6.1	16 h	[110]/2018
Ag-Cu	-1.10	0.1 M NaHCO_3	PEM	CH_4 (58 %); H_2 (21 %)	8.31	1 h	[111]/2019
Zn (hexagonal NPs)	-0.85	0.5 M KHCO_3	AEM	CO (80 %); H_2 (20 %)	9.5	30 h	[121]/2016

Cu ₂ O film (0.2 µm thick)	-0.99	0.1 M KHCO ₃	AEM	C ₂ H ₄ (33 %); H ₂ (26 %)	14	70 min	[91]/ 2015
Au nanoneedles	-0.35	0.5 M KHCO ₃	PEM	CO (95 %); H ₂ (5 %)	15	8 h	[95]/ 2016
ZnO nanosheets	-1.10	0.1 M KHCO ₃	PEM	CO (83 %); H ₂ (17 %)	16	40 min	[42]/ 2018
Cu NPs/Si	-1.38	0.1 M KHCO ₃	N/M	C ₂ H ₄ (40 %); H ₂ (20 %)	17	65 min	[122]/ 2017
Cu ₂ O film (3.6 µm thick)	-0.99	0.1 M KHCO ₃	AEM	H ₂ (39 %); C ₂ H ₄ (34 %); C ₂ H ₅ OH (16 %)	35	70 min	[91]/ 2015
Cu NPs (<15 nm)	-1.10	0.1 M KHCO ₃	N/M	H ₂ (60 %); CO (25 %)	40	10 min	[75]/ 2014
CuSe	-1.18	[BMIM]PF ₆ - CH ₃ CN-H ₂ O ^d	PEM	CH ₃ OH (78 %); HCOOH (21 %)	42	25 h	[52]/ 2019
Cu ₁₀ Zn ₉₀ (alloy)	-1.35	0.1 M KHCO ₃	AEM	H ₂ (55 %); CO (45 %)	45	N/A	[109]/ 2019
Cu NPs	-1.20	0.1 M KOH	AEM	C ₂ H ₄ (38 %); C ₂ H ₅ OH (32 %)	52	3 h	[105]/ 2020
Cu ₇₀ Zn ₃₀	-1.35	0.1 M KHCO ₃	AEM	CH ₄ (70 %); H ₂ (25 %)	53	N/A	[109]/ 2019
Nanodefected Cu nanosheet	-1.18	0.1 M K ₂ SO ₄	PEM	C ₂ H ₄ (83 %); H ₂ (17 %)	58.8	14 h	[99]/ 2020
Cu with N-doped carbon layer	-0.68	1.0 M KOH	N/M	C ₂ H ₅ OH (52 %); C ₂ H ₄ (38 %)	300	15 h	[123]/ 2020

^a: type of membrane used to separate the cathode and anode compartments, AEM (anion-exchange membrane), PEM (proton-exchange membrane), or N/M when no membrane was used (standard three-electrode cell); ^b: total current density; ^c: N/A, not available;

^d: [BIMM]-PF₆, 1-butyl-3-methylimidazolium hexafluorophosphate.

1.5 ERCO₂ mechanisms on copper surfaces

Since the pioneering work of Hori *et al.* [67,68], copper has been recognized as a unique material for ERCO₂. It is the only pure metal capable of reducing CO₂ to products requiring more than two-electron transfer with significant efficiency [40,66]. At the same time, it has been proven to be highly efficient for CO and formate production (two-electron products) [90,124,125]. As a result, considerable research efforts have been devoted to clarifying the mechanism of the ERCO₂ reaction on copper. However, there is still little agreement after three decades of work, **Figure 1.7** [12].

In general, most of the proposed ERCO₂ mechanisms agree that the limiting step in the generation of 2e⁻ products is the CO₂ adsorption, followed by its reduction to form the first reaction intermediate. However, the chemical identity of this first intermediate and how it is generated remains elusive [124]. Initially, and following the work of Hori *et al.* [67], it was proposed that CO₂ is reduced through one common first intermediate, the carboxylate anion radical (CO₂^{•-}). According to this mechanism, the ERCO₂ initiates with the CO₂ adsorption, forming *CO₂. Then, *CO₂ captures an electron and transfers it to the central carbon atom, bending the linear structure of CO₂ and thus weakening the C=O bond. A new chemical bond between CO₂ and active sites on the catalyst surface is then generated, forming CO₂^{•-}, as indicated by Equation (1.10) [30,31]. Alternatively, a more contemporary model, based on DFT simulations, suggests that the first reaction intermediate is carboxyl (*COOH) or formyloxyl (*OCHO), which is formed via a concerted proton-electron transfer (CPET) step, as shown in Equations (1.11) and (1.12) [31,126].



According to the model proposed by the DFT studies, the distinction between the formate and CO pathways seems to be related to the adsorption configuration of the first

reaction intermediate (through the C or O atom) [12]. Computational studies performed by Nørskov and co-workers demonstrated that $^*\text{COOH}$ is more likely the first intermediate for CO formation, while $^*\text{OCHO}$ was proposed as the key intermediate for formate production [126,127]. Alternatively, Chernyshova *et al.* used operando spectroscopic techniques to provide evidence that the first intermediate for formate and CO production is indeed $^*\text{CO}_2^-$, as initially postulated [124]. According to the authors, this intermediate is coordinated to the catalyst surface through one of its C–O bonds. Furthermore, it was proposed that formate is produced via activation of the Cu–C and C–O bonds, while stabilizing the Cu–O bond results in CO formation. Thus, although different intermediates are suggested, the strength of Cu–C and Cu–O bonds appears to govern the selectivity for CO and formate production [12].

While the formate pathway is considered a dead-end, CO is widely accepted as a key intermediate for the production of higher reduced products ($> 2e^-$) [128]. Beyond CO, the limiting step in C_1 formation is believed to be CO protonation, while CO dimerization is accepted as the rate-determining step in C_2 formation [12,31,128]. Within the C_1 pathway, the selectivity toward methane and methanol is of particular relevance, as methanol is a more valuable product [12]. The first comprehensive investigation of C_1 production on copper was reported by Peterson *et al.*, who proposed that the key step in hydrocarbons formation is the protonation of $^*\text{CO}$ to $^*\text{CHO}$, which is accompanied by cleavage of the C=O bond and generation of C–H bonds [129,130]. Kuhl *et al.* studied the CO_2 reduction to methanol and methane over several transition metals, including copper. The authors observed that the onset potential for both products is closely related, indicating a mechanism in which these products share a common limiting step [131]. According to the work of Cheng *et al.*, $^*\text{CHO}$ is protonated to $^*\text{CH}_2\text{O}$, being this intermediate a possible branch point between methanol ($^*\text{CH}_2\text{O} \rightarrow ^*\text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$) and methane ($^*\text{CH}_2\text{O} \rightarrow ^*\text{CH} \rightarrow ^*\text{CH}_2 \rightarrow ^*\text{CH}_3 \rightarrow \text{CH}_4$) pathways [132]. The oxophilicity of the catalyst surface may play an important role in determining the selectivity between these two products. Methanol production involves the cleavage of only one C–O bond of the CO_2 molecule, while both C–O bonds must be broken to produce methane. Thus,

a strong oxygen binding affinity can favor the break of the second C–O bond, enhancing methane production [131].

While several experimental and theoretical studies suggested that CO dimerization is a critical step in C₂ formation, many aspects are still up for debate [31,133,134]. In particular, it is unclear whether CO coupling is an electrochemical step involving a rate-limiting electron transfer [133] or purely a chemical step not comprising a rate-limiting electron transfer [135]. Moreover, C–C coupling can occur between two adsorbed CO molecules (*CO + *CO) [110,134,135] or an adsorbed and a free CO molecule (*CO + CO) [133,136]. Other studies also suggest the coupling between species such as *CHO and *COH [30,31]. As reported, the key intermediates for C₂ commodities production are formed following dimerization, possibly *OCCO, *OCCHO, and *OCCOH [30]. According to the literature, the *OCCO intermediate is directly generated from the C–C coupling [134], while *OCCHO and *OCCOH can be obtained from a CPET to *OCCO, or by the direct reaction of *CO with *CHO and *COH, respectively [30,134]. Ethylene and ethanol are two typical C₂ products, which can be produced from the same C₂ intermediates but have different energy barriers and preferred formation pathways [30].

The formation of higher-order (C₃₊) hydrocarbons has also been observed on copper, with the maximum FE of 72 % recorded for isopropanol production [137]. Propanol and isopropanol are the most commonly reported C₃ products [137–139], with trace amounts of propionaldehyde, hydroxyacetone, acetone, and allyl alcohol also identified [140]. The elementary steps involved in the formation of these C₃ products have not been thoroughly investigated so far. However, C–C coupling between *CO and *C₂H₄ precursors was proposed as a route for propanol formation [141].

In short, the adsorption state and binding strength of the reaction intermediates determine the splitting of the reaction pathways. Despite significant research efforts, many aspects of the proposed mechanisms remain unclear or even controversial [12,30,31]. The fact is that only a few possible intermediates have been experimentally identified due to current instrument limitations; thus, the complete reaction pathways have yet to be confirmed [29].

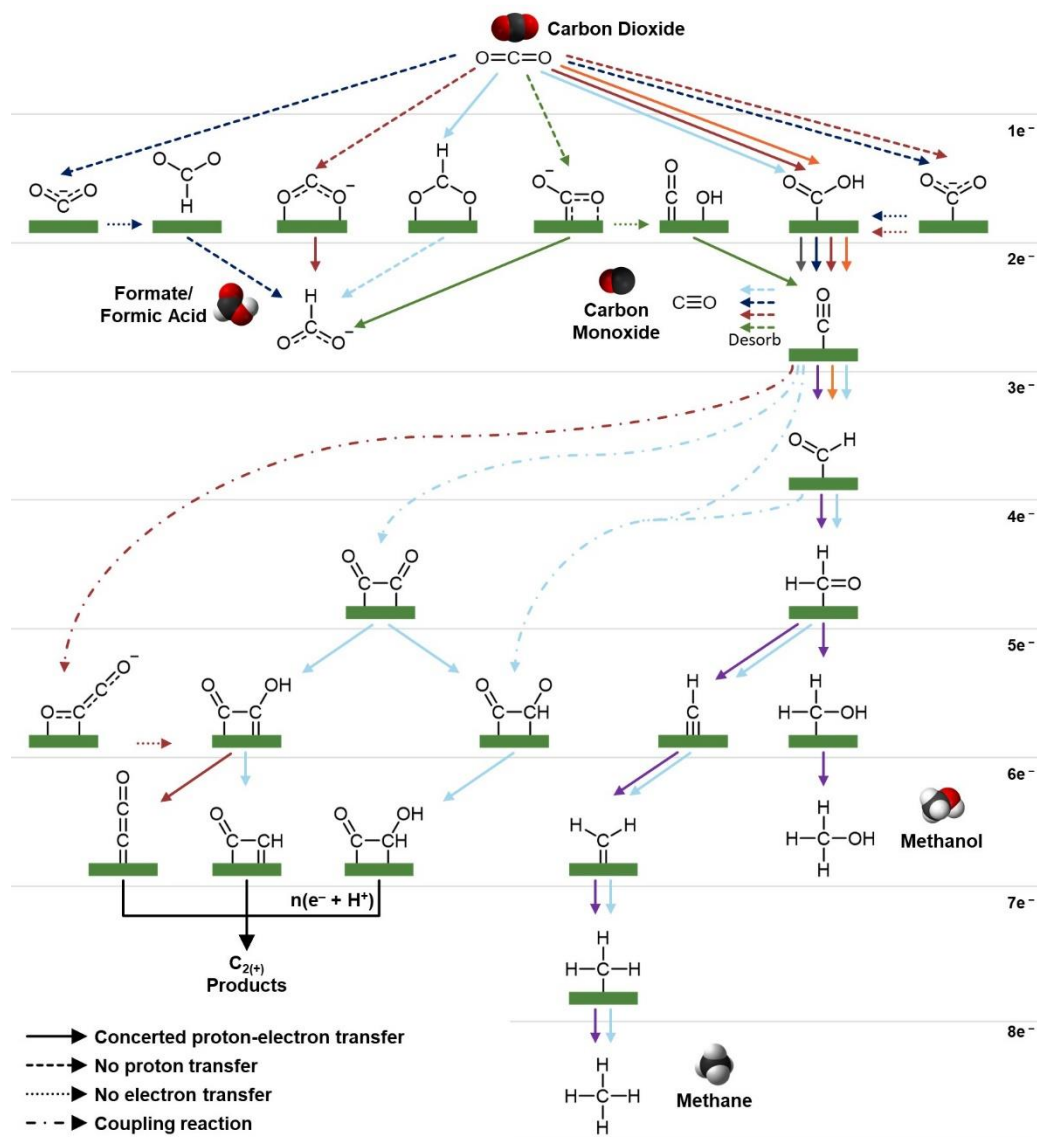


Figure 1.7. Possible ERCo₂ mechanisms on copper-based catalysts, adapted from [12]. The different colors of the arrows identify the various reaction pathways proposed in the literature: — Hori *et al.* [67]; — Peterson *et al.* [129] and Kuhl *et al.* [140]; — Kortlever *et al.* [142]; — Cheng *et al.* [132]; — Feaster *et al.* [126] and Liu *et al.* [143]; and, — Chernyshova *et al.* [124].

1.6 Objectives and outline of this work

The need to reach net-zero CO₂ emissions has prompted the question, "*How can the circular carbon dioxide economy be achieved?*". Inevitably, sustainable CO₂ capture and utilization technologies must be developed to close the carbon cycle. After 4.5 billion years of evolution, nature has shown us that this is the right strategy to handle energy and feedstocks production. In this context, electrochemical technologies for CO₂ conversion are of great importance and can enable the transition to a more sustainable chemical and energy industry.

Despite significant progress, the Achilles' heel of the CO₂ electrochemical reduction remains the poor activity and selectivity of the catalysts. Accordingly, this work aims to contribute to the development of copper-based ERCO₂ catalysts and to provide a detailed structure-activity relationship.

Chapter 1 introduces the ERCO₂. It discusses important aspects of the working principles of ERCO₂ and provides an overview of the main technical barriers to the future commercialization of the technology. Special focus is given to the latest advancements in metal-based catalysts, mainly copper, for selective electrochemical CO₂ conversion to desired valuable products. Moreover, a summary of proposed reaction mechanisms on copper surfaces and potential strategies for improving the ERCO₂ catalysts are presented.

Chapter 2 presents the solvothermal route as a simple and potentially scalable method for producing CuZn oxide catalysts. The influence of the synthesis conditions (*i.e.*, reaction time) on the physicochemical and electrochemical characteristics of the developed materials is explored in this chapter.

Chapter 3 focuses on the influence of several post-synthesis treatments on the ER CO_2 activity of the developed CuZn oxide catalyst (synthesized within 15 h). Furthermore, the synergetic effect between copper and zinc species is addressed.

Chapter 4 studies electrochemical anodization as a synthesis method to produce self-supported copper oxide catalysts (as an alternative to the *traditional* powder catalysts developed in **Chapter 2**). This chapter also explores the influence of catalyst morphology on ER CO_2 activity and presents electrochemical measurements in two different cell designs.

Chapter 5 reports a series of CuBi catalysts prepared using the materials developed in **Chapter 4**. Moreover, the influence of the electrolyte on catalytic performance is addressed, and the nature of the species formed following CO_2 adsorption is studied and correlated with the product selectivity.

Finally, in **Chapter 6**, the main conclusions and future work suggestions are presented.

Nomenclature

Abbreviation	Definition
AEM	Anion-exchange membrane
BECCS	Biomass energy with carbon capture and storage
CCS	Carbon capture and sequestration
CCU	Carbon capture and utilization
CPET	Concerted proton-electron transfer
DAC	Direct air capture
DFT	Density functional theory
e^-	Electron
ECSA	Electrochemical active surface area
EE	Energy efficiency
EOR	Enhanced oil recovery
ERCO ₂	Electrochemical reduction of CO ₂
EU	European Union
FE	Faradaic efficiency
HER	Hydrogen evolution reaction
IPCC	Intergovernmental Panel on Climate Change
N/A	Not available
N/M	No membrane
NPs	Nanoparticles
NWs	Nanowires
OER	Oxygen evolution reaction
PEM	Proton-exchange membrane
PEMFC	Proton-exchange membrane fuel cell
PVP	Polyvinylpyrrolidone
RWGS	Reverse water gas shift
SDG	Sustainable development goals
SOFC	Solid oxide fuel cell
TOP	Tri- <i>n</i> -octylphosphine
UNFCCC	United Nations Framework Convention on Climate Change

Greek Symbol	Definition	Unit
ΔE^0	Difference between the standard potential for OER (anode) and ERCO ₂ (cathode)	V
η	Overpotential	mV
η_{EE}	Energy efficiency	%
η_{FE}	Faradaic efficiency	%

Variable	Definition	Unit
A	Electrode geometric surface area	cm ²
E	Experimental electrochemical potential	V
E^0	Standard redox potential	V
E_{eq}	Equilibrium potential under reaction conditions	V
F	Faraday constant ($F = 96\,485\text{ C mol}^{-1}$)	C mol ⁻¹
J_{total}	Total current density	mA cm ⁻¹
k	Product formation rate	μmol h ⁻¹ cm ⁻²
n	Number of moles of product produced	mol
q	Total charge	C
Q	Reaction quotient	
R	Universal gas constant ($R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$)	J mol ⁻¹ K ⁻¹
t	Duration of each electrochemical test	h
T	Temperature	K
z	Number of electrons exchanged	

References

- [1] H. Yang, X. Wang, Q. Hu, X. Chai, X. Ren, Q. Zhang, J. Liu, C. He, Recent progress in self-supported catalysts for CO₂ electrochemical reduction, *Small Methods*. (2020) 1900826. <https://doi.org/10.1002/smt.201900826>.
- [2] Pro Oxygen, The World's CO₂ Home Page, (2021). <https://www.co2.earth/> (accessed October 25, 2021).
- [3] Intergovernmental Panel on Climate Change, Special report on emissions scenarios, Cambridge University Press, Cambridge, 2020.
- [4] Q. Lu, J. Rosen, Y. Zhou, G.S. Hutchings, Y.C. Kimmel, J.G. Chen, F. Jiao, A selective and efficient electrocatalyst for carbon dioxide reduction, *Nat. Commun.* 5 (2014) 3242. <https://doi.org/10.1038/ncomms4242>.
- [5] D. Kim, S. Lee, J.D. Ocon, B. Jeong, J.K. Lee, J. Lee, Insights into an autonomously formed oxygen-evacuated Cu₂O electrode for the selective production of C₂H₄ from CO₂, *Phys. Chem. Chem. Phys.* 17 (2015) 824–830. <https://doi.org/10.1039/C4CP03172E>.
- [6] X. Xiao, Y. Xu, X. Lv, J. Xie, J. Liu, C. Yu, Electrochemical CO₂ reduction on copper nanoparticles-dispersed carbon aerogels, *J. Colloid Interface Sci.* 545 (2019) 1–7. <https://doi.org/10.1016/j.jcis.2019.03.005>.
- [7] United Nations Framework Convention on Climate Change, Report on the conference of the parties on its 21st session, held in Paris from 30 November to 13 December 2015, Geneva, 2016.
- [8] World Meteorological Organization, State of the global climate 2020: unpacking the indicators, WMO, 2021. <https://public.wmo.int/en/our-mandate/climate/wmo-statement-state-of-globalclimate>
- [9] V. Clement, K.K. Rigaud, A. de Sherbinin, B. Jones, S. Adamo, J. Schewe, N. Sadiq, E. Shabahat, Groundswell part 2: Acting on internal climate migration, World Bank, Washington, DC., 2021. <https://openknowledge.worldbank.org/handle/10986/36248>.

-
- [10] A.A. Khan, M. Tahir, Recent advancements in engineering approach towards design of photo-reactors for selective photocatalytic CO₂ reduction to renewable fuels, *J. CO₂ Util.* 29 (2019) 205–239. <https://doi.org/10.1016/j.jcou.2018.12.008>.
- [11] O.S. Bushuyev, P. De Luna, C.T. Dinh, L. Tao, G. Saur, J. van de Lagemaat, S.O. Kelley, E.H. Sargent, What should we make with CO₂ and how can we make it?, *Joule*. 2 (2018) 825–832. <https://doi.org/10.1016/j.joule.2017.09.003>.
- [12] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E.L. Stephens, K. Chan, C. Hahn, J.K. Nørskov, T.F. Jaramillo, I. Chorkendorff, Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte, *Chem. Rev.* 119 (2019) 7610–7672. <https://doi.org/10.1021/acs.chemrev.8b00705>.
- [13] M.H. Barecka, J.W. Ager, A.A. Lapkin, Carbon neutral manufacturing via on-site CO₂ recycling, *iScience*. 24 (2021) 102514. <https://doi.org/10.1016/j.isci.2021.102514>.
- [14] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T.F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design, *Science* 355 (2017) eaad4998. <https://doi.org/10.1126/science.aad4998>.
- [15] European Commision, COM(2021) Fit for 55: Delivering the EU’s 2030 climate target on the way to climate neutrality, 2021.
- [16] European Commision, COM(2013) A 2030 framework for climate and energy policies, 2013.
- [17] European Commision, COM(2011) A Roadmap for moving to a competitive low carbon economy in 2050, 2011.
- [18] S. Chu, Y. Cui, N. Liu, The path towards sustainable energy, *Nat. Mater.* 16 (2017) 16–22. <https://doi.org/10.1038/nmat4834>.

- [19] L. Fan, C. Xia, F. Yang, J. Wang, H. Wang, Y. Lu, Strategies in catalysts and electrolyzer design for electrochemical CO₂ reduction toward C₂₊ products, *Sci. Adv.* 6 (2020) eaay3111. <https://doi.org/10.1126/sciadv.aay3111>.
- [20] Global CCS Institute, Global status of CCS, Melbourne, 2021.
- [21] R.G. Grim, Z. Huang, M.T. Guarnieri, J.R. Ferrell, L. Tao, J.A. Schaidle, Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO₂ utilization, *Energy Environ. Sci.* 13 (2020) 472–494. <https://doi.org/10.1039/C9EE02410G>.
- [22] I. Ghiat, T. Al-Ansari, A review of carbon capture and utilisation as a CO₂ abatement opportunity within the EWF nexus, *J. CO₂ Util.* 45 (2021) 101432. <https://doi.org/10.1016/j.jcou.2020.101432>.
- [23] R. Bellamy, J. Lezaun, J. Palmer, Perceptions of bioenergy with carbon capture and storage in different policy scenarios, *Nat. Commun.* 10 (2019) 743. <https://doi.org/10.1038/s41467-019-08592-5>.
- [24] S. Haikola, J. Anshelm, A. Hansson, Limits to climate action - Narratives of bioenergy with carbon capture and storage, *Polit. Geogr.* 88 (2021) 102416. <https://doi.org/10.1016/j.polgeo.2021.102416>.
- [25] S. V. Hanssen, V. Daioglou, Z.J.N. Steinmann, J.C. Doelman, D.P. Van Vuuren, M.A.J. Huijbregts, The climate change mitigation potential of bioenergy with carbon capture and storage, *Nat. Clim. Chang.* 10 (2020) 1023–1029. <https://doi.org/10.1038/s41558-020-0885-y>.
- [26] G. Centi, E.A. Quadrelli, S. Perathoner, Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries, *Energy Environ. Sci.* 6 (2013) 1711–1731. <https://doi.org/10.1039/c3ee00056g>.

-
- [27] E. V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazábal, J. Pérez-Ramírez, Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes, *Energy Environ. Sci.* 6 (2013) 3112–3135. <https://doi.org/10.1039/c3ee41272e>.
- [28] J. Zeng, T. Rino, K. Bejtka, M. Castellino, A. Sacco, M.A. Farkhondehfar, A. Chiodoni, F. Drago, C.F. Pirri, Coupled Copper–Zinc Catalysts for electrochemical reduction of carbon dioxide, *ChemSusChem*. 13 (2020) 4128–4139. <https://doi.org/10.1002/cssc.202000971>.
- [29] V.C. Hoang, V.G. Gomes, N. Kornienko, Metal-based nanomaterials for efficient CO₂ electroreduction: Recent advances in mechanism, material design and selectivity, *Nano Energy*. 78 (2020) 105311. <https://doi.org/10.1016/j.nanoen.2020.105311>.
- [30] J. Yu, J. Wang, Y. Ma, J. Zhou, Y. Wang, P. Lu, J. Yin, R. Ye, Z. Zhu, Z. Fan, Recent progresses in electrochemical carbon dioxide reduction on copper-based catalysts toward multicarbon products, *Adv. Funct. Mater.* 31 (2021) 2102151. <https://doi.org/10.1002/adfm.202102151>.
- [31] Y.Y. Birdja, E. Pérez-Gallent, M.C. Figueiredo, A.J. Göttele, F. Calle-Vallejo, M.T.M. Koper, Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels, *Nat. Energy*. 4 (2019) 732–745. <https://doi.org/10.1038/s41560-019-0450-y>.
- [32] J. Pan, H.A. Hansen, T. Vegge, Vanadium oxynitrides as stable catalysts for electrochemical reduction of nitrogen to ammonia: the role of oxygen, *J. Mater. Chem. A*. 8 (2020) 24098–24107. <https://doi.org/10.1039/D0TA08313E>.
- [33] R. Küngas, Review—Electrochemical CO₂ reduction for CO production: comparison of low- and high-temperature electrolysis technologies, *J. Electrochem. Soc.* 167 (2020) 044508. <https://doi.org/10.1149/1945-7111/ab7099>.

- [34] J.-B. Vennekötter, T. Scheuermann, R. Sengpiel, M. Wessling, The electrolyte matters: Stable systems for high rate electrochemical CO₂ reduction, *J. CO₂ Util.* 32 (2019) 202–213. <https://doi.org/10.1016/j.jcou.2019.04.007>.
- [35] D. Gao, R.M. Arán-Ais, H.S. Jeon, B. Roldan Cuenya, Rational catalyst and electrolyte design for CO₂ electroreduction towards multicarbon products, *Nat. Catal.* 2 (2019) 198–210. <https://doi.org/10.1038/s41929-019-0235-5>.
- [36] M.E. Royer, Réduction de l'acide carbonique en acide formique, *Compt. Rend. Acad. Sci.* 70 (1870) 731.
- [37] P.R. Yaashikaa, P. Senthil Kumar, S.J. Varjani, A. Saravanan, A review on photochemical, biochemical and electrochemical transformation of CO₂ into value-added products, *J. CO₂ Util.* 33 (2019) 131–147. <https://doi.org/10.1016/j.jcou.2019.05.017>.
- [38] J. Qiao, Y. Liu, F. Hong, J. Zhang, A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels, *Chem. Soc. Rev.* 43 (2014) 631–675. <https://doi.org/10.1039/C3CS60323G>.
- [39] W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang, Z. Jin, Progress and perspective of electrocatalytic CO₂ reduction for renewable carbonaceous fuels and chemicals, *Adv. Sci.* 5 (2018) 1700275. <https://doi.org/10.1002/advs.201700275>.
- [40] D.D. Zhu, J.L. Liu, S.Z. Qiao, Recent advances in inorganic heterogeneous electrocatalysts for reduction of carbon dioxide, *Adv. Mater.* 28 (2016) 3423–3452. <https://doi.org/10.1002/adma.201504766>.
- [41] C. Wang, M. Cao, X. Jiang, M. Wang, Y. Shen, A catalyst based on copper-cadmium bimetal for electrochemical reduction of CO₂ to CO with high faradaic efficiency, *Electrochim. Acta.* 271 (2018) 544–550. <https://doi.org/10.1016/j.electacta.2018.03.156>.

- [42] Z. Geng, X. Kong, W. Chen, H. Su, Y. Liu, F. Cai, G. Wang, J. Zeng, Oxygen vacancies in ZnO nanosheets enhance CO₂ electrochemical reduction to CO, *Angew. Chem. Int. Ed.* 57 (2018) 6054–6059. <https://doi.org/10.1002/anie.201711255>.
- [43] W. Yang, K. Dastafkan, C. Jia, C. Zhao, Design of electrocatalysts and electrochemical cells for carbon dioxide reduction reactions, *Adv. Mater. Technol.* 3 (2018) 1700377. <https://doi.org/10.1002/admt.201700377>.
- [44] X. Chang, T. Wang, J. Gong, CO₂ photo-reduction: insights into CO₂ activation and reaction on surfaces of photocatalysts, *Energy Environ. Sci.* 9 (2016) 2177–2196. <https://doi.org/10.1039/C6EE00383D>.
- [45] Z. Sun, T. Ma, H. Tao, Q. Fan, B. Han, Fundamentals and challenges of electrochemical CO₂ reduction using two-dimensional materials, *Chem.* 3 (2017) 560–587. <https://doi.org/10.1016/j.chempr.2017.09.009>.
- [46] Q. Li, J. Fu, W. Zhu, Z. Chen, B. Shen, L. Wu, Z. Xi, T. Wang, G. Lu, J. Zhu, S. Sun, Tuning Sn-catalysis for electrochemical reduction of CO₂ to CO via the core/shell Cu/SnO₂ structure, *J. Am. Chem. Soc.* 139 (2017) 4290–4293. <https://doi.org/10.1021/jacs.7b00261>.
- [47] G.O. Larrazábal, A.J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, Solvothermally-prepared Cu₂O electrocatalysts for CO₂ reduction with tunable selectivity by the introduction of p-block elements, *ChemSusChem.* 10 (2017) 1255–1265. <https://doi.org/10.1002/cssc.201601578>.
- [48] E.L. Clark, J. Resasco, A. Landers, J. Lin, L.-T. Chung, A. Walton, C. Hahn, T.F. Jaramillo, A.T. Bell, Standards and protocols for data acquisition and reporting for studies of the electrochemical reduction of carbon dioxide, *ACS Catal.* 8 (2018) 6560–6570. <https://doi.org/10.1021/acscatal.8b01340>.
- [49] M. Ma, K. Djanashvili, W.A. Smith, Selective electrochemical reduction of CO₂ to CO on CuO-derived Cu nanowires, *Phys. Chem. Chem. Phys.* 17 (2015) 20861–20867. <https://doi.org/10.1039/C5CP03559G>.

- [50] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, CO₂ electroreduction to formate: Continuous single-pass operation in a filter-press reactor at high current densities using Bi gas diffusion electrodes, *J. CO₂ Util.* 34 (2019) 12–19. <https://doi.org/10.1016/j.jcou.2019.05.035>.
- [51] A.J. Bard, L.R. Faulkner, *Electrochemical methods: Fundamentals and applications*, 2nd edition, John Wiley & Sons, 2001.
- [52] D. Yang, Q. Zhu, C. Chen, H. Liu, Z. Liu, Z. Zhao, X. Zhang, S. Liu, B. Han, Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts, *Nat. Commun.* 10 (2019) 677. <https://doi.org/10.1038/s41467-019-08653-9>.
- [53] M.L. Pegis, J.A.S. Roberts, D.J. Wasylenko, E.A. Mader, A.M. Appel, J.M. Mayer, Standard reduction potentials for oxygen and carbon dioxide couples in acetonitrile and n,n-dimethylformamide, *Inorg. Chem.* 54 (2015) 11883–11888. <https://doi.org/10.1021/acs.inorgchem.5b02136>.
- [54] M.-J. Cheng, E.L. Clark, H.H. Pham, A.T. Bell, M. Head-Gordon, Quantum mechanical screening of single-atom bimetallic alloys for the selective reduction of CO₂ to C₁ hydrocarbons, *ACS Catal.* 6 (2016) 7769–7777. <https://doi.org/10.1021/acscatal.6b01393>.
- [55] Y. Peng, T. Wu, L. Sun, J.M. V. Nsanzimana, A.C. Fisher, X. Wang, Selective electrochemical reduction of CO₂ to ethylene on nanopores-modified copper electrodes in aqueous solution, *ACS Appl. Mater. Interfaces.* 9 (2017) 32782–32789. <https://doi.org/10.1021/acsami.7b10421>.
- [56] Y. Chen, M.W. Kanan, Tin oxide dependence of the CO₂ reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts, *J. Am. Chem. Soc.* 134 (2012) 1986–1989. <https://doi.org/10.1021/ja2108799>.
- [57] S. Jin, Z. Hao, K. Zhang, Z. Yan, J. Chen, Advances and challenges for the electrochemical reduction of CO₂ to CO: From fundamentals to industrialization, *Angew. Chem. Int. Ed.* 60 (2021) 20627–20648. <https://doi.org/10.1002/anie.202101818>.

- [58] J. Durst, A. Rudnev, A. Dutta, Y. Fu, J. Herranz, V. Kaliginedi, A. Kuzume, A.A. Permyakova, Y. Paratcha, P. Broekmann, T.J. Schmidt, Electrochemical CO₂ reduction – A critical view on fundamentals, materials and applications, *Chimia* 69 (2015) 769–776. <https://doi.org/10.2533/chimia.2015.769>.
- [59] M. Jouny, W. Luc, F. Jiao, General techno-economic analysis of CO₂ electrolysis systems, *Ind. Eng. Chem. Res.* 57 (2018) 2165–2177. <https://doi.org/10.1021/acs.iecr.7b03514>.
- [60] W. Reutemann, H. Kieczka, Formic Acid, in: ULLMANN'S Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2000. https://doi.org/10.1002/14356007.a12_013.
- [61] O.G. Sánchez, Y.Y. Birdja, M. Bulut, J. Vaes, T. Breugelmans, D. Pant, Recent advances in industrial CO₂ electroreduction, *Curr. Opin. Green Sustain. Chem.* 16 (2019) 47–56. <https://doi.org/10.1016/j.cogsc.2019.01.005>.
- [62] D. Raciti, K.J. Livi, C. Wang, Highly dense Cu nanowires for low-overpotential CO₂ reduction, *Nano Lett.* 15 (2015) 6829–6835. <https://doi.org/10.1021/acs.nanolett.5b03298>.
- [63] D. Ren, J. Fong, B.S. Yeo, The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction, *Nat. Commun.* 9 (2018) 925. <https://doi.org/10.1038/s41467-018-03286-w>.
- [64] M. Schreier, F. Héroguel, L. Steier, S. Ahmad, J.S. Luterbacher, M.T. Mayer, J. Luo, M. Grätzel, Solar conversion of CO₂ to CO using earth-abundant electrocatalysts prepared by atomic layer modification of CuO, *Nat. Energy.* 2 (2017) 17087. <https://doi.org/10.1038/nenergy.2017.87>.
- [65] J.-J. Velasco-Vélez, T. Jones, D. Gao, E. Carbonio, R. Arrigo, C.-J. Hsu, Y.-C. Huang, C.-L. Dong, J.-M. Chen, J.-F. Lee, P. Strasser, B. Roldan Cuenya, R. Schlögl, A. Knop-Gericke, C.-H. Chuang, The role of the copper oxidation state in the electrocatalytic reduction of CO₂ into valuable hydrocarbons, *ACS Sustainable Chem. Eng.* 7 (2019) 1485–1492. <https://doi.org/10.1021/acssuschemeng.8b05106>.

- [66] D. Raciti, C. Wang, Recent advances in CO₂ reduction electrocatalysis on copper, *ACS Energy Lett.* 3 (2018) 1545–1556. <https://doi.org/10.1021/acsenrgylett.8b00553>.
- [67] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media, *Electrochim. Acta.* 39 (1994) 1833–1839. [https://doi.org/10.1016/0013-4686\(94\)85172-7](https://doi.org/10.1016/0013-4686(94)85172-7).
- [68] Y. Hori, K. Kikuchi, S. Suzuki, Production of CO and CH₄ in electrochemical reduction of CO₂ at metal electrodes in aqueous hydrogencarbonate solution, *Chem. Lett.* 14 (1985) 1695–1698. <https://doi.org/10.1246/cl.1985.1695>.
- [69] H. Ooka, J. Huang, K.S. Exner, The Sabatier principle in electrocatalysis: Basics, limitations, and extensions, *Front. Energy Res.* 9 (2021). <https://doi.org/10.3389/fenrg.2021.654460>.
- [70] J.-P. Jones, G.K.S. Prakash, G.A. Olah, Electrochemical CO₂ reduction: Recent advances and current trends, *Isr. J. Chem.* 54 (2014) 1451–1466. <https://doi.org/10.1002/ijch.201400081>.
- [71] W. Luo, W. Xie, M. Li, J. Zhang, A. Züttel, 3D hierarchical porous indium catalyst for highly efficient electroreduction of CO₂, *J. Mater. Chem. A.* 7 (2019) 4505–4515. <https://doi.org/10.1039/C8TA11645H>.
- [72] A. Dutta, M. Rahaman, N.C. Luedi, M. Mohos, P. Broekmann, Morphology matters: Tuning the product distribution of CO₂ electroreduction on oxide-derived Cu foam Catalysts, *ACS Catal.* 6 (2016) 3804–3814. <https://doi.org/10.1021/acscatal.6b00770>.
- [73] L. Cao, D. Raciti, C. Li, K.J.T. Livi, P.F. Rottmann, K.J. Hemker, T. Mueller, C. Wang, Mechanistic insights for low-overpotential electroreduction of CO₂ to CO on Copper nanowires, *ACS Catal.* 7 (2017) 8578–8587. <https://doi.org/10.1021/acscatal.7b03107>.

- [74] W. Tang, A.A. Peterson, A.S. Varela, Z.P. Jovanov, L. Bech, W.J. Durand, S. Dahl, J.K. Nørskov, I. Chorkendorff, The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO₂ electroreduction, *Phys. Chem. Chem. Phys.* 14 (2012) 76–81. <https://doi.org/10.1039/C1CP22700A>.
- [75] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, Particle size effects in the catalytic electroreduction of CO₂ on Cu nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 6978–6986. <https://doi.org/10.1021/ja500328k>.
- [76] D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang, X. Bao, Size-dependent electrocatalytic reduction of CO₂ over Pd nanoparticles, *J. Am. Chem. Soc.* 137 (2015) 4288–4291. <https://doi.org/10.1021/jacs.5b00046>.
- [77] H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B.R. Cuenya, Exceptional size-dependent activity enhancement in the electroreduction of CO₂ over Au nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 16473–16476. <https://doi.org/10.1021/ja508879j>.
- [78] M. Valenti, N.P. Prasad, R. Kas, D. Bohra, M. Ma, V. Balasubramanian, L. Chu, S. Gimenez, J. Bisquert, B. Dam, W.A. Smith, Suppressing H₂ evolution and promoting selective CO₂ electroreduction to CO at low overpotentials by alloying Au with Pd, *ACS Catal.* 9 (2019) 3527–3536. <https://doi.org/10.1021/acscatal.8b04604>.
- [79] C. Kim, T. Möller, J. Schmidt, A. Thomas, P. Strasser, Suppression of competing reaction channels by Pb adatom decoration of catalytically active Cu surfaces during CO₂ electroreduction, *ACS Catal.* 9 (2019) 1482–1488. <https://doi.org/10.1021/acscatal.8b02846>.
- [80] D. Kim, J. Resasco, Y. Yu, A.M. Asiri, P. Yang, Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles, *Nat. Commun.* 5 (2014) 4948. <https://doi.org/10.1038/ncomms5948>.

- [81] W. Luo, X. Nie, M.J. Janik, A. Asthagiri, Facet dependence of CO₂ reduction paths on Cu electrodes, *ACS Catal.* 6 (2016) 219–229. <https://doi.org/10.1021/acscatal.5b01967>.
- [82] F.-Y. Gao, R.-C. Bao, M.-R. Gao, S.-H. Yu, Electrochemical CO₂-to-CO conversion: Electrocatalysts, electrolytes, and electrolyzers, *J. Mater. Chem. A.* 8 (2020) 15458–15478. <https://doi.org/10.1039/D0TA03525D>.
- [83] A.A. Peterson, L.C. Grabow, T.P. Brennan, B. Shong, C. Ooi, D.M. Wu, C.W. Li, A. Kushwaha, A.J. Medford, F. Mbuga, L. Li, J.K. Nørskov, Finite-size effects in O and CO adsorption for the late transition metals, *Top. Catal.* 55 (2012) 1276–1282. <https://doi.org/10.1007/s11244-012-9908-x>.
- [84] J. Kleis, J. Greeley, N.A. Romero, V.A. Morozov, H. Falsig, A.H. Larsen, J. Lu, J.J. Mortensen, M. Dulak, K.S. Thygesen, J.K. Nørskov, K.W. Jacobsen, Finite size effects in chemical bonding: from small clusters to solids, *Catal. Letters.* 141 (2011) 1067–1071. <https://doi.org/10.1007/s10562-011-0632-0>.
- [85] H.S. Jeon, I. Sinev, F. Scholten, N.J. Divins, I. Zegkinoglou, L. Pielsticker, B.R. Cuenya, Operando evolution of the structure and oxidation state of size-controlled Zn nanoparticles during CO₂ electroreduction, *J. Am. Chem. Soc.* 140 (2018) 9383–9386. <https://doi.org/10.1021/jacs.8b05258>.
- [86] W. Zhu, R. Michalsky, Ö. Metin, H. Lv, S. Guo, C.J. Wright, X. Sun, A.A. Peterson, S. Sun, Monodisperse Au nanoparticles for selective electrocatalytic reduction of CO₂ to CO, *J. Am. Chem. Soc.* 135 (2013) 16833–16836. <https://doi.org/10.1021/ja409445p>.
- [87] J.A. Trindell, J. Clausmeyer, R.M. Crooks, Size stability and H₂/CO selectivity for Au nanoparticles during electrocatalytic CO₂ reduction, *J. Am. Chem. Soc.* 139 (2017) 16161–16167. <https://doi.org/10.1021/jacs.7b06775>.
- [88] M. Bernal, A. Bagger, F. Scholten, I. Sinev, A. Bergmann, M. Ahmadi, J. Rossmeisl, B.R. Cuenya, CO₂ electroreduction on copper-cobalt nanoparticles: Size and composition effect, *Nano Energy.* 53 (2018) 27–36. <https://doi.org/10.1016/j.nanoen.2018.08.027>.

- [89] Z. Yin, D. Gao, S. Yao, B. Zhao, F. Cai, L. Lin, P. Tang, P. Zhai, G. Wang, D. Ma, X. Bao, Highly selective palladium-copper bimetallic electrocatalysts for the electrochemical reduction of CO₂ to CO, *Nano Energy*. 27 (2016) 35–43. <https://doi.org/10.1016/j.nanoen.2016.06.035>.
- [90] C.W. Li, M.W. Kanan, CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films, *J. Am. Chem. Soc.* 134 (2012) 7231–7234. <https://doi.org/10.1021/ja3010978>.
- [91] D. Ren, Y. Deng, A.D. Handoko, C.S. Chen, S. Malkhandi, B.S. Yeo, Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(I) oxide catalysts, *ACS Catal.* 5 (2015) 2814–2821. <https://doi.org/10.1021/cs502128q>.
- [92] F.S. Roberts, K.P. Kuhl, A. Nilsson, High selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts, *Angew. Chem. Int. Ed.* 54 (2015) 5179–5182. <https://doi.org/10.1002/anie.201412214>.
- [93] K. Jiang, Y. Huang, G. Zeng, F.M. Toma, W.A. Goddard, A.T. Bell, Effects of surface roughness on the electrochemical reduction of CO₂ over Cu, *ACS Energy Lett.* 5 (2020) 1206–1214. <https://doi.org/10.1021/acsenergylett.0c00482>.
- [94] S. Sen, D. Liu, G.T.R. Palmore, Electrochemical reduction of CO₂ at copper nanofoams, *ACS Catal.* 4 (2014) 3091–3095. <https://doi.org/10.1021/cs500522g>.
- [95] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C.T. Dinh, F. Fan, C. Cao, F.P.G. de Arquer, T.S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S.O. Kelley, E.H. Sargent, Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration, *Nature*. 537 (2016) 382–386. <https://doi.org/10.1038/nature19060>.
- [96] J. Resasco, L.D. Chen, E. Clark, C. Tsai, C. Hahn, T.F. Jaramillo, K. Chan, A.T. Bell, Promoter effects of alkali metal cations on the electrochemical reduction of carbon dioxide, *J. Am. Chem. Soc.* 139 (2017) 11277–11287. <https://doi.org/10.1021/jacs.7b06765>.

- [97] D. Raciti, L. Cao, K.J.T. Livi, P.F. Rottmann, X. Tang, C. Li, Z. Hicks, K.H. Bowen, K.J. Hemker, T. Mueller, C. Wang, Low-overpotential electroreduction of carbon monoxide using copper nanowires, *ACS Catal.* 7 (2017) 4467–4472. <https://doi.org/10.1021/acscatal.7b01124>.
- [98] G. Li, G.R. Blake, T.T.M. Palstra, Vacancies in functional materials for clean energy storage and harvesting: The perfect imperfection, *Chem. Soc. Rev.* 46 (2017) 1693–1706. <https://doi.org/10.1039/C6CS00571C>.
- [99] B. Zhang, J. Zhang, M. Hua, Q. Wan, Z. Su, X. Tan, L. Liu, F. Zhang, G. Chen, D. Tan, X. Cheng, B. Han, L. Zheng, G. Mo, Highly electrocatalytic ethylene production from CO₂ on nanodeficient Cu nanosheets, *J. Am. Chem. Soc.* 142 (2020) 13606–13613. <https://doi.org/10.1021/jacs.0c06420>.
- [100] P. Devi, K. Malik, E. Arora, S. Bhattacharya, V. Kalendra, K. V. Lakshmi, A. Verma, J.P. Singh, Selective electrochemical reduction of CO₂ to CO on CuO/In₂O₃ nanocomposites: Role of oxygen vacancies, *Catal. Sci. Technol.* 9 (2019) 5339–5349. <https://doi.org/10.1039/C9CY01396B>.
- [101] X. Feng, K. Jiang, S. Fan, M.W. Kanan, Grain-boundary-dependent CO₂ electroreduction activity, *J. Am. Chem. Soc.* 137 (2015) 4606–4609. <https://doi.org/10.1021/ja5130513>.
- [102] R.G. Mariano, K. McKelvey, H.S. White, M.W. Kanan, Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations, *Science* 358 (2017) 1187–1192. <https://doi.org/10.1126/science.aao3691>.
- [103] K.-S. Kim, W.J. Kim, H.-K. Lim, E.K. Lee, H. Kim, Tuned chemical bonding ability of Au at grain boundaries for enhanced electrochemical CO₂ reduction, *ACS Catal.* 6 (2016) 4443–4448. <https://doi.org/10.1021/acscatal.6b00412>.
- [104] A.R. Woldu, Y. Wang, A.H. Shah, X. Zhang, T. He, Efficient reduction of CO₂ to CO over grain boundary rich gold film reconstructed by O₂ plasma treatment, *Appl. Catal. A Gen.* 625 (2021) 118333. <https://doi.org/10.1016/j.apcata.2021.118333>.

- [105] Z. Chen, T. Wang, B. Liu, D. Cheng, C. Hu, G. Zhang, W. Zhu, H. Wang, Z.-J. Zhao, J. Gong, Grain-boundary-rich copper for efficient solar-driven electrochemical CO₂ reduction to ethylene and ethanol, *J. Am. Chem. Soc.* 142 (2020) 6878–6883. <https://doi.org/10.1021/jacs.0c00971>.
- [106] B. Hammer, J.K. Nørskov, Electronic factors determining the reactivity of metal surfaces, *Surf. Sci.* 343 (1995) 211–220. [https://doi.org/10.1016/0039-6028\(96\)80007-0](https://doi.org/10.1016/0039-6028(96)80007-0).
- [107] L. Ou, W. Long, J. Huang, Y. Chen, J. Jin, Theoretical insight into effect of doping of transition metal M (M = Ni, Pd and Pt) on CO₂ reduction pathways on Cu(111) and understanding of origin of electrocatalytic activity, *RSC Adv.* 7 (2017) 11938–11950. <https://doi.org/10.1039/C6RA28815D>.
- [108] D. Higgins, A.T. Landers, Y. Ji, S. Nitopi, C.G. Morales-Guio, L. Wang, K. Chan, C. Hahn, T.F. Jaramillo, Guiding electrochemical carbon dioxide reduction toward carbonyls using copper silver thin films with interphase miscibility, *ACS Energy Lett.* 3 (2018) 2947–2955. <https://doi.org/10.1021/acsenergylett.8b01736>.
- [109] H.S. Jeon, J. Timoshenko, F. Scholten, I. Sinev, A. Herzog, F.T. Haase, B. Roldan Cuenya, Operando insight into the correlation between the structure and composition of CuZn nanoparticles and their selectivity for the electrochemical CO₂ reduction, *J. Am. Chem. Soc.* 141 (2019) 19879–19887. <https://doi.org/10.1021/jacs.9b10709>.
- [110] Y. Feng, Z. Li, H. Liu, C. Dong, J. Wang, S.A. Kulinich, X. Du, Laser-prepared CuZn alloy catalyst for selective electrochemical reduction of CO₂ to ethylene, *Langmuir*. 34 (2018) 13544–13549. <https://doi.org/10.1021/acs.langmuir.8b02837>.
- [111] H. Zhang, X. Chang, J.G. Chen, W.A. Goddard, B. Xu, M.-J. Cheng, Q. Lu, Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane, *Nat. Commun.* 10 (2019) 3340. <https://doi.org/10.1038/s41467-019-11292-9>.

- [112] J. He, K.E. Dettelbach, D.A. Salvatore, T. Li, C.P. Berlinguette, High-throughput synthesis of mixed-metal electrocatalysts for CO₂ reduction, *Angew. Chem. Int. Ed.* 56 (2017) 6068–6072. <https://doi.org/10.1002/anie.201612038>.
- [113] D.A. Torelli, S.A. Francis, J.C. Crompton, A. Javier, J.R. Thompson, B.S. Brunschwig, M.P. Soriaga, N.S. Lewis, Nickel–gallium-catalyzed electrochemical reduction of CO₂ to highly reduced products at low overpotentials, *ACS Catal.* 6 (2016) 2100–2104. <https://doi.org/10.1021/acscatal.5b02888>.
- [114] W. Zhu, B.M. Tackett, J.G. Chen, F. Jiao, Bimetallic electrocatalysts for CO₂ reduction, *Top. Curr. Chem.* 376 (2018) 41. <https://doi.org/10.1007/s41061-018-0220-5>.
- [115] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Adsorption of CO accompanied with simultaneous charge transfer on copper single crystal electrodes related with electrochemical reduction of CO₂ to hydrocarbons, *Surf. Sci.* 335 (1995) 258–263. [https://doi.org/10.1016/0039-6028\(95\)00441-6](https://doi.org/10.1016/0039-6028(95)00441-6).
- [116] M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper, *J. Electroanal. Chem.* 594 (2006) 1–19. <https://doi.org/10.1016/j.jelechem.2006.05.013>.
- [117] G. Liu, J.C. Yu, G.Q. (Max) Lu, H.-M. Cheng, Crystal facet engineering of semiconductor photocatalysts: Motivations, advances and unique properties, *Chem. Commun.* 47 (2011) 6763–6783. <https://doi.org/10.1039/c1cc10665a>.
- [118] Z. Wang, G. Yang, Z. Zhang, M. Jin, Y. Yin, Selectivity on etching: creation of high-energy facets on copper nanocrystals for CO₂ electrochemical reduction, *ACS Nano.* 10 (2016) 4559–4564. <https://doi.org/10.1021/acsnano.6b00602>.
- [119] D. Gao, F. Scholten, B. Roldan Cuenya, Improved CO₂ electroreduction performance on plasma-activated Cu catalysts via electrolyte design: Halide effect, *ACS Catal.* 7 (2017) 5112–5120. <https://doi.org/10.1021/acscatal.7b01416>.

- [120] W. Zhu, L. Zhang, P. Yang, C. Hu, Z. Luo, X. Chang, Z. Zhao, J. Gong, Low-coordinated edge sites on ultrathin palladium nanosheets boost carbon dioxide electroreduction performance, *Angew. Chem. Int. Ed.* 57 (2018) 11544–11548. <https://doi.org/10.1002/anie.201806432>.
- [121] D.H. Won, H. Shin, J. Koh, J. Chung, H.S. Lee, H. Kim, S.I. Woo, Highly efficient, selective, and stable CO₂ electroreduction on a hexagonal Zn catalyst, *Angew. Chem. Int. Ed.* 55 (2016) 9297–9300. <https://doi.org/10.1002/anie.201602888>.
- [122] M. Padilla, O. Baturina, J.P. Gordon, K. Artyushkova, P. Atanassov, A. Serov, Selective CO₂ electroreduction to C₂H₄ on porous Cu films synthesized by sacrificial support method, *J. CO₂ Util.* 19 (2017) 137–145. <https://doi.org/10.1016/j.jcou.2017.03.006>.
- [123] X. Wang, Z. Wang, F.P. García de Arquer, C.-T. Dinh, A. Ozden, Y.C. Li, D.-H. Nam, J. Li, Y.-S. Liu, J. Wicks, Z. Chen, M. Chi, B. Chen, Y. Wang, J. Tam, J.Y. Howe, A. Proppe, P. Todorović, F. Li, T.-T. Zhuang, C.M. Gabardo, A.R. Kirmani, C. McCallum, S.-F. Hung, Y. Lum, M. Luo, Y. Min, A. Xu, C.P. O'Brien, B. Stephen, B. Sun, A.H. Ip, L.J. Richter, S.O. Kelley, D. Sinton, E.H. Sargent, Efficient electrically powered CO₂-to-ethanol via suppression of deoxygenation, *Nat. Energy*. 5 (2020) 478–486. <https://doi.org/10.1038/s41560-020-0607-8>.
- [124] I. V. Chernyshova, P. Somasundaran, S. Ponnuram, On the origin of the elusive first intermediate of CO₂ electroreduction, *PNAS* 115 (2018) E9261–E9270. <https://doi.org/10.1073/pnas.1802256115>.
- [125] R. Kas, K.K. Hummadi, R. Kortlever, P. de Wit, A. Milbrat, M.W.J. Luiten-Olieman, N.E. Benes, M.T.M. Koper, G. Mul, Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction, *Nat. Commun.* 7 (2016) 10748. <https://doi.org/10.1038/ncomms10748>.

- [126] J.T. Feaster, C. Shi, E.R. Cave, T. Hatsukade, D.N. Abram, K.P. Kuhl, C. Hahn, J.K. Nørskov, T.F. Jaramillo, Understanding selectivity for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide on metal electrodes, *ACS Catal.* **7** (2017) 4822–4827. <https://doi.org/10.1021/acscatal.7b00687>.
- [127] J.S. Yoo, R. Christensen, T. Vegge, J.K. Nørskov, F. Studt, Theoretical insight into the trends that guide the electrochemical reduction of carbon dioxide to formic acid, *ChemSusChem.* **9** (2016) 358–363. <https://doi.org/10.1002/cssc.201501197>.
- [128] X. Zhi, A. Vasileff, Y. Zheng, Y. Jiao, S.-Z. Qiao, Role of oxygen-bound reaction intermediates in selective electrochemical CO₂ reduction, *Energy Environ. Sci.* **14** (2021) 3912–3930. <https://doi.org/10.1039/D1EE00740H>.
- [129] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels, *Energy Environ. Sci.* **3** (2010) 1311–1315. <https://doi.org/10.1039/c0ee00071j>.
- [130] A.A. Peterson, J.K. Nørskov, Activity Descriptors for CO₂ Electroreduction to methane on transition-metal catalysts, *J. Phys. Chem. Lett.* **3** (2012) 251–258. <https://doi.org/10.1021/jz201461p>.
- [131] K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, T.F. Jaramillo, Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces, *J. Am. Chem. Soc.* **136** (2014) 14107–14113. <https://doi.org/10.1021/ja505791r>.
- [132] T. Cheng, H. Xiao, W.A. Goddard, Free-energy barriers and reaction mechanisms for the electrochemical reduction of CO on the Cu(100) surface, including multiple layers of explicit solvent at pH 0, *J. Phys. Chem. Lett.* **6** (2015) 4767–4773. <https://doi.org/10.1021/acs.jpcclett.5b02247>.
- [133] F. Calle-Vallejo, M.T.M. Koper, Theoretical considerations on the electroreduction of CO to C₂ species on Cu(100) electrodes, *Angew. Chem. Int. Ed.* **52** (2013) 7282–7285. <https://doi.org/10.1002/anie.201301470>.

- [134] J.H. Montoya, C. Shi, K. Chan, J.K. Nørskov, Theoretical insights into a CO dimerization mechanism in CO₂ electroreduction, *J. Phys. Chem. Lett.* 6 (2015) 2032–2037. <https://doi.org/10.1021/acs.jpcclett.5b00722>.
- [135] L. Wang, S.A. Nitopi, E. Bertheussen, M. Orazov, C.G. Morales-Guio, X. Liu, D.C. Higgins, K. Chan, J.K. Nørskov, C. Hahn, T.F. Jaramillo, Electrochemical carbon monoxide reduction on polycrystalline copper: effects of potential, pressure, and pH on selectivity toward multicarbon and oxygenated products, *ACS Catal.* 8 (2018) 7445–7454. <https://doi.org/10.1021/acscatal.8b01200>.
- [136] A.J. Garza, A.T. Bell, M. Head-Gordon, Mechanism of CO₂ reduction at copper surfaces: Pathways to C₂ products, *ACS Catal.* 8 (2018) 1490–1499. <https://doi.org/10.1021/acscatal.7b03477>.
- [137] A. V. Rayer, E. Reid, A. Kataria, I. Luz, S.J. Thompson, M. Lail, J. Zhou, M. Soukri, Electrochemical carbon dioxide reduction to isopropanol using novel carbonized copper metal organic framework derived electrodes, *J. CO₂ Util.* 39 (2020) 101159. <https://doi.org/10.1016/j.jcou.2020.101159>.
- [138] M. Rahaman, K. Kiran, I.Z. Montiel, V. Grozovski, A. Dutta, P. Broekmann, Selective n-propanol formation from CO₂ over degradation-resistant activated PdCu alloy foam electrocatalysts, *Green Chem.* 22 (2020) 6497–6509. <https://doi.org/10.1039/D0GC01636E>.
- [139] T.-T. Zhuang, Y. Pang, Z.-Q. Liang, Z. Wang, Y. Li, C.-S. Tan, J. Li, C.T. Dinh, P. De Luna, P.-L. Hsieh, T. Burdyny, H.-H. Li, M. Liu, Y. Wang, F. Li, A. Proppe, A. Johnston, D.-H. Nam, Z.-Y. Wu, Y.-R. Zheng, A.H. Ip, H. Tan, L.-J. Chen, S.-H. Yu, S.O. Kelley, D. Sinton, E.H. Sargent, Copper nanocavities confine intermediates for efficient electrosynthesis of C₃ alcohol fuels from carbon monoxide, *Nat. Catal.* 1 (2018) 946–951. <https://doi.org/10.1038/s41929-018-0168-4>.
- [140] K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces, *Energy Environ. Sci.* 5 (2012) 7050–7059. <https://doi.org/10.1039/c2ee21234j>.

- [141] D. Ren, N.T. Wong, A.D. Handoko, Y. Huang, B.S. Yeo, Mechanistic insights into the enhanced activity and stability of agglomerated Cu nanocrystals for the electrochemical reduction of carbon dioxide to n-propanol, *J. Phys. Chem. Lett.* 7 (2016) 20–24. <https://doi.org/10.1021/acs.jpcllett.5b02554>.
- [142] R. Kortlever, J. Shen, K.J.P. Schouten, F. Calle-Vallejo, M.T.M. Koper, Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide, *J. Phys. Chem. Lett.* 6 (2015) 4073–4082. <https://doi.org/10.1021/acs.jpcllett.5b01559>.
- [143] X. Liu, P. Schlexer, J. Xiao, Y. Ji, L. Wang, R.B. Sandberg, M. Tang, K.S. Brown, H. Peng, S. Ringe, C. Hahn, T.F. Jaramillo, J.K. Nørskov, K. Chan, pH effects on the electrochemical reduction of CO₂ towards C₂ products on stepped copper, *Nat. Commun.* 10 (2019) 32. <https://doi.org/10.1038/s41467-018-07970-9>.

CHAPTER 2

Influence of Synthesis Time on the Properties
of Bimetallic CuZn Oxide Catalysts for CO₂
Electrochemical Reduction

Adapted from the article

Azenha, C., Pereira, A., Mateos-Pedrero, C., Mendes, A., “Influence of synthesis time on the properties of bimetallic CuZn oxide catalysts for CO₂ electrochemical reduction”, submitted to Journal of CO₂ Utilization, February 2022.

Influence of Synthesis Time on the Properties of Bimetallic CuZn Oxide Catalysts for CO₂ Electrochemical Reduction

2.1 Abstract

A bimetallic CuZn oxide catalyst was synthesized by a simple one-pot solvothermal method, considering different reaction times (5 h, 15 h, and 25 h). By changing the synthesis time, it was possible to control several physicochemical properties, including particle size, morphology, and strength of Cu-Zn interaction. Furthermore, the influence of different properties on the electrochemical reduction of CO₂ (ERCO₂) was evaluated, and a remarkable effect on product distribution was observed. Namely, the number of ERCO₂ products decreased with the increasing duration of the synthesis. For catalysts with a synthesis time of 5 h, a mixture of CO, ethanol, methanol, and isopropanol was obtained, while only CO and ethanol were detected after 25 h of synthesis. The distinct electrocatalytic behavior is assigned to the binding affinity of the reaction intermediates, which controls the product distribution of ERCO₂, and strongly depends on the catalyst properties, especially the strength of Cu-Zn interaction.

Keywords: CO₂ valorization; CO₂ electroreduction; copper-zinc; synthesis time; product distribution.

2.2 Introduction

The excessive CO₂ emissions caused by the combustion of fossil fuels have been the primary trigger of climate change, already accounting for an increase in the global average temperature of 1.0 °C above pre-industrial levels [1,2]. Despite the goal set by the 2015 Paris Agreement (*i.e.*, limit global warming to an increase of 1.5 °C), recent projections suggest that the world is still heading for a 3.2 °C global temperature rise by 2100 [3,4], demanding urgent and aggressive actions. Rising global temperature has contributed to more frequent and severe extreme weather events, fueling other potential worldwide crises, like climate change displacement [2,3]. According to current indicators, up to 216 million climate migrants are expected by 2050 [3].

Technologies for the direct CO₂ conversion to valuable products, not requiring hydrogen sources, are of particular interest for the transition to a more sustainable economy [5]. Among emerging technologies, CO₂ electrochemical reduction (ERCO₂) is projected to be the first to reach the necessary technological readiness level [5–7]. However, some challenges need to be overcome. CO₂ is a fully oxidized, thermodynamically stable molecule with two linear double bonds, displaying ultralow reactivity [6,8]. Thus, a considerable amount of energy is required to overcome the thermodynamic barrier for CO₂ activation, resulting in sluggish kinetics and low energy efficiency [9]. Additionally, the ERCO₂ reaction is intrinsically complex given the multiple possible reaction pathways and end products. Hence, selectivity is another critical challenge for the design and operation of the ERCO₂ process [10]. The practical implementation of this technology requires then the development of catalysts with high activity and selectivity [9,11]. Despite great research efforts, a catalyst that meets the required selectivity at industrial relevant CO₂ conversion rates has not yet been reported [5].

Copper is unique among the materials explored as ERCO₂ catalysts. It is the only pure metal capable of reducing CO₂ to products requiring more than two electron transfers, with considerable faradaic efficiency (*i.e.*, hydrocarbons, aldehydes, and alcohols) [8]. In addition, Cu-based catalysts have proved to be highly efficient for CO and formate production (two-electron products) [12–14]. In general, the 2e[−] transfer products can be

produced with low overpotential and high faradaic efficiencies. However, substantially higher overpotentials and lower efficiencies are observed for multi-electron transfer products [15]. Despite the lack of consensus, most of the proposed ER CO_2 mechanisms agree that CO_2 adsorption, followed by its reduction to the first reaction intermediate, is the limiting step in the generation of $2e^-$ products [8,15]. The distinction between formate and CO pathways seems to be related to the adsorption configuration of this first reaction intermediate (through the C or O atom) [8]. While the formate pathway is considered a dead-end, CO is widely accepted as a key intermediate for the production of higher reduced products ($> 2e^-$) [10]. Beyond CO, the limiting step in C_1 formation is believed to be CO protonation, while CO dimerization is accepted as the rate-determining step in C_2 formation [8,10,15].

Recently, catalyst engineering was identified as an effective strategy to improve the ER CO_2 performance of Cu-based catalysts. Catalyst engineering allows the modulation of chemical state, surface structure, atomic arrangements, and electronic properties, creating different/new catalytic active sites [11]. As a result, the CO_2 activation energy is lowered to enhance the reaction activity, and the binding energy of key reaction intermediates can be tuned to improve the selectivity [16]. Typical methods of catalyst engineering include the control of the composition [17], morphology [18,19], crystal phase [20], and defects [21,22]. Meanwhile, the chemical growth of bulk or nanometer-sized materials inevitably involves the process of precipitation of a solid phase from a solution. Thus, a good understanding of the process and parameters controlling the precipitation (*e.g.*, reaction time, temperature, concentration) helps to improve the engineering of the final material to the desired characteristics [23].

This chapter provides a detailed analysis of the influence of the synthesis time on the physicochemical properties of bimetallic CuZn oxide catalysts produced by a one-pot solvothermal route. Moreover, the ER CO_2 activity of the developed catalysts was assessed, considering different synthesis stages, and correlated with their physicochemical characteristics. This work contributes to the fundamental understanding of the synthesis mechanism and the structure-activity relationship, and it is expected to assist in the design of more efficient ER CO_2 catalysts.

2.3 Experimental

2.3.1 Catalyst synthesis

Bimetallic CuZn oxide catalysts were prepared from the reduction of Cu(II) and Zn(II) precursors by a one-pot solvothermal method adapted from the literature [24], **Figure 2.1**. All reagents were used without any pre-treatment. For a target Cu:Zn atomic ratio of 1.54, the appropriated amount of $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ (6.07 mmol, Sigma-Aldrich, $\geq 99.0\%$) and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (3.93 mmol, Alfa Aesar, $\geq 97\%$) was dissolved in ethylene glycol (100 mL, Sigma-Aldrich, 99.8 %) under vigorous stirring. After forming a homogeneous solution, the mixture was transferred to a 200 mL Teflon autoclave. The sealed autoclave was heated at $140\text{ }^\circ\text{C}$ for 5 h, 15 h, or 25 h and then allowed to cool down to room temperature. The obtained precipitate was collected by centrifugation, washed several times with ultrapure water ($18.2\text{ M}\Omega\text{ cm}^{-1}$ at $25\text{ }^\circ\text{C}$, Millipore Milli-Q system), and dried overnight at $80\text{ }^\circ\text{C}$ in a vacuum oven. Monometallic Cu and Zn control samples were also produced following the same protocol.

The catalysts were labeled according to the synthesis duration, using the following nomenclature, CuZn_X, where X represents the synthesis time (5 h, 15 h, or 25 h).

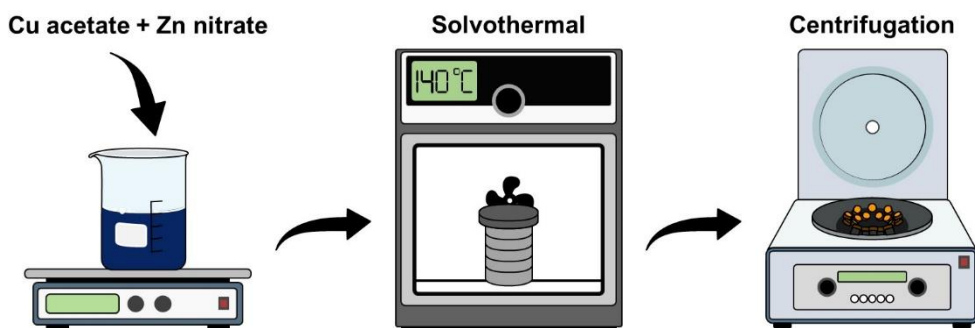


Figure 2.1. Synthesis of bimetallic CuZn oxide catalysts.

2.3.2 Electrode preparation

Electrodes were prepared by spraying a catalyst ink on a gas diffusion layer (GDL), according to a method reported in the literature [24]. Catalysts inks were prepared by

mixing 25 mg of the respective catalyst powder, 25 μL of Nafion dispersion (5 wt. % in water and 1-propanol, Alfa Aesar), 2.5 mL of ultrapure water (Millipore Milli-Q system), and 2.5 mL of 2-propanol (VWR Chemicals, $\geq 99.9\%$). The suspension was ultra-sonicated for 30 min and then sprayed with an airbrush on the microporous layer of a GDL (Sigracet 35BC, SGL Group, 6 cm^2 area), which had been placed on a hot plate at a temperature of 100 $^{\circ}\text{C}$. It is important to note that the catalyst inks were prepared considering 50 % weight loss during the airbrushing process. Thus, a catalyst loading of 2 mg cm^{-2} was typically obtained. This value was verified by weighting the GDL before and after deposition. Before the electrochemical characterization, the electrodes were prepared by cutting the GDL into 1 cm^2 squares.

2.3.3 Material characterization

The morphology and element distribution were obtained by high-resolution scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, JEOL JSM 6301F/Oxford INCA Energy 350).

The crystal structure was studied using X-ray diffraction (XRD, PANalytical X'Pert Pro) operating in Bragg-Brentano focusing geometry and using Cu $K\alpha$ radiation at wavelengths Cu $K\alpha 1 = 1.5406 \text{ \AA}$ and Cu $K\alpha 2 = 1.54443 \text{ \AA}$. Data was collected at 2θ angles (20-100 $^{\circ}$), with a step size of 0.017 $^{\circ}$, and the Rietveld refinement was applied for phase identification. The Debye-Scherrer equation was used to determine the average crystallite size (nm) – Equation (2.1).

$$d = \frac{K \lambda}{\beta \cos \theta} \quad (2.1)$$

In this equation, K represents the crystallite-shape factor, λ is the wavelength of the X-ray beam used, β denotes the full width at half maximum (FWHM), and θ is the Bragg angle. The average particle size was estimated assuming that all particles have the same spherical shape and size, so K was 0.9.

X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra HAS) was used to analyze the surface element composition. Vision and CasaXPS software were used for data acquisition and analysis, respectively. The analysis was carried out with a monochromatic Al K α X-ray source (1486.6 eV), operating at 15 kV (90 W), in fixed analyzer transmission (FAT) mode, with a pass energy of 40 eV for regions and 80 eV for survey. Data acquisition was performed with a pressure lower than 1.0×10^{-6} Pa, using a charge neutralization system. Binding energies (BE) were calibrated based on the C 1s line at 285 eV from adventitious carbon. The spectra were modelled using Shirley-type background subtraction and peak fitting with Gaussian-Lorentzian peak shape, following literature recommendation [25–27].

The reducibility of the catalysts was studied by H₂ temperature-programmed reduction (H₂-TPR, ChemBET Pulsar TPR/TPD). In a typical TPR experiment, approximately 25 mg of sample was placed in a U-shaped quartz reactor and held by quartz wool. Samples were pretreated at 120 °C for 30 min under He flow. After the samples cooled to 50 °C, a flow of 20 % H₂/Ar (20 mL min⁻¹) was pulsed, and samples were heated from 50 °C to 600 °C. The hydrogen consumption was measured by a thermal conductivity detector (TCD).

The CO adsorption was studied by CO temperature-programmed desorption (CO-TPD, ChemBET Pulsar TPR/TPD). Samples were pretreated at 120 °C for 30 min under He flow. After the samples cooled to 50 °C, a flow of 10 % CO/He (20 mL min⁻¹) was continuously pulsed for 1 h at 50 °C. Afterward, the CO desorption was monitored by TCD between 50 °C and 750 °C under He flow (20 mL min⁻¹).

The surface area of the catalysts was determined using the multi-point Brunauer-Emmett-Teller method (BET, Quantachrome Autosorb AS-1) at -196 °C. Before the analysis, the samples were outgassed in vacuum at 80 °C overnight. The pore size distribution was calculated by the Barret-Joyner-Halenda (BJH) method, using the nitrogen desorption branch of the isotherm.

The work function (WF) of the developed catalysts was determined using an ultra-high vacuum Kelvin Probe (KP Technology, Series 10) at ambient conditions.

2.3.4 Electrochemical measurements

Electrochemical measurements were performed at room temperature and atmospheric pressure in a conventional three-electrode electrochemical cell, **Figure 2.2**. The working electrode was the prepared CuZn electrodes with a geometric area of 1 cm^2 . A carbon rod and an Ag/AgCl/Sat. KCl electrode served as the counter electrode and the reference electrode, respectively. The electrolyte used was 150 mL of an aqueous solution of 0.1 M KHCO_3 (Alfa Aesar, 99.95% trace metals basis), prepared with ultrapure water (Millipore Milli-Q system). Otherwise specified, all potentials in this study are in the RHE scale; thus, the applied potentials measured against Ag/AgCl were converted using the following relation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{ pH} + 0.197$.

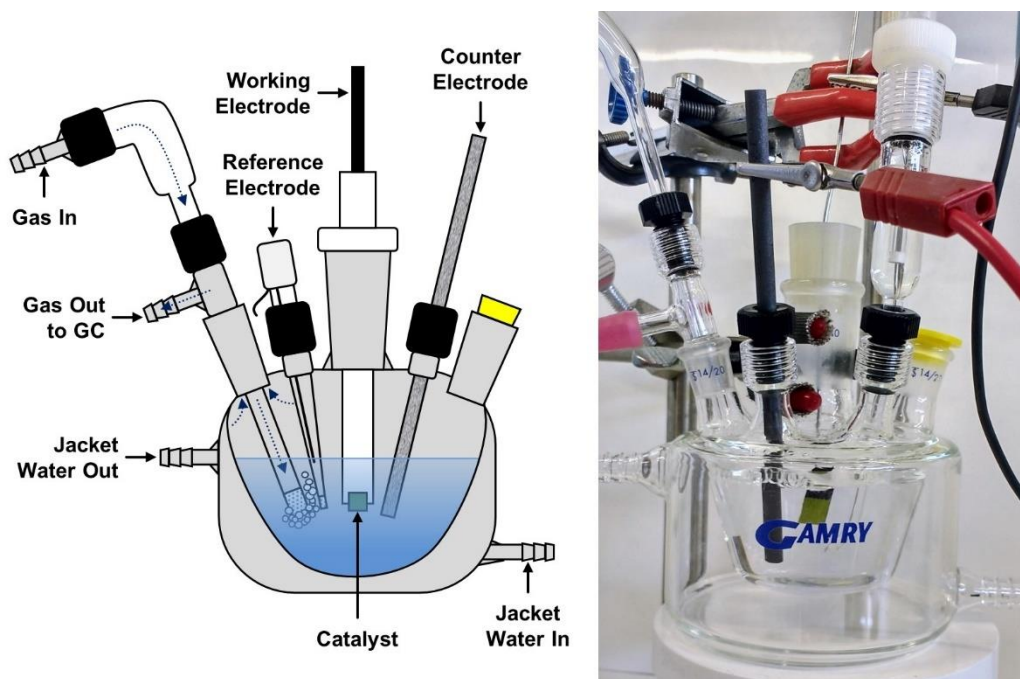


Figure 2.2. Conventional three-electrode electrochemical cell.

Linear sweep voltammetry (LSV), with a scan rate of 20 mV s^{-1} , was carried out using an IM6ex electrochemical workstation (Zahner) in N_2 or CO_2 -saturated electrolyte (the electrolyte was purged with N_2 or CO_2 for 30 min before the measurements and a

blanketing atmosphere was kept during the reads). The potential was swept from $-0.1 \text{ V}_{\text{Ag/AgCl}}$ to $-1.8 \text{ V}_{\text{Ag/AgCl}}$, and the current density was recorded. The results presented consider the average of six scans.

Double-layer capacitance measurements were used to estimate the electrochemical active surface area (ECSA) of the electrodes. Cyclic voltammograms (CV) were acquired in N_2 -saturated 0.1 M KHCO_3 at multiple scan rates ($5 \text{ mV s}^{-1} - 100 \text{ mV s}^{-1}$), considering a non-faradaic region of the voltammogram. The slope of the non-faradaic current density vs. scan rate provided the capacitance value.

The electrochemical oxidation/reduction behavior of the CuZn catalysts in the working electrolyte was studied by cyclic voltammetry. CV curves were recorded with a scan rate of 50 mV s^{-1} between $-1.0 \text{ V}_{\text{Ag/AgCl}}$ and $1.2 \text{ V}_{\text{Ag/AgCl}}$, in N_2 -purged electrolyte.

2.3.5 CO_2 electrochemical reduction and product analysis

Electrolysis experiments were performed under atmospheric conditions using the three-electrode electrochemical cell previously described, **Figure 2.3**. The electrolyte was a solution of 0.1 M KHCO_3 saturated with CO_2 . For each potential tested, the experiments lasted 90 min and were performed using fresh electrodes and electrolytes.

Gas-phase products generated during CO_2 electrolysis were analyzed by gas chromatography (GC, GC-2010 Plus, Shimadzu), using He as the carrier gas. The GC was equipped with a barrier ionization discharge detector and two columns, Pora-Plot Q (Agilent) and HP-Molesieve (Agilent). GC runs were initiated 20 min after starting the electrolysis and subsequently performed every 15 min. Only the third to the seventh GC measurements were used in the data analysis to ensure that the reported data refers to steady-state conditions.

Liquid products were collected at the end of the electrolysis and analyzed by headspace-GC (Nexis GC-2030, Shimadzu) equipped with a TRB-624 column (Teknokroma), using He as the carrier gas. All measurements were recorded in duplicate to ensure reproducibility.

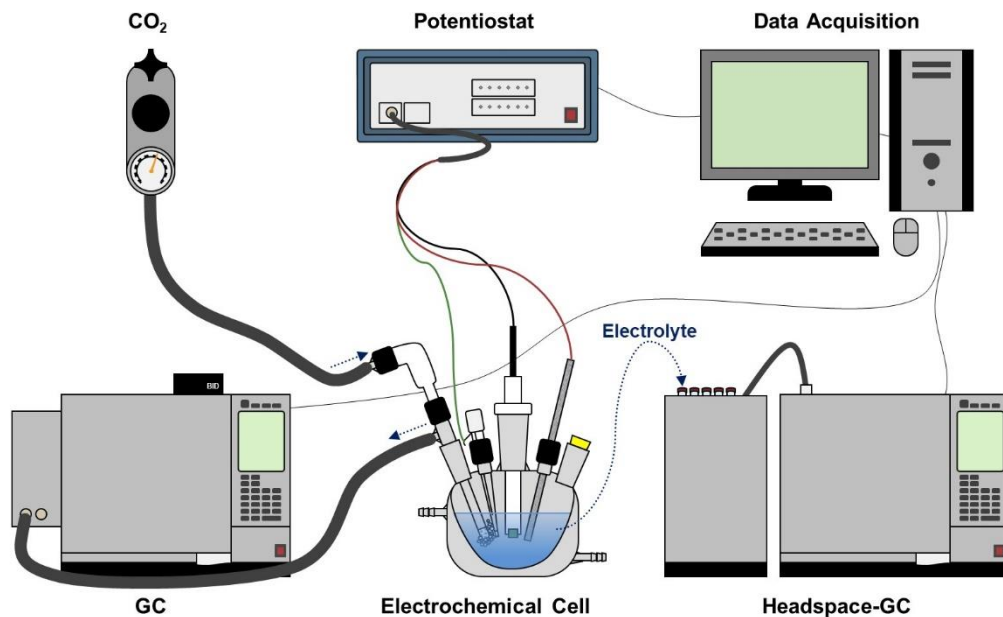


Figure 2.3. Experimental set-up for the ER CO_2 tests.

The faradaic efficiency (FE), product formation rate, and overpotential were calculated according to Equations (1.5), (1.6), and (1.7), respectively. The overpotential for CO production was determined considering an equilibrium potential under reaction conditions (E_{eq}) of $-0.59 \pm 0.01 \text{ V}_{\text{RHE}}$ (vs. $E^0 = -0.52 \text{ V}_{\text{RHE}}$), which was calculated according to Equation (1.8).

2.4 Results and discussion

2.4.1 Physicochemical properties of the developed catalysts

The morphology and microstructure of the prepared catalysts were examined by SEM-EDS, **Figure 2.4** and Appendix A. According to the obtained micrographs, CuZn_5 is mainly an amorphous material with some cauliflower-like structures observed (typical of ZnO). On the other hand, a higher degree of heterogeneity is observed for

CuZn_15, which exhibits some spherical particles. EDS analysis suggests that these particles are composed of a copper-rich core coated with a mixed copper-zinc oxide (Figure A.2, Appendix A). CuZn_25 shows a well-defined hollow spherical structure with two shells. The outer shell presents a smooth surface and is mainly made of copper and zinc oxide, while the inner shell shows a granular structure formed by small copper granules (Figure A.3, Appendix A). The average particle size was determined to be *ca.* 10 μm .

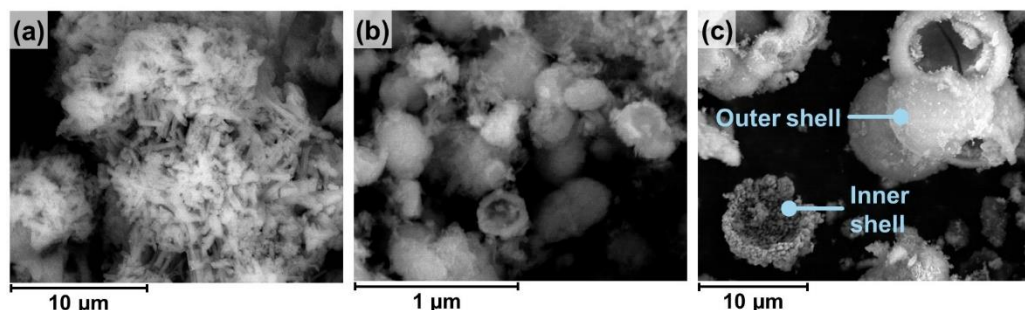


Figure 2.4. SEM images of (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.

XRD was used to evaluate the crystal structure of the prepared CuZn catalysts, **Figure 2.5**. The XRD pattern of CuZn_5 shows only a few broad peaks of low intensity, indicating that this sample is mostly amorphous, in good agreement with SEM results. Notwithstanding, diffraction peaks at 2θ values of 31.8° (100), 34.4° (002), and 36.3° (101) indicate the formation of ZnO with wurtzite structure. Additional peaks at 23.9° (021), 39.4° (130), and 53.3° (132) denote the presence of the $\text{Cu}(\text{OH})_2$ phase.

For sample CuZn_15, intense diffraction lines are observed at 36.3° (111) and 42.4° (200), ascribed to Cu_2O with cuprite structure. Once again, the main diffraction lines of the ZnO phase are present; however, with higher intensity when compared to CuZn_5, indicating higher crystallinity. Accordingly, the ZnO crystallite size was estimated to be *ca.* 9.1 nm and 17.2 nm for CuZn_5 and CuZn_15, respectively (**Table 2.1**). CuZn_15 presents only a residual amount of $\text{Cu}(\text{OH})_2$, suggesting that the major fraction of crystalline Cu^{2+} was reduced to Cu^+ . The presence of ethylene glycol, which acts as a reducing agent, can explain the observed copper reduction. The diffraction pattern of

CuZn_25 indicates that Cu_2O and ZnO phases are still present after 25 h of synthesis. However, this sample shows two new sets of diffraction lines: the first ascribed to metallic Cu at 43.3° (111) and 50.4° (200), and the second to a CuZn intermetallic compound at 25.5° (101), 42.1° (110), and 50.4° (113). Therefore, the results indicate that longer syntheses increase the degree of interaction between copper and zinc and promote the reduction of copper oxide species formed during the initial stages to metallic copper.

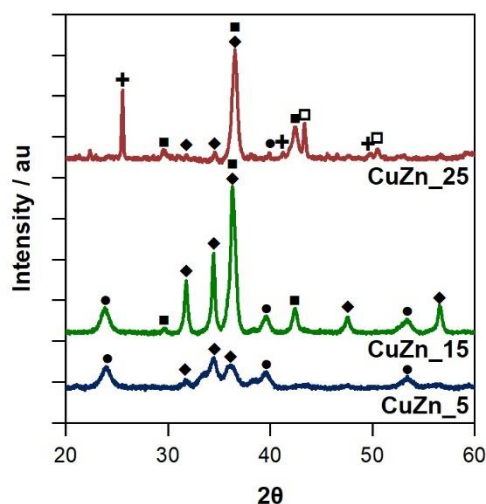


Figure 2.5. XRD pattern of the developed catalysts. ■ Cu_2O (JCPDS card no. 05-0667), □ Cu^0 (JCPDS card no. 04-0836), ● $\text{Cu}(\text{OH})_2$ (JCPDS card no. 80-0656), ◆ ZnO (JCPDS card no. 36-1451), and + CuZn (JCPDS card no. 26-0571).

The textural properties of the developed catalysts were studied by N_2 physisorption technique (**Figure 2.6**, **Table 2.2**). According to the IUPAC classification, all catalysts present type IV isotherms with type H2 hysteresis, typical of materials with mesoporous structures and pores with an ink-bottle shape [28]. Results also indicate that the specific surface area (S_{BET}) decreased with the increasing synthesis time, which is explained by the increase in the degree of crystallization and particle size. All samples present a polymodal pore size distribution; however, CuZn_5 and CuZn_25 are dominated by small-diameter pores (*ca.* 4 nm) while CuZn_15 presents larger pores (*ca.* 15 nm),

Figure 2.6b. Thus, the higher pore volume recorded for CuZn_15 is related to their larger pore size. In turn, the lower S_{BET} , compared to CuZn_5, suggests that CuZn_15 presents a lower number of pores. Undoubtedly, these results indicate that the textural properties of the catalysts are influenced by the synthesis conditions, namely the synthesis time.

Table 2.1. Average crystallite size estimated from XRD data using the Scherrer equation.

Sample	Mean crystallite size (nm)				
	Cu^0	Cu_2O	$\text{Cu}(\text{OH})_2$	ZnO	CuZn
CuZn_5h	--	--	7.7 ± 0.9	9.1 ± 1.1	--
CuZn_15h	--	13.7 ± 3.0	8.0 ± 0.3	17.2 ± 5.0	--
CuZn_25h	44.8 ± 7.0	14.6 ± 3.0	--	18.7 ± 5.0	52.4 ± 3.0

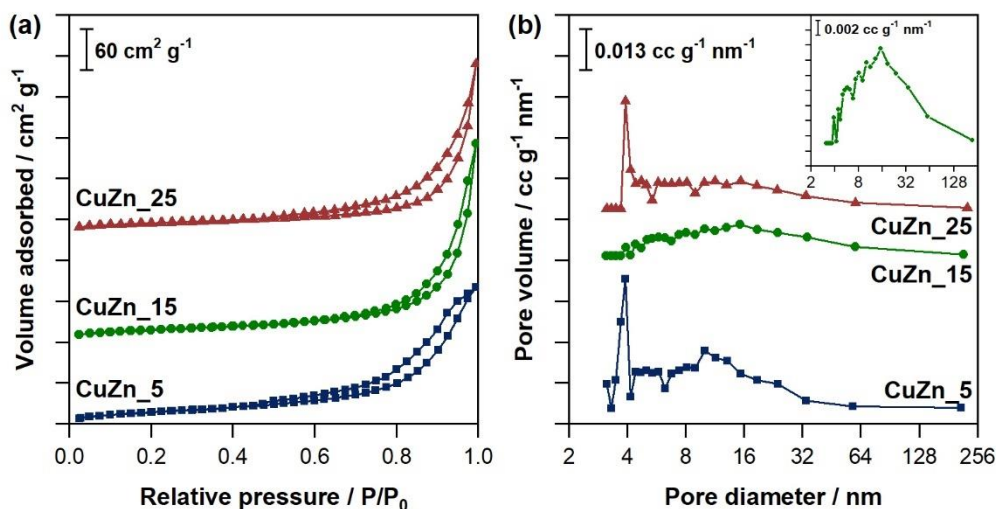


Figure 2.6. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of CuZn_5, CuZn_15, and CuZn_25.

Interestingly, the double-layer capacitance of the electrodes produced with the CuZn catalysts (**Table 2.2**) is not in line with the S_{BET} (**Figure 2.7**), as previously reported by other authors [29]. On the other hand, **Figure 2.7** shows a correlation between pore volume and the double-layer capacitance, suggesting that porosity is a critical parameter that affects the properties of the electrodes.

Table 2.2. Textural and electrical properties of the developed catalysts.

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_{pore} (cc g^{-1})	Cu:Zn at. ratio ^a	C_{dl} ^b (mF cm^{-2})
CuZn_5	66.8	0.33	1.50	2.36
CuZn_15	54.4	0.45	1.69	5.04
CuZn_25	43.4	0.40	1.70	3.80

^a: atomic ratio according to SEM-EDX results obtained for the electrodes prepared with the CuZn catalysts (Figure A.4, Appendix A); ^b: double-layer capacitance.

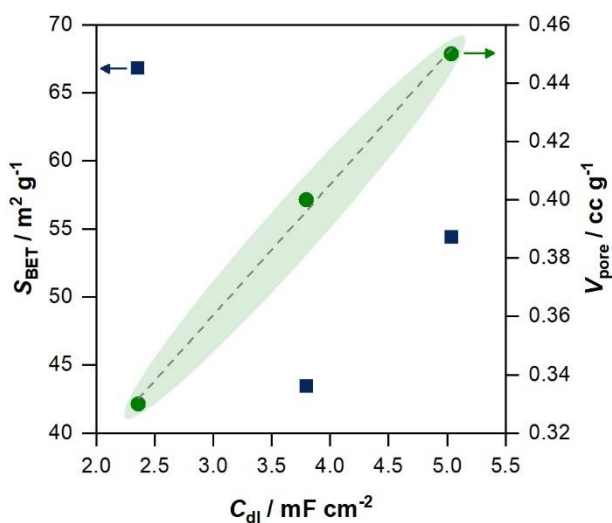


Figure 2.7. Correlation between the BET-specific surface area and pore volume with the double-layer capacitance of the electrodes.

The reducibility of the catalysts was studied by H₂-TPR, **Figure 2.8a**. Since no reduction signal was observed at *ca.* 500 °C (ZnO reduction region [30], **Figure 2.8b**), all recorded peaks are attributed to the reduction of copper species.

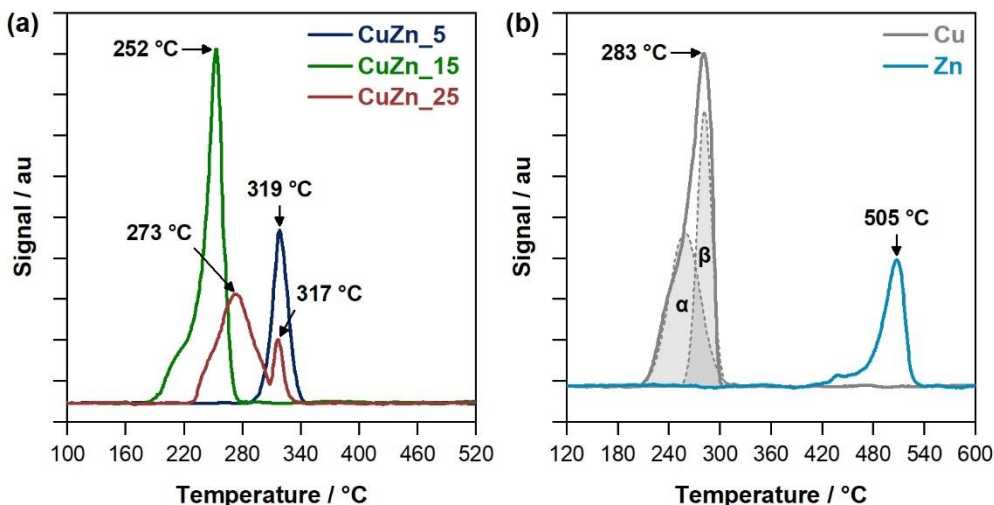


Figure 2.8. (a) H₂-TPR profile of CuZn_5, CuZn_15 and CuZn_25. (b) H₂-TPR profile of Cu and Zn single element catalysts synthesized according to the same procedure used to prepare the CuZn bimetallic catalysts within 15 h of synthesis. TPR profile indicates that the reduction of copper and zinc species occurs at 283 °C and 505 °C, respectively. Moreover, the H₂ consumption peak of the copper sample can be deconvoluted into two Gaussian peaks centered at *ca.* 259 °C (α) and 282 °C (β). These double peaks have been previously assigned to a stepwise reduction of surface dispersed CuO species from Cu²⁺ to Cu⁺ (α), closely followed by the reduction of Cu⁺ to Cu⁰ (β) [31].

CuZn_15 sample displays a narrow and intense reduction peak, indicative of copper particles with homogenous size. Moreover, hydrogen consumption occurred at a considerably lower temperature than that reported for bulk Cu₂O reduction (above 350 °C) [32]. This behavior can be explained by the smaller particle size of the synthesized catalysts and higher surface area compared to bulk Cu₂O (*ca.* 0.10 m² g⁻¹), which exposes more Cu⁺ species. Moreover, literature reports that copper reducibility

can be enhanced by the interaction with ZnO [33]. Thus, the recorded peak at 252 °C is attributed to the reduction of small Cu^+ particles in intimate contact with ZnO. TPR profile of CuZn_25 shows two reduction features, suggesting the presence of two distinct copper species. The low-temperature peak (273 °C) is attributed to the reduction of Cu^+ in strong interaction with ZnO, as observed for CuZn_15. According to SEM results, these particles are part of the outer shell of the catalyst structure. The higher reduction temperature compared to CuZn_15 can be related to the larger particle size of CuZn_25. On the other hand, the high-temperature reduction peak (317 °C) is ascribed to the reduction of isolated Cu^+ from the copper inner shell. For the CuZn_5 sample, only one narrow reduction peak is observed at 319 °C associated with the reduction of mainly amorphous Cu^{2+} , which behaves as bulk-CuO [32].

The surface composition and electronic structure of the developed CuZn catalysts were examined by XPS, **Figure 2.9**. For all samples, the peak-fit of the Cu $2p_{3/2}$ region shows two photoelectron peaks at *ca.* 934.5 eV and *ca.* 932.3 eV, **Figure 2.9a**. According to the literature, the high BE peak (934.5 eV) is ascribed to $\text{Cu}(\text{OH})_2$ [27], suggesting that some $\text{Cu}(\text{OH})_2$ impurities are present on the catalyst surface, even after 25 h of synthesis. It should be noted that XRD indicated that $\text{Cu}(\text{OH})_2$ is formed during the early stages of the solvothermal synthesis and later reduced to Cu^+ and Cu^0 species, being absent in the bulk structure of CuZn_25. Notwithstanding, XPS also indicates that the amount of surface Cu^{2+} decreases with increasing synthesis time, from 42.7 % after 5 h of synthesis to 21.7 % after 25 h (**Table 2.3**). The low BE peak (932.6 eV) can be attributed to Cu^+ and/or Cu^0 . Literature reports statistically similar BE values for metal Cu and most Cu^+ species [34]. Thus, the modified Auger parameter and the Auger peak shape provide a more accurate assignment for these species [26,27]. A modified Auger parameter of 1848.7 eV was obtained for all samples (**Table 2.3**), consistent with literature values for Cu_2O (1849 ± 0.6 eV) [35].

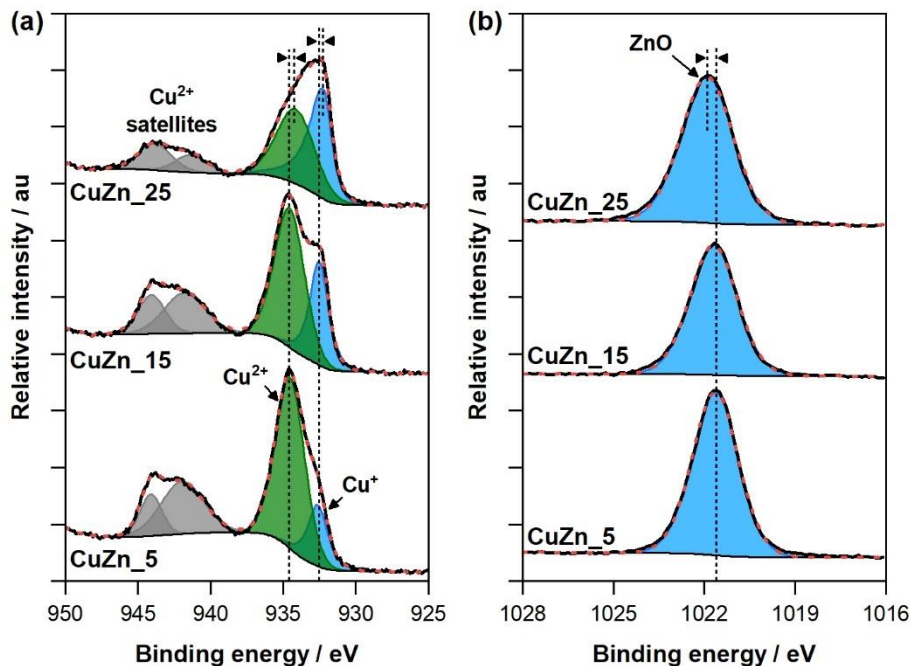


Figure 2.9. (a) Cu 2p_{3/2} and (b) Zn 2p_{3/2} XPS spectra of the CuZn catalysts.

Table 2.3. Zn 2p_{3/2}, Cu 2p_{3/2}, Cu and Zn LMM, and modified Auger parameter values for the developed CuZn catalysts. Curve-fitting parameters.

Sample	Compound	BE ^a (eV)	FWHM ^b (eV)	Peak shape	KE ^c (eV)	FWHM (eV)	Peak shape	α' (eV)	At. % ^d
CuZn_5	Cu ₂ O	932.6	1.58	GL(80)	916.1	3.62	GL(70)	1848.7	6.8
	Cu(OH) ₂	934.5	2.35	GL(30)	916.1	3.62	GL(70)	1850.7	42.7
	ZnO	1021.6	1.78	GL(30)	987.6	2.71	GL(30)	2009.2	59.5
CuZn_15	Cu ₂ O	932.6	1.50	GL(80)	916.1	3.77	GL(70)	1848.7	11.4
	Cu(OH) ₂	934.5	2.43	GL(30)	916.1	3.77	GL(70)	1850.6	42.2
	ZnO	1021.6	1.83	GL(30)	987.2	2.92	GL(30)	2009.2	46.5
CuZn_25	Cu ₂ O	932.3	1.29	GL(80)	916.4	3.26	GL(70)	1848.7	20.3
	Cu(OH) ₂	934.2	2.84	GL(30)	916.4	3.26	GL(70)	1850.5	21.7
	ZnO	1021.9	2.03	GL(30)	987.2	2.90	GL(30)	2009.2	58.0

^a: binding energy; ^b: full width at half maximum; ^c: kinetic energy; α' : modified Auger parameter;

^d: calculated according to Cu 2p_{3/2} and Zn 2p_{3/2}.

XPS also indicates that CuZn_5 has a negligible amount of Cu_2O (6.8 %), though this value increases with the increasing synthesis time, reaching 20.3 % for CuZn_25. Therefore, this result suggests that Cu_2O is not formed during the initial synthesis stage; instead, it results from the reduction of Cu^{2+} species (in agreement with XRD). On the other hand, the Zn $2p_{3/2}$ region, **Figure 2.9b**, presents only one peak at *ca.* 1021.6 eV with a modified Auger parameter of 2009.2 eV, indicating the presence of ZnO [25,26]. **Figure 2.9** and **Table 2.3** also evidence a positive shift of 0.3 eV in the Zn $2p_{3/2}$ region of CuZn_25, while the equivalent down-shift was observed in the Cu $2p_{3/2}$ region. These deviations are attributed to the charge transfer during the formation of the CuZn intermetallic compound (XRD results), where copper acts as an electron acceptor [36,37].

As mentioned earlier, catalysts were synthesized through a simple and potentially scalable one-pot solvothermal route. This method exploits the solubility of an inorganic substance (*e.g.*, copper and zinc acetate) in an appropriate solvent (*e.g.*, ethylene glycol) at elevated temperature and pressure and, subsequent crystallization of the dissolved material from the fluid [23]. Moreover, this method offers an easy way to tailor the properties of the obtained nanomaterials by simply changing different reaction parameters, including reaction time, temperature, reaction medium, and pressure. For instance, Yan *et al.* reported that the morphology of ceria nanoparticles can be controlled by tuning the reaction time without the assistance of surfactants or templates [38], dismissing the use of complex purification techniques. As suggested by the characterization results, in this work, the reaction time also has a remarkable effect on the properties of the developed catalysts.

Based on the above results, it is proposed that during the first stage of the solvothermal process, $\text{Cu}(\text{OH})_2$ and ZnO start to nucleate and precipitate, mainly as an amorphous material, following the growth mechanism proposed by other authors [39–41]. Later, after forming the first structures, the initial crystals start to agglomerate to minimize their surface energy, resulting in particle growth. Moreover, it was observed that at this point, core-shell type microspheres are produced with a copper-rich core and a mixed copper-zinc oxide shell. $\text{Cu}(\text{OH})_2$ is also partially reduced to Cu_2O . According to

Li *et al.*, acetaldehyde molecules, formed by the dehydration of ethylene glycol at high temperature, are responsible for this reduction [39]. On the other hand, more electropositive cations, as Zn^{2+} cannot be reduced due to the mild reducing power of the glycol solution [42]. During the later stages, Cu_2O is further reduced to Cu^0 , and the two-shelled hollow spheres are produced. Literature reports that, for longer syntheses, crystallites located in the central region of the spheres are gradually removed, shaping a hollow structure [43]. This phenomenon is observed since the inner crystallites are formed in the early stages of nucleation and growth and, thus, usually are smaller and present lower crystallinity. To minimize the Gibbs energy of these crystallites/particles, they dissolve and subsequently re-grow on the surface of larger crystals [43,44]. Likewise, it is assumed that in the present work, hollow spheres are generated in the last stage of the synthesis through Ostwald ripening, with subsequent particle growth, as already reported for Cu_2O and ZnO particles [39,40]. **Figure 2.10** illustrates the proposed mechanism, with the identification of the main steps: (1) nucleation, (2) crystal growth and formation of the core-shell microspheres, and (3) Ostwald ripening.

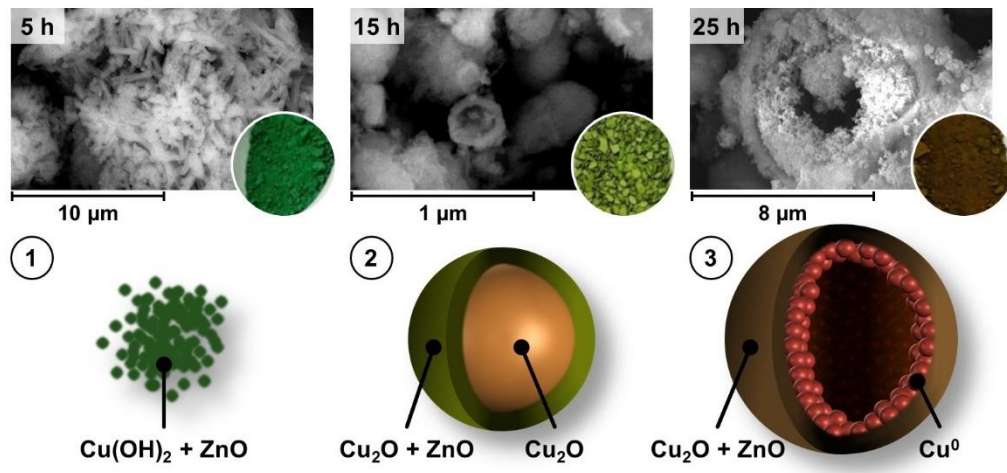


Figure 2.10. Proposed formation mechanism of two-shelled hollow spheres *via* a simple one-pot solvothermal route. The mechanism involves three main stages: (1) nucleation, (2) crystal growth and formation of the core-shell microspheres, and (3) Ostwald ripening. Inserts in SEM images show digital photographs of the obtained catalyst powders.

SEM images of the monometallic copper and zinc samples (**Figure 2.11**) show that hollow spheres are formed when only the copper precursor is present in the solvothermal medium. Thus, it is proposed that copper deposition mainly controls the formation of hollow spheres. On the other hand, ZnO nanoplates with smoother surfaces are obtained when only zinc is precipitated. Therefore, zinc seems to be responsible for the smooth surface of the outer shell observed for the CuZn_25 sample.

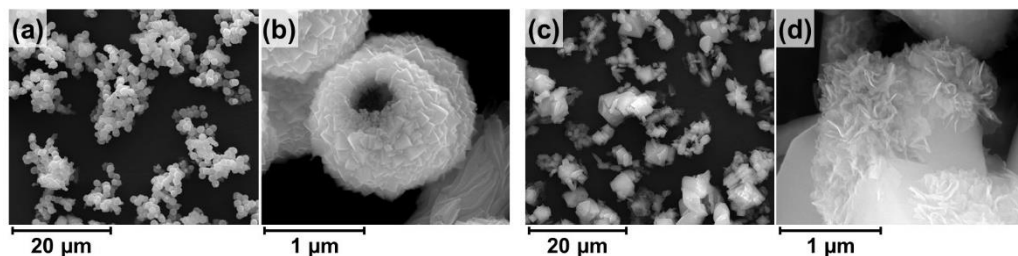


Figure 2.11. (a, c) Low and (b, d) high magnification SEM images of (a, b) copper and (c, d) zinc monometallic samples.

2.4.2 Electrochemical CO_2 reduction

The first evaluation of the catalytic activity of the developed CuZn-based catalysts was assessed by LSV in N_2 and CO_2 -saturated 0.1 M KHCO_3 , using a conventional three-electrode cell (**Figure 2.12**). The faradaic current observed when using N_2 -saturated electrolyte is associated with the hydrogen evolution reaction (HER), while the current response in the presence of CO_2 comprehends the contribution of HER and ER CO_2 . As illustrated, all samples generated higher current density when the electrolyte was saturated with CO_2 , suggesting that the developed catalysts are active for the ER CO_2 . Moreover, **Figure 2.12** indicates that the synthesis conditions had some effect on the overall current density recorded under CO_2 -saturated electrolyte, with the CuZn_25 sample displaying the lowest current response. In turn, considering the differences between the CO_2 and N_2 polarization curves as an indication of the ER CO_2 activity [45], it can be concluded that increasing the synthesis time of the catalysts results in a massive reduction of the CO_2 reduction activity, especially at higher overpotentials.

Figure 2.12 also denotes that the onset potential is higher for the catalyst prepared with 25 h of synthesis.

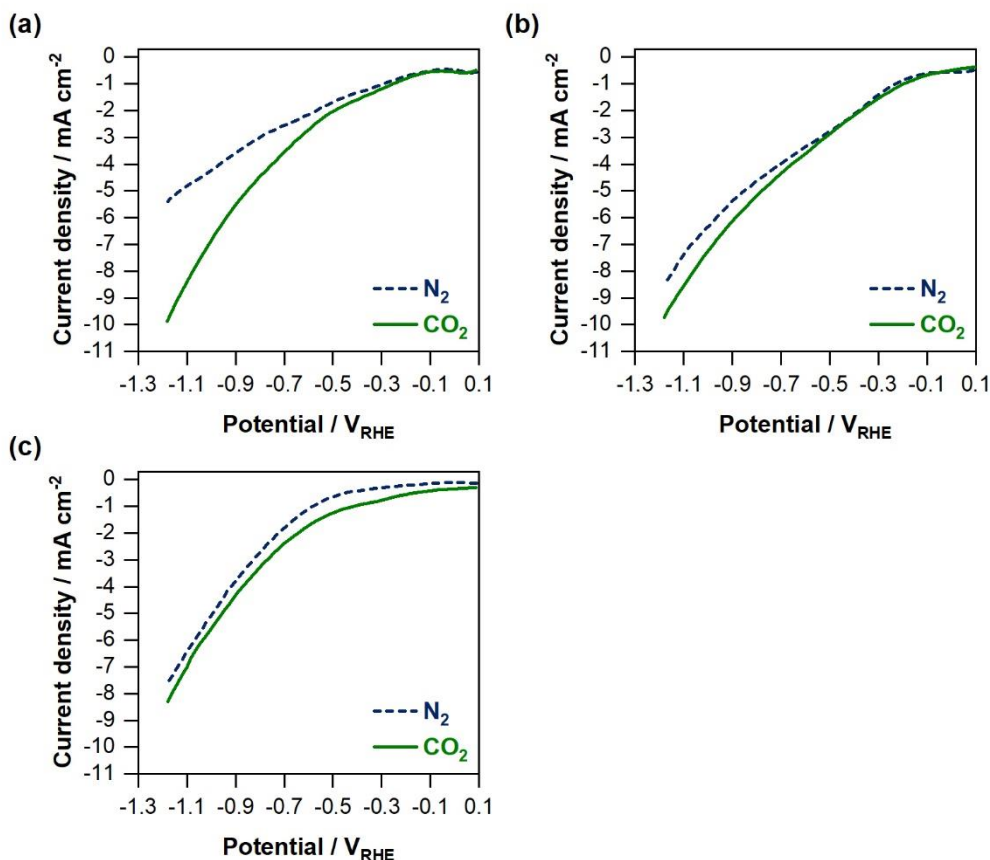


Figure 2.12. IR-corrected LSV polarization curves at cathodic potentials in N_2 (dashed lines) and CO_2 -saturated (full lines) 0.1 M KHCO_3 for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25. Scan rate, 20 mV s^{-1} .

After the initial LSV measurements, the activity of the CuZn catalysts toward CO_2 reduction was assessed by potentiostatic measurements at selected potentials from -0.7 V to -1.4 V, using a three-electrode cell. An aqueous solution of 0.1 M KHCO_3 , saturated with CO_2 , was used as electrolyte. The evolved gaseous products were quantified during the electrolysis by GC, and liquid products were analyzed by headspace-GC at the end of the reaction. Six products, including H_2 , were detected, and their FE added up between

97.2 % and 104.7 % (Tables A.1-A.3, Appendix A). **Figure 2.13** shows some fluctuations in the current density during the initial 10-15 min of electrolysis, possibly due to conditioning effects. However, after reaching the steady-state, the geometric current densities remained stable over the duration of the electrolysis (90 minutes).

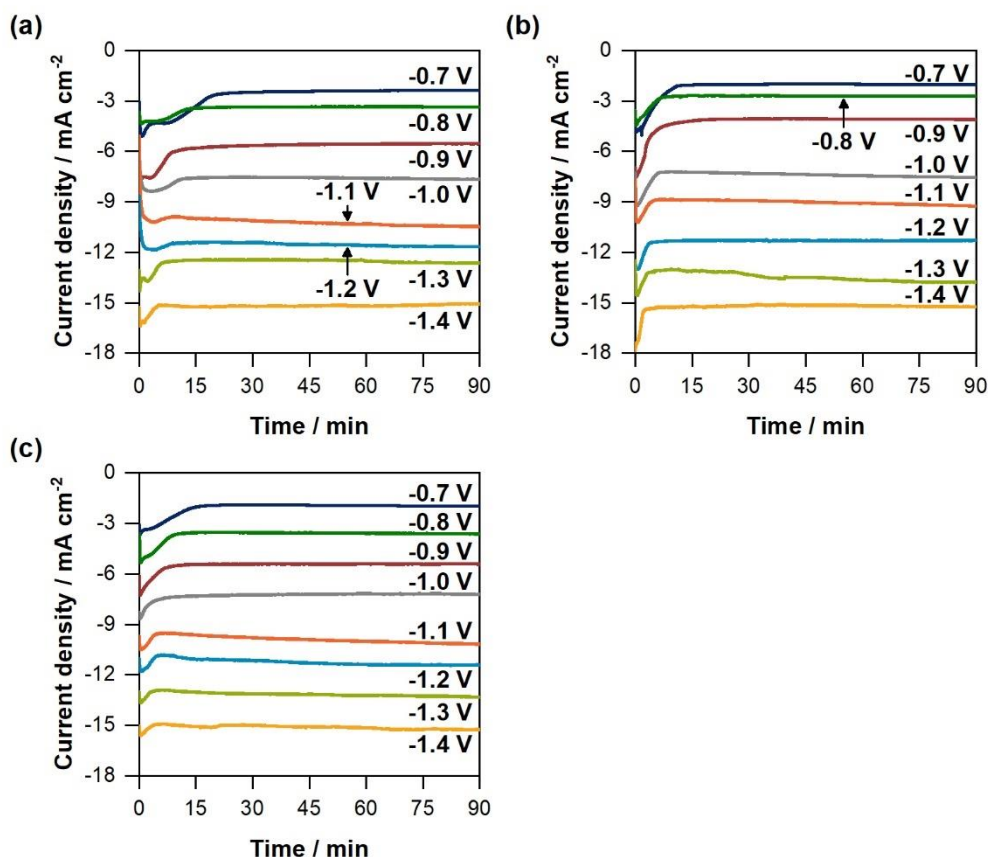


Figure 2.13. Chronoamperometric curves at various potentials for CO_2 reduction in CO_2 -saturated 0.1 M KHCO_3 for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.

The total current density and FE values recorded during the electrolysis experiments at constant potential are illustrated in **Figure 2.14**. In contrast to what was suggested by the LSV measurements, **Figure 2.14a** shows that the current density is not affected by the synthesis time. Previous studies using CuZn catalysts for ER CO_2 showed that the catalytic activity is mainly controlled by the catalyst bulk composition. In particular, it

is reported that the current density monotonically decreases as Zn content increases in a CuZn system [17,46]; this behavior was assigned to the conductivity of the materials. As acknowledged, copper is three times more conductive than zinc; therefore, a higher amount of copper can reduce the resistance of the CuZn catalyst, increasing the charge transport and consequently the catalytic activity (current density) [47]. The differences observed during the LSV measurements may be related to the fact that LSV is potentiodynamic in nature, and thus it does not represent a true steady-state [48].

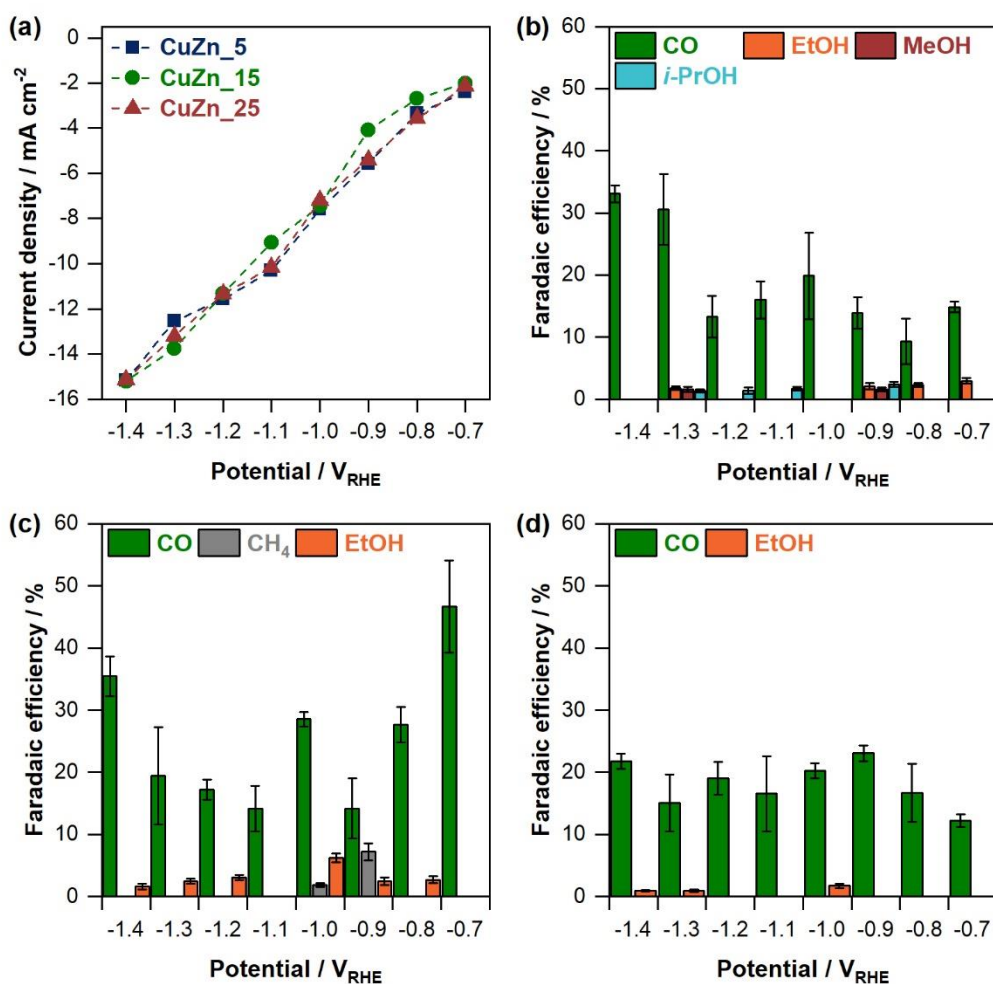


Figure 2.14. (a) Total current density and faradaic efficiency over (b) CuZn_5, (c) CuZn_15, and (d) CuZn_25 at different applied potentials.

Electrochemical results summarized in Tables A.1-A.3 (Appendix A) indicate that H_2 , output from the parasitic HER, was the main product, in agreement with previous reports. H_2 FE values above 40 % are typically found in the literature for CuZn systems with similar composition (quasi-equiatomic), measured under similar conditions (*i.e.*, electrolyte and cell configuration) [17,49,50]. Regarding the CO_2 electrolysis, CO was identified as the main reaction product for all catalysts and potential range studied, as illustrated in **Figure 2.14**. Nevertheless, the catalytic results show that the synthesis time of the catalysts influences the product distribution. A major effect is a decrease in the number of ER CO_2 products with the increasing hours of synthesis. For CuZn_5 (**Figure 2.14b**), four reaction products were identified, *i.e.*, CO, ethanol, methanol, and 2-propanol; three different compounds were obtained with CuZn_15, namely CO, methane, and ethanol (**Figure 2.14c**); and only CO and ethanol were produced when using CuZn_25 (**Figure 2.14d**).

As discussed, CO was obtained as the main ER CO_2 product for all catalysts. In particular, for CuZn_5, it was observed that the CO selectivity increased when more reducing potentials were applied (**Figure 2.14b**). The maximum FE for CO (33.1 %) was recorded at -1.4 V. Methanol was also obtained as a CO_2 -electrolysis product, however, with very low selectivity (maximum FE of 1.6 %). In addition, C_{2+} compounds were detected, in agreement with previous reports for unalloyed CuZn systems [17,46,49]. In the present work, ethanol was preferentially produced at low overpotential. The maximum FE values, between 2-3 %, were achieved for a potential range of -0.7 V to -0.9 V. However, these values are far from the FE reported by Ren and co-workers, which obtained a selectivity of 29.1 % using a CuZn catalyst, at -1.05 V_{RHE} [17]. The authors concluded that by varying the amount of Zn, it is possible to tune the selectivity for ethanol, with a maximum production achieved for a Cu:Zn atomic ratio of 4. In line with the cited work, the low ethanol selectivity of CuZn_5 can be associated with the composition of the catalyst (Cu:Zn atomic ratio of 1.54). Finally, 2-propanol was detected with a maximum FE of 2.5 % at -0.9 V.

As opposed to the results obtained with CuZn_5 catalyst, sample CuZn_15 shows higher CO production at lower overpotential (**Figure 2.14c**). The maximum FE for CO

production was recorded at -0.7 V, representing an overpotential of only 110 mV, under the current operating conditions. Nonetheless, the production yield was very low ($19.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$; Table A.2, Appendix A). Results also indicate that it is possible to increase the production rate by 5.7-times, to $110.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$, when working at a higher overpotential (810 mV). Methane and ethanol were also produced, displaying a maximum FE value of 7.2 % and 6.2 %, respectively. According to the reaction mechanisms proposed by several authors, methane and methanol production share the same pathway [8,51–53], with $^*\text{CHOH}$ identified as a possible branch point [52] (* indicates surface sites). The main difference between the electrosynthesis of methanol vs. methane is that methanol production requires only one C–O bond of the CO_2 molecule to be broken, while for methane both C–O bonds must be cleaved. Thus, according to Kuhl *et al.*, the oxophilicity of the catalyst plays a crucial role in controlling the methane/methanol selectivity [54]. A strong oxygen binding affinity favors the cleavage of the second C–O bond, enhancing methane production. Accordingly, comparing the evolved product distribution trend for CuZn_5 and CuZn_15 catalysts, it is reasonable to assume that CuZn_15 has a stronger oxygen affinity, favoring methane production over methanol. According to the characterization results, this effect may result from the more complex structure of CuZn_15. As discussed, CuZn_15 presents core-shell type microspheres with a Cu_2O core and $\text{Cu}_2\text{O}/\text{ZnO}$ shell, contrary to the amorphous structure of CuZn_5. Thus, Zn, which is more oxophilic than Cu [37], is preferentially exposed on the surface of CuZn_15. CV curves indicate that the oxidation of CuZn_15 starts at a lower potential than CuZn_5, suggesting that the surface of CuZn_15 is oxidized more readily than CuZn_5 (**Figure 2.15**). Thereby, the results support the hypothesis that CuZn_15 has a stronger oxygen affinity.

CuZn_25 shows a relatively stable CO selectivity for the whole range of potential studied, with the FE never exceeding 25 % (**Figure 2.14d**). Besides CO, ethanol was obtained as ERCO_2 product, with a maximum FE of 1.7 % at -1.0 V. As previously mentioned, the lowest number of reaction products was achieved for this sample (only CO and ethanol). According to the literature, the strong Cu-Zn interaction (possibly an alloy) observed for CuZn_25 can explain this behavior [46].

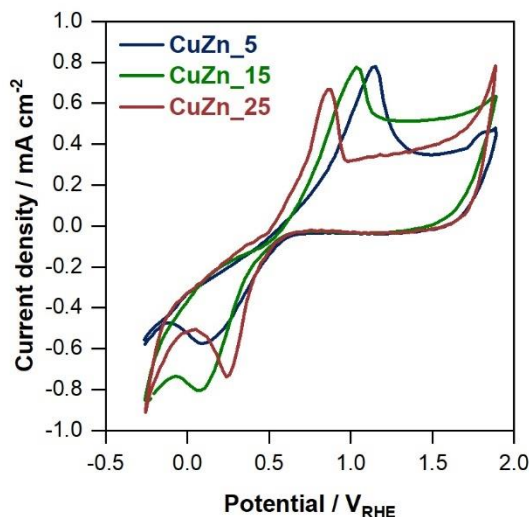


Figure 2.15. IR-corrected cyclic voltammograms of CuZn_5, CuZn_15, and CuZn_25 in N_2 -purged 0.1 M KHCO_3 solution. Scan rate, 50 mV s^{-1} .

Although the mechanism of C_2 production is still controversial, CO dimerization has been widely accepted as the most plausible pathway [8,55]. As a result, increasing the near-surface concentration of CO should improve the selectivity toward C_2 products. At the same time, copper is reported to facilitate C–C coupling reactions [17,55]. Therefore, establishing a Cu-bimetallic structure by adding a second metal, which is highly active for the CO_2 -to-CO reduction (*e.g.*, Zn), is an effective strategy to boost the production of C_2 compounds [56]. From this perspective, the role of Zn during the electrolysis is to continuously produce an *in situ* source of mobile CO. The CO molecules then diffuse to adjacent Cu sites and react with other C_1 intermediates (probably *CO) [17,46,57]. However, when a CuZn alloy is formed, the Cu sites lose the functionality to further reduce CO intermediates, enhancing the production of CO. The formation of an alloy shifts the *d*-band center of Cu away from the Fermi level [46,58], increasing the occupancy of the antibonding states and thus weakening the binding energy of *CO (Hammer-Nørskov *d*-band model) [59,60]. It is worth mentioning that the synergetic effect between copper and zinc in the developed CuZn catalysts will be explored in Chapter 3.

CO-TPD experiments were performed to confirm the different adsorption behavior of CO on the prepared catalysts (**Figure 2.16**). The CO-TPD profiles clearly show a negative shift in the main desorption peak from 595 °C to 518 °C, increasing the synthesis time. Moreover, for CuZn_25, an additional well-defined peak is observed at 340 °C. Thus, the results confirm that the CO binding strength decreases for longer syntheses, which can be explained by the increased Cu-Zn interaction (electronic effects), promoting CO production over C₂ products. Besides the electronic effects, the particle size can also account for the differences observed in the CO binding strength and, thus, evolved product distribution. Characterization results indicated that longer syntheses also lead to particle growth. According to Reske *et al.*, an increased particle size reduces the population of undercoordinated sites, weakening the binding of *CO and *H [61]. Similar size-dependent adsorption behavior was also observed for Au [62] and Pd nanoparticles [63].

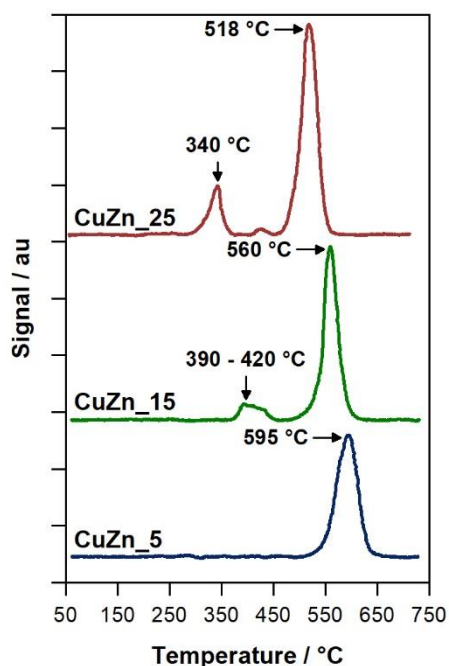


Figure 2.16. CO-TPD profile of CuZn_5, CuZn_15, and CuZn_25.

The work function (WF) of the prepared CuZn oxide catalysts was determined to further understand their electrocatalytic behavior and the obtained electroreduction products, **Figure 2.17**. As illustrated, the WF of the bimetallic samples is lower than that of the pure copper oxide surface, in agreement with the literature [64]. As a result, less energy is required to remove an electron from the bimetallic surfaces.

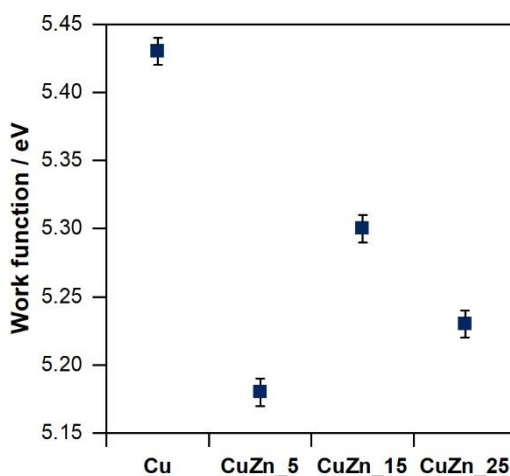


Figure 2.17. Work function of the developed CuZn catalysts and Cu single element catalyst.

CuZn_5 shows the lowest WF value among the prepared catalysts, suggesting that electrons are easily removed from their surface and become readily available for CO_2 reduction. Thus, the low WF of this material can explain the higher production of more reduced products, namely ethanol, methanol, and 2-propanol. In comparison, CuZn_15 has a higher WF, resulting in less reduced products. As previously discussed, C_3 products (*i.e.*, 2-propanol) were not identified when this sample was used as catalyst. Finally, CuZn_25 shows an intermediate WF value, higher than CuZn_5 but lower than CuZn_15. Thus, considering only the WF, it would be expected to observe the production of more reduced products, others than CO. However, as discussed, this sample produced mainly CO. This behavior can be related to the low adsorption affinity for CO. Despite the low WF, which indicates that electrons are readily available for reducing CO_2 , and then the CO intermediate, the catalyst is unable to stabilize CO on its

surface. Thus, CO is easily desorbed from the catalytic surface and emerges as the main ER CO_2 product.

The structural integrity of the developed catalysts under electrolysis conditions was evaluated by SEM. Images were acquired before and after the CO_2 electrolysis, as illustrated in **Figure 2.18**. The images of the electrodes before the ER CO_2 experiments show particle aggregation on the surface of CuZn_5 and CuZn_25 catalysts. In contrast, a very homogeneous surface, with small granular particles, is observed on the surface of CuZn_15. After electrolysis, structural losses were observed for CuZn_5 and CuZn_25; in particular, the morphology of CuZn_5 changed entirely. Although the current density and FE remained stable during electrolysis for catalysts CuZn_5 and CuZn_25, indicating no apparent deactivation, these results suggest some stability problems. Catalyst CuZn_15, on the other hand, showed higher structural integrity under the operating conditions.

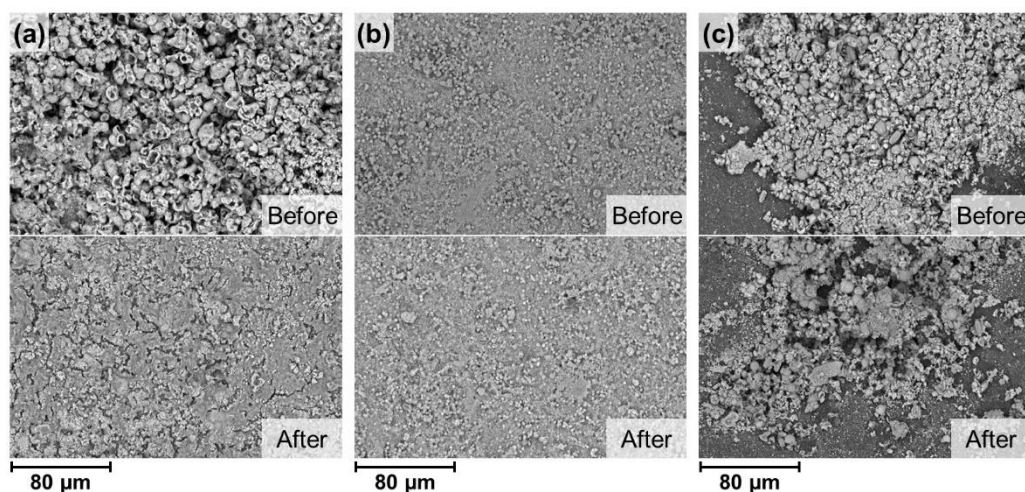


Figure 2.18. SEM images of the electrodes prepared with the developed catalysts, (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25, before and after the ER CO_2 reaction at -1.4 V.

2.5 Conclusions

Bimetallic CuZn oxide catalysts were synthesized following a simple one-pot solvothermal route. The influence of the synthesis time on the physicochemical and electrochemical characteristics of the developed materials was successfully assessed.

According to the present results, it is proposed that this synthetic route leads to the production of two shelled hollow spheres, with a copper-rich inner shell and a mixed copper-zinc oxide outer shell. Moreover, it is suggested that the synthesis starts with the nucleation of copper and zinc, followed by crystal growth and formation of core-shell microstructures. Later, Ostwald ripening is responsible for shaping the hollow spheres and particle growth. It was also observed that longer synthesis promotes the reduction of Cu^{2+} species to Cu^+ and Cu^0 , and strengthens the interaction between copper and zinc, ultimately forming a CuZn intermetallic compound.

Furthermore, it was concluded that the electrocatalytic behavior for CO_2 reduction is strongly affected by the synthesis time. With the increasing synthesis time, the number of ER CO_2 products obtained decreases due to the strengthening of the copper-zinc interaction. Accordingly, when a CuZn bimetallic structure is formed, copper loses the ability to reduce CO_2 to hydrocarbons and alcohols. This loss of functionality was assigned to a different electronic ligand effect, with decreased binding energy for CO. Thus, CO is easily desorbed from the catalyst surface, resulting in an increased CO production. Moreover, the obtained results indicate that the oxophilicity of the catalyst increases when a well-defined core-shell structure is formed, with zinc preferentially exposed on the shell, which governs the methanol/methane selectivity. The work function of the catalysts is also critical in controlling the product distribution, with more reduced products ($\text{C}_{2(+)}$) being produced when the work function value is lower, *i.e.*, less energy is required to remove electrons from the catalytic surface.

Although the present results did not constitute a breakthrough in the catalytic activity values for the ER CO_2 , it clearly demonstrates the strong influence of the synthesis method, in particular the solvothermal reaction time, on the catalytic properties of Cu-Zn oxide catalysts, even keeping the bulk catalyst composition.

Acknowledgments

Azenha, C., is grateful to the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant (reference SFRH/BD/128768/2017). This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); project FCT POCI-01-0145-FEDER-030357 - “Taylor made porphyrinoids for emerging efficient solar energy devices”, funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. The authors also acknowledge P. Tavares from UME-UTAD for the XRD analyses and CEMUP for the XPS analysis.

Nomenclature

Abbreviation	Definition
Ag/AgCl	Silver/silver chloride reference electrode
At. %	Atomic ratio
BE	Binding energy
BET	Brunauer-Emmett-Teller method
BJH	Barret-Joyner-Halenda method
CO-TPD	Carbon monoxide temperature-programmed desorption
CV	Cyclic voltammetry
e^-	Electron
ECSA	Electrochemical active surface area
ER CO_2	Electrochemical reduction of CO_2
FAT	Fixed analyzer transmission
FE	Faradaic efficiency
FWHM	Full width at half maximum
GC	Gas chromatography
GDL	Gas diffusion layer
H_2 -TPR	Hydrogen temperature-programmed reduction
HER	Hydrogen evolution reaction
JCPDS	Joint committee on powder diffraction standards
KE	Kinetic energy
LSV	Linear sweep voltammetry
RHE	Reversible hydrogen electrode
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
TCD	Thermal conductivity detector
WF	Work function
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Greek Symbol	Definition	Unit
α'	Modified Auger parameter	eV
β	Full width at half maximum	rad
θ	Bragg angle	rad
λ	Wavelength of the X-ray beam	nm

Variable	Definition	Unit
C_{dl}	Double-layer capacitance	mF cm ⁻²
d	Crystallite size	nm
E^0	Standard redox potential	V
$E_{Ag/AgCl}$	Potential of the Ag/AgCl reference electrode	V
E_{eq}	Equilibrium potential under reaction conditions	V
E_{RHE}	Potential in the RHE scale	V
K	Crystallite-shape factor	
S_{BET}	Specific surface area	m ² g ⁻¹
V_{pore}	Pore volume	cc g ⁻¹

References

- [1] Intergovernmental Panel on Climate Change, Summary for policymakers. In: Global warming of 1.5 °C, Geneva, Switzerland, 2018.
- [2] World Meteorological Organization, State of the global climate 2020: Unpacking the indicators, WMO, 2021. <https://public.wmo.int/en/our-mandate/climate/wmo-statement-state-of-globalclimate>.
- [3] V. Clement, K.K. Rigaud, A. de Sherbinin, B. Jones, S. Adamo, J. Schewe, N. Sadiq, E. Shabahat, Groundswell part 2: Acting on internal climate migration, Washington, DC., 2021. <https://openknowledge.worldbank.org/handle/10986/36248>.
- [4] United Nations Environment Programme, Emissions gap report 2019. Executive summary, Nairobi, 2019.
- [5] M.H. Barecka, J.W. Ager, A.A. Lapkin, Carbon neutral manufacturing via on-site CO_2 recycling, IScience. 24 (2021) 102514. <https://doi.org/10.1016/j.isci.2021.102514>.
- [6] O.S. Bushuyev, P. De Luna, C.T. Dinh, L. Tao, G. Saur, J. van de Lagemaat, S.O. Kelley, E.H. Sargent, What should we make with CO_2 and how can we make it?, Joule. 2 (2018) 825–832. <https://doi.org/10.1016/j.joule.2017.09.003>.
- [7] S. Garg, M. Li, A.Z. Weber, L. Ge, L. Li, V. Rudolph, G. Wang, T.E. Rufford, Advances and challenges in electrochemical CO_2 reduction processes: An engineering and design perspective looking beyond new catalyst materials, J. Mater. Chem. A. 8 (2020) 1511–1544. <https://doi.org/10.1039/C9TA13298H>.
- [8] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E.L. Stephens, K. Chan, C. Hahn, J.K. Nørskov, T.F. Jaramillo, I. Chorkendorff, Progress and perspectives of electrochemical CO_2 reduction on copper in aqueous electrolyte, Chem. Rev. 119 (2019) 7610–7672. <https://doi.org/10.1021/acs.chemrev.8b00705>.

- [9] V.C. Hoang, V.G. Gomes, N. Kornienko, Metal-based nanomaterials for efficient CO₂ electroreduction: Recent advances in mechanism, material design and selectivity, *Nano Energy*. 78 (2020) 105311. <https://doi.org/10.1016/j.nanoen.2020.105311>.
- [10] X. Zhi, A. Vasileff, Y. Zheng, Y. Jiao, S.-Z. Qiao, Role of oxygen-bound reaction intermediates in selective electrochemical CO₂ reduction, *Energy Environ. Sci.* 14 (2021) 3912–3930. <https://doi.org/10.1039/D1EE00740H>.
- [11] J. Yu, J. Wang, Y. Ma, J. Zhou, Y. Wang, P. Lu, J. Yin, R. Ye, Z. Zhu, Z. Fan, Recent progresses in electrochemical carbon dioxide reduction on copper-based catalysts toward multicarbon products, *Adv. Funct. Mater.* 31 (2021) 2102151. <https://doi.org/10.1002/adfm.202102151>.
- [12] I. V. Chernyshova, P. Somasundaran, S. Ponnuram, On the origin of the elusive first intermediate of CO₂ electroreduction, *PNAS*. 115 (2018) E9261–E9270. <https://doi.org/10.1073/pnas.1802256115>.
- [13] C.W. Li, M.W. Kanan, CO₂ Reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films, *J. Am. Chem. Soc.* 134 (2012) 7231–7234. <https://doi.org/10.1021/ja3010978>.
- [14] R. Kas, K.K. Hummadi, R. Kortlever, P. de Wit, A. Milbrat, M.W.J. Luiten-Olieman, N.E. Benes, M.T.M. Koper, G. Mul, Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction, *Nat. Commun.* 7 (2016) 10748. <https://doi.org/10.1038/ncomms10748>.
- [15] Y.Y. Birdja, E. Pérez-Gallent, M.C. Figueiredo, A.J. Göttle, F. Calle-Vallejo, M.T.M. Koper, Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels, *Nat. Energy*. 4 (2019) 732–745. <https://doi.org/10.1038/s41560-019-0450-y>.
- [16] D. Gao, R.M. Arán-Ais, H.S. Jeon, B. Roldan Cuenya, Rational catalyst and electrolyte design for CO₂ electroreduction towards multicarbon products, *Nat. Catal.* 2 (2019) 198–210. <https://doi.org/10.1038/s41929-019-0235-5>.

- [17] D. Ren, B.S.-H. Ang, B.S. Yeo, Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu_xZn catalysts, *ACS Catal.* 6 (2016) 8239–8247. <https://doi.org/10.1021/acscatal.6b02162>.
- [18] A. Dutta, M. Rahaman, N.C. Luedi, M. Mohos, P. Broekmann, Morphology matters: Tuning the product distribution of CO_2 electroreduction on oxide-derived Cu foam catalysts, *ACS Catal.* 6 (2016) 3804–3814. <https://doi.org/10.1021/acscatal.6b00770>.
- [19] F.S. Roberts, K.P. Kuhl, A. Nilsson, High Selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts, *Angew. Chem. Int. Ed.* 54 (2015) 5179–5182. <https://doi.org/10.1002/anie.201412214>.
- [20] Y. Chen, Z. Fan, J. Wang, C. Ling, W. Niu, Z. Huang, G. Liu, B. Chen, Z. Lai, X. Liu, B. Li, Y. Zong, L. Gu, J. Wang, X. Wang, H. Zhang, Ethylene selectivity in electrocatalytic CO_2 reduction on Cu nanomaterials: A crystal phase-dependent study, *J. Am. Chem. Soc.* 142 (2020) 12760–12766. <https://doi.org/10.1021/jacs.0c04981>.
- [21] P. Devi, K. Malik, E. Arora, S. Bhattacharya, V. Kalendra, K. V. Lakshmi, A. Verma, J.P. Singh, Selective electrochemical reduction of CO_2 to CO on $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites: role of oxygen vacancies, *Catal. Sci. Technol.* 9 (2019) 5339–5349. <https://doi.org/10.1039/C9CY01396B>.
- [22] A. Eilert, F. Cavalca, F.S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E.J. Crumlin, H. Ogasawara, D. Friebe, L.G.M. Pettersson, A. Nilsson, Subsurface oxygen in oxide-derived copper electrocatalysts for carbon dioxide reduction, *J. Phys. Chem. Lett.* 8 (2017) 285–290. <https://doi.org/10.1021/acs.jpclett.6b02273>.
- [23] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chemistry and properties of nanocrystals of different shapes, *Chem. Rev.* 105 (2005) 1025–1102. <https://doi.org/10.1021/cr030063a>.

- [24] G.O. Larrazábal, A.J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, Solvothermally-prepared Cu₂O electrocatalysts for CO₂ reduction with tunable selectivity by the introduction of p-block elements, *ChemSusChem*. 10 (2017) 1255–1265. <https://doi.org/10.1002/cssc.201601578>.
- [25] F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei, A. Rossi, Nanosized surface films on brass alloys by XPS and XAES, *RSC Adv.* 6 (2016) 31277–31289. <https://doi.org/10.1039/C5RA23135C>.
- [26] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.* 257 (2010) 887–898. <https://doi.org/10.1016/j.apsusc.2010.07.086>.
- [27] M.C. Biesinger, Advanced analysis of copper X-ray photoelectron spectra, *Surf. Interface Anal.* 49 (2017) 1325–1334. <https://doi.org/10.1002/sia.6239>.
- [28] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (2015) 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- [29] D. Hursán, A.A. Samu, L. Janovák, K. Artyushkova, T. Asset, P. Atanassov, C. Janáky, Morphological attributes govern carbon dioxide reduction on n-doped carbon electrodes, *Joule*. 3 (2019) 1719–1733. <https://doi.org/10.1016/j.joule.2019.05.007>.
- [30] J. Qi, X. Hu, The loss of ZnO as the support for metal catalysts by H₂ reduction, *Phys. Chem. Chem. Phys.* 22 (2020) 3953–3958. <https://doi.org/10.1039/C9CP06093F>.
- [31] G. Águila, S. Guerrero, P. Araya, Influence of the crystalline structure of ZrO₂ on the activity of Cu/ZrO₂ catalysts on the water gas shift reaction, *Catal. Commun.* 9 (2008) 2550–2554. <https://doi.org/10.1016/j.catcom.2008.07.011>.

- [32] R. Poreddy, C. Engelbrekt, A. Riisager, Copper oxide as efficient catalyst for oxidative dehydrogenation of alcohols with air, *Catal. Sci. Technol.* 5 (2015) 2467–2477. <https://doi.org/10.1039/C4CY01622J>.
- [33] G. Fierro, M. Lo Jacono, M. Inversi, P. Porta, F. Cioci, R. Lavecchia, Study of the reducibility of copper in CuO-ZnO catalysts by temperature-programmed reduction, *Appl. Catal. A: Gen.* 137 (1996) 327–348. [https://doi.org/10.1016/0926-860X\(95\)00311-8](https://doi.org/10.1016/0926-860X(95)00311-8).
- [34] A. V. Naumkin, A. Kraut-Vass, S.W. Gaarenstroom, C.J. Powell, NIST standard reference database 20, Version 4.1, (2012).
- [35] I. Beinik, M. Hellström, T.N. Jensen, P. Broqvist, J. V. Lauritsen, Enhanced wetting of Cu on ZnO by migration of subsurface oxygen vacancies, *Nat. Commun.* 6 (2015) 8845. <https://doi.org/10.1038/ncomms9845>.
- [36] L. Zhu, H. Li, Z. Liu, P. Xia, Y. Xie, D. Xiong, Synthesis of the 0D/3D CuO/ZnO heterojunction with enhanced photocatalytic activity, *J. Phys. Chem. C.* 122 (2018) 9531–9539. <https://doi.org/10.1021/acs.jpcc.8b01933>.
- [37] L. Wang, H. Peng, S. Lamaison, Z. Qi, D.M. Koshy, M.B. Stevens, D. Wakerley, J.A. Zamora Zeledón, L.A. King, L. Zhou, Y. Lai, M. Fontecave, J. Gregoire, F. Abild-Pedersen, T.F. Jaramillo, C. Hahn, Bimetallic effects on Zn-Cu electrocatalysts enhance activity and selectivity for the conversion of CO_2 to CO, *Chem Catal.* 1 (2021) 663–680. <https://doi.org/10.1016/j.checat.2021.05.006>.
- [38] L. Yan, R. Yu, J. Chen, X. Xing, Template-free hydrothermal synthesis of CeO_2 nano-octahedrons and nanorods: Investigation of the morphology evolution, *Cryst. Growth Des.* 8 (2008) 1474–1477. <https://doi.org/10.1021/cg800117v>.
- [39] S.-K. Li, C.-H. Li, F.-Z. Huang, Y. Wang, Y.-H. Shen, A.-J. Xie, Q. Wu, One-pot synthesis of uniform hollow cuprous oxide spheres fabricated by single-crystalline particles via a simple solvothermal route, *J. Nanoparticle Res.* 13 (2011) 2865–2874. <https://doi.org/10.1007/s11051-010-0175-0>.

- [40] T. Ihara, H. Wagata, T. Kogure, K. Katsumata, K. Okada, N. Matsushita, Template-free solvothermal preparation of ZnO hollow microspheres covered with *c* planes, RSC Adv. 4 (2014) 25148–25154. <https://doi.org/10.1039/C4RA02877E>.
- [41] X. Deng, Q. Zhang, E. Zhou, C. Ji, J. Huang, M. Shao, M. Ding, X. Xu, Morphology transformation of Cu₂O sub-microstructures by Sn doping for enhanced photocatalytic properties, J. Alloys Compd. 649 (2015) 1124–1129. <https://doi.org/10.1016/j.jallcom.2015.07.124>.
- [42] L. Poul, S. Ammar, N. Jouini, F. Fievet, F. Villain, Synthesis of inorganic compounds (metal, oxide and hydroxide) in polyol medium: A versatile route related to the sol-gel process, J. Sol-Gel Sci. Technol. 26 (2003) 261–265. <https://doi.org/10.1023/A:1020763402390>.
- [43] C.C. Yec, H.C. Zeng, Synthesis of complex nanomaterials via Ostwald ripening, J. Mater. Chem. A. 2 (2014) 4843–4851. <https://doi.org/10.1039/C3TA14203E>.
- [44] B. Liu, X. Hu, Hollow micro- and nanomaterials: synthesis and applications, in: Adv. Nanomater. Pollut. Sens. Environ. Catal., Elsevier, 2020: pp. 1–38. <https://doi.org/10.1016/B978-0-12-814796-2.00001-0>.
- [45] D. Kim, S. Lee, J.D. Ocon, B. Jeong, J.K. Lee, J. Lee, Insights into an autonomously formed oxygen-evacuated Cu₂O electrode for the selective production of C₂H₄ from CO₂, Phys. Chem. Chem. Phys. 17 (2015) 824–830. <https://doi.org/10.1039/C4CP03172E>.
- [46] H.S. Jeon, J. Timoshenko, F. Scholten, I. Sinev, A. Herzog, F.T. Haase, B. Roldan Cuenya, Operando insight into the correlation between the structure and composition of CuZn nanoparticles and their selectivity for the electrochemical CO₂ reduction, J. Am. Chem. Soc. 141 (2019) 19879–19887. <https://doi.org/10.1021/jacs.9b10709>.

- [47] J. Zeng, T. Rino, K. Bejtka, M. Castellino, A. Sacco, M.A. Farkhondehfar, A. Chiodoni, F. Drago, C.F. Pirri, Coupled copper–zinc catalysts for electrochemical reduction of carbon dioxide, *ChemSusChem*. 13 (2020) 4128–4139. <https://doi.org/10.1002/cssc.202000971>.
- [48] S. Anantharaj, S. Noda, M. Driess, P.W. Menezes, The pitfalls of using potentiodynamic polarization curves for tafel analysis in electrocatalytic water splitting, *ACS Energy Lett.* 6 (2021) 1607–1611. <https://doi.org/10.1021/acsenergylett.1c00608>.
- [49] Y. Feng, Z. Li, H. Liu, C. Dong, J. Wang, S.A. Kulinich, X. Du, Laser-prepared CuZn alloy catalyst for selective electrochemical reduction of CO_2 to ethylene, *Langmuir*. 34 (2018) 13544–13549. <https://doi.org/10.1021/acs.langmuir.8b02837>.
- [50] H. Hu, Y. Tang, Q. Hu, P. Wan, L. Dai, X.J. Yang, In-situ grown nanoporous Zn-Cu catalysts on brass foils for enhanced electrochemical reduction of carbon dioxide, *Appl. Surf. Sci.* 445 (2018) 281–286. <https://doi.org/10.1016/j.apsusc.2018.03.146>.
- [51] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels, *Energy Environ. Sci.* 3 (2010) 1311–1315. <https://doi.org/10.1039/c0ee00071j>.
- [52] T. Cheng, H. Xiao, W.A. Goddard, Free-energy barriers and reaction mechanisms for the electrochemical reduction of CO on the Cu(100) surface, including multiple layers of explicit solvent at pH 0, *J. Phys. Chem. Lett.* 6 (2015) 4767–4773. <https://doi.org/10.1021/acs.jpcllett.5b02247>.
- [53] R. Kortlever, J. Shen, K.J.P. Schouten, F. Calle-Vallejo, M.T.M. Koper, Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide, *J. Phys. Chem. Lett.* 6 (2015) 4073–4082. <https://doi.org/10.1021/acs.jpcllett.5b01559>.

- [54] K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, T.F. Jaramillo, Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces, *J. Am. Chem. Soc.* 136 (2014) 14107–14113. <https://doi.org/10.1021/ja505791r>.
- [55] Y. Zheng, A. Vasileff, X. Zhou, Y. Jiao, M. Jaroniec, S.-Z. Qiao, Understanding the roadmap for electrochemical reduction of CO₂ to multi-carbon oxygenates and hydrocarbons on copper-based catalysts, *J. Am. Chem. Soc.* 141 (2019) 7646–7659. <https://doi.org/10.1021/jacs.9b02124>.
- [56] S. Dongare, N. Singh, H. Bhunia, P.K. Bajpai, Electrochemical reduction of CO₂ using oxide based Cu and Zn bimetallic catalyst, *Electrochim. Acta.* 392 (2021) 138988. <https://doi.org/10.1016/j.electacta.2021.138988>.
- [57] J. Gao, H. Zhang, X. Guo, J. Luo, S.M. Zakeeruddin, D. Ren, M. Grätzel, Selective C–C coupling in carbon dioxide electroreduction via efficient spillover of intermediates as supported by operando raman spectroscopy, *J. Am. Chem. Soc.* 141 (2019) 18704–18714. <https://doi.org/10.1021/jacs.9b07415>.
- [58] P.T. Andrews, L.A. Hisscott, X-ray photoelectron spectroscopy of some Cu–Zn alloys, *J. Phys. F: Met. Phys.* 5 (1975) 1568–1572. <https://doi.org/10.1088/0305-4608/5/8/016>.
- [59] K. Liu, M. Ma, L. Wu, M. Valenti, D. Cardenas-Morcoso, J.P. Hofmann, J. Bisquert, S. Gimenez, W.A. Smith, Electronic effects determine the selectivity of planar Au–Cu bimetallic thin films for electrochemical CO₂ reduction, *ACS Appl. Mater. Interfaces.* 11 (2019) 16546–16555. <https://doi.org/10.1021/acsami.9b01553>.
- [60] B. Hammer, J.K. Nørskov, Electronic factors determining the reactivity of metal surfaces, *Surf. Sci.* 343 (1995) 211–220. [https://doi.org/10.1016/0039-6028\(96\)80007-0](https://doi.org/10.1016/0039-6028(96)80007-0).
- [61] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, Particle size effects in the catalytic electroreduction of CO₂ on Cu nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 6978–6986. <https://doi.org/10.1021/ja500328k>.

- [62] H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B.R. Cuenya, Exceptional size-dependent activity enhancement in the electroreduction of CO_2 over Au nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 16473–16476. <https://doi.org/10.1021/ja508879j>.
- [63] D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang, X. Bao, Size-dependent electrocatalytic reduction of CO_2 over Pd nanoparticles, *J. Am. Chem. Soc.* 137 (2015) 4288–4291. <https://doi.org/10.1021/jacs.5b00046>.
- [64] P. Rochana, J. Wilcox, A theoretical study of CO adsorption on FeCo(100) and the effect of alloying, *Surf. Sci.* 605 (2011) 681–688. <https://doi.org/10.1016/j.susc.2011.01.003>.

CHAPTER 3

Tuning the Selectivity of Cu₂O/ZnO Catalyst
for CO₂ Electrochemical Reduction

Adapted from the article

Azenha, C., Mateos-Pedrero, C., Lagarteira, T., Mendes, A., “Tuning the selectivity of Cu₂O/ZnO catalyst for CO₂ electrochemical reduction”, submitted to ACS Applied Energy Materials, March 2022.

Tuning the Selectivity of Cu₂O/ZnO Catalyst for CO₂ Electrochemical Reduction

3.1 Abstract

Different post-synthesis procedures were employed for enhancing the performance of catalyst CuZn_15 (described in Chapter 2) to the electrochemical reduction of CO₂ (ERCO₂). Namely, when an *in situ* potential cycling treatment was applied, the selectivity to CO increased 2-fold compared to the untreated catalyst, reaching 65.7 % of faradaic efficiency with a partial current density of -11.9 mA cm⁻² at -1.4 V_{RHE}. The enhanced CO₂-to-CO conversion was attributed to the increased number of oxygen vacancies and the strengthening of the copper-zinc synergy, which helps to stabilize Cu⁺ species. In general, the explored procedures successfully controlled critical physicochemical parameters that govern the catalytic behavior such as oxidation state, oxygen defects, crystallite size, and the strength of the copper-zinc interaction.

Keywords: CO₂ valorization; CO₂ electroreduction; potential cycling; copper-zinc; syngas; selectivity.

3.2 Introduction

World energy consumption has grown tremendously in the past two decades due to unprecedented economic development and population growth, especially in Asian countries [1]. On that account, excessive CO₂ emissions have triggered severe environmental problems, presenting an urgent and potentially irreversible threat to human life, which demand an urgent and vigorous response [2,3]. Creating a global-scale sustainable energy system for the future, while preserving our environment, is then one of the most crucial endeavors of our time [4].

The capture of CO₂ from air and point sources, such as power plants, followed by its conversion into chemical feedstocks and fuels, is a possible strategy for carbon recycling and a pathway to a circular carbon economy [3]. Among the many approaches under development, CO₂ electrochemical reduction (ERCO₂) is an elegant long-term approach with several advantages already identified [3,5,6]. For instance, the electrocatalytic process can be carried out under atmospheric conditions [6]. As driving force, electrical energy can be obtained from intermittent renewable energy sources (*e.g.*, solar, wind, and hydro), thus not contributing to new CO₂ emissions [7,8].

Despite being a promising technology, the ERCO₂ still faces scientific challenges, hindering its large-scale implementation [9]. The performance of the CO₂ electrolysis is primarily affected by sluggish reaction kinetics, owing to the large energy barrier for CO₂ activation, which explains the urgent need to develop efficient catalysts [10,11]. Moreover, the hydrogen evolution reaction (HER) competes with ERCO₂, whose kinetics is substantially more favorable, decreasing the overall efficiency of the process. Additionally, the poor reaction selectivity for the target product is a critical problem [5,9,12]. Among the various possible products, CO is pointed out as an emerging entry point for ERCO₂ into the market due to its large global demand and ease of production [13], already attracting industrial interest [14]. In particular, syngas, a mixture of CO and H₂, is one of the most important precursors for many commodities and chemicals, including high-energy-density fuels (*e.g.*, methanol, ammonia, and

synthetic petroleum) [15,16]. As syngas is mainly produced from fossil fuels, there is an opportunity to establish sustainable pathways for its production [16,17].

Noble metal-based catalysts (including Au, Ag, and Pd) are considered the current state-of-the-art catalysts for the electrochemical reduction of CO₂ to CO [5,18]. These metals exhibit optimal binding energy for reaction intermediates (*i.e.*, COOH and CO), which explains their superior catalytic activity and selectivity [18,19]. Over the last years, several successful strategies have been reported to improve the catalytic performance for CO production [18,20–23]. Mistry *et al.* concluded that the catalytic activity of Au nanoparticles is size-dependent, showing a drastic increase in current density with decreasing particle size. Moreover, the particle size greatly influences product selectivity; larger particles (7.7 nm) favor CO production, while the HER becomes dominant for sizes smaller than 5 nm [20]. The size effect was also reported for Pd catalysts. However, in contrast to Au catalysts, the CO production increases as the size decreases, while the HER is favored for larger particles [21]. Although the particle size affects different materials distinctly, it is reported that the particle size modifies the adsorption energy of the reaction intermediates on the catalyst surface, which in turn controls the catalytic activity [18]. Morphology is another critical parameter to tune the ERCO₂ performance. Liu and co-workers demonstrated that triangular Ag nanoplates exhibit enhanced current density and higher CO faradaic efficiency (FE) compared to similarly-sized Ag particles and bulk Ag. The improved performance was attributed to the optimum edge-to-corner ratio of triangular Ag nanoplates, which can efficiently reduce the reaction energy barrier [22]. Another effective approach to control the adsorption energy of intermediates and, thereby, further improve the performance of metal catalysts, is to increase the number of low-coordinated sites on the catalyst surface, as reported by Zhu *et al.* [23].

Nevertheless, the scarcity and high cost of noble metals require that future development of catalysts for CO production focus on reducing or replacing these metals. In this context, Zn emerges as the most promising alternative [18]. The suitable intermediate adsorption energy of Zn results in high FE for CO production, usually above 80 % [24,25]. However, Zn has low intrinsic activity [17], hindering CO productivity.

One potential strategy to improve the catalytic performance is the use of bimetallic catalysts. These materials show particular electronic and geometric structures that result in synergistic effects, promoting ER CO_2 [12,26]. Cu-Zn bimetallic systems have recently gained attention since Cu and Zn are low-cost sustainable materials [9,10,17,27,28]. Moreover, these systems are already well-studied and widely used in important industrial processes (*e.g.*, methanol synthesis) [29]. Copper has three times more electrical conductivity than zinc. As a result, the incorporation of Cu into Zn can reduce the resistance of the catalyst material and thus enhance charge transport, decreasing the reaction overpotential and ultimately resulting in higher catalytic activity. Meanwhile, the presence of Zn is expected to inhibit the H_2 formation, owing to its low activity toward the HER [9].

The present work studies the influence of different post-synthesis procedures on the catalytic performance of the CuZn oxide catalyst, produced with 15 h synthesis (Chapter 2). In particular, it is proposed that *in situ* conditioning approaches can be integrated with CO_2 electrolysis to tune the CO/ H_2 production ratio. A thorough search of the relevant literature suggests that this work demonstrates for the first time that the composition of syngas produced through the ER CO_2 can be controlled using *in situ* potential cycling procedures. So far, this fine-tuning has mainly been achieved by changing the catalyst properties during the synthesis stage.

3.3 Experimental

3.3.1 Catalyst synthesis

The catalysts were synthesized using the solvothermal-route described in Chapter 2 and considering 15 h of synthesis. Cu and Zn single-element catalysts were also synthesized using the same protocol. Lastly, a physical mixture of the appropriate amount of Cu and Zn single-element catalysts was prepared considering the target of Cu:Zn atomic ratio of 1.54.

In this chapter, catalysts were named according to their composition: CuZn (bicomponent CuZn catalyst); Cu (Cu single-element); Zn (Zn single-element); CuZn_{mix} (physical mixture of Cu and Zn).

3.3.2 Electrode preparation

The electrodes were prepared by airbrush deposition of a catalyst suspension on the microporous layer of a gas diffusion layer (GDL), as described in Chapter 2.

3.3.3 Conditioning/post-synthesis treatments

Ex situ and *in situ* procedures were employed to activate the catalyst, **Figure 3.1**. The *ex situ* conditioning was performed before the electrode preparation. The catalyst powder was reduced under H₂ atmosphere (150 mL min⁻¹) for 30 min at 240 °C or 300 °C. The *in situ* activation consisted of applying a series of potential cycles before the electrocatalytic reduction of CO₂. Cyclic voltammetry (CV) was performed at room temperature and atmospheric pressure in 0.1 M KHCO₃ saturated with N₂. 50 CV cycles were scanned at 50 mV s⁻¹, ranging from -1.0 V_{Ag/AgCl} to 1.2 V_{Ag/AgCl}. The CVs were either initiated from the anodic scan (causing catalyst oxidation) or the cathodic scan (causing catalyst reduction).

It is worth mentioning that the number of CV cycles applied – 50 – was sufficient for reaching a cyclic steady state, *i.e.*, the last five voltammogram cycles overlap, showing that the structural modifications were complete.

The conditioned catalysts were labeled according to the following nomenclature, X_Y, where X represents the catalyst composition and Y the conditioning conditions: 240 or 300 for the reduction temperature in °C (*ex situ* conditioning); AS or CS for CVs initiated from the anodic or the cathodic scan (*in situ* conditioning).

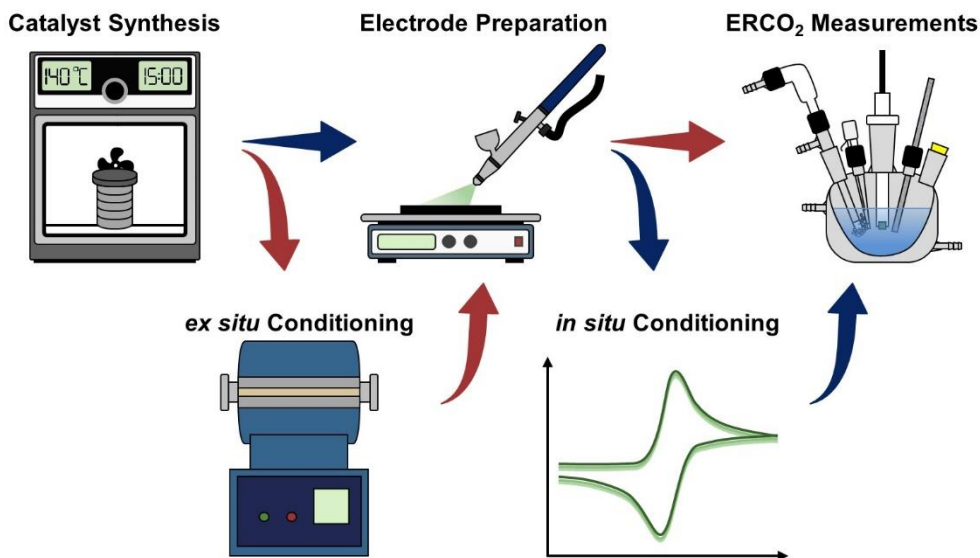


Figure 3.1. Experimental procedure for the evaluation of the different conditioning approaches: *in situ* – blue arrows, and *ex situ* – red arrows.

3.3.4 Electrochemical measurements

All electrochemical measurements were performed at atmospheric conditions of temperature and pressure in a conventional three-electrode electrochemical cell, as described in Chapter 2. All potentials in this chapter are on the RHE scale.

Linear sweep voltammetry (LSV) measurements were conducted according to the protocol described in Chapter 2. Electrochemical impedance spectroscopy (EIS) measurements were performed in CO₂-saturated 0.1 M KHCO₃ at -0.8 V with an amplitude of 10 mV and frequency ranging from 1 MHz to 1 mHz. The data obtained were fitted against an equivalent circuit [30] using the ZView software (Version 3.5, Scribner Associates, USA). Double-layer capacitance measurements were used to estimate the electrochemical active surface area (ECSA) of the electrodes, as described in Chapter 2.

3.3.5 CO₂ reduction electrolysis and product analysis

The electrolysis experiments were performed at atmospheric conditions, following the protocol described in Chapter 2. Likewise, gas-phase and liquid products were quantified by gas chromatography (GC) and headspace-GC, respectively. Each experiment lasted 120 min. The faradaic efficiency and product formation rate were determined to evaluate the electrochemical performance of the catalysts.

3.3.6 Physicochemical characterization

The morphology and element distribution were obtained by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, Phenom XL Desktop SEM) and high-resolution transmission electron microscopy analysis (HR-TEM, FEI Titan G2 ChemiSTEM) with an acceleration voltage of 200 kV. The average particle size was calculated from the measurement of 100 particles.

X-ray diffraction (XRD, PANalytical X'Pert Pro) and X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra HAS) were used to study the crystal structure and the surface chemical composition, respectively, as detailed in Chapter 2. It is worth mentioning that, after preparation, the samples were stored and transported in N₂ atmosphere to avoid possible oxidation due to air exposure, which could compromise the XPS analysis. The amount of surface Cu(II) was calculated according to XPS results, following literature [31], Equation (3.1).

$$\text{Cu(II)} = \frac{B (1 + (A_{1s}/B_s))}{A_t + B} \quad (3.1)$$

In this equation, A_t is the total area of the main emission, B stands for the shake-up peak areas, and A_{1s}/B_s is the ratio of the main peak/shake-up peak areas (1.59 at pass energies of 40 eV).

The reducibility of the catalysts was studied by H₂ temperature-programmed reduction (H₂-TPR, ChemBET Pulsar TPR/TPD) – details provided in Chapter 2. The CO₂

adsorption was studied by CO₂ temperature-programmed desorption (CO₂-TPD, ChemBET Pulsar TPR/TPD), following the protocol used for the CO-TPD experiments (Chapter 2). Briefly, samples were pretreated at 120 °C under He flow, followed by CO₂ adsorption at 50 °C. Then, the CO₂ desorption was monitored using a thermal conductivity detector (TCD) from 50 °C to 700 °C.

3.4 Results and discussion

3.4.1 Physicochemical properties of the as-prepared CuZn catalyst

The crystalline structure of the as-prepared catalyst was characterized by XRD. **Figure 3.2** shows the XRD pattern of the prepared catalyst as powder and after electrode preparation.

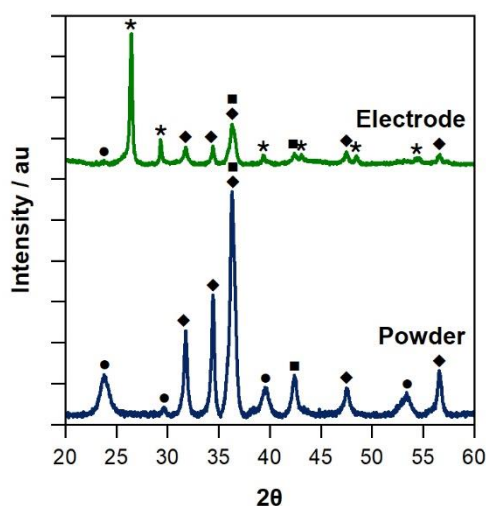


Figure 3.2. XRD pattern of the CuZn catalyst, as-prepared and after electrode production. ■ Cu₂O (JCPDS card no. 05-0667), ● Cu(OH)₂ (JCPDS card no. 80-0656), ◆ ZnO (JCPDS card no. 36-1451), and * GDL.

As observed, the powder sample shows diffraction peaks of the Cu₂O phase with cuprite structure at 36.3° (111) and 42.4° (200). The average crystallite size, estimated from the Debye-Scherrer equation, is 13.7 ± 3 nm. Diffraction peaks assigned to the wurtzite structure of ZnO are also observed at 31.8° (100), 34.4° (002), 36.2° (101), 47.5° (102), and 56.6° (110), with an average crystallite size of 17.2 ± 5 nm. Furthermore, the diffraction peak at 2θ value of 23.8° (021) suggests the presence of traces of Cu(OH)₂ phase. No significant changes are observed after the electrode production, suggesting that the catalyst structure was maintained. However, the XRD pattern becomes dominated by the intense diffraction lines of the GDL, mainly at 26.5° and 29.3°.

Surface atomic composition and valence state of the main elements were analyzed by XPS; Cu and Zn single-element catalysts were also analyzed for comparison purposes, **Figure 3.3**.

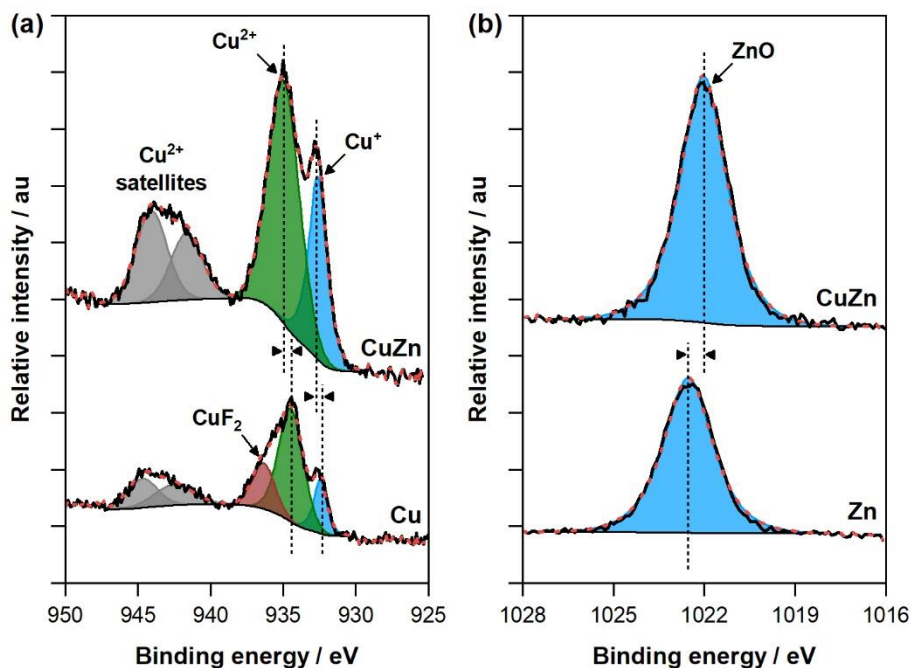


Figure 3.3. (a) Cu 2p_{3/2} and (b) Zn 2p_{3/2} XPS spectra of the CuZn catalyst and Cu and Zn single-element samples.

The Cu 2p_{3/2} photoelectron spectrum of CuZn shows two distinct peaks centered at 934.9 eV and 932.6 eV, **Figure 3.3a**. According to the literature, the high binding energy (BE) component (934.9 eV) is ascribed to Cu²⁺ as part of Cu(OH)₂, and the low BE peak (932.6 eV) can be attributed to Cu⁺ and/or Cu⁰ species [32]. Since the XPS Cu 2p region shows only marginal differences between Cu⁰ and Cu⁺, the chemical differentiation of these states usually relies on the peak shape of the Cu LMM Auger emission [32,33]. The Auger peak at 916.2 eV suggests the presence of Cu⁺, which is confirmed by the modified Auger parameter of 1848.8 eV, consistent with literature values for Cu₂O (1849 ± 0.6 eV) [34], **Table 3.1**. For the Cu sample, an additional peak is observed at 936.3 eV. This peak was assigned to the formation of CuF₂ during the electrode preparation due to the presence of Nafion solution. The same trend is not observed for CuZn, although fluorine (F) is detected in the survey spectrum (Appendix A, Figure A.9).

Table 3.1. Zn 2p_{3/2}, Cu 2p_{3/2}, Cu LMM, Zn LMM, and modified Auger parameter values for the as-prepared catalysts. Curve-fitting parameters.

Sample	Compound	BE ^a (eV)	FWHM ^b (eV)	Peak shape	KE ^c (eV)	FWHM (eV)	Peak shape	α' (eV)	At. % ^d
Cu	Cu ₂ O	932.4	1.06	GL(80)	916.5	2.24	GL(70)	1848.9	29.5
	Cu(OH) ₂	934.4	2.01	GL(30)	916.5	2.24	GL(70)	1850.9	48.9
	CuF ₂	936.3	2.08	GL(30)	915.6	2.25	GL(30)	1851.9	29.5
Zn	ZnO	1022.5	1.94	GL(70)	987.0	2.89	GL(30)	2009.5	100
CuZn	Cu ₂ O	932.6	1.36	GL(80)	916.2	2.94	GL(70)	1848.8	11.1
	Cu(OH) ₂	934.9	2.42	GL(30)	916.2	2.94	GL(70)	1850.7	44.9
	ZnO	1022.0	1.86	GL(70)	987.4	3.11	GL(30)	2009.4	44.0

^a: binding energy; ^b: full width at half maximum; ^c: kinetic energy; α': modified Auger parameter;

^d: calculated according to Cu 2p_{3/2} and Zn 2p_{3/2}.

For the Zn 2p_{3/2} region, **Figure 3.3b**, only one peak is observed at 1022.0 eV with a modified Auger parameter of 2009.4 eV, suggesting the presence of ZnO [31,35]. A

positive shift of *ca.* 0.4 eV is observed for the Cu 2p_{3/2} region in CuZn compared to the single-element sample (Cu), while the opposite behavior was recorded for the Zn 2p_{3/2} region concerning the monometallic Zn counterpart. As reported for CuZn alloys, the bimetallic bonding induces a positive shift in the core level of Cu and the reverse down-shift on the Zn core level. These changes result from charge transfer within the heteronuclear metal-to-metal bond and other phenomena, such as rehybridization in Cu valence levels [36]. The same tendency seems valid in this work, although no evidence of an alloy formation was observed. Thus, the shift in the BEs suggests that a strong interaction between Cu₂O and ZnO is present.

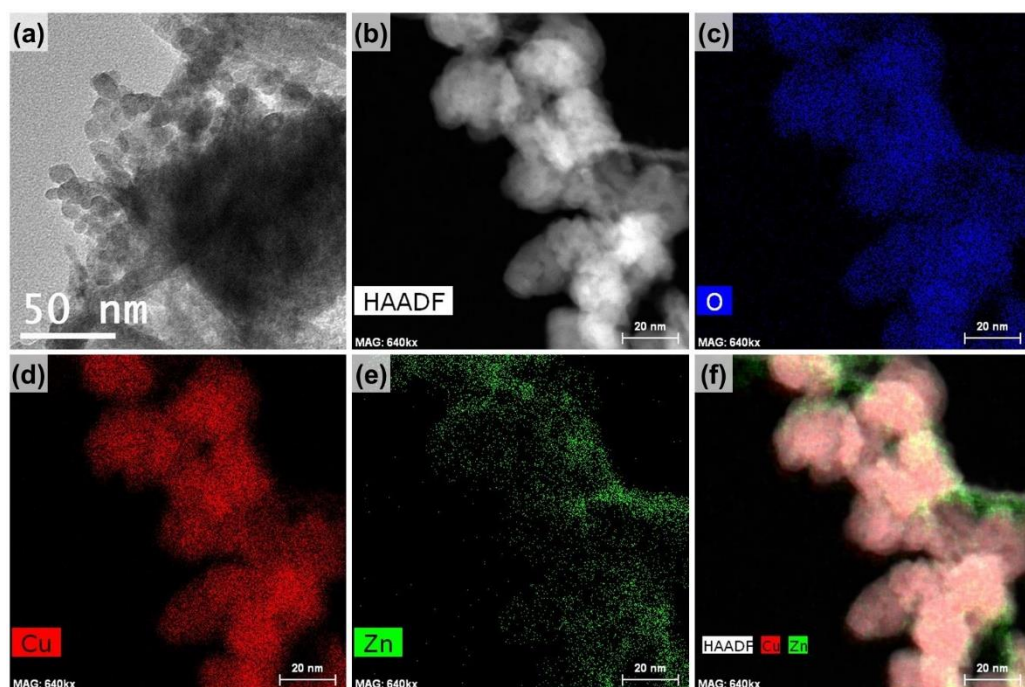


Figure 3.4. (a) TEM image of the as-prepared CuZn catalyst power, (b) representative HAADF-STEM image, and (c-d) energy dispersive X-ray spectroscopy maps of (c) O, (d) Cu, (e) Zn, and (f) superposition of Cu and Zn.

TEM and HAADF-STEM micrographs of the CuZn catalyst are shown in **Figure 3.4**. The results suggest that the catalyst particles are spherical with a core-shell structure (particle size of *ca.* 13 ± 4 nm). EDS elemental composition analysis indicates that the

core is mainly copper, covered by a Zn-rich shell. This evidence is supported by the XRD and XPS results. The Cu:Zn atomic ratio calculated according to the XRD results is 1.59, a value very close to the target of 1.54. In turn, a value of 1.27 is obtained from the XPS, suggesting that the surface is slightly rich in zinc (**Table 3.2**). However, it should be mentioned that copper is also present on the catalyst surface.

The reducibility of the prepared CuZn catalyst and the single-element counterparts were assessed by TPR, **Figure 3.5**. TPR profile indicates that the reduction of Cu and Zn samples occurs at 283 °C and 505 °C, respectively. Moreover, the H₂ consumption peak of the Cu sample can be deconvoluted into two Gaussian peaks centered at *ca.* 259 °C (α) and 282 °C (β). These double peaks were previously assigned to a stepwise reduction of surface-dispersed CuO species from Cu²⁺ to Cu⁺ (α), closely followed by the reduction from Cu⁺ to Cu⁰ (β) [37]. On the other hand, the reduction peak of CuZn is more symmetrical and sharper than that observed for the Cu sample. In addition, it is also shifted to a lower reduction temperature, and no reduction feature was observed in the temperature range of the ZnO reduction. This result endorses the existence of a strong interaction between copper and zinc (refer to XPS results), where the ZnO increases the reducibility of copper [38].

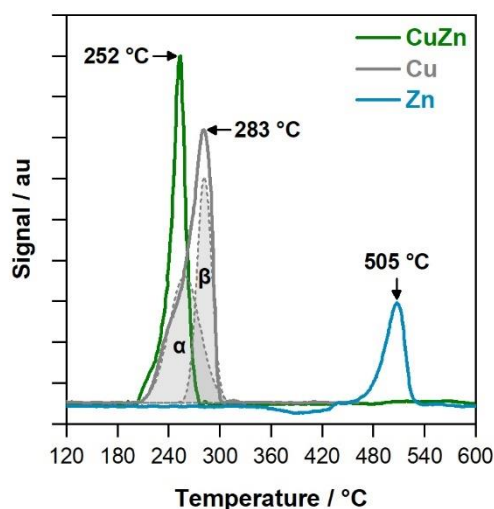


Figure 3.5. H₂-TPR profile of CuZn, and Cu and Zn single-element catalysts.

3.4.2 Influence of the conditioning on the physicochemical properties

The design of efficient catalysts for CO₂ reduction to CO involves optimizing the binding energy of key reaction intermediates (*COOH and *CO) and/or suppressing the HER. These properties can be tuned by controlling the physicochemical properties of the catalysts, including particle size, morphology, and surface modifications [18]. Thus, to understand how the conditioning affects the physicochemical properties of the CuZn catalyst and, consequently, the electrochemical activity, the prepared electrodes were characterized by several techniques and compared with the reference sample – unconditioned CuZn catalyst. As discussed in detail below, the conditioning procedures studied either resulted in severe structural modification (*ex situ*) or slight surface rearrangement (*in situ*).

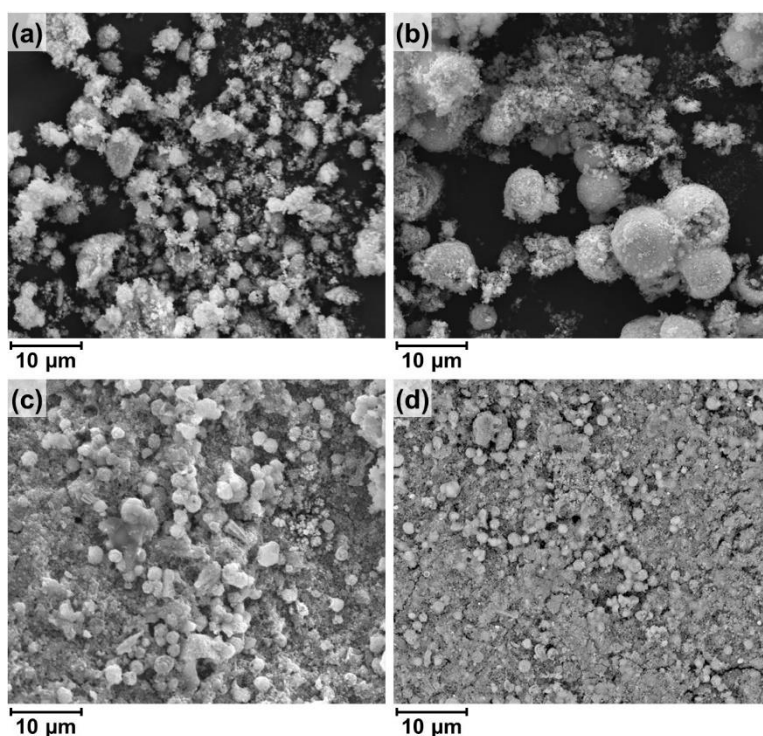


Figure 3.6. SEM images of (a) CuZn₂₄₀, (b) CuZn₃₀₀, (c) CuZn_{AS}, and (d) CuZn_{CS}.

SEM images acquired after conditioning suggest that the conditioning procedures do not affect the catalyst morphology. As illustrated in **Figure 3.6**, all samples exhibit particle aggregates comprehending some spherical structures, in agreement with the core-shell structure identified for the reference CuZn sample. However, it is also observed that the particle size increased after H₂ reduction at 300 °C. Double-layer capacitance measurements were carried out to estimate the electrochemical active surface area (ECSA). As summarized in **Table 3.2**, the capacitance values obtained after *in situ* conditioning are very close to the value of 5.04 mF cm⁻² recorded for the CuZn sample, suggesting that the ECSA was kept after conditioning. On the other hand, a slight reduction of the capacitance was observed for samples reduced *ex situ*, indicating a decrease in the ECSA. CuZn_300 presents the lowest value (3.19 mF cm⁻²), representing a decrease of 1.6-times compared to the CuZn reference, which can be explained by the increase in particle size (SEM results).

Figure 3.7a shows the XRD pattern of the CuZn catalyst before and after *ex situ* conditioning. The diffractograms of CuZn_240 and CuZn_300 do not exhibit the main diffraction lines of Cu₂O and Cu(OH)₂ phases, as observed for the as-prepared CuZn sample. On the other hand, new intense diffraction peaks appeared at 43.3° (111) and 50.4° (200), indicating that the copper species were reduced to metallic Cu during the thermal treatment under H₂ atmosphere. Diffraction peaks assigned to the wurtzite structure of ZnO are also detected after *ex situ* reduction. These findings are in good agreement with the XPS results (**Table 3.3**), which indicate that the catalytic surface is mainly composed of Cu⁰ and ZnO after *ex situ* reduction. Moreover, and in agreement with SEM analysis, **Figure 3.7a** suggests that increasing the reduction temperature increases the Cu⁰ particle size, possibly due to sintering effects. CuZn_300 presents larger Cu⁰ crystallites (33.0 ± 2 nm) than CuZn_240 (16.0 ± 1 nm), **Table 3.2**. Meanwhile, the ZnO crystallite size increased with the reduction treatment but was not affected by the reduction temperature.

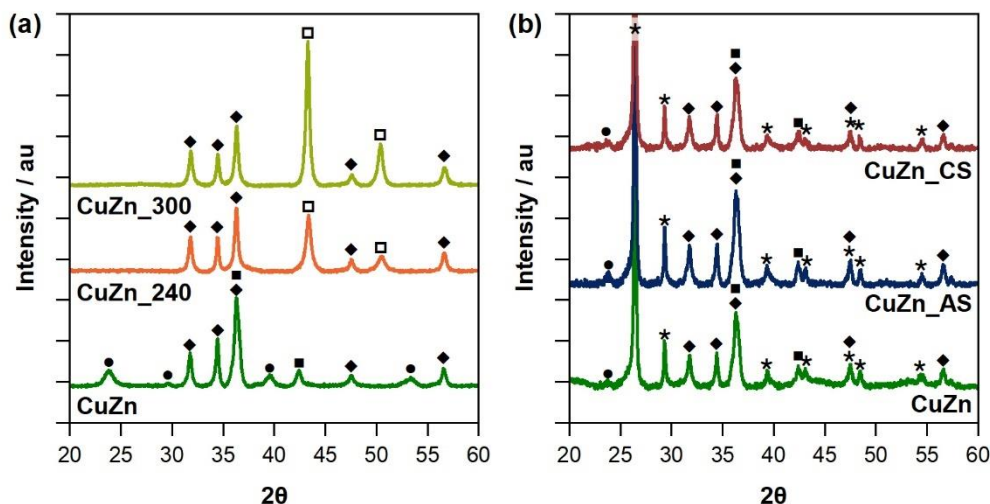


Figure 3.7. XRD patterns of the CuZn catalyst before and after (a) *ex situ* and (b) *in situ* conditioning. ■ Cu₂O (JCPDS card no. 05-0667), ● Cu(OH)₂ (JCPDS card no. 80-0656), □ Cu⁰ (JCPDS card no. 04-0836), ◆ ZnO (JCPDS card no. 36-1451), and * GDL. Note: the XRD patterns in (a) concern powder samples and (b) samples after the electrode preparation, as indicated by the presence of diffraction lines from the GDL.

Table 3.2. Physicochemical and electrical properties of the electrodes, before and after conditioning.

Sample	Mean crystallite size (nm) ^a			% surface Cu ²⁺ /Cu ⁺ ^b	Cu:Zn atomic ratio		<i>C</i> _{dl} ^c (mF cm ⁻²)
	Cu ⁰	Cu ₂ O	ZnO		XRD	XPS	
CuZn	--	13.7 ± 3	17.2 ± 5	80/20	1.59	1.27	5.04
CuZn_240	16.0 ± 1	--	46.0 ± 5	--	1.31	1.23	3.88
CuZn_300	33.0 ± 2	--	42.0 ± 3	--	1.32	1.25	3.19
CuZn_AS	--	14.5 ± 4	18.2 ± 6	67/33	1.54	1.17	5.15
CuZn_CS	--	12.9 ± 4	17.1 ± 5	73/27	1.51	1.18	4.26

^a: estimated from XRD according to the Scherrer equation; ^b: % of copper species as Cu²⁺ and Cu⁺ calculated from the XPS data according to the literature [31]; ^c: double-layer capacitance.

Opposite to what was observed after the *ex situ* reduction, the *in situ* potential cycling did not result in a complete reduction of the copper species to Cu^0 , as evidenced by XRD (**Figure 3.7b**). According to the XRD, no significant differences were observed between the reference sample (CuZn) and the catalysts after conditioning (CuZn_AS and CuZn_CS). The main diffraction lines of Cu_2O , $\text{Cu}(\text{OH})_2$, and ZnO are still present, and the average crystallite size was maintained (**Table 3.2**). Thus, the results suggest that the bulk structure of the catalyst was not affected. On the other hand, the XPS analysis indicates some rearrangement of the catalytic surface. As shown in **Table 3.2**, although Cu^{2+} is the predominant copper species, both *in situ* procedures increased the fraction of Cu^+ on the catalyst surface. Moreover, this phenomenon is more evident when the CV cycles were initiated from the anodic scan (CuZn_AS).

Table 3.3. Zn 2p_{3/2}, Cu 2p_{3/2}, Cu and Zn LMM, and modified Auger parameter values for the catalysts after conditioning. Curve-fitting parameters.

Sample	Compound	BE (eV)	FWHM (eV)	Peak shape	KE (eV)	FWHM (eV)	Peak shape	α' (eV)	At. %
CuZn_240	Cu^0	932.4	1.17	GL(90)	918.5	1.54	GL(80)	1850.9	40.2
	$\text{Cu}(\text{OH})_2$	934.1	2.77	GL(70)	916.5	2.45	GL(70)	1850.6	12.5
	ZnO	1022.2	1.90	GL(70)	987.3	2.93	GL(30)	2009.5	47.3
CuZn_300	Cu^0	932.3	1.11	GL(90)	918.5	1.52	GL(80)	1850.8	41.7
	$\text{Cu}(\text{OH})_2$	934.2	2.33	GL(70)	916.5	2.53	GL(70)	1850.7	11.3
	ZnO	1022.1	1.85	GL(70)	987.4	3.12	GL(30)	2009.5	47.0
CuZn_AS	Cu_2O	932.3	1.32	GL(80)	916.4	2.66	GL(70)	1848.7	17.4
	$\text{Cu}(\text{OH})_2$	934.7	2.48	GL(30)	916.4	2.66	GL(70)	1851.1	36.5
	ZnO	1022.0	1.86	GL(70)	987.4	3.31	GL(30)	2009.4	46.1
CuZn_CS	Cu_2O	932.6	1.27	GL(80)	916.2	2.63	GL(70)	1848.8	14.8
	$\text{Cu}(\text{OH})_2$	934.9	2.48	GL(30)	916.2	2.63	GL(70)	1851.1	39.3
	ZnO	1022.0	1.81	GL(70)	987.4	3.37	GL(30)	2009.4	45.9

The BE of the Cu 2p_{3/2} and Zn 2p_{3/2} regions are summarized in **Tables 3.1** and **3.3**. No chemical shift was observed in the Cu 2p core level of CuZn_CS compared to the CuZn

reference (932.6 eV and 934.9 eV for Cu₂O and Cu(OH)₂, respectively). However, a slight negative shift of *ca.* 0.3 eV was found for CuZn_AS. Although this is a minor shift, it suggests a slightly higher electron density around the copper atoms for CuZn_AS.

The O 1s core peak spectrum shows asymmetrical features indicating the presence of multi-component oxygen species. As illustrated in **Figure 3.8**, the oxygen peak was fitted by five Gaussian peaks. According to the literature, the higher BE peak (535.6 eV) is attributed to fluorinated compounds (O-Fx) [39], the peak at 532.8 eV is ascribed to chemisorbed oxygenated species on the surface (*e.g.*, hydroxyl anions or adsorbed O₂ and H₂O; O_C) [40,41], and the peak at 532.1 eV is assigned to O²⁻ ions in oxygen-deficient regions (*i.e.*, oxygen atoms adjacent to an oxygen vacancy; O_V) [42]. Finally, the peaks at 531.2 eV and 530.0 eV are attributed to lattice oxygen of ZnO (O_L Zn²⁺) and Cu₂O (O_L Cu⁺), respectively [41,42]. Thus, the O_V/O_{total} ratio can be used as an indirect measure of the presence of oxygen vacancies. As summarized in **Table 3.4**, the application of CV cycles starting from the anodic scan increases the number of oxygen vacancies. In contrast, the opposite behavior is observed when the CV initiates by the cathodic scan. Accordingly, CuZn_AS is the sample with the highest concentration of surface oxygen defects.

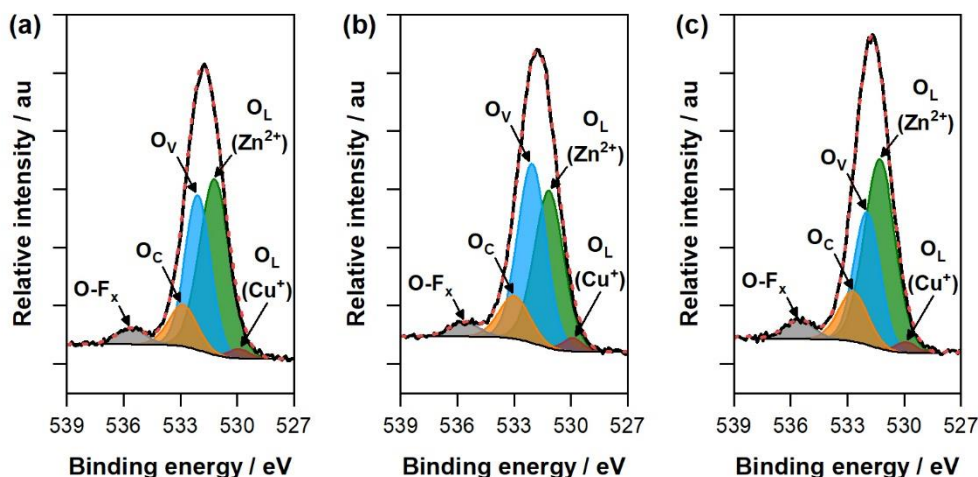


Figure 3.8. O 1s XPS spectra of (a) CuZn, (b) CuZn_AS, and (c) CuZn_CS.

Table 3.4. O 1s values for the as-prepared catalyst and after conditioning. Curve-fitting parameters.

Sample	Compound	BE (eV)	FWHM (eV)	Peak shape	O _v /O _{total}
CuZn	O _L (Cu ²⁺)	530.0	1.20	GL(30)	0.36
	O _L (Zn ²⁺)	531.2	1.85	GL(30)	
	O _v	532.1	1.56	GL(30)	
	O _c	532.8	1.74	GL(30)	
	O-Fx	535.6	1.74	GL(30)	
CuZn_AS	O _L (Cu ²⁺)	530.0	1.21	GL(30)	0.44
	O _L (Zn ²⁺)	531.1	1.85	GL(30)	
	O _v	532.1	1.75	GL(30)	
	O _c	532.8	1.90	GL(30)	
	O-Fx	535.6	1.81	GL(30)	
CuZn_CS	O _L (Cu ²⁺)	530.0	1.22	GL(30)	0.30
	O _L (Zn ²⁺)	531.2	1.89	GL(30)	
	O _v	532.0	1.60	GL(30)	
	O _c	532.7	1.81	GL(30)	
	O-Fx	535.6	1.82	GL(30)	

3.4.3 Influence of the conditioning on the electrochemical activity

The electrocatalytic activity of the CuZn electrode, before and after conditioning, was initially assessed by linear sweep voltammetry (LSV) in N₂- or CO₂-saturated electrolyte, using a standard three-electrode cell, **Figure 3.9**.

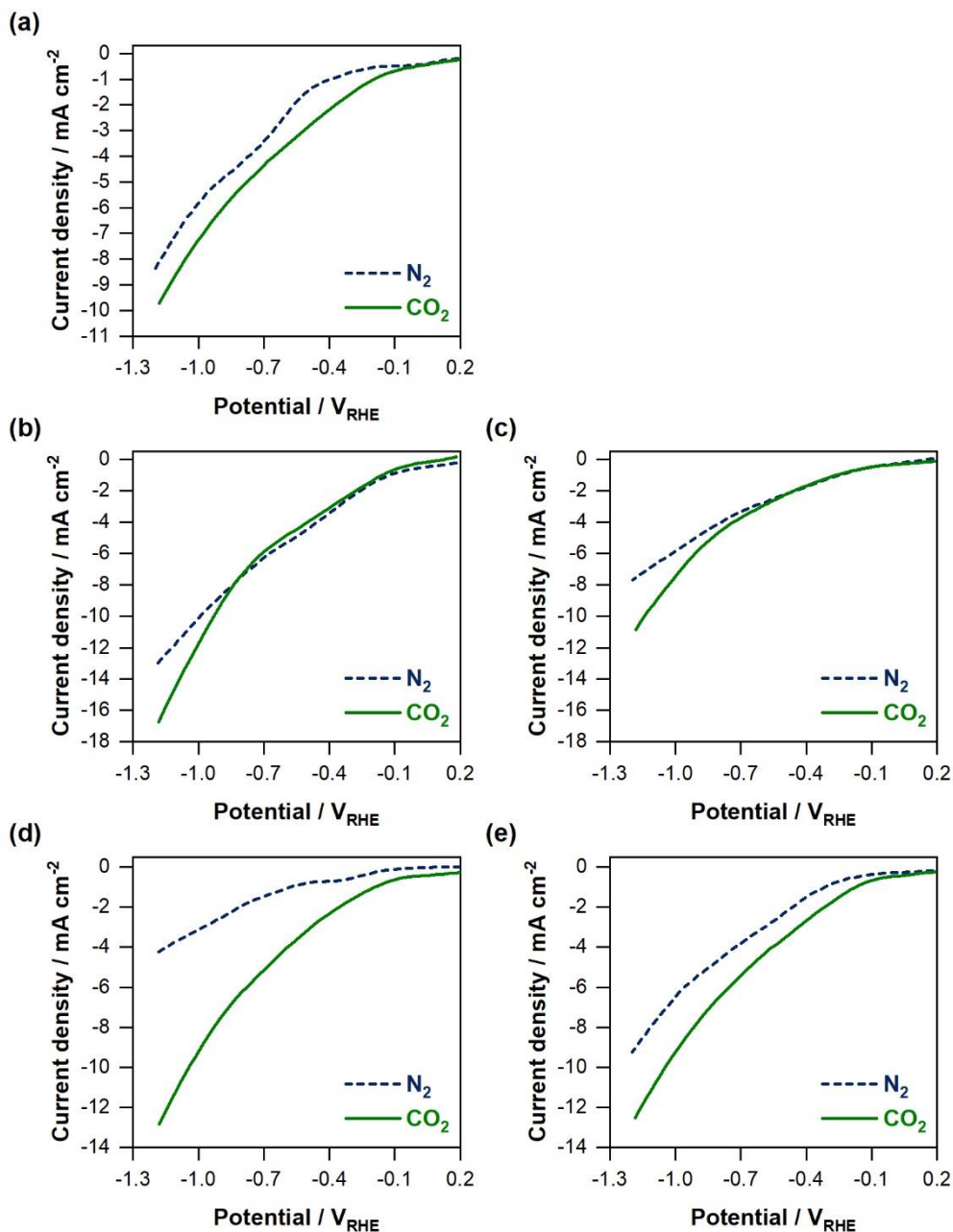


Figure 3.9. IR-corrected LSV at cathodic potentials in N₂ (dashed lines) and CO₂-saturated (full lines) 0.1 M KHCO₃ for (a) CuZn catalyst as-prepared (reference sample) and after conditioning: (b) CuZn₂₄₀, (c) CuZn₃₀₀, (d) CuZn_{AS}, and (e) CuZn_{CS}. Scan rate, 20 mV s⁻¹.

All samples show higher current density when CO₂ is present in the reaction media, suggesting that all samples have electrochemical activity for the ERCO₂. Comparing the faradaic currents recorded at negative potentials, it is clear that: (i) the conditioning strongly affects the performance of the CuZn catalyst; (ii) the total current density recorded under CO₂ atmosphere is higher for the conditioned samples than the untreated CuZn catalyst, suggesting that the conditioning increases the catalytic activity; (iii) the type of conditioning applied has a marked influence in the ERCO₂ selectivity. The difference between the curves recorded under N₂- and CO₂-saturated electrolyte can be used as an indication of the ERCO₂ activity [43]. Thus, it is noticed that the *in situ* anodic scan (AS) conditioning resulted in a remarkable improvement of the ERCO₂ selectivity compared to the reference sample (**Figure 3.9d**).

After this preliminary evaluation, the activity of the CuZn electrode, before and after conditioning, was accessed by potentiostatic measurements for 120 min at selected potentials from -0.6 V to -1.4 V, using a conventional three-electrode system and CO₂-saturated 0.1 M KHCO₃ as electrolyte. The geometric current density remained stable throughout the experiments, regardless of the conditioning procedure and applied potential (Figure A.12, Appendix A). GC analysis indicates that H₂ and CO were the main gas products. Likewise, ethanol and methanol were identified as liquid products, usually with low faradaic efficiency (FE < 5 %). The total FE for the detected products was 98 ± 2 % (Tables A.4-A.14, Appendix A); thus, other products are not expected at all or in considerable amounts.

Figure 3.10 illustrates the current density and faradaic efficiency recorded during the constant-potential electrolysis; it should be noted that only products with FE > 1 % are shown.

In agreement with the LSV results, the CuZn reference catalyst presents very high selectivity to H₂ evolution. As illustrated, the H₂ FE reaches values above 65 % for all potentials tested – **Figure 3.10b**. Considering the ERCO₂ products, CO was detected as the main reaction product, with the highest FE of 35.4 % recorded at -1.4 V. Besides CO, ethanol was also produced, with a maximum FE value of 4.7 % at -1.0 V.

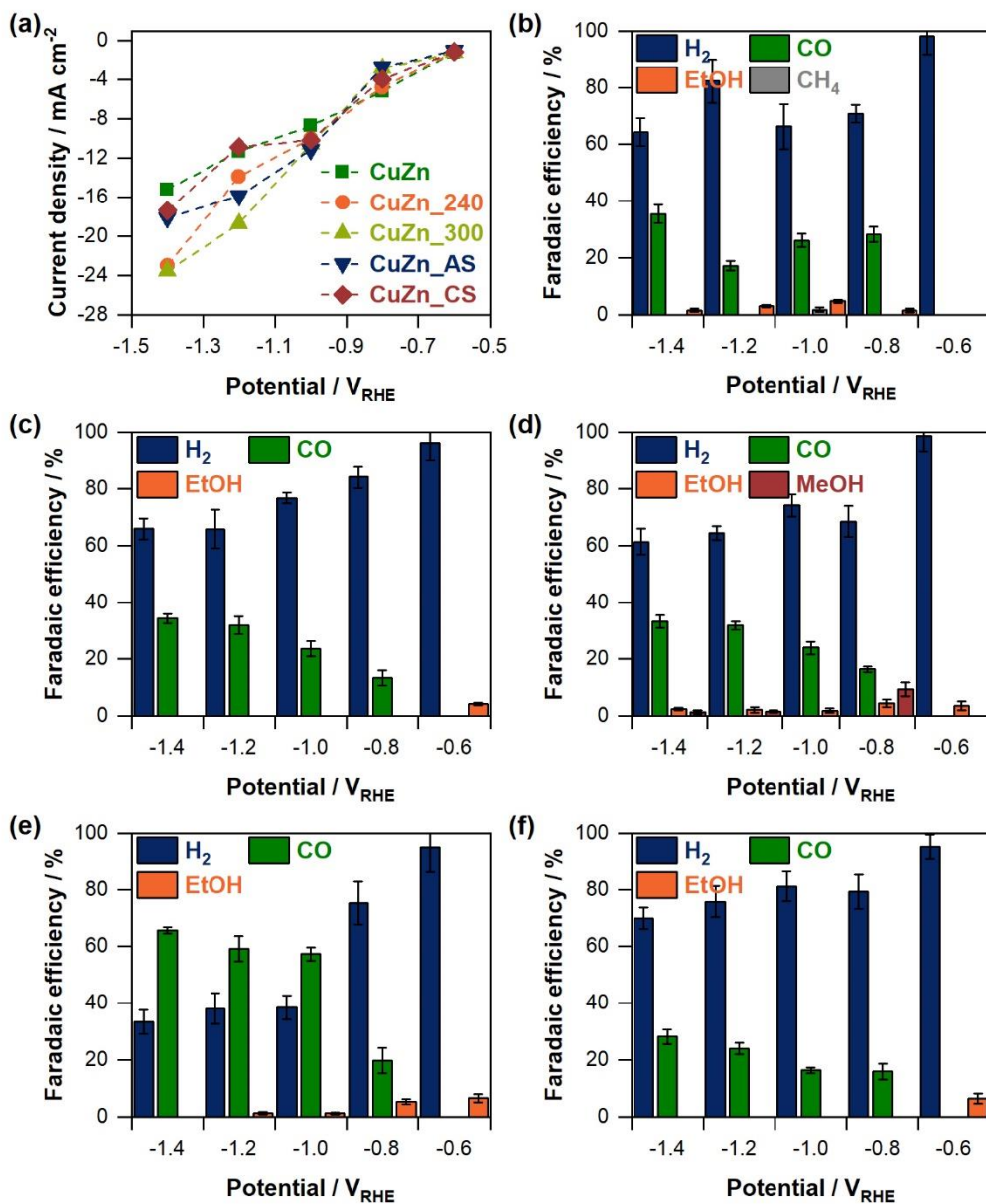


Figure 3.10. (a) Total current density and faradaic efficiency over (b) CuZn, (c) CuZn₂₄₀, (d) CuZn₃₀₀, (e) CuZn_{AS}, and (f) CuZn_{CS} at different applied potentials.

In general, reducing the catalyst under H₂ atmosphere (*ex situ* conditioning) increased the current density (**Figure 3.10a**). However, no significant differences were observed in the H₂ FE values, which remained high. CuZn_240 and CuZn_300 reached FE values for H₂ production > 60 %, regardless of the applied potential. Thus, the current improvement is mainly associated with increased activity of the parasitic HER. In fact, for an applied potential of -1.4 V, the H₂ evolution rate increased from 200.2 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ (CuZn) to 309.6 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ and 295.4 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ for CuZn_240 and CuZn_300, respectively, which represents a 1.5-fold increase in the H₂ production yield. Interestingly, **Figures 3.10c** and **d** show that increasing the reduction temperature causes a slight reduction of the HER activity, which is more noticeable at -0.8 V. Moreover, hydrocarbon production was favored after the catalyst reduction at 300 °C, especially for low applied potentials. As illustrated, at -0.8 V, methanol and ethanol were produced with an FE of 9.3 % and 4.4 %, respectively. Nevertheless, the CO selectivity of CuZn_300 remained low, accounting for only 33.2 % of the overall current density at -1.4 V.

For most of the potentials studied, the *in situ* conditioning also positively affected the overall activity. Compared to the CuZn reference catalyst, a slightly higher current density was recorded for CuZn_AS and CuZn_CS. As observed, H₂ remained the main product when the catalyst was subjected to 50 CV cycles starting from the cathodic scan (CuZn_CS); the H₂ evolution for the reference and CuZn_CS catalysts was similar (FE > 60 %). Notwithstanding, at -1.2 V, the HER activity decreased slightly while the CO production increased 1.4-times compared with the reference catalyst – CuZn. On the other hand, starting the CV from the anodic scan (CuZn_AS) resulted in a remarkable improvement of the selectivity for CO production, being the HER inhibited. In the potential range of -1.4 V to -1.0 V, the H₂ FE did not exceed 40 %, representing an average reduction in the HER activity of 48 % compared to the CuZn catalyst (**Figures 3.10b** and **e**). Moreover, for the same potential range, CuZn_AS is 2 to 3-times more selective for CO production. The maximum FE for CO was 65.7 % recorded at -1.4 V, with a partial current density of -11.9 mA cm⁻².

The CO₂-to-CO conversion efficiency achieved with CuZn_AS is still far from the values reported for noble metal catalysts. For instance, an FE > 95 % for a total current density of -22 mA cm⁻² was obtained using Au nanoneedles as catalyst [44]. Zhu *et al.* also reported a hexagonal Pd nanosheet that achieved a CO FE of 94 % at -0.5 V_{RHE}, without any decay after a stability test of 8 h [23]. Theoretical studies demonstrated that Au and Ag are probably the most effective materials for the electrochemical CO₂ conversion to CO. These catalysts can bind *COOH (* specifies an adsorption site) firmly enough to promote the activation and reduction of CO₂, and *CO weakly enough that CO is easily desorbed from the surface [18]. However, due to the scarcity and high cost of noble metals, the ERCO₂ to CO should avoid using these metals.

Most non-noble metals are not suitable for the adsorption of *COOH and *CO intermediates. Due to its proper intermediate adsorption energy, Zn is considered the most promising candidate to replace noble metals [18]. Won *et al.* reported a hexagonal Zn catalyst that exhibited an FE for CO production of 80 %, stable over 30 h of electrolysis at -0.85 V_{RHE} in 0.5 M KHCO₃ [24]. However, this value was obtained with a low current density (-9.5 mA cm⁻²), hindering CO productivity (142.9 μmol h⁻¹ cm⁻²).

In the present work, Cu and Zn monometallic catalysts were also tested for the ERCO₂, **Figure 3.11**. As observed, the Zn catalyst presents a superior CO FE, reaching *ca.* 80 % for all potentials tested. Even so, the maximum current density of -9.2 mA cm⁻², recorded at -1.4 V, translates into a production yield of 152.6 μmol h⁻¹ cm⁻². In comparison, at the same applied potential, CuZn_AS reached a CO production rate of 244.1 μmol h⁻¹ cm⁻², representing a 1.6-fold improvement (Tables A.7 and A.11, Appendix A). Thus, the present results suggest that bimetallic CuZn catalysts are promising candidates to replace noble metals catalysts for the ERCO₂ to CO. Despite the lower CO FE of CuZn compared to monometallic Zn catalysts, the higher current density provided by CuZn materials makes them more suitable for use in flow cell systems, which work at higher current densities. Moreover, these results clearly show that the ERCO₂ activity and selectivity strongly depend on the conditioning procedure. In particular, the *in situ* potential cycling can be employed to control the CO to H₂ production ratio (syngas composition), which can be attractive for industrial applications. For instance, at -1.0 V, an H₂/CO ratio of

2.5, 5.0, and 0.7 was obtained for CuZn, CuZn_CS, and CuZn_AS, respectively. Whereas the first value is suitable for methanol synthesis or Fischer-Tropsch processes, a ratio > 3 is more appropriate for methane synthesis reaction [20], and < 1 is required for alcohol synthesis or Fischer-Tropsch processes using iron catalysts [45].

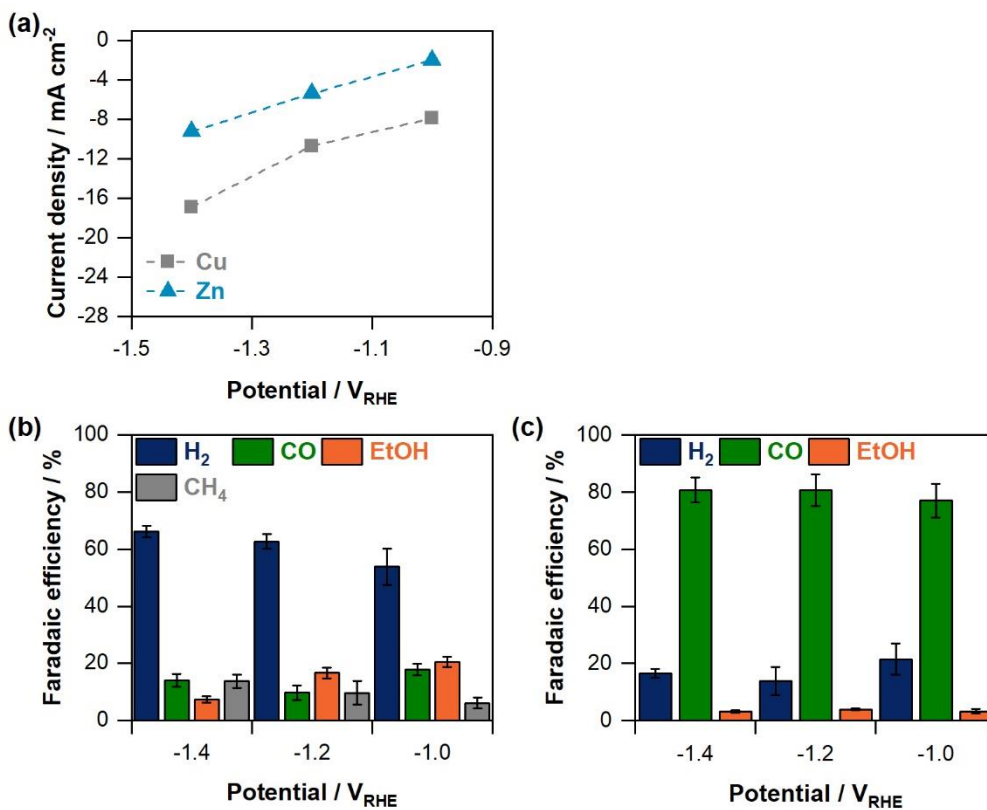


Figure 3.11. (a) Total current density and faradaic efficiency over (b) Cu and (c) Zn single-element catalysts at different applied potentials.

3.4.4 Influence of the physicochemical properties on the electrocatalytic activity

The physicochemical properties of the catalysts suggest that the conditioning procedures mainly affect the particle size, oxidation state, and oxygen vacancies. The particle size of copper plays a critical role in controlling the activity and selectivity of Cu-catalysts during CO₂ electrolysis, as proposed by Reske *et al.* [46]. These authors reported that the formation of CO and H₂ is enhanced by decreasing the particle size, especially below 5 nm. Similar results were obtained by Bernal *et al.* for a CuCo bimetallic system. However, studying CuCo catalysts with particle sizes ranging from *ca.* 1 nm to 20 nm, the authors also concluded that as particles grow in size, the ERCO₂ is favored (*vs.* HER) due to a decrease in the content of undercoordinated sites [47]. It is universally acknowledged that the higher occurrence of undercoordinated sites results in a perturbed electronic structure, increasing the reactivity of catalysts [18]. Nevertheless, for transition metals, it is also true that reducing the coordination number increases the binding energy to intermediate reaction species, mainly *CO, hindering its desorption. Furthermore, the lower surface mobility of *CO also prevents its further reduction to form hydrocarbons on the Cu surface. Thus, catalysts with very small particle size (< 3 nm) favor H₂ formation and are less active for CO₂ reduction [18,46]. The same trend is observed in this study for samples reduced *ex situ*. As previously discussed, the *ex situ* conditioning increased the current density, which is mainly associated with a higher H₂ production (H₂ FE > 60 % for CuZn_240 and CuZn_300). Nevertheless, it was also observed that increasing the reduction temperature resulted in a slight reduction of the HER activity and promoted the formation of hydrocarbons (CuZn_300). This behavior can now be explained by the increase in the size of the Cu⁰ crystallite (Table 3.2).

The oxidation state of copper is another critical parameter that influences the catalytic activity. Literature suggests that Cu⁺ species favor CO₂ reduction activity and selectivity. Moreover, it is reported that the presence of Cu⁺ is associated with a reduction in the reaction onset potential [48,49]. Cu⁺, as well as Cu⁰, also promotes the dissociative adsorption of CO₂ to produce CO, which is then available for the subsequent

hydrogenation into C_1 and C_2 products [50]. Density functional theory (DFT) calculations performed by De Luna *et al.* suggest that the presence of surface oxides (Cu^+) reduces the formation energy of key intermediates, such as $OCCOH^*$, favoring ethylene production [51]. On the other hand, studies by Velasco-Vélez *et al.* suggest that Cu^{2+} is likely not active for reducing CO_2 . Copper carbonates are generated on Cu^{2+} oxides, hindering effective charge transport due to the formation of a passivation layer, ultimately resulting in catalyst deactivation [50]. Accordingly, several authors have already recognized the superior performance of Cu^+ for CO_2 conversion. However, the reported studies concern the CO_2 conversion to C_1 and C_2 products, other than CO. As discussed above, XPS results (**Table 3.2**) suggest that the surface of CuZn_AS is slightly richer in Cu^+ than CuZn_CS and CuZn. Thus, the higher selectivity of CuZn_AS toward the CO_2 -to-CO conversion can be related to the higher content of surface Cu^+ .

Nevertheless, according to the literature, the higher number of Cu^+ species would be expected to increase the production of more reduced products, not CO. Thus, monometallic Cu catalyst was also electrochemically tested and characterized to confirm this hypothesis (**Figure 3.12**, **Table 3.5**). XPS indicates that the population of Cu^+ surface species doubled after the *in situ* potential cycling, ensuring that when the CV starts from the anodic scan (*i.e.*, catalyst oxidation), a fraction of surface copper is reduced from Cu^{2+} to Cu^+ . Moreover, in good agreement with the literature, the predominance of Cu^+ is associated with improved selectivity for C_2 (ethanol) production. The enhanced selectivity for C_2H_5OH production is especially noted at high potential; a 3.4-fold improvement was recorded at -1.4 V. At the same applied potential, the HER activity is also 1.4-times lower. Undoubtedly these results show that the Cu^+ favors the $ERCO_2$. However, it cannot explain why CO production was promoted for CuZn_AS. Accordingly, a synergetic effect between copper and zinc should be present, as discussed in more detail below (section 3.4.5).

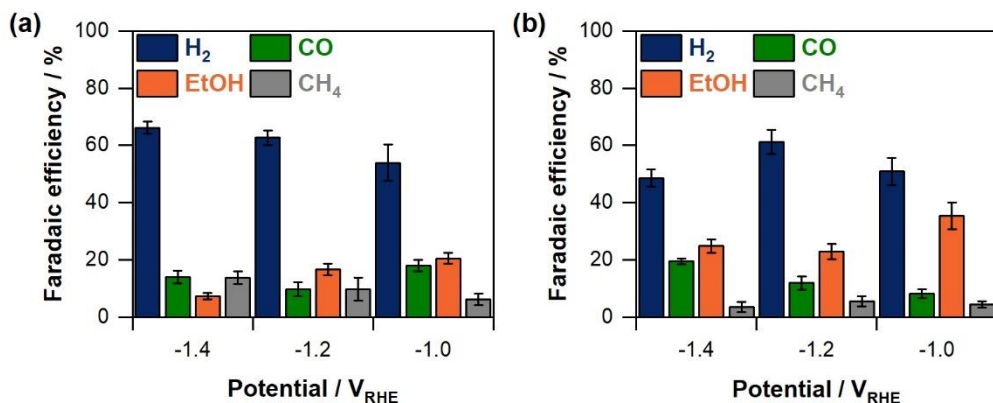


Figure 3.12. Faradaic efficiency over (a) Cu and (b) Cu_AS at different applied potentials.

Table 3.5. Physicochemical properties of the monometallic Cu electrode, before and after *in situ* conditioning (anodic scan).

Sample	Cu ₂ O Mean crystallite size (nm)	% surface Cu ²⁺ /Cu ⁺
Cu	12.3 ± 4	70/30
Cu_AS	11.9 ± 3	34/66

The physicochemical characterization also suggests that the conditioning affects the number of O-defects on the catalyst surface. Surface oxygen vacancies are proposed to take part in many chemical reactions and play central roles in controlling the adsorption and activation of CO₂, serving as active sites for CO₂ adsorption [52,53]. For instance, Lee *et al.* studied the adsorption of CO₂ at oxygen vacancy defects on the surface of TiO₂ [54]. The authors found that one oxygen atom of the CO₂ molecule is readily adsorbed on the oxygen vacancy, which is then healed by an O atom released upon dissociation of the C–O bond. Moreover, of the two C–O bonds present in the CO₂, only the one engaged in the bond with the oxygen vacancy dissociates. As a result, the presence of this type of surface defects on metal oxides lowers the energy barrier for CO₂ activation [18,52,54]. Recently, Gao *et al.* demonstrated that oxygen (II) vacancies facilitate CO₂ adsorption and stabilize reaction intermediates, once again lowering the

rate-limiting activation barrier [55]. In the present study, a higher number of surface oxygen defects is also associated with improved ER CO_2 performance for CO production. As discussed, CuZn_AS presents a slightly higher number of oxygen vacancies than CuZn_CS and CuZn, accounting for the higher FE for CO formation.

EIS was used to gain further insights into the reaction kinetics. The potentiostat EIS tests were conducted at -0.8 V since, according to the literature, the reaction kinetics is controlled by charge transfer processes in the low overpotential region [56]. **Figure 3.13** shows the Nyquist plots obtained for CuZn, CuZn_AS, and CuZn_CS. As expected, the EIS analysis suggests that the presence of O-vacancies resulted in improved electric conductivity, enhancing charge transport [55]. Comparing the values obtained for the charge transfer resistance (R_{ct}) (**Table 3.6**) with the O_v/O_{total} ratio (**Table 3.4**) is clear that a correlation between both variables is present; the R_{ct} decreases with the increasing number of oxygen defects in the following order CuZn_CS < CuZn < CuZn_AS. This result suggests that the CO_2 activation kinetics is promoted by the introduction of oxygen vacancies, which in turn enhances the faradaic process.

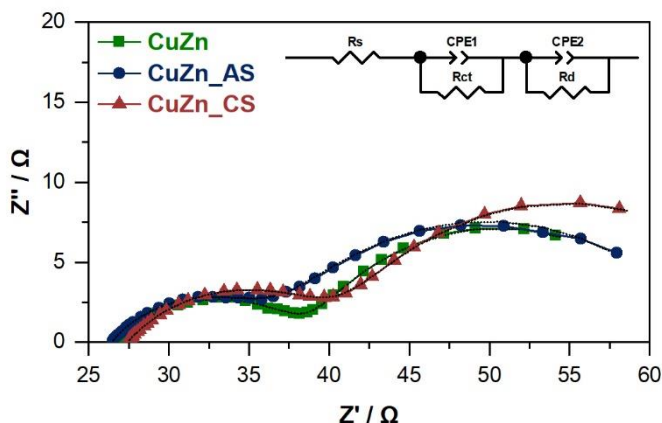


Figure 3.13. Nyquist plots, with fitting curves (dashed lines), of CuZn, CuZn_AS, and CuZn_CS in CO_2 -saturated 0.1 M KHCO_3 with a frequency from 1 MHz to 100 mHz and 10 mV of amplitude. The equivalent circuit model is shown on the insert. R_s stands for the electrolyte resistance, R_{ct} for the charge transfer resistance, and R_d is the diffusion resistance. The double-layer capacitance is distributed between the charge transfer and diffusion processes and is represented by constant phase elements (CPE_1 and CPE_2).

Table 3.6. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -0.8 V (error percentage for each element is given in parentheses).

Elements	CuZn	CuZn_AS	CuZn_CS
R_s (Ω cm ⁻²)	26.75 (0.08)	26.44 (0.09)	27.42 (0.06)
CPE ₁ -T (F cm ⁻²)	8.41×10^{-4} (3.35)	1.19×10^{-3} (5.59)	1.43×10^{-3} (2.67)
CPE ₁ -P	0.52 (0.71)	0.56 (1.16)	0.54 (0.61)
R_{ct} (Ω cm ⁻²)	12.22 (0.62)	10.47 (1.56)	13.76 (0.62)
CPE ₂ -T (F cm ⁻²)	3.57×10^{-2} (0.73)	1.94×10^{-2} (1.03)	3.37×10^{-2} (0.66)
CPE ₂ -P	0.68 (0.83)	0.64 (1.12)	0.70 (0.49)
R_d (Ω cm ⁻²)	23.66 (1.17)	26.75 (1.34)	27.95 (0.49)

The intrinsic reason why the oxygen vacancies facilitate the CO₂ activation was further investigated. **Figure 3.14** shows the CO₂-TPD profiles of the CuZn reference and the catalyst after *in situ* conditioning. As observed, CuZn presents the main CO₂ desorption peak at 527 °C. However, after potential cycling, a deviation in the desorption temperature and peak intensity was recorded, which depends on the initial sweep direction of the CV. When the CV was initiated by the cathodic scan (CuZn_CS), the intensity of the peak and the desorption temperature decreased, suggesting slightly lower CO₂ binding strength and adsorption capacity. On the other hand, starting the CV by the anodic scan (CuZn_AS) resulted in a positive shift in the desorption temperature to 549 °C and increased peak intensity, indicating enhanced binding affinity and CO₂ adsorption. Therefore, the CO₂-TPD experiments suggest that the boosted CO₂-to-CO activity of CuZn_AS can be attributed to the improved binding strength of CO₂, which results in part from the increment of O-vacancies after *in situ* conditioning (anodic scan).

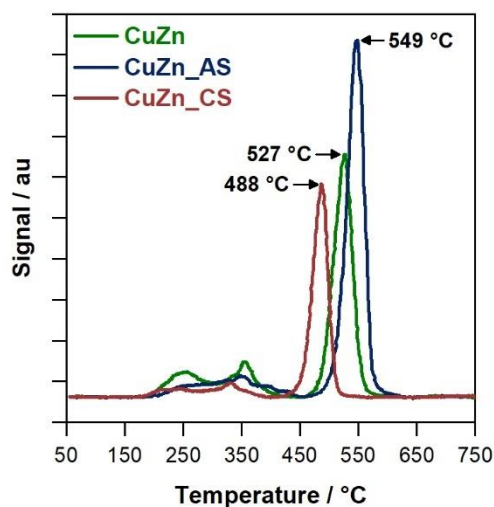


Figure 3.14. CO₂-TPD profiles for CuZn, CuZn_AS, and CuZn_CS.

3.4.5 Cu₂O-ZnO synergy

Hitherto, our results show that, for the prepared CuZn catalyst, the presence of Cu⁺ species and a high number of oxygen defects promotes the ERCO₂ to CO. However, as previously mentioned, a synergetic effect between copper and zinc seems to account for the higher performance of CuZn_AS toward CO production. Thus, the catalytic activity of the CuZn catalyst was compared to control samples to determine how the interaction of the copper and zinc phases affects its properties and performance. The three control samples were the monometallic Cu and Zn catalysts and a physical mixture of these two (CuZn_{mix}). The control samples were physicochemically characterized and tested for the ERCO₂ before and after *in situ* anodic potential sweeping (AS).

According to the TPR and SEM-EDX results (**Figures 3.15** and **3.16**), CuZn_{mix} mainly comprises a phase-segregated mixture of copper and zinc, contrary to what was observed for CuZn. Accordingly, this result endorses the hypothesis that CuZn is made of copper and zinc particles in intimate interaction.

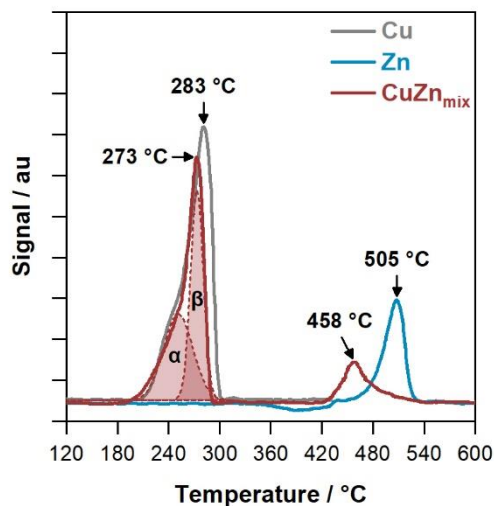


Figure 3.15. H₂-TPR profile of the CuZn catalyst prepared by a physical mixture of Cu and Zn single-element powders; profiles of Cu and Zn samples are also shown for comparison purposes. As observed, the CuZn_{mix} sample displays two well-defined reduction peaks ascribed to the reduction of copper (low-temperature peak) and zinc (high-temperature peak) species.

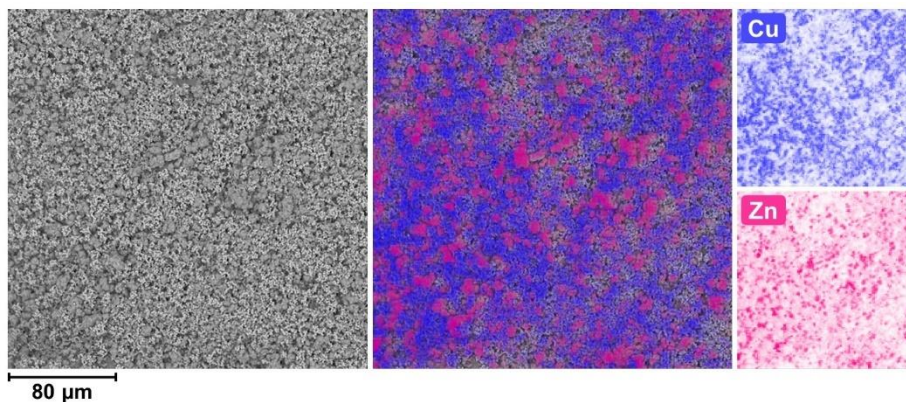


Figure 3.16. SEM micrographs and EDS mapping pictures of the CuZn catalyst prepared by a physical mixture of Cu and Zn single-element powders.

As illustrated in **Figure 3.12a**, a mixture of CO, CH₄, and C₂H₅OH was obtained as ERCO₂ products for Cu single-element catalyst. Moreover, as previously discussed, the C₂H₅OH selectivity was enhanced after *in situ* conditioning, which is attributed to the higher number of surface Cu⁺ species (**Figure 3.12b**). In good agreement with the literature, Zn monometallic catalyst is highly selective for CO production, reaching 80 % of FE (**Figure 3.17a**). However, as already mentioned, the total current density is very low inhibiting CO productivity. Besides, no major difference was observed after *in situ* conditioning (**Figure 3.17b**).

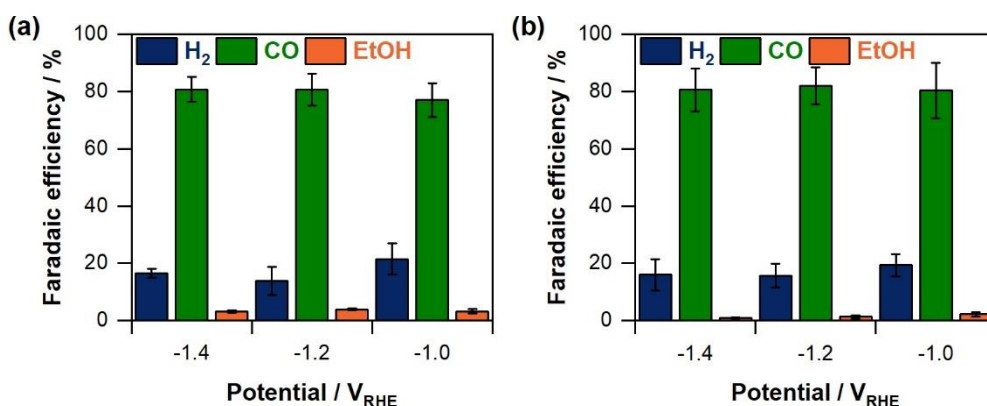


Figure 3.17. Faradaic efficiency over (a) Zn and (b) Zn_AS at different applied potentials.

The physical mixture of Cu and Zn catalysts resulted in an intermediate electrocatalytic behavior between the two monometallic samples. The total current density values obtained for CuZn_{mix} are close to those recorded for Cu catalyst (**Figure 3.18a**), which can be explained by the presence of copper that enhances the electric conductivity and allows obtaining higher activity, as previously reported for CuZn catalysts [9]. Regarding the product distribution, a mixture of CO, CH₄, and C₂H₅OH was produced; still, with higher FE for CO production than Cu catalyst (for the range of potential tested, CuZn_{mix} is *ca.* 1.7-times more selective for CO formation). Moreover, CuZn_{mix} is slightly less active for the HER than the Cu sample (**Figure 3.18b**). Similar to the Cu catalyst, the ethanol selectivity increased after the anodic potential sweep. Nevertheless, no

significant difference was observed concerning the CO FE, suggesting that the CO production is mainly governed by the zinc moieties on the catalyst surface (**Figure 3.18c**). Thus, it is proposed that CuZn_{mix} presents two distinct active sites: (i) Zn-clusters that promote the ERCO₂ to CO and are not affected by the conditioning; and (ii) Cu-rich zones, more selective for the HER and the ERCO₂ to ethanol, whose activity can be controlled through conditioning.

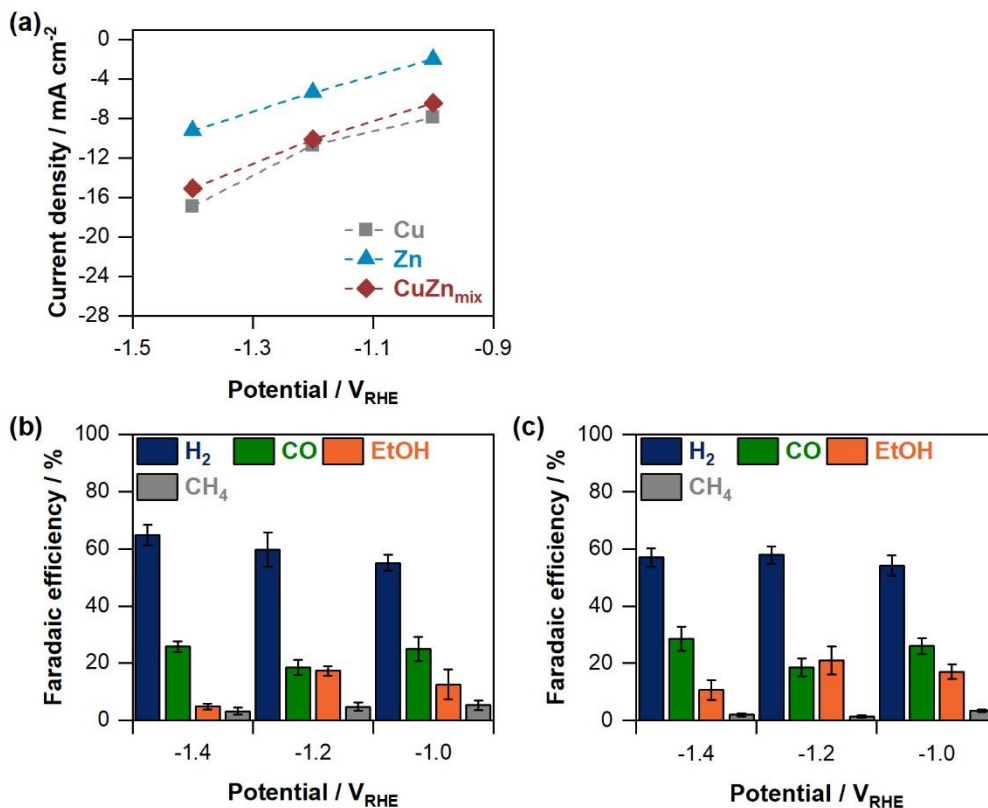


Figure 3.18. (a) Total current density and faradaic efficiency over (b) CuZn_{mix}, and (c) CuZn_{mix}_AS at different applied potentials.

On the other hand, CuZn presents quite different electrocatalytic behavior compared to CuZn_{mix} (**Figure 3.19**). For CuZn, the ethanol production is almost negligible, and the electrocatalytic activity is strongly influenced by the anodic potential cycling. After conditioning, CO production was strongly promoted at the expense of the H₂ evolution.

Thus, for CuZn, it is suggested that Cu-Zn in intimate contact are the active centers for the ER CO_2 – assumption supported by the characterization results.

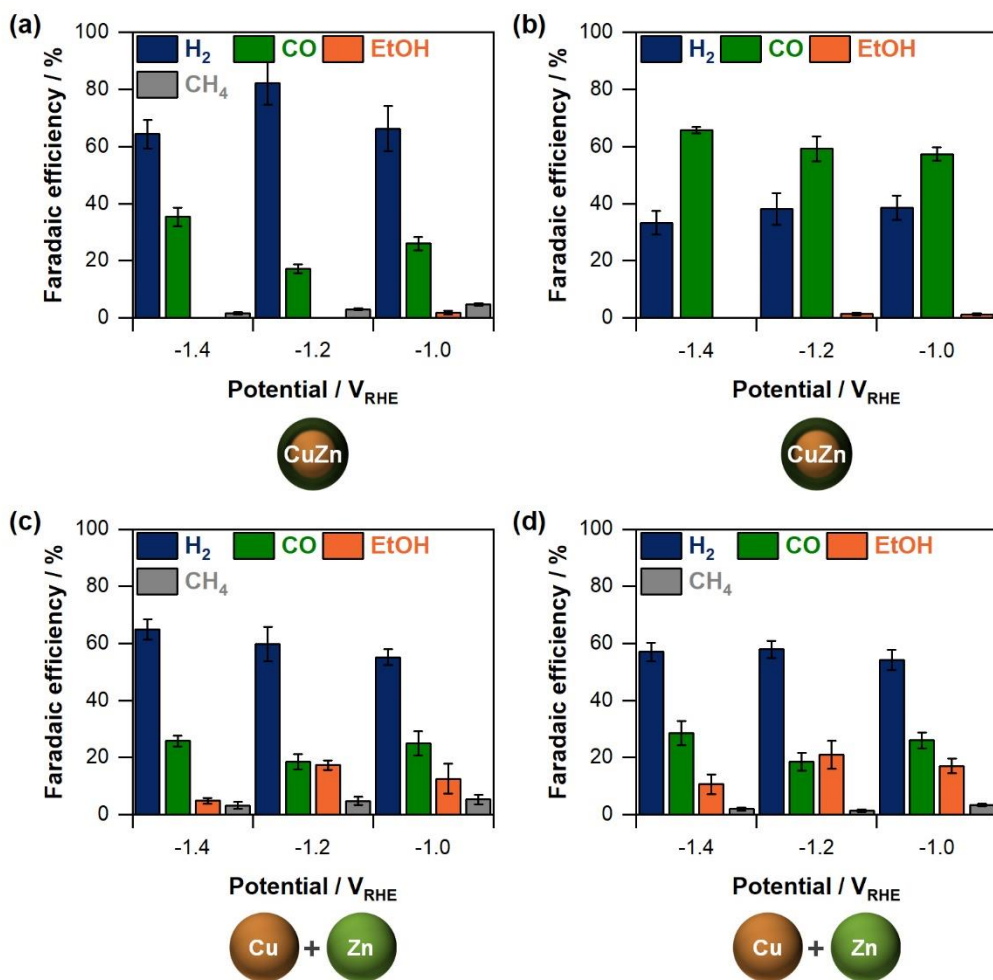


Figure 3.19. Comparison between the FE values obtained for (a, b) CuZn and (c, d) CuZn_{mix}, (a, c) before and (b, d) after *in situ* anodic conditioning.

Compared with CuZn_{mix}, it is proposed that the particular electronic structure of the CuZn active centers resulted in significantly different nature of the electroactive species and, thus, adsorbate binding energy. Therefore, it is considered that the active centers present in the CuZn sample promote the stabilization of key intermediates (possibly

*COOH), as described for other bimetallic systems [12,26,57,58]. Moreover, it is reported that the production of products that require a larger number of reaction steps involves the stabilization of both *CO and *H since adsorbed CO is successively protonated to evolve as hydrocarbon species [12]. Thus, the decreased ethanol selectivity of CuZn can be attributed to a low binding strength of *CO and *H on the catalyst surface.

However, it cannot be discarded that geometric effects can also be present. As reported, the CO production is essentially governed by the binding strength of *COOH and *CO; *i.e.*, to enhance the CO selectivity, a catalyst must stabilize *COOH more strongly than *CO so that CO₂ readily activates to COOH and desorbs as CO [18,59]. For monometallic systems, the binding strength of different intermediates scales together (scaling relation). On the other hand, bimetallic catalysts can potentially stabilize *COOH relative to *CO by forming one additional bond at the oxygen end with an oxophilic element on the catalyst surface [12,17]. Owing to the mentioned uncertainty, *in situ*/operando experiments must be conducted. With these advanced techniques, it is possible to reveal the real active sites, the formed intermediates, and the local environment, enabling the elucidation of the reaction mechanism with good reliability. Nevertheless, in **Figure 3.20**, a possible reaction mechanism is proposed for CuZn and CuZn_{mix}, considering the typical three reaction steps [12,18,58] (* denotes an active catalytic site):



First, CO₂ is adsorbed on the catalytic surface and then reduced by incoming electrons, coupled with adsorbed protons, resulting in *COOH formation. Afterward, *COOH reacts with another proton and electron to produce *CO, followed by its desorption from the catalyst surface (non-electrochemical process) [18,26].

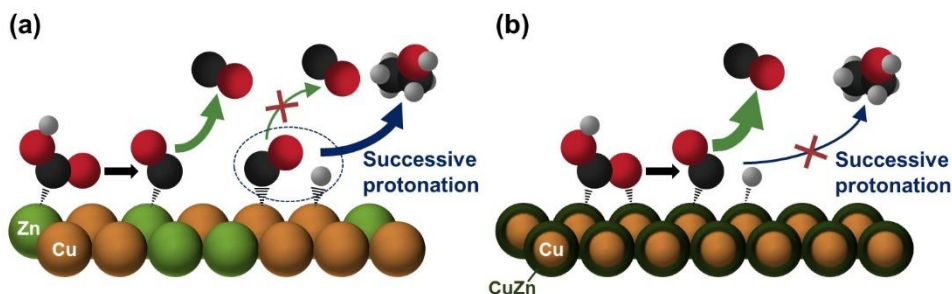


Figure 3.20. Schematic showing the proposed reaction mechanism on the surface of (a) CuZn_{mix} and (b) CuZn. Filled circles with black are C, red are O, and light grey are H. The stroke weight indicates the relative intermediate binding strength. Colored arrows indicate the pathway to CO (green) and ethanol (blue) production; larger arrows indicate higher product formation.

The results clearly indicate that a synergetic effect between copper and zinc is present for CuZn. However, understanding how this synergy is affected by the conditioning (specifically for *in situ*) is also essential; it can provide useful information to better comprehend the improved ER_{CO₂} to CO performance of CuZn_AS. **Figure 3.21** illustrates the gradual evolution of the CV profile of CuZn_AS and CuZn_CS. With the approach of the 50th cycle, the current density reaches a constant pattern, indicating that a cyclic steady-state is reached. In both cases, cathodic and anodic peaks are observed and ascribed to the reduction and oxidation of copper species. This assignment was made considering that no redox activity was measured for Zn single-element sample (Figure A.13, Appendix A) in the potential window tested.

Since the characterization techniques indicate that CuZn has a mixture of Cu²⁺ and Cu⁺, the anodic peak observed for CuZn_AS is attributed to the Cu⁺ to Cu²⁺ oxidation. In turn, the reverse reduction process (Cu²⁺ to Cu⁺) occurred during the down scan, in good agreement with previous studies and the standard redox potential of Cu²⁺/Cu⁺ ($E^0 = 0.159 \text{ V}_{\text{RHE}}$) [60–62]. After completing the conditioning treatment, a negative shift in the cathodic peak potential was observed, followed by increased peak intensity. As summarized in **Table 3.7**, the peak-to-peak separation (ΔE_p) value increased, indicating

that the degree of irreversibility of the Cu²⁺ to Cu⁺ reduction increased. This behavior explains the higher content of Cu⁺ for CuZn_AS (**Table 3.2**). Moreover, it is proposed that a stronger copper-zinc interaction is responsible for the stabilization of surface Cu⁺ species, as reported for Cu/ZnO-Al₂O₃ [63]. Starting the CVs with the anodic scan results in the oxidation of Cu⁺ to Cu²⁺, leaving an incomplete 3d-subshell. In turn, this incomplete subshell promotes the electron transfer from ZnO to Cu²⁺, strengthening the interaction between both elements. The BE of the core level of copper supports this hypothesis, as previously described [64,65]. **Tables 3.1** and **3.3** show that the BE of Cu 2p_{3/2} shifted to low energies by *ca.* 0.3 eV compared to CuZn, confirming the electron transfer during the *in situ* anodic conditioning and, thus, strong ligand effect from neighboring zinc atoms [17].

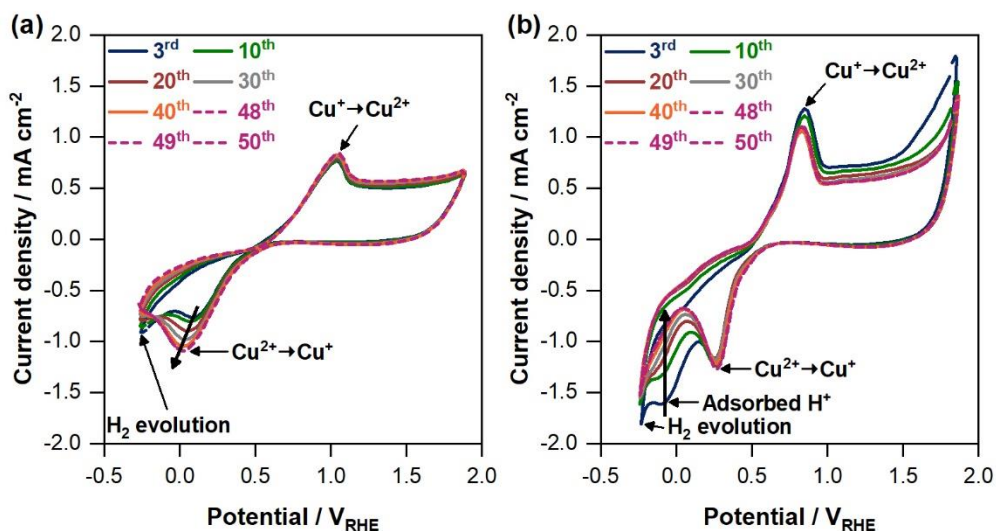


Figure 3.21. IR-corrected CVs in N₂-saturated 0.1 M KHCO₃, (a) starting from the anodic scan (AS) and (b) starting from the cathodic scan (CS).

Similarly, the Cu²⁺ to Cu⁺ reduction and the reverse Cu⁺ to Cu²⁺ oxidation processes were observed for CuZn_CS. However, in this case, the ΔE_p is closer to the standard value for a reversible redox reaction (59 mV z⁻¹), suggesting higher reversibility when compared to CuZn_AS. This behavior may account for the less pronounced increase in

surface Cu^+ after the *in situ* cathodic conditioning (**Table 3.2**). CuZn_CS also shows one additional cathodic peak during the first CV cycles at -0.12 V. According to the trends of the standard redox potentials for copper (0.52 V_{RHE} for Cu^+/Cu^0 , 0.34 V_{RHE} for $\text{Cu}^{2+}/\text{Cu}^0$, and 0.16 V_{RHE} for $\text{Cu}^{2+}/\text{Cu}^+$) [66], this peak cannot be attributed to the reduction of other copper species. During the down scan of the voltage, the Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^0$ reductions are thermodynamically more favorable than $\text{Cu}^{2+}/\text{Cu}^+$. Thus, if these reactions were taking place, new reduction peaks would be observed at higher potential. Thereby, this peak is assigned to the reduction of protons to adsorbed atomic hydrogen, as proposed by the literature [61]. The adsorption of H^+ was absent for CuZn_AS, which may be related to the lower HER activity of this sample.

Table 3.7. Summary of cyclic voltammetry results obtained for CuZn_AS and CuZn_CS.

Sample	CV cycle	E_{pa} (V)	i_{pa} (mA cm^{-1})	E_{pc} (V)	i_{pc} (mA cm^{-1})	ΔE_{p} (V)
CuZn_AS	3 rd	1.04	0.61	0.10	-0.74	0.94
	50 th	1.04	0.78	0.02	-1.06	1.02
CuZn_CS	3 rd	0.85	1.01	0.27	-1.20	0.58
	50 th	0.83	0.94	0.27	-1.26	0.56

E_{pa} : anodic peak potential; i_{pa} : anodic peak current; E_{pc} : cathodic peak potential; i_{pc} : cathodic peak current; ΔE_{p} : peak-to-peak separation.

In summary, the copper-zinc synergy appears unaffected by the cathodic potential sweep (CS). On the other hand, during the anodic potential sweep (AS), the interaction between copper and zinc species is strengthened, resulting in the stabilization of Cu^+ on the catalyst surface and, thus, enhanced CO_2 -to-CO conversion.

An overview of the influence of the post-synthesis treatments on the physicochemical structure and activity of the $\text{Cu}_2\text{O}/\text{ZnO}$ catalyst is provided in **Table 3.8**.

Table 3.8. Influence of the different post-synthesis treatments on the physicochemical structure of the catalysts and electrochemical behavior. A structure-activity relationship is also presented.

Sample	Physicochemical structure	Electrochemical behavior	Structure-Activity relationship
CuZn	- Core-shell structure (Cu-rich core + Zn-rich shell) - Bulk structure (XRD): Cu₂O (14 nm); ZnO (17 nm) - Surface structure (XPS): Cu⁺ (11 %); Cu²⁺ (45 %); Zn²⁺ (44 %) - Copper-zinc interaction	High HER activity (H₂ FE > 65 % for the entire potential range)	Synergetic effect between copper and zinc species promotes the CO₂-to-CO conversion
CuZn_240	- Severe modification of the bulk structure: Cu⁰ (16 nm); ZnO (46 nm) (Reduction of copper species to metallic copper and crystallite growth)	- Increased current density - High HER activity (H₂ FE > 60 % for the entire potential range)	
CuZn_300	- Severe modification of the bulk structure: Cu⁰ (33 nm); ZnO (42 nm) (Reduction of copper species to metallic copper and crystallite growth)	- Increased current density - Slight reduction of the HER activity - Favored hydrocarbon production (methanol and ethanol)	Increased Cu⁰ crystallite size promotes hydrocarbon formation and reduces the HER activity
CuZn_AS	- No changes in the bulk structure - Slight surface rearrangement: Increase in the fraction of Cu⁺ surface species (↑1.7-fold) - Increased number of O-defects - Stronger copper-zinc interaction	- Increased current density - Remarkable improvement of CO production (maximum FE of 65.7 % at -1.4 V) - Inhibition of the HER activity (H₂ FE < 48 % for the entire potential range)	- Cu⁺ favors the ERCO₂ - O-defects improve the binding strength of CO₂ and enhance the charge transport, favoring CO production - Stronger copper-zinc interaction reinforces the enhancement of CO₂-to-CO conversion
CuZn_CS	- No changes in the bulk structure - Slight surface rearrangement: Increase in the fraction of Cu⁺ surface species (↑1.4-fold) - Decreased number of O-defects	- Increased current density - High HER activity (H₂ FE > 60 % for the entire potential range)	- Cu⁺ favors the ERCO₂ - Decreased concentration of O-vacancies results in higher charge transport resistance and decreased CO₂ binding strength

3.5 Conclusions

In this chapter, the influence of post-synthesis procedures on the electrocatalytic performance of a Cu₂O/ZnO catalyst was investigated. Both *ex situ* and *in situ* conditioning methods were implemented as an easy tool for tuning the ERCO₂ selectivity of the developed catalyst. In particular, it is reported that the CO/H₂ production ratio can be controlled (syngas composition).

The *ex situ* conditioning (reduction under H₂ atmosphere) resulted in severe structural modifications. Accordingly, the overall catalytic activity increased, however, due to a considerable increase in the HER activity. On the other hand, the electrochemical conditioning (*in situ*, 50 CV cycles) resulted in a slight surface rearrangement. It is proposed that starting the CV cycles from the anodic scan promotes an electron transfer from zinc to copper species, increasing the interaction and synergetic effect between both elements. In turn, the stronger copper-zinc interaction helps to stabilize the Cu⁺ species at the catalyst surface. Moreover, the number of oxygen defects on the catalyst surface increases after the potential cycling, improving the CO₂ binding strength and adsorption capacity. These slight rearrangements remarkably boosted the CO₂-to-CO conversion, with the CuZn_AS sample reaching the maximum FE for CO production of 65.7 % at -1.4 V, with a partial current density of -11.9 mA cm⁻².

The present results open new perspectives for improving the ERCO₂ selectivity under unfavorable operating conditions by highlighting the importance of post-synthesis procedures. Moreover, the results suggest that bimetallic CuZn catalysts are promising candidates to replace noble metals for the ERCO₂ to CO.

Acknowledgments

Azenha, C., is grateful to the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant (reference SFRH/BD/128768/2017). This work was performed under the project “SunStorage - Harvesting and storage of solar energy”, with reference

POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through COMPETE 2020 - Operational Programme for Competitiveness and Internationalisation (OPCI), and by national funds, through FCT - Fundação para a Ciência e a Tecnologia I.P. This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC). This work was carried out in part through the use of the INL Advanced Electron Microscopy, Imaging and Spectroscopy Facility. The authors also acknowledge P. Tavares from UME-UTAD for XRD analyses and CEMUP for XPS analyses.

Nomenclature

Abbreviation	Definition
AS	Anodic potential sweep
BE	Binding energy
CO ₂ -TPD	Carbon dioxide temperature-programmed desorption
CPE	Constant phase element
CS	Cathodic potential sweep
CV	Cyclic voltammetry
DFT	Density functional theory
ECSA	Electrochemical active surface area
EIS	Electrochemical impedance spectroscopy
ERCO ₂	Electrochemical reduction of CO ₂
FE	Faradaic efficiency
FWHM	Full width at half maximum
GC	Gas chromatography
GDL	Gas diffusion layer
H ₂ -TPR	Hydrogen temperature-programmed reduction
HADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
HER	Hydrogen evolution reaction
HR-TEM	High-resolution transmission electron microscopy
JCPDS	Joint committee on powder diffraction standards
KE	Kinetic energy
LSV	Linear sweep voltammetry
O _c	Chemisorbed oxygenated species
O _L	Lattice oxygen
O _v	Oxygen vacancy
RHE	Reversible hydrogen electrode
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
TCD	Thermal conductivity detector
TPR	Temperature-programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Greek Symbol	Definition	Unit
α'	Modified Auger parameter	eV
ΔE_p	Peak-to-peak separation	V

Variable	Definition	Unit
A_{1s}/B_s	Ratio of the main XPS peak/shake-up areas	
A_t	Total area of the main XPS emission	
B	XPS shake-up areas	
C_{dl}	Double-layer capacitance	mF cm ⁻²
E^0	Standard redox potential	V
E_{pa}	Anodic peak potential	V
E_{pc}	Cathodic peak potential	V
i_{pa}	Anodic peak current	mA cm ⁻²
i_{pc}	Cathodic peak current	mA cm ⁻²
R_{ct}	Charge transfer resistance	Ω cm ⁻²
R_d	Diffusion resistance	Ω cm ⁻²
R_s	Electrolyte resistance	Ω cm ⁻²
z	Number of electrodes exchanged	

References

- [1] T. Zhang, H. Zhong, Y. Qiu, X. Li, H. Zhang, Zn electrode with a layer of nanoparticles for selective electroreduction of CO₂ to formate in aqueous solutions, *J. Mater. Chem. A*. 4 (2016) 16670–16676. <https://doi.org/10.1039/C6TA07000K>.
- [2] Y. Wang, J. Liu, Y. Wang, A.M. Al-Enizi, G. Zheng, Tuning of CO₂ reduction selectivity on metal electrocatalysts, *Small*. 13 (2017) 1701809. <https://doi.org/10.1002/sml.201701809>.
- [3] L. Fan, C. Xia, F. Yang, J. Wang, H. Wang, Y. Lu, Strategies in catalysts and electrolyzer design for electrochemical CO₂ reduction toward C₂₊ products, *Sci. Adv.* 6 (2020) eaay3111. <https://doi.org/10.1126/sciadv.aay3111>.
- [4] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T.F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design, *Science* 355 (2017) eaad4998. <https://doi.org/10.1126/science.aad4998>.
- [5] V.C. Hoang, V.G. Gomes, N. Kornienko, Metal-based nanomaterials for efficient CO₂ electroreduction: Recent advances in mechanism, material design and selectivity, *Nano Energy*. 78 (2020) 105311. <https://doi.org/10.1016/j.nanoen.2020.105311>.
- [6] S. Garg, M. Li, A.Z. Weber, L. Ge, L. Li, V. Rudolph, G. Wang, T.E. Rufford, Advances and challenges in electrochemical CO₂ reduction processes: An engineering and design perspective looking beyond new catalyst materials, *J. Mater. Chem. A*. 8 (2020) 1511–1544. <https://doi.org/10.1039/C9TA13298H>.
- [7] D. Ren, J. Fong, B.S. Yeo, The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction, *Nat. Commun.* 9 (2018) 925. <https://doi.org/10.1038/s41467-018-03286-w>.

- [8] W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang, Z. Jin, Progress and perspective of electrocatalytic CO₂ reduction for renewable carbonaceous fuels and chemicals, *Adv. Sci.* 5 (2018) 1700275. <https://doi.org/10.1002/advs.201700275>.
- [9] J. Zeng, T. Rino, K. Bejtka, M. Castellino, A. Sacco, M.A. Farkhondehfal, A. Chiodoni, F. Drago, C.F. Pirri, Coupled copper–zinc catalysts for electrochemical reduction of carbon dioxide, *ChemSusChem*. 13 (2020) 4128–4139. <https://doi.org/10.1002/cssc.202000971>.
- [10] J. Albo, A. Sáez, J. Solla-Gullón, V. Montiel, A. Irabien, Production of methanol from CO₂ electroreduction at Cu₂O and Cu₂O/ZnO-based electrodes in aqueous solution, *Appl. Catal. B: Environ.* 176–177 (2015) 709–717. <https://doi.org/10.1016/j.apcatb.2015.04.055>.
- [11] C. Wang, M. Cao, X. Jiang, M. Wang, Y. Shen, A catalyst based on copper-cadmium bimetal for electrochemical reduction of CO₂ to CO with high faradaic efficiency, *Electrochim. Acta.* 271 (2018) 544–550. <https://doi.org/10.1016/j.electacta.2018.03.156>.
- [12] D. Kim, J. Resasco, Y. Yu, A.M. Asiri, P. Yang, Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold-copper bimetallic nanoparticles, *Nat. Commun.* 5 (2014) 4948. <https://doi.org/10.1038/ncomms5948>.
- [13] R.G. Grim, Z. Huang, M.T. Guarnieri, J.R. Ferrell, L. Tao, J.A. Schaidle, Transforming the carbon economy: Challenges and opportunities in the convergence of low-cost electricity and reductive CO₂ utilization, *Energy Environ. Sci.* 13 (2020) 472–494. <https://doi.org/10.1039/C9EE02410G>.
- [14] O.G. Sánchez, Y.Y. Birdja, M. Bulut, J. Vaes, T. Breugelmans, D. Pant, Recent advances in industrial CO₂ electroreduction, *Curr. Opin. Green Sustain. Chem.* 16 (2019) 47–56. <https://doi.org/10.1016/j.cogsc.2019.01.005>.

- [15] J.R. Rostrup-Nielsen, J. Sehested, J.K. Nørskov, Hydrogen and synthesis gas by steam- and CO₂ reforming, in *Advances in Catalysis*: pp. 65–139. [https://doi.org/10.1016/S0360-0564\(02\)47006-X](https://doi.org/10.1016/S0360-0564(02)47006-X).
- [16] R. Küngas, Review—Electrochemical CO₂ reduction for CO production: comparison of low- and high-temperature electrolysis technologies, *J. Electrochem. Soc.* 167 (2020) 044508. <https://doi.org/10.1149/1945-7111/ab7099>.
- [17] L. Wang, H. Peng, S. Lamaison, Z. Qi, D.M. Koshy, M.B. Stevens, D. Wakerley, J.A. Zamora Zeledón, L.A. King, L. Zhou, Y. Lai, M. Fontecave, J. Gregoire, F. Abild-Pedersen, T.F. Jaramillo, C. Hahn, Bimetallic effects on Zn-Cu electrocatalysts enhance activity and selectivity for the conversion of CO₂ to CO, *Chem Catal.* 1 (2021) 663–680. <https://doi.org/10.1016/j.checat.2021.05.006>.
- [18] F.-Y. Gao, R.-C. Bao, M.-R. Gao, S.-H. Yu, Electrochemical CO₂-to-CO conversion: Electrocatalysts, Electrolytes, and electrolyzers, *J. Mater. Chem. A.* 8 (2020) 15458–15478. <https://doi.org/10.1039/D0TA03525D>.
- [19] M. Zhao, Y. Gu, P. Chen, Z. Xin, H. Zhu, B. Wang, K. Zhu, S. Yan, Z. Zou, Highly selective electrochemical CO₂ reduction to CO using a redox-active couple on low-crystallinity mesoporous ZnGa₂O₄ catalyst, *J. Mater. Chem. A.* 7 (2019) 9316–9323. <https://doi.org/10.1039/C9TA00562E>.
- [20] H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B.R. Cuenya, Exceptional size-dependent activity enhancement in the electroreduction of CO₂ over Au nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 16473–16476. <https://doi.org/10.1021/ja508879j>.
- [21] D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang, X. Bao, Size-dependent electrocatalytic reduction of CO₂ over Pd nanoparticles, *J. Am. Chem. Soc.* 137 (2015) 4288–4291. <https://doi.org/10.1021/jacs.5b00046>.
- [22] S. Liu, H. Tao, L. Zeng, Q. Liu, Z. Xu, Q. Liu, J.-L. Luo, Shape-dependent electrocatalytic reduction of CO₂ to CO on triangular silver nanoplates, *J. Am. Chem. Soc.* 139 (2017) 2160–2163. <https://doi.org/10.1021/jacs.6b12103>.

- [23] W. Zhu, L. Zhang, P. Yang, C. Hu, Z. Luo, X. Chang, Z.-J. Zhao, J. Gong, Low-coordinated edge sites on ultrathin palladium nanosheets boost carbon dioxide electroreduction performance, *Angew. Chem. Int. Ed.* 57 (2018) 11544–11548. <https://doi.org/10.1002/anie.201806432>.
- [24] D.H. Won, H. Shin, J. Koh, J. Chung, H.S. Lee, H. Kim, S.I. Woo, Highly Efficient, Selective, and Stable CO₂ electroreduction on a hexagonal Zn catalyst, *Angew. Chem. Int. Ed.* 55 (2016) 9297–9300. <https://doi.org/10.1002/anie.201602888>.
- [25] J. Rosen, G.S. Hutchings, Q. Lu, R. V. Forest, A. Moore, F. Jiao, Electrodeposited Zn dendrites with enhanced CO selectivity for electrocatalytic CO₂ reduction, *ACS Catal.* 5 (2015) 4586–4591. <https://doi.org/10.1021/acscatal.5b00922>.
- [26] Z. Yin, D. Gao, S. Yao, B. Zhao, F. Cai, L. Lin, P. Tang, P. Zhai, G. Wang, D. Ma, X. Bao, Highly selective palladium-copper bimetallic electrocatalysts for the electrochemical reduction of CO₂ to CO, *Nano Energy.* 27 (2016) 35–43. <https://doi.org/10.1016/j.nanoen.2016.06.035>.
- [27] Y. Feng, Z. Li, H. Liu, C. Dong, J. Wang, S.A. Kulinich, X. Du, Laser-prepared CuZn alloy catalyst for selective electrochemical reduction of CO₂ to ethylene, *Langmuir.* 34 (2018) 13544–13549. <https://doi.org/10.1021/acs.langmuir.8b02837>.
- [28] D. Ren, B.S.-H. Ang, B.S. Yeo, Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu_xZn catalysts, *ACS Catal.* 6 (2016) 8239–8247. <https://doi.org/10.1021/acscatal.6b02162>.
- [29] A. Le Valant, C. Comminges, C. Tisseraud, C. Canaff, L. Pinard, Y. Pouilloux, The Cu–ZnO synergy in methanol synthesis from CO₂ , Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu + ZnO mechanical mixtures, *J. Catal.* 324 (2015) 41–49. <https://doi.org/10.1016/j.jcat.2015.01.021>.

- [30] J. Zeng, K. Bejtka, W. Ju, M. Castellino, A. Chiodoni, A. Sacco, M.A. Farkhondehfal, S. Hernández, D. Rentsch, C. Battaglia, C.F. Pirri, Advanced Cu-Sn foam for selectively converting CO₂ to CO in aqueous solution, *Appl. Catal. B: Environ.* 236 (2018) 475–482. <https://doi.org/10.1016/j.apcatb.2018.05.056>.
- [31] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.* 257 (2010) 887–898. <https://doi.org/10.1016/j.apsusc.2010.07.086>.
- [32] M.C. Biesinger, Advanced analysis of copper X-ray photoelectron spectra, *Surf. Interface Anal.* 49 (2017) 1325–1334. <https://doi.org/10.1002/sia.6239>.
- [33] G.O. Larrazábal, A.J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, Solvothermally-prepared Cu₂O Electrocatalysts for CO₂ reduction with tunable selectivity by the introduction of p-block elements, *ChemSusChem.* 10 (2017) 1255–1265. <https://doi.org/10.1002/cssc.201601578>.
- [34] I. Beinik, M. Hellström, T.N. Jensen, P. Broqvist, J. V. Lauritsen, Enhanced wetting of Cu on ZnO by migration of subsurface oxygen vacancies, *Nat. Commun.* 6 (2015) 8845. <https://doi.org/10.1038/ncomms9845>.
- [35] F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei, A. Rossi, Nanosized surface films on brass alloys by XPS and XAES, *RSC Adv.* 6 (2016) 31277–31289. <https://doi.org/10.1039/C5RA23135C>.
- [36] J.A. Rodriguez, J. Hrbek, Photoemission studies of zinc-noble metal alloys: Zn-Cu, Zn-Ag, and Zn-Au films on Ru(001), *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* 11 (1993) 1998–2002. <https://doi.org/10.1116/1.578398>.
- [37] G. Águila, S. Guerrero, P. Araya, Influence of the crystalline structure of ZrO₂ on the activity of Cu/ZrO₂ catalysts on the water gas shift reaction, *Catal. Commun.* 9 (2008) 2550–2554. <https://doi.org/10.1016/j.catcom.2008.07.011>.

- [38] M.M. Günter, T. Ressler, R.E. Jentoft, B. Bems, Redox behavior of copper oxide/zinc oxide catalysts in the steam reforming of methanol studied by in situ x-ray diffraction and absorption spectroscopy, *J. Catal.* 203 (2001) 133–149. <https://doi.org/10.1006/jcat.2001.3322>.
- [39] M. Kim, J.-H. Seo, D. Zhao, S.-C. Liu, K. Kim, K. Lim, W. Zhou, E. Waks, Z. Ma, Transferrable single crystalline 4H-SiC nanomembranes, *J. Mater. Chem. C.* 5 (2017) 264–268. <https://doi.org/10.1039/C6TC04480H>.
- [40] Y. Wang, Y. Lü, W. Zhan, Z. Xie, Q. Kuang, L. Zheng, Synthesis of porous Cu₂O/CuO cages using Cu-based metal–organic frameworks as templates and their gas-sensing properties, *J. Mater. Chem. A.* 3 (2015) 12796–12803. <https://doi.org/10.1039/C5TA01108F>.
- [41] M. Claros, M. Setka, Y.P. Jimenez, S. Vallejos, AACVD Synthesis and Characterization of Iron and Copper Oxides Modified ZnO structured films, *Nanomaterials.* 10 (2020) 471. <https://doi.org/10.3390/nano10030471>.
- [42] N.M. Vuong, N.D. Chinh, B.T. Huy, Y.-I. Lee, CuO-decorated ZnO hierarchical nanostructures as efficient and established sensing materials for H₂S gas sensors, *Sci. Rep.* 6 (2016) 26736. <https://doi.org/10.1038/srep26736>.
- [43] D. Kim, S. Lee, J.D. Ocon, B. Jeong, J.K. Lee, J. Lee, Insights into an autonomously formed oxygen-evacuated Cu₂O electrode for the selective production of C₂H₄ from CO₂, *Phys. Chem. Chem. Phys.* 17 (2015) 824–830. <https://doi.org/10.1039/C4CP03172E>.
- [44] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C.T. Dinh, F. Fan, C. Cao, F.P.G. de Arquer, T.S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S.O. Kelley, E.H. Sargent, Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration, *Nature.* 537 (2016) 382–386. <https://doi.org/10.1038/nature19060>.

- [45] Y. Liu, D. Yuan, D. Ji, Z. Li, Z. Zhang, B. Wang, H. Wu, Syngas production: diverse H_2/CO range by regulating carbonates electrolyte composition from $\text{CO}_2/\text{H}_2\text{O}$ via co-electrolysis in eutectic molten salts, *RSC Adv.* 7 (2017) 52414–52422. <https://doi.org/10.1039/C7RA07320H>.
- [46] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, Particle size effects in the catalytic electroreduction of CO_2 on Cu nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 6978–6986. <https://doi.org/10.1021/ja500328k>.
- [47] M. Bernal, A. Bagger, F. Scholten, I. Sinev, A. Bergmann, M. Ahmadi, J. Rossmeisl, B.R. Cuenya, CO_2 electroreduction on copper-cobalt nanoparticles: Size and composition effect, *Nano Energy.* 53 (2018) 27–36. <https://doi.org/10.1016/j.nanoen.2018.08.027>.
- [48] H. Mistry, A.S. Varela, C.S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E.A. Stach, J.C. Yang, P. Strasser, B.R. Cuenya, Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene, *Nat. Commun.* 7 (2016) 12123. <https://doi.org/10.1038/ncomms12123>.
- [49] D. Raciti, C. Wang, Recent Advances in CO_2 reduction electrocatalysis on copper, *ACS Energy Lett.* 3 (2018) 1545–1556. <https://doi.org/10.1021/acsenerylett.8b00553>.
- [50] J.-J. Velasco-Vélez, T. Jones, D. Gao, E. Carbonio, R. Arrigo, C.-J. Hsu, Y.-C. Huang, C.-L. Dong, J.-M. Chen, J.-F. Lee, P. Strasser, B. Roldan Cuenya, R. Schlögl, A. Knop-Gericke, C.-H. Chuang, The role of the copper oxidation state in the electrocatalytic reduction of CO_2 into valuable hydrocarbons, *ACS Sustainable Chem. Eng.* 7 (2019) 1485–1492. <https://doi.org/10.1021/acssuschemeng.8b05106>.
- [51] P. De Luna, R. Quintero-Bermudez, C.-T. Dinh, M.B. Ross, O.S. Bushuyev, P. Todorović, T. Regier, S.O. Kelley, P. Yang, E.H. Sargent, Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction, *Nat. Catal.* 1 (2018) 103–110. <https://doi.org/10.1038/s41929-017-0018-9>.

- [52] X. Chang, T. Wang, J. Gong, CO₂ photo-reduction: insights into CO₂ activation and reaction on surfaces of photocatalysts, *Energy Environ. Sci.* 9 (2016) 2177–2196. <https://doi.org/10.1039/C6EE00383D>.
- [53] P. Devi, K. Malik, E. Arora, S. Bhattacharya, V. Kalendra, K. V. Lakshmi, A. Verma, J.P. Singh, Selective electrochemical reduction of CO₂ to CO on CuO/In₂O₃ nanocomposites: role of oxygen vacancies, *Catal. Sci. Technol.* 9 (2019) 5339–5349. <https://doi.org/10.1039/C9CY01396B>.
- [54] J. Lee, D.C. Sorescu, X. Deng, Electron-induced dissociation of CO₂ on TiO₂ (110), *J. Am. Chem. Soc.* 133 (2011) 10066–10069. <https://doi.org/10.1021/ja204077e>.
- [55] S. Gao, Z. Sun, W. Liu, X. Jiao, X. Zu, Q. Hu, Y. Sun, T. Yao, W. Zhang, S. Wei, Y. Xie, Atomic layer confined vacancies for atomic-level insights into carbon dioxide electroreduction, *Nat. Commun.* 8 (2017) 14503. <https://doi.org/10.1038/ncomms14503>.
- [56] D. Li, J. Wu, T. Liu, J. Liu, Z. Yan, L. Zhen, Y. Feng, Tuning the pore structure of porous tin foam electrodes for enhanced electrochemical reduction of carbon dioxide to formate, *Chem. Eng. J.* 375 (2019) 122024. <https://doi.org/10.1016/j.cej.2019.122024>.
- [57] S. Rasul, D.H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo, K. Takanabe, A highly selective copper-indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO₂ to CO, *Angew. Chem. Int. Ed.* 54 (2015) 2146–2150. <https://doi.org/10.1002/anie.201410233>.
- [58] Y. Wang, L. Cao, N.J. Libretto, X. Li, C. Li, Y. Wan, C. He, J. Lee, J. Gregg, H. Zong, D. Su, J.T. Miller, T. Mueller, C. Wang, Ensemble effect in bimetallic electrocatalysts for CO₂ reduction, *J. Am. Chem. Soc.* 141 (2019) 16635–16642. <https://doi.org/10.1021/jacs.9b05766>.
- [59] A.A. Peterson, J.K. Nørskov, Activity descriptors for CO₂ electroreduction to methane on transition-metal catalysts, *J. Phys. Chem. Lett.* 3 (2012) 251–258. <https://doi.org/10.1021/jz201461p>.

- [60] S. González, M. Pérez, M. Barrera, A.R. González Elípe, R.M. Souto, Mechanism of copper passivation in aqueous sodium carbonate–bicarbonate solution derived from combined x-ray photoelectron spectroscopic and electrochemical data, *J. Phys. Chem. B.* 102 (1998) 5483–5489. <https://doi.org/10.1021/jp981069k>.
- [61] A. Eilert, F. Cavalca, F.S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E.J. Crumlin, H. Ogasawara, D. Friebe, L.G.M. Pettersson, A. Nilsson, Subsurface oxygen in oxide-derived copper electrocatalysts for carbon dioxide reduction, *J. Phys. Chem. Lett.* 8 (2017) 285–290. <https://doi.org/10.1021/acs.jpcclett.6b02273>.
- [62] W. Tang, A.A. Peterson, A.S. Varela, Z.P. Jovanov, L. Bech, W.J. Durand, S. Dahl, J.K. Nørskov, I. Chorkendorff, The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO₂ electroreduction, *Phys. Chem. Chem. Phys.* 14 (2012) 76–81. <https://doi.org/10.1039/C1CP22700A>.
- [63] Q. Wang, Z. Yu, J. Feng, P. Fornasiero, Y. He, D. Li, Insight into the effect of dual active Cu⁰/Cu⁺ sites in a Cu/ZnO–Al₂O₃ catalyst on 5-hydroxymethylfurfural hydrodeoxygenation, *ACS Sustainable Chem. Eng.* 8 (2020) 15288–15298. <https://doi.org/10.1021/acssuschemeng.0c05235>.
- [64] L. Zhu, H. Li, Z. Liu, P. Xia, Y. Xie, D. Xiong, Synthesis of the 0D/3D CuO/ZnO heterojunction with enhanced photocatalytic activity, *J. Phys. Chem. C.* 122 (2018) 9531–9539. <https://doi.org/10.1021/acs.jpcc.8b01933>.
- [65] F. Liao, Y. Huang, J. Ge, W. Zheng, K. Tedsree, P. Collier, X. Hong, S.C. Tsang, Morphology-dependent interactions of ZnO with Cu nanoparticles at the materials' interface in selective hydrogenation of CO₂ to CH₃OH, *Angew. Chem. Int. Ed.* 50 (2011) 2162–2165. <https://doi.org/10.1002/anie.201007108>.
- [66] S. Tappertzhofen, H. Mündelein, I. Valov, R. Waser, Nanoionic transport and electrochemical reactions in resistively switching silicon dioxide, *Nanoscale.* 4 (2012) 3040–3043. <https://doi.org/10.1039/c2nr30413a>.

CHAPTER 4

Enhancement of the Electrochemical Reduction
of CO₂ to Methanol and Suppression of H₂
Evolution Over CuO Nanowires

Adapted from the article

*Azenha, C., Mateos-Pedrero, C., Alvarez-Guerra, M., Irabien, A., Mendes, A.,
“Enhancement of the electrochemical reduction of CO₂ to methanol and suppression of
H₂ evolution over CuO nanowires”, *Electrochimica Acta*, 2020, 363 (137207).*

Enhancement of the Electrochemical Reduction of CO₂ to Methanol and Suppression of H₂ Evolution Over CuO Nanowires

4.1 Abstract

A highly efficient copper-catalyst (noble metal-free) was developed for the electrochemical reduction of CO₂ (ERCO₂) to methanol. Due to the nanowire structure of the catalyst, a remarkable ERCO₂ selectivity was achieved, while the competing H₂ evolution reaction (HER) was significantly suppressed for the overall range of potential tested. The developed copper-catalyst (CuO NWs) outperforms the single metal Cu-catalysts in aqueous environment. Under atmospheric conditions, methanol was produced at an overpotential of 410 mV with a faradaic efficiency (FE) of 66.4 %, and 64.9 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ of production yield, which represents a 1.5-fold improvement over the previously reported value of 43 $\mu\text{mol h}^{-1} \text{cm}^{-2}$. Interestingly, when the developed CuO NWs was used as a gas diffusion electrode (GDE) in a filter-press cell (more *real* industrial configuration), methanol remained the major ERCO₂ product, with the same FE (66 %).

Keywords: CO₂ electroreduction; copper-based catalysts; copper(II) oxide; methanol; selectivity; GDE-electrodes.

4.2 Introduction

The increasing global CO₂ concentration, mainly from extensive fossil fuel utilization, is a serious environmental threat that is considered one of the major causes of climate change [1,2]. The electrochemical reduction of CO₂ (ERCO₂) to fuels and chemical feedstock, using renewable electricity, represents one promising approach for reducing anthropogenic CO₂ emissions and developing a sustainable energy system [3–5]. However, this desired approach imposes major technological challenges before its implementation in large-scale applications [1]. CO₂ is a fully oxidized and thermodynamically stable molecule. Thus, developing a suitable catalyst, capable of achieving a stable and cost-effective process with high efficiency and selectivity at low overpotential is crucial [2,4].

In aqueous environment, the ERCO₂ reaction competes in selectivity with the hydrogen evolution reaction (HER), particularly at low applied potentials [6]. Therefore, tuning the ERCO₂ activity and selectivity to the target product while suppressing the HER is critical for improving the energy efficiency of the process [7]. Metal electrodes have been the focus of extensive ERCO₂ research in aqueous solutions at ambient conditions [8]. However, since the earliest studies by Hori *et al.*, it has been identified that most metals preferentially produce H₂ under electrocatalytic conditions, even in the presence of CO₂ [9]. This occurs because the overpotential of the HER is usually lower compared to ERCO₂ overpotential. As a result, metals that are active for ERCO₂ are also active for HER [10,11]. Systematic studies have been carried out to improve the ERCO₂ selectivity by controlling the morphology of the electrodes [12–15] and electronic properties (bimetallic alloys) [7,16]. However, up to now, the search for pure metal catalysts that favor ERCO₂ over HER has proved infertile [11]; in fact, effective suppression of the HER has only been reported using precious bimetallic catalysts (AuPd and PbCu) [7,16].

Recent studies have shown that the production of electrodes with nanostructured surfaces is a path for better efficiency and selectivity, in particular for Cu-based catalysts. For instance, Cu₂O rods were used for the production of CO and formic acid with

faradaic efficiencies (FE) of *ca.* 40 % and 33 %, respectively [17]. Sen *et al.* reported that copper foams provide high surface roughness, hierarchical porosity, and confinement of reactive species, resulting in the production of formic acid with an FE of 37 % at -0.9 V_{RHE} [18]. Ethylene and ethanol were identified as ER CO_2 products using polyhedron Cu_2O particles as catalyst, whose FE can be tuned by varying the thickness of the Cu_2O overlayers [19]. It was also reported that multicarbon product formation, mainly ethylene, is favored on copper cubic facets [20]. More recently, Cu nanowires (NWs) were identified as advanced electrocatalysts for CO_2 and CO electroreduction by Raciti *et al.* [3,21] and Ma *et al.* [2]. Especially for the ER CO_2 , this type of catalyst requires an overpotential as low as 300 mV to reach a total current density of -1 mA cm⁻², and enables the production of CO with FE of *ca.* 60 % [3].

In the present chapter, high surface area CuO NWs were produced using a simple method and non-precious metals. The developed catalyst was initially tested for ER CO_2 using a conventional three-electrode system, showing remarkable activity and selectivity for methanol production under atmospheric conditions and using an ionic liquid-free electrolyte. The catalyst stability under reaction conditions was also assessed and improved, resulting in no apparent deactivation after 2 h of electrolysis. Finally, the CuO NWs electrode was evaluated in a continuous ER CO_2 device, working in a gas diffusion electrode (GDE) configuration.

4.3 Experimental

4.3.1 Electrode preparation

Electrodes were prepared by the anodization of a bare Cu foam, following a procedure adapted from the work of Wang *et al.* [22], **Figure 4.1**. Cu foam with a thickness of 80 μm (MTI Corp USA) was successively washed with acetone (Sigma-Aldrich, 99.9 %), ultrapure water (18.2 M Ω cm⁻¹ at 25 °C, Millipore Milli-Q system), and 3.0 M HCl (Fluka, 37 %) for 30 min under ultrasonic condition to remove organic

contaminants and possible oxide layers on the surface. Then, it was rinsed with ultrapure water and dried at 80 °C in a vacuum oven before being used as the working electrode. A three-electrode setup was used with a carbon rod as counter electrode and an Ag/AgCl/Sat. KCl as reference electrode, connected to an IM6ex electrochemical workstation (Zahner). The electrolyte was 1.0 M KOH (Merck) solution, which was deaerated by bubbling N₂ for at least 30 min before experiments. The Cu foam was electrochemically anodized at room temperature and constant current density of 10 mA cm⁻² for 10 min to form Cu(OH)₂ NWs. After anodization, samples were rinsed with ultrapure water and annealed at 150 °C for 1.5 h under static air for dehydration of Cu(OH)₂ to CuO.

A thin layer of TiO₂ was deposited on the surface of the CuO NWs by atomic layer deposition (ALD) to increase the catalyst stability. The deposition was conducted on a Beneq thin-film system (TFS 200, Beneq Corporation), according to previous work [23]. Titanium isopropoxide (C₁₂H₂₈O₄Ti ≥ 97 %, Sigma Aldrich) was used as precursor, and distilled water (H₂O) as oxidizing agent, at 225 °C. Ultrahigh-purity nitrogen was used as reactant carrier and purge gas, and the reactor was maintained at 400 Pa.

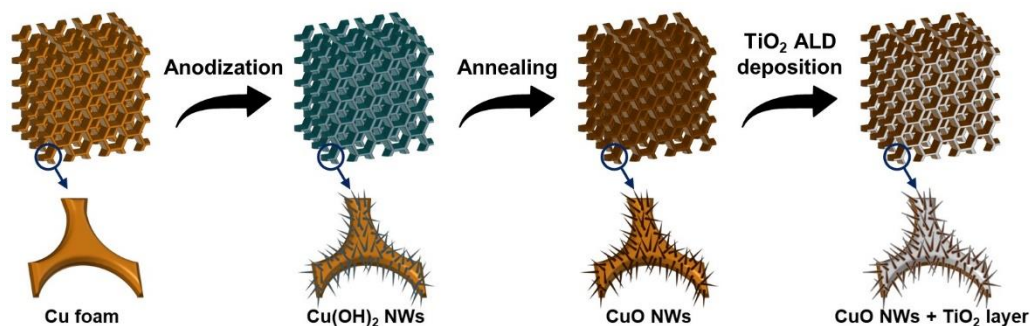


Figure 4.1. Experimental procedure used to prepare the CuO NWs electrodes.

4.3.2 Physicochemical characterization

The morphology and element distribution were obtained by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, Phenom XL Desktop SEM). The crystal structure was studied using X-ray diffraction (XRD, PANalytical

X'Pert Pro), while X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra HAS) was used to identify the surface chemical composition and valence state, as detailed in Chapter 2.

The CO_2 adsorption was studied by CO_2 temperature-programmed desorption (CO_2 -TPD, ChemBET Pulsar TPR/TPD), following a protocol similar to that used for the CO-TPD experiments (Chapter 2). In short, samples were pretreated at 120 °C under He flow, followed by CO_2 adsorption at 50 °C. Afterward, the CO_2 desorption was monitored by a quadrupole MS (Pfeiffer Vacuum OmniStar GSD 320) from 50 °C to 700 °C.

4.3.3 Electrochemical measurements

All electrochemical measurements were performed at atmospheric conditions of temperature and pressure in a conventional three-electrode electrochemical cell, as described in Chapter 2. All potentials in this chapter are on the RHE scale.

Linear sweep voltammetry (LSV) measurements were conducted according to the protocol described in Chapter 2. Electrochemical impedance spectroscopy (EIS) was also performed according to the protocol described in Chapter 3, for an applied potential of -0.8 V and -1.2 V. Adsorption affinity of OH^- as surrogate of CO_2^* was examined by oxidative LSV at 20 mV s^{-1} in N_2 -saturated 0.1 M NaOH.

Surface roughness factors of the developed electrodes were determined by measuring the double-layer capacitance in N_2 -saturated 0.1 M KHCO_3 . Cyclic voltammograms (CV) were acquired in N_2 -saturated 0.1 M KHCO_3 , at multiple scan rates (5 mV s^{-1} – 100 mV s^{-1}), considering a non-faradaic region of the voltammogram. The obtained values were then normalized to a polycrystalline Cu foil (standard reference) to obtain the surface roughness factors [2]. Prior to the CV measurements, the copper foil (thickness 0.25 mm, 99.98 % trace metals, Sigma-Aldrich) was electropolished using a solution of 70 vol. % H_3PO_4 (85.9 %, Fisher Scientific) as electrolyte. The current density was fixed at 4.7 mA cm^{-2} , and the polishing time was 30 min [24].

Due to the porous nature and heterogeneous structure of the developed electrodes, resistance was determined by applying a compression pressure with a MultiTest-1d (Mecmesin) force testing system. An electrode sample with 1 cm² was sandwiched between two gold-coated steel plates and inserted between the compression plates. A current between 10 mA and 30 mA passed through the electrode material, and the voltage drop across the gold coated plates was recorded with an Autolab (Metrohm).

4.3.4 CO₂ reduction electrolysis and product analysis

The electrolysis experiments were conducted under atmospheric conditions, following the protocol described in Chapter 2. Likewise, gas-phase product and liquid products were quantified by gas chromatography (GC) and headspace-GC, respectively. Each experiment lasted 120 min. The faradaic efficiency and product formation rate were determined to evaluate the electrochemical performance of the electrodes. The overpotential for methanol production was determined considering an equilibrium potential under reaction conditions (E_{eq}) of -0.40 ± 0.01 V_{RHE} (vs. $E^0 = -0.38$ V_{RHE}), which was calculated according to Equation (1.8). The same E_{eq} value was used for determining the cell energy efficiency according to Equation (1.9).

4.3.5 Filter-press tests

Selected electrodes were tested on a filter-press cell at ambient conditions of pressure and temperature, using an experimental setup described in previous works [25,26] (**Figure 4.2**). A Nafion 117 cation exchange membrane was used to separate the cathode and anode compartments, and the geometric electrode area was 10 cm². A tinned steel mesh was used as current collector and a dimensionally stable anode [DSA/O₂ (Ir- MMO (mixed metal oxide) on platinum)] as counter electrode. A leak-free Ag/AgCl 3.4 mol L⁻¹ KCl reference electrode was assembled close to the surface of the cathode. An aqueous solution of 0.1 M KHCO₃ (PanReac, > 99 % purity) and 1.0 M KOH (PanReac, 85 % purity) was used as catholyte and anolyte, respectively. Experiments were conducted at

galvanostatic conditions (-45 mA cm^{-2}), with the current supplied by the potentiostat (MSTAT 4, Arbin Instruments). Each test lasted 90 min and was performed in continuous mode with a single pass of the catholyte and anolyte through the cell with a flow rate of $0.57 \text{ mL min}^{-1} \text{ cm}^{-2}$, using two peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group). Pure gaseous CO_2 was fed to the cell at a flow rate of 200 mL min^{-1} . To ensure the reproducibility of the results, each test was conducted in duplicate on different days.

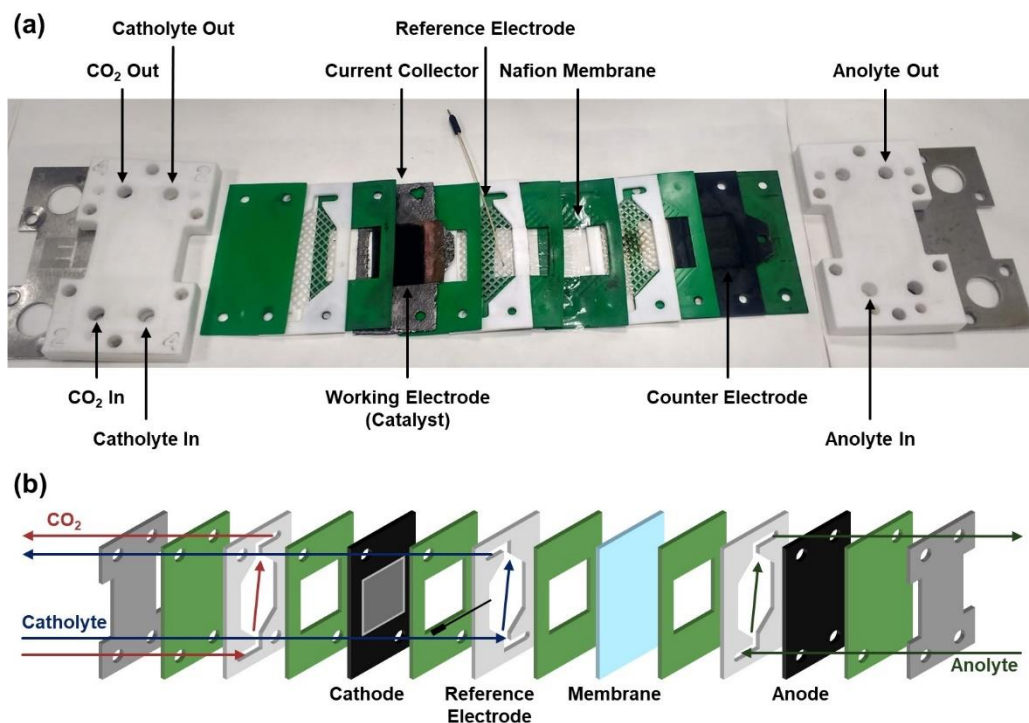


Figure 4.2. (a) Disassembled filter-press cell and (b) working principle of the filter-press cell for continuous CO_2 electrolysis.

Gas products were analyzed online every 30 min with a micro gas chromatograph (490 Micro GC, Agilent) equipped with four channels (columns: PBQ + MS5A, PoraPLOT U, CP-Sil 5 CB, and CP-WAX 52 CB). Liquid samples were also collected every 30 min and analyzed by ion chromatography (Dionex ICS 1100, Thermo Scientific) to obtain the formate concentration. The chromatographic system was

equipped with an AS9-HC column, and analysis was carried out using a solution of 4.5 mmol L^{-1} of Na_2CO_3 as the eluent at a flow rate of 1 mL min^{-1} . Methanol and ethanol production were accessed by headspace GC (GCMS-QP 2010 Ultra, Shimadzu) equipped with a DB-624 column (Agilent), using He as the carrier gas.

4.4 Results and discussion

4.4.1 Electrode characterization

A Cu foam was used as a substrate for producing CuO NWs electrodes for the ERCO_2 , using a method adapted from the literature [22]. First, $\text{Cu}(\text{OH})_2$ NWs were obtained through the electrochemical anodization of the Cu foam in an aqueous solution of NaOH. According to Wang *et al.* [22], Cu^0 atoms on the surface of the foam are oxidized to Cu^{2+} , which then reacts with OH^- from the electrolyte solution to form $\text{Cu}(\text{OH})_2$. During annealing, the dehydration of $\text{Cu}(\text{OH})_2$ NWs gives rise to porous CuO NWs. The formation of the various Cu species is easily noticed by the successive color change from red (Cu^0) of the pristine foam to navy blue ($\text{Cu}(\text{OH})_2$) after anodization and, finally, to brownish-black (CuO) after annealing (**Figure 4.3**). It is important to notice that the thickness and morphology of the NWs can be tuned by changing the operation conditions (reaction temperature and time, electrolyte concentration, and current density) [22].

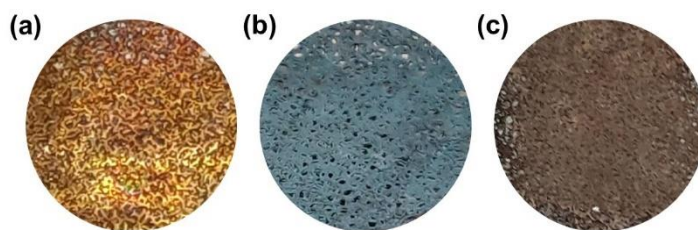


Figure 4.3. Digital photographs of (a) Cu foam, (b) $\text{Cu}(\text{OH})_2$ NWs, and (c) CuO NWs.

The morphology of the various samples collected at different stages of the electrode preparation was characterized by SEM, as illustrated in **Figure 4.4**. As the substrate, the bare pristine foam presents a smooth surface and a 3D interconnected network with a pore size ranging from 100 μm to 300 μm (**Figure 4.4a**). However, after anodization, the 3D skeleton of the Cu foam is evenly covered by $\text{Cu}(\text{OH})_2$ NWs with 4-5 nm in length and 0.3-0.6 nm in width (**Figures 4.4b** and **c**). The nanowire morphology and size are maintained after annealing, as depicted in **Figure 4.4d**.

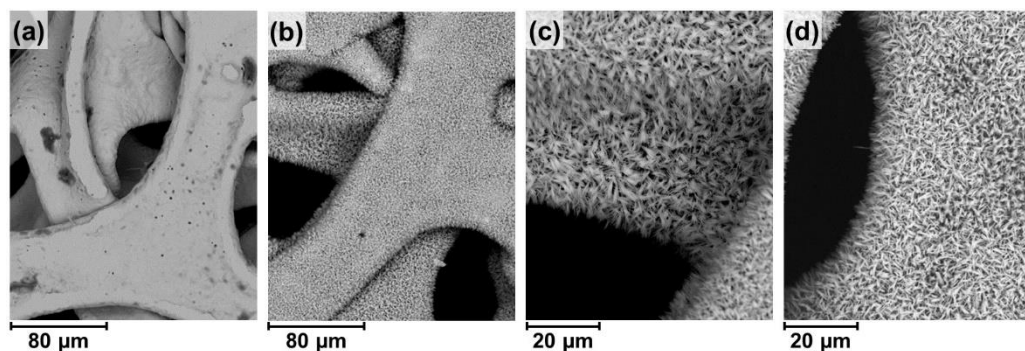


Figure 4.4. SEM image of (a) Cu foam, (b, c) low- and high-magnification of $\text{Cu}(\text{OH})_2$ NWs, and (d) CuO NWs.

The crystal structure of the prepared samples was investigated by XRD. All samples exhibit strong peaks at 43.3° , 50.4° , and 74.1° ascribed to Cu^0 (**Figure 4.5**), which correspond to the bulk structure of the Cu foam substrate. Since the anodization is a surface phenomenon, no changes in the bulk structure of the sample were expected after treatment. However, and in agreement with the trend reported by Wang *et al.* [22], the main diffraction peaks of $\text{Cu}(\text{OH})_2$ (35 nm, Debye-Scherrer) are detected after anodization. After thermal annealing, broad diffraction peaks at 35.8° (11-1) and 38.7° (111) evidence the appearance of CuO, which confirms the dehydration of most $\text{Cu}(\text{OH})_2$. Compared to $\text{Cu}(\text{OH})_2$ NWs, the broader peaks observed for CuO NWs indicate a decrease in crystallite size (21 nm, Debye-Scherrer). A very weak reflection at 23.9° suggests that some $\text{Cu}(\text{OH})_2$ is still present in the annealed sample.

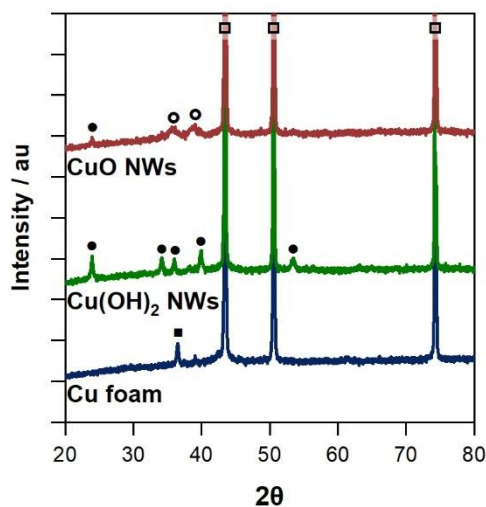


Figure 4.5. XRD pattern of the developed electrodes. $\square$ Cu^0 (JCPDS card no. 04-0836), $\bullet$ CuO (JCPDS card no. 48-1548), $\blacksquare$ Cu_2O (JCPDS card no. 05-0667), and $\bullet$ $\text{Cu}(\text{OH})_2$ (JCPDS card no. 80-0656).

Table 4.1. Cu $2p_{3/2}$, Cu Auger LMM, and modified Auger parameter values for the electrodes. Curve-fitting parameters.

Sample	Compound	BE ^a (eV)	FWHM ^b (eV)	Peak shape	KE ^c (eV)	FWHM (eV)	Peak shape	α' (eV)	At. % ^d
Cu foam	Cu_2O	932.9	1.10	GL(80)	915.9	2.20	GL(70)	1848.7	69.1 ^e
	Cu^0	932.9	1.10	GL(80)	918.2	1.80	GL(80)	1851.1	30.9 ^e
$\text{Cu}(\text{OH})_2$ NWs	$\text{Cu}(\text{OH})_2$	934.4	2.50	GL(70) T(1.5)	916.5	2.10	GL(70)	1850.9	100.0
CuO NWs	CuO	933.6	2.40	GL(70) T(1.5)	917.4	2.10	GL(30)	1851.0	100.0

^a: binding energy; ^b: full width at half maximum; ^c: kinetic energy; α' : modified Auger parameter;

^d: unless otherwise specified, calculated according to Cu $2p_{3/2}$; ^e: calculated according to Cu LMM.

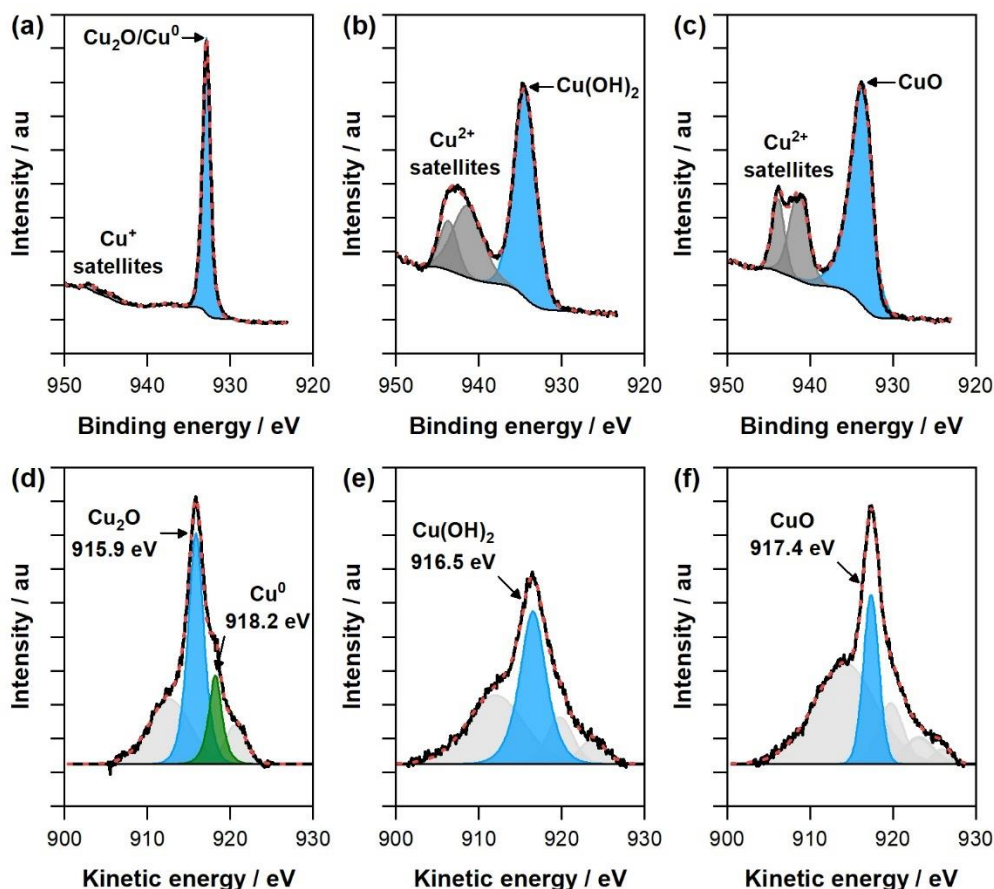


Figure 4.6. (a-c) Cu 2p_{3/2} XPS and (d-f) Cu Auger LMM spectra for (a, d) Cu foam, (b, e) Cu(OH)₂ NWs, and (c, f) CuO NWs.

The surface of the various samples was studied by XPS. **Figure 4.6** and **Table 4.1** summarize the obtained results. For the bare Cu foam, the peak-fit of the Cu 2p_{3/2} core level gives a single narrow peak centered at 932.9 eV (**Figure 4.6a**) that can be attributed to Cu⁰ and/or Cu⁺. Thus, the chemical speciation of copper was based on the Cu LMM Auger peak [27]. The Auger peak-shape illustrated in **Figure 4.6d** suggests that copper is present, at least, in two different oxidation states characterized by the main peak at 915.9 eV (Cu⁺, 69.1 at. %) and the shoulder at 918.2 eV (Cu⁰, 30.9 at. %). After anodization (**Figure 4.6b**), the Cu 2p_{3/2} peak shifted to higher binding energy (BE;

934.4 eV), and strong shake-up satellite peaks emerged, endorsing the formation of $\text{Cu}(\text{OH})_2$. For the annealed sample (**Figure 4.6c**), the values of the Cu $2p_{3/2}$ (933.6 eV) and Cu LMM (917.4 eV) peaks are consistent with the presence of CuO [27].

4.4.2 Electrochemical performance and stability

The electrocatalytic activity of the prepared electrodes was initially assessed by LSV in N_2 or CO_2 -saturated electrolyte, using a standard three-electrode cell, **Figure 4.7**. The LSV curve of the Cu foam recorded in N_2 environment exhibits a clear reduction peak at *ca.* 0.30 V, which can be attributed to the reduction of Cu^+ to Cu^0 [28]. XRD and XPS already evidenced the presence of Cu_2O . For $\text{Cu}(\text{OH})_2$ NWs and CuO NWs, two cathodic signals (C_I and C_{II} , Figure A.15, Appendix A) are observed, which were associated with the sequential reduction of Cu^{2+} to Cu^+ and Cu^+ to Cu^0 [28,29].

Under CO_2 -atmosphere, the Cu foam exhibited a total current density of -14.3 mA cm^{-2} at -1.2 V . However, no significant differences are observed compared to the LSV response under N_2 -saturated electrolyte, suggesting that the water electrolysis is the dominant reaction (**Figure 4.7a**). Considering the same applied potential range, both $\text{Cu}(\text{OH})_2$ NWs and CuO NWs produced much higher current densities than the bare Cu foam. For instance, a current of -25.0 mA cm^{-2} was recorded at -1.2 V for $\text{Cu}(\text{OH})_2$ NWs, representing a *ca.* 2-fold increase (**Figure 4.7b**). For CuO NWs, a notable current density of -56.8 mA cm^{-2} was registered at the same applied potential (improvement by 4-fold, **Figure 4.7c**).

The increase in surface area after forming the nanowires can explain the current density enhancement observed for $\text{Cu}(\text{OH})_2$ NWs and CuO NWs. As shown in **Table 4.2**, $\text{Cu}(\text{OH})_2$ NWs and CuO NWs present a capacitance of 10.3 mF cm^{-2} and 9.82 mF cm^{-2} , respectively. This result indicates that the roughness factors are 11 times higher than that of Cu foam (capacitance of 0.93 mF cm^{-2}). On the other hand, $\text{Cu}(\text{OH})_2$ NWs and CuO NWs have similar roughness factors, suggesting that the higher current density measured for CuO NWs is indicative of higher activity.

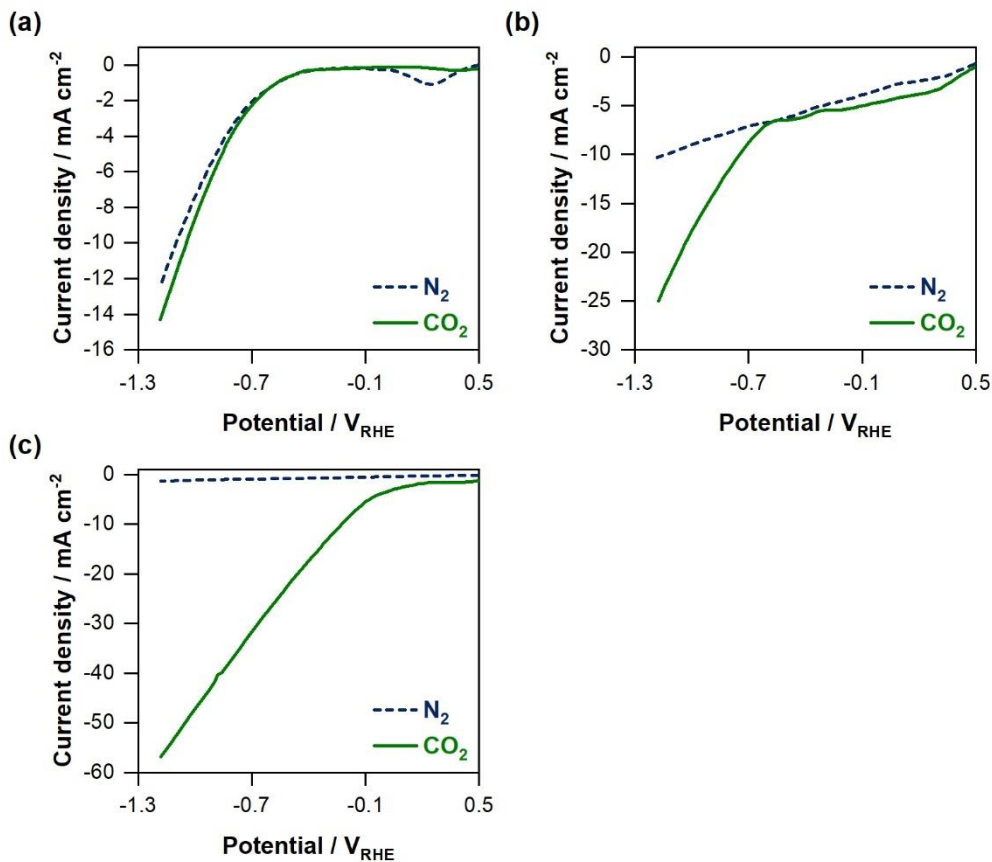


Figure 4.7. IR-corrected LSV curves at cathodic potentials in N_2 (dashed lines) and CO_2 -saturated (full lines) 0.1 M KHCO_3 for (a) Cu foam, (b) $\text{Cu}(\text{OH})_2$ NWs, and (c) CuO NWs. Scan rate, 20 mV s^{-1} .

Table 4.2. Capacitance values and surface roughness factors of the developed electrodes.

Sample	Capacitance (mF cm^{-2})	Roughness factor
Polycrystalline Cu foil ^a	0.28	1.00
Cu foam	0.93	3.32
$\text{Cu}(\text{OH})_2$ NWs	10.3	36.8
CuO NWs	9.82	35.1

^a: the obtained capacitance value of 0.28 mF cm^{-2} is in agreement with the literature [30].

In addition to the high activity, this preliminary test suggests that CuO NWs is highly selective for the ER CO_2 . For the overall range of potential tested, the total current density recorded under N_2 -environment is almost negligible (*ca.* -1 mA cm^{-2}), evidencing that the HER competing reaction was strongly suppressed (**Figure 4.7c**). In contrast, in the presence of CO_2 , the current density sharply increased, indicating high activity/selectivity for CO_2 reduction. Additionally, the onset potential shifted positively from -0.44 V (Cu foam) to 0.04 V (CuO NWs), which denotes that the electrocatalytic activity is enhanced for the CuO NWs electrode. Thus, less energy is needed to initiate CO_2 reduction. It is also worth mentioning that most of the surface CuO was reduced to Cu^0 during the ER CO_2 ; thus, Cu^0 is the active state of copper (**Figure 4.8**).

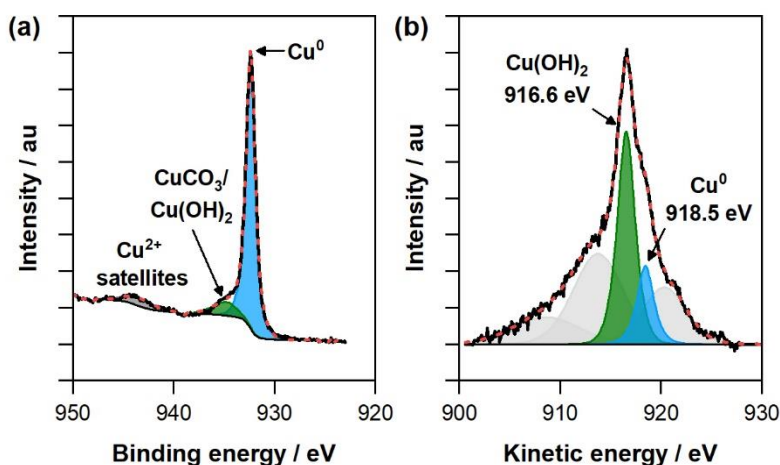


Figure 4.8. (a) Cu 2p_{3/2} XPS and (b) Cu Auger LMM spectra of CuO NWs after ER CO_2 .

The stability of the developed CuO NWs electrode was evaluated by short-term electrolysis at an applied potential of -1.2 V , **Figure 4.9a**. After 2 h of operation, the current density dropped from -56.8 mA cm^{-2} to -18.2 mA cm^{-2} , indicating that the CuO NWs electrode will not be stable under long-term electrolysis. According to SEM results (**Figures 4.9b** and **c**), the decrease in activity can be related to some structural damage of the nanowires during the reaction.

To improve the stability of the electrode, a TiO_2 layer with *ca.* 5 nm of thickness was deposited by ALD. This technique has already been identified as a viable tool to add ultrathin corrosion protective layers (TiO_2 , Al_2O_3 , ZnO , HfO , and ZrO_2) to copper surfaces [31,32]. In the present work, ALD TiO_2 was successfully used to improve the stability of an ER CO_2 catalyst; after the TiO_2 incorporation, the current density remained stable at -32.0 mA cm^{-2} during the 2 h test (**Figure 4.9a**). Literature reports that Cu NWs are stable under ER CO_2 conditions over 1 h without further treatment [2]. However, in the cited work, the electrolysis was carried out at less cathodic potentials than those used in this study ($-0.6 \text{ V}_{\text{RHE}}$). Thus, the results presented here may be related to the more reductive environment to which the CuO NWs electrode was exposed, which damages the structure of the NWs. The addition of the TiO_2 layer increases the structural robustness, resulting in high catalytic stability, and enables the operation at more cathodic potentials.

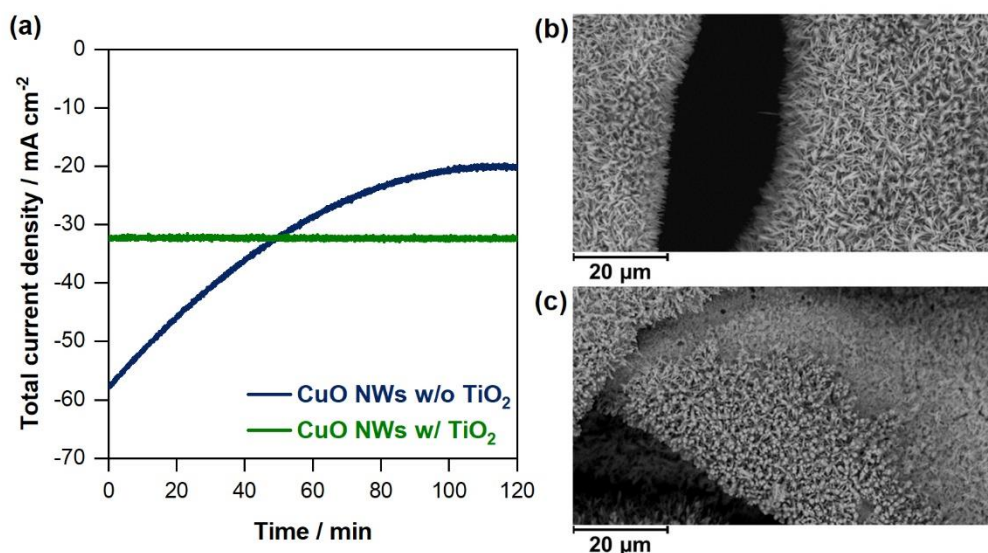


Figure 4.9. (a) Dependence of the total current density over time for the CuO NWs sample, with and without the TiO_2 protection layer, recorded at -1.2 V . SEM image of the CuO NWs electrode without the TiO_2 layer (b) before and (c) after 2 h of electrolysis.

Moreover, TiO_2 has a negligible impact on the electrode conductivity and ERCO_2 product distribution (discussed in detail in the next section), **Figure 4.10**. Regarding the conductivity, **Figure 4.10a** indicates that the area-specific resistance (ASR) increased by *ca.* 4.8-fold after anodization and only 1.2-times when the TiO_2 was deposited, reaching a value of $0.2 \Omega \text{ cm}^{-2}$ for a compression pressure of 1 MPa.

On the other hand, it is also observed that the addition of the TiO_2 layer reduces the total current density (-56.8 mA cm^{-2} without TiO_2 and -32.0 mA cm^{-2} with TiO_2). According to SEM-EDS and CO_2 -TPD-MS results (Appendix A, Figures A.17 and A.18), this behavior can be explained by the blockage of some CuO active centers. From here, all results reported concern electrodes with the TiO_2 protective layer.

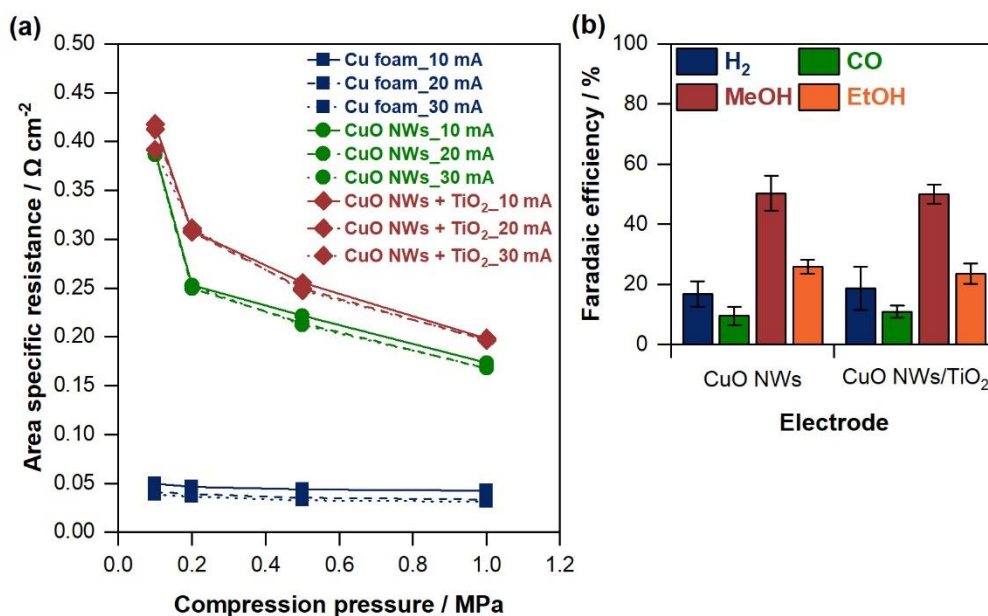


Figure 4.10. (a) Area-specific resistance vs. compression pressure for Cu foam and CuO NWs with and without TiO_2 , at multiple applied current densities. (b) Faradaic efficiency over CuO NWs with and without TiO_2 at -1.2 V .

4.4.3 Electrochemical CO_2 reduction

The activity of the prepared electrodes toward the CO_2 reduction was assessed by potentiostatic measurements for 120 min at selected potentials from -0.6 V to -1.2 V, using a conventional three-electrode system and CO_2 -saturated 0.1 M KHCO_3 as electrolyte. The geometric current density remained stable throughout the electrolysis, regardless of the electrode and applied potential (Figure A.19, Appendix A). GC analysis revealed that H_2 and CO were the only gas products. Similarly, methanol and ethanol were identified as the main liquid products, with propanol also detected for some samples but with a negligible faradaic efficiency ($\text{FE} < 2\%$).

The current density and FE recorded during the constant-potential electrolysis of CO_2 over the different electrodes are displayed in **Figure 4.11**. As expected, the bare copper foam presents quite high values of FE for H_2 production, reaching *ca.* 80 % for each potential tested (**Figure 4.11b**). This result is in agreement with the work of Min *et al.*, which reported *ca.* 85 % of H_2 FE for a commercial Cu foam tested under similar conditions at -0.45 V_{RHE} [33]. Moreover, it confirms that this electrode is not suitable for ER CO_2 due to its low selectivity, as suggested by the LSV. Other studies reported in the literature show Cu foams with lower H_2 FE, for instance, 60 % [18] and 16 % [13] at -0.7 V_{RHE} . However, these values were obtained with electrodeposited Cu foams and not commercial materials.

After anodization, the H_2 FE decreased to an average value of 45 %, representing a 1.7-fold reduction compared to the Cu foam (**Figure 4.11c**). Methanol and ethanol were also detected, however, with low FE (*ca.* 10 % and 5 % for methanol and ethanol, respectively).

The unique nanostructure of the nanowires formed after anodization was found to effectively decrease the HER activity. Notwithstanding, the H_2 electrolysis was further inhibited by the dehydration of $\text{Cu}(\text{OH})_2$ to CuO, as depicted in **Figure 4.11d**. After annealing, the H_2 FE remained below 15 % in the potential range of -0.6 V to -1.0 V, evidencing that CuO NWs is 5.3-times less HER selective when compared to the Cu foam. Besides, alcohols emerged as the main ER CO_2 products. Ethanol was produced

with a maximum FE value of 23.5 % recorded at -1.2 V, and the methanol FE exceeded 50 % in the tested potential range. Particularly at -0.8 V, methanol was selectively produced with an FE of 66.4 % and a production yield of $64.9 \mu\text{mol h}^{-1} \text{cm}^{-2}$; a value 1.5-times higher than the literature reference ($43 \mu\text{mol h}^{-1} \text{cm}^{-2}$) [34]. At the same applied potential (-0.8 V), the overpotential for the ERCO_2 to methanol was 410 mV (under the current operating conditions). The energy efficiency for methanol production was also assessed; 31.2 % at -0.8 V, with a maximum of 32.7 % achieved at -0.6 V.

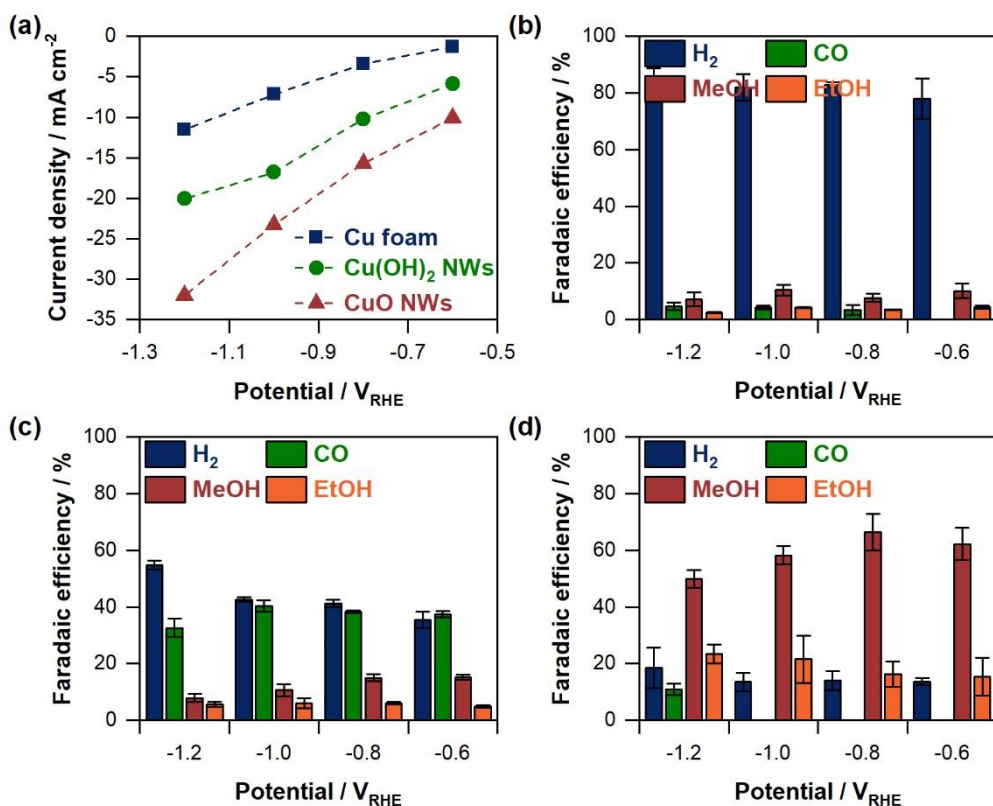


Figure 4.11. (a) Total current density and faradaic efficiency over (b) Cu foam, (c) Cu(OH)_2 NWs, and (d) CuO NWs at different applied potentials.

Concerning the methanol production, the values obtained with the CuO NWs electrode are very close to those reported by Yang *et al.* over CuSe electrodes (FE of 77.6 %, total current density of -41.5 mA cm^{-2} , and overpotential of 285 mV) [35]. Moreover, since

the current density decreased after the incorporation of the TiO_2 protective layer, it is expected that further improvement of the protective layer will result in the performance enhancement of the developed electrode.

Among other properties, the ideal catalyst for ER CO_2 should be effective in inhibiting the HER, and much work has been devoted to this topic [7,12–16]. However, hitherto an effective suppression of the HER has only been achieved using precious metals-containing catalysts [7,16]. Recently, Kim *et al.* reported an unprecedented suppression of the HER for a bimetallic catalyst consisting of Pd adatom decoration of active Cu surfaces; a selectivity of 90 % for the CO_2 reduction was achieved at $-1.14 \text{ V}_{\text{RHE}}$ [16]. The other remarkable example is the nearly 100 % selectivity for ER CO_2 attained using an AuPd bimetallic catalyst, reported by Valenti *et al.* [7]. On the other hand, for pure metals electrodes, the promotion of ER CO_2 over HER has proved infertile [4,11,36]. For instance, it is reported that the FE for HER is *ca.* 30 % on Cu surfaces at $-1.05 \text{ V}_{\text{RHE}}$ [36] and 50 % on CuO at $-1.1 \text{ V}_{\text{RHE}}$ [4]. In contrast, the developed CuO NWs electrode presents an FE for H_2 evolution of only 13.5 % at -1.0 V . Thus, regarding the inhibition of the H_2 production, the developed electrode has a performance comparable to the state-of-the-art precious metal electrodes and outperforms the single Cu-catalysts in aqueous environment. Moreover, the CuO NWs electrode has the advantage of being highly selective for ER CO_2 to methanol.

4.4.4 Understanding the superior performance of CuO NWs

Further electrocatalytic characterization was performed to disclose the crucial factors affecting the electrocatalytic process and the superior performance of CuO NWs.

The results from the Tafel analysis are given in **Figure 4.12a**. The Tafel slope measured for the Cu foam of 136 mV dec^{-1} agrees with previous reports ($130 \pm 7 \text{ mV dec}^{-1}$) [37], and indicates a rate-determining initial electron transfer to CO_2 to form an adsorbed $\text{CO}_2^{\cdot-}$ intermediate [8,37]. The overpotential required for this step is typically large due to the poor stabilization of $\text{CO}_2^{\cdot-}$ by the metal surface [8]. In contrast, electrokinetics data for $\text{Cu}(\text{OH})_2$ NWs and CuO NWs support a mechanism that implies a faster

first-electron transfer step prior to a chemical rate-determining step (theoretical value of 59 mV dec^{-1}) [1,38]. Mechanistic divergence from the rate-determining $1e^-$ transfer suggests that active sites on the surfaces of $\text{Cu}(\text{OH})_2$ NWs and CuO NWs provide better stabilization to $\text{CO}_2^{\cdot-}$. The faster kinetics recorded when $\text{Cu}(\text{OH})_2$ NWs and CuO NWs are used as electrodes can be explained, in part, by the field-induced reagent concentration theory (FIRC) [39]. According to the FIRC, nanostructured electrodes can improve the slow kinetics imposed by the low CO_2 concentration close to the catalytic active sites. As reported, the presence of K^+ can stabilize the adsorption of reaction intermediates (*e.g.*, $\text{CO}_2^{\cdot-}$) [40], and the high local electric fields created by high-curvature structures (*e.g.*, tip of nanowires) tend to concentrate electrolyte cations near CO_2 reduction sites. Thus, it seems logical to assume that the particular morphology of the CuO NWs and $\text{Cu}(\text{OH})_2$ NWs supported on a 3D substrate provides better stabilization of $\text{CO}_2^{\cdot-}$, explaining the observed faster kinetics.

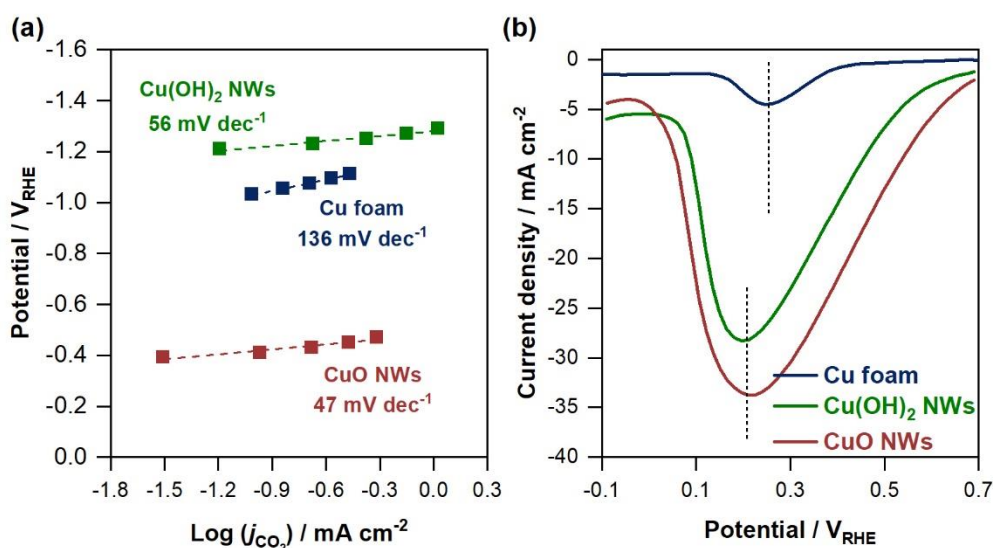


Figure 4.12. (a) Tafel plots of the CO_2 reduction partial current density. (b) IR-corrected single oxidative LSV scans at 50 mV s^{-1} in N_2 -saturated 0.1 M NaOH .

To confirm the change in the binding affinity of $\text{CO}_2^{\cdot-}$, the adsorption of OH^- as a surrogate for $\text{CO}_2^{\cdot-}$ was studied. The current response was measured following single

oxidative LSV scans from -0.1 V to 0.7 V, **Figure 4.12b**. As shown, surface OH^- adsorption on CuO NWs and $\text{Cu}(\text{OH})_2$ NWs occurs at a potential *ca.* 50 mV lower than that observed for Cu foam. The potential shift indicates higher binding energy between reaction sites and intermediates and, thus, stronger stabilization of $\text{CO}_2^{\cdot-}$ on the surface of the CuO NWs and $\text{Cu}(\text{OH})_2$ NWs [41,42], following the mechanism proposed by the Tafel analysis.

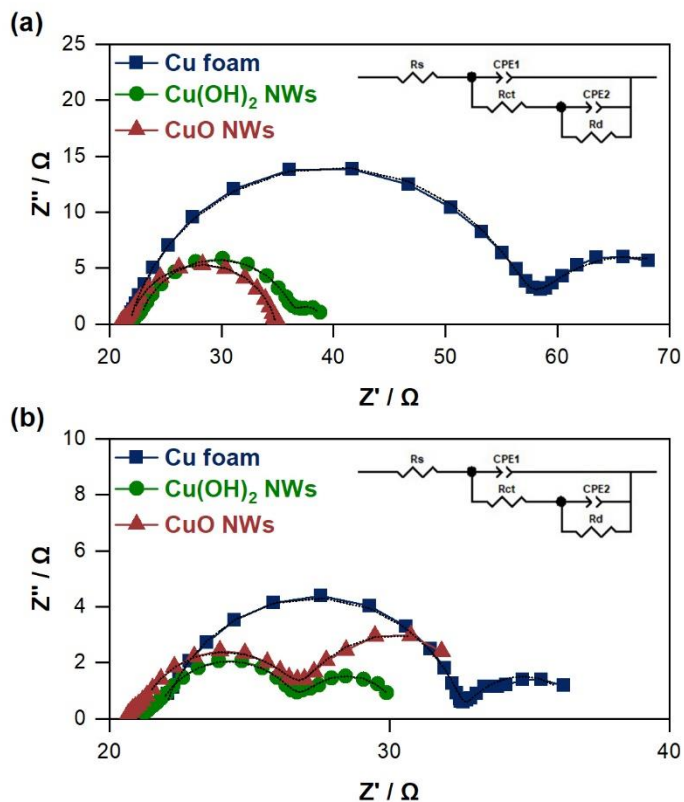


Figure 4.13. Nyquist plots, with fitting curves (dashed lines), of the prepared electrodes in CO_2 -saturated 0.1 M KHCO_3 with a frequency from 1 MHz to 10 mHz, and 10 mV amplitude at (a) -0.8 V and (b) -1.2 V. The equivalent circuit model is shown on the insert. R_s stands for the electrolyte resistance, R_{ct} for the charge transfer resistance, and R_d is the diffusion resistance. The double-layer capacitance is distributed between the charge transfer and diffusion processes and is represented by constant phase elements (CPE_1 and CPE_2).

EIS measurements were performed to further investigate the effect of the catalyst structure on the kinetics of the CO₂ reduction, **Figure 4.13**. EIS tests were carried out at -0.8 V and -1.2 V. According to the literature, at low overpotential, the charge transfer process controls the reaction kinetics, whereas mass diffusion dominates at high overpotential [41]. The obtained Nyquist plots were fitted by the equivalent circuit model shown in **Figure 4.13** insert [43], and the corresponding fitted results are summarized in **Tables 4.3** and **4.4**. According to the EIS fitting, all electrodes present similar electrolyte resistance (R_s), with an average value of $22.5 \Omega \text{ cm}^{-2}$ due to the same electrolyte condition and reactor. At the same time, obvious differences are observed in the charge transfer resistance (R_{ct}) and diffusion resistance (R_d). Results obtained at -0.8 V (**Figure 4.13a**) show that the R_{ct} decreased by 2.5-fold after anodization, suggesting that the presence of the nanowires enhances the electronic interaction at the reaction interfaces during electrolysis. As a result of the FIRC effect, the adsorption energy barrier of CO₂ decreased, facilitating the electron transfer to form CO₂^{•-} [44]. Moreover, the R_d also decreased, being negligible for CuO NWs, indicating that a pore network was created that guides the diffusion of CO₂ to the active centers. The same pattern is observed for the EIS data acquired at -1.2 V; however, as expected, the R_d is slightly higher (**Figure 4.13b**).

Table 4.3. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -0.8 V (error percentage for each element is given in parentheses).

Elements	Cu foam	Cu(OH) ₂ NWs	CuO NWs
$R_s (\Omega \text{ cm}^{-2})$	23.77 (0.18)	22.62 (0.24)	21.78 (0.25)
CPE ₁ -T (F cm ⁻²)	7.51×10^{-4} (1.55)	8.91×10^{-3} (1.69)	1.54×10^{-2} (1.12)
CPE ₁ -P	0.84 (0.38)	0.87 (0.80)	0.87 (0.67)
$R_{ct} (\Omega \text{ cm}^{-2})$	35.99 (0.41)	14.18 (0.82)	13.08 (0.61)
CPE ₂ -T (F cm ⁻²)	3.46×10^{-1} (5.11)	3.61 (7.98)	--
CPE ₂ -P	0.74 (3.19)	1.04 (5.98)	--
$R_d (\Omega \text{ cm}^{-2})$	17.81 (5.13)	2.27 (9.13)	--

Table 4.4. Values of the equivalent electric circuit elements fitted in the Nyquist plots obtained at -1.2 V (error percentage for each element is given in parentheses).

Elements	Cu foam	Cu(OH) $_2$ NWs	CuO NWs
R_s ($\Omega \text{ cm}^{-2}$)	23.90 (0.04)	21.65 (0.15)	21.05 (0.17)
CPE $_1$ -T (F cm^{-2})	7.46×10^{-4} (3.75)	9.83×10^{-3} (2.88)	1.64×10^{-2} (2.20)
CPE $_1$ -P	0.86 (0.82)	0.85 (1.12)	0.85 (1.09)
R_{ct} ($\Omega \text{ cm}^{-2}$)	10.78 (0.72)	5.22 (1.24)	5.60 (1.26)
CPE $_2$ -T (F cm^{-2})	9.61×10^{-1} (6.96)	9.63×10^{-1} (4.23)	9.97×10^{-1} (3.51)
CPE $_2$ -P	0.78 (4.35)	0.85 (1.93)	0.89 (1.66)
R_d ($\Omega \text{ cm}^{-2}$)	4.20 (5.53)	3.55 (2.40)	6.69 (2.88)

As previously mentioned, CO and methanol were selectively produced over Cu(OH) $_2$ NWs and CuO NWs surfaces, respectively. However, structural effects cannot explain the different reaction selectivity of Cu(OH) $_2$ NWs and CuO NWs. Thus, it is suggested that the chemical environment is the key to the observed differences. As evidenced by XPS, the BE of Cu 2p core level of Cu(OH) $_2$ NWs is 0.8 eV higher when compared to CuO NWs (Table 4.1). The higher BE suggests that the electron density around Cu $^{2+}$ decreased, possibly due to the electrons in the outer shell of the Cu $^{2+}$ being attracted by the O–H bond. The higher electronic density of the CuO NWs indicates higher basicity and, therefore, higher CO $_2$ and CO adsorption capacity. This evidence suggests that CuO NWs is capable of stabilizing the CO intermediate, resulting in the conversion of CO $_2$ to high-reduced products, like methanol. In contrast, the lower CO affinity of Cu(OH) $_2$ NWs, with respect to CuO NWs, leads to its facile desorption and, thus, gaseous CO production.

4.4.5 CO $_2$ reduction in a gas-phase GDE configuration

It is important to highlight that the direct synthesis of the CuO NWs on the surface of a copper foam enables the direct application of the developed electrode in a gas-phase GDE configuration.

GDE reactors provide some significant advantages over the liquid-phase systems. They overcome the low solubility of CO_2 in aqueous electrolytes (33 mM), which hinders high productivity, and are suitable for continuous operation and industrial scale-up [45,46]. Thus, as the GDE configurations are closer to *real* industrial technology, Cu foam and CuO NWs were tested in a filter-press cell working at a constant current density of -45 mA cm^{-2} , according to previous reports [25,26]. All tests were carried out at atmospheric conditions in a continuous mode, with a single pass of the catholyte and anolyte through the electrochemical cell. **Figure 4.14** presents the obtained FE and product rate formation.

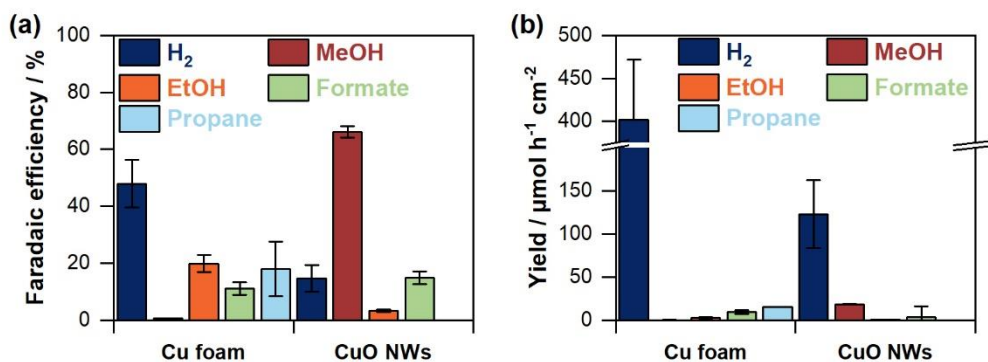


Figure 4.14. (a) Faradaic efficiencies and (b) production yield for Cu foam and CuO NWs, working on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell, working at a current density of -45 mA cm^{-2} .

As observed, the H_2 production from the HER reaction accounts for 47.9 % of the total FE for the Cu foam, with a partial current density of -21.6 mA cm^{-2} . This value is lower when compared to *ca.* 80 % recorded using the three-electrode cell (**Figure 4.11b**), suggesting that the HER is less promoted in the GDE configuration. Thus, besides the advantages already discussed, this result highlights that a major benefit of the GDE configuration, over liquid-phase systems, is the inhibition of the competing HER. For CuO NWs, an H_2 FE < 15 % was achieved, in agreement with the results obtained in the conventional cell, being HCOO^- also identified as ERCO_2 product (FE of 14.9 %). Notwithstanding, methanol was the major ERCO_2 product with an FE of 66.1 % (partial

current density of -29.7 mA cm^{-2}) and a formation rate of $18.5 \mu\text{mol h}^{-1} \text{ cm}^{-2}$. The FE is comparable to the value obtained at -0.8 V in the conventional system; however, the production yield decreased by 3.5-fold, possibly due to the larger area of the electrode (10 cm^2). Thus, the achieved methanol yield is lower when compared to the values reported by Le *et al.* using Cu_2O as electrode (*ca.* $43 \mu\text{mol h}^{-1} \text{ cm}^{-2}$) but was recorded with a higher FE value (66 % vs. 38 % reported by Le *et al.*) [34].

4.5 Conclusions

The developed CuO NWs catalyst proved to be very efficient for the ER CO_2 . In aqueous environment, a high current density was obtained (-56.8 mA cm^{-2} at -1.2 V); however not stable during 2 h of electrolysis. The stability issues were overcome by depositing a thin layer of TiO_2 on the catalyst surface, and methanol was selectively produced using the developed catalyst with an FE of 66.4 % at -0.8 V (overpotential of 410 mV). The energy efficiency was 31.2 %, and the production yield was $64.9 \mu\text{mol h}^{-1} \text{ cm}^{-2}$. These are quite promising values obtained with a single metal catalyst. Moreover, since the current work has been focused on demonstrating the concept and feasibility of this class of catalysts, future work will target the improvement of catalytic performance.

The remarkable catalytic activity of CuO NWs was attributed to the particular nanostructure of the nanowires that lowers the CO_2 adsorption energy barrier, enhancing the electron transfer to form $\text{CO}_2^{\cdot-}$. The stabilization of the $\text{CO}_2^{\cdot-}$ intermediate is also facilitated by CuO NWs, resulting in the conversion of CO_2 to more reduced products (methanol). Moreover, the newly formed pore network drives the CO_2 to the active sites, decreasing the diffusion resistance.

The performance of the CuO NWs catalyst was also explored in a continuous-GDE reactor configuration. The direct application of this type of material on a GDE configuration was confirmed, and methanol was obtained as the main ER CO_2 product with high efficiency (FE of 66.1 % and partial current density of -29.7 mA cm^{-2}).

Acknowledgments

Azenha, C., is grateful to the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant (reference SFRH/BD/128768/2017). This work was performed under the project “SunStorage - Harvesting and storage of solar energy”, with reference POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through COMPETE 2020 - Operational Programme for Competitiveness and Internationalisation (OPCI), and by national funds, through FCT - Fundação para a Ciência e a Tecnologia I.P. The authors are thankful to POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia and NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Nomenclature

Abbreviation	Definition
ALD	Atomic layer deposition
ASR	Area-specific resistance
BE	Binding energy
CO_2 -TPD	Carbon dioxide temperature-programmed desorption
CO_2 -TPD-MS	Carbon dioxide temperature-programmed desorption combined with mass spectrometry
CPE	Constant phase element
CV	Cyclic voltammetry
DAS	Dimensionally stable anode
e^-	Electron
EIS	Electrochemical impedance spectroscopy
ER CO_2	Electrochemical reduction of CO_2
FE	Faradaic efficiency
FIRC	Field-induced reagent concentration theory
FWHM	Full width at half maximum
GC	Gas chromatography
GDE	Gas diffusion electrode
HER	Hydrogen evolution reaction
JCPDS	Joint committee on powder diffraction standards
KE	Kinetic energy
LSV	Linear sweep voltammetry
MMO	Mixed metal oxide
NWs	Nanowires
RHE	Reversible hydrogen electrode
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Greek Symbol	Definition	Unit
α'	Modified Auger parameter	eV

Variable	Definition	Unit
E^0	Standard redox potential	V
E_{eq}	Equilibrium potential under reaction conditions	V
R_{ct}	Charge transfer resistance	$\Omega \text{ cm}^{-2}$
R_{d}	Diffusion resistance	$\Omega \text{ cm}^{-2}$
R_{s}	Electrolyte resistance	$\Omega \text{ cm}^{-2}$

References

- [1] Q. Lu, J. Rosen, Y. Zhou, G.S. Hutchings, Y.C. Kimmel, J.G. Chen, F. Jiao, A selective and efficient electrocatalyst for carbon dioxide reduction, *Nat. Commun.* 5 (2014) 3242. <https://doi.org/10.1038/ncomms4242>.
- [2] M. Ma, K. Djanashvili, W.A. Smith, Selective electrochemical reduction of CO_2 to CO on CuO-derived Cu nanowires, *Phys. Chem. Chem. Phys.* 17 (2015) 20861–20867. <https://doi.org/10.1039/C5CP03559G>.
- [3] D. Raciti, K.J. Livi, C. Wang, Highly dense Cu nanowires for low-overpotential CO_2 reduction, *Nano Lett.* 15 (2015) 6829–6835. <https://doi.org/10.1021/acs.nanolett.5b03298>.
- [4] D. Ren, J. Fong, B.S. Yeo, The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction, *Nat. Commun.* 9 (2018) 925. <https://doi.org/10.1038/s41467-018-03286-w>.
- [5] M. Schreier, F. Héroguel, L. Steier, S. Ahmad, J.S. Luterbacher, M.T. Mayer, J. Luo, M. Grätzel, Solar conversion of CO_2 to CO using earth-abundant electrocatalysts prepared by atomic layer modification of CuO, *Nat. Energy.* 2 (2017) 17087. <https://doi.org/10.1038/nenergy.2017.87>.
- [6] M.-J. Cheng, E.L. Clark, H.H. Pham, A.T. Bell, M. Head-Gordon, Quantum mechanical screening of single-atom bimetallic alloys for the selective reduction of CO_2 to C_1 Hydrocarbons, *ACS Catal.* 6 (2016) 7769–7777. <https://doi.org/10.1021/acscatal.6b01393>.
- [7] M. Valenti, N.P. Prasad, R. Kas, D. Bohra, M. Ma, V. Balasubramanian, L. Chu, S. Gimenez, J. Bisquert, B. Dam, W.A. Smith, Suppressing H_2 evolution and promoting selective CO_2 electroreduction to CO at low overpotentials by alloying Au with Pd, *ACS Catal.* 9 (2019) 3527–3536. <https://doi.org/10.1021/acscatal.8b04604>.

- [8] Y. Chen, C.W. Li, M.W. Kanan, Aqueous CO₂ Reduction at very low overpotential on oxide-derived Au nanoparticles, *J. Am. Chem. Soc.* 134 (2012) 19969–19972. <https://doi.org/10.1021/ja309317u>.
- [9] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media, *Electrochim. Acta.* 39 (1994) 1833–1839. [https://doi.org/10.1016/0013-4686\(94\)85172-7](https://doi.org/10.1016/0013-4686(94)85172-7).
- [10] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels, *Energy Environ. Sci.* 3 (2010) 1311–1315. <https://doi.org/10.1039/c0ee00071j>.
- [11] Z. Zhao, G. Lu, Computational screening of near-surface alloys for CO₂ electroreduction, *ACS Catal.* 8 (2018) 3885–3894. <https://doi.org/10.1021/acscatal.7b03705>.
- [12] W. Luo, W. Xie, M. Li, J. Zhang, A. Züttel, 3D hierarchical porous indium catalyst for highly efficient electroreduction of CO₂, *J. Mater. Chem. A.* 7 (2019) 4505–4515. <https://doi.org/10.1039/C8TA11645H>.
- [13] A. Dutta, M. Rahaman, N.C. Luedi, M. Mohos, P. Broekmann, Morphology matters: Tuning the product distribution of CO₂ electroreduction on oxide-derived Cu foam catalysts, *ACS Catal.* 6 (2016) 3804–3814. <https://doi.org/10.1021/acscatal.6b00770>.
- [14] W. Tang, A.A. Peterson, A.S. Varela, Z.P. Jovanov, L. Bech, W.J. Durand, S. Dahl, J.K. Nørskov, I. Chorkendorff, The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO₂ electroreduction, *Phys. Chem. Chem. Phys.* 14 (2012) 76–81. <https://doi.org/10.1039/C1CP22700A>.
- [15] L. Cao, D. Raciti, C. Li, K.J.T. Livi, P.F. Rottmann, K.J. Hemker, T. Mueller, C. Wang, Mechanistic insights for low-overpotential electroreduction of CO₂ to CO on copper nanowires, *ACS Catal.* 7 (2017) 8578–8587. <https://doi.org/10.1021/acscatal.7b03107>.

- [16] C. Kim, T. Möller, J. Schmidt, A. Thomas, P. Strasser, Suppression of competing reaction channels by Pb adatom decoration of catalytically active Cu surfaces during CO_2 electroreduction, *ACS Catal.* 9 (2019) 1482–1488. <https://doi.org/10.1021/acscatal.8b02846>.
- [17] C.W. Li, M.W. Kanan, CO_2 Reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu_2O films, *J. Am. Chem. Soc.* 134 (2012) 7231–7234. <https://doi.org/10.1021/ja3010978>.
- [18] S. Sen, D. Liu, G.T.R. Palmore, Electrochemical reduction of CO_2 at copper nanofoams, *ACS Catal.* 4 (2014) 3091–3095. <https://doi.org/10.1021/cs500522g>.
- [19] D. Ren, Y. Deng, A.D. Handoko, C.S. Chen, S. Malkhandi, B.S. Yeo, Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(I) oxide catalysts, *ACS Catal.* 5 (2015) 2814–2821. <https://doi.org/10.1021/cs502128q>.
- [20] F.S. Roberts, K.P. Kuhl, A. Nilsson, High selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts, *Angew. Chem. Int. Ed.* 54 (2015) 5179–5182. <https://doi.org/10.1002/anie.201412214>.
- [21] D. Raciti, L. Cao, K.J.T. Livi, P.F. Rottmann, X. Tang, C. Li, Z. Hicks, K.H. Bowen, K.J. Hemker, T. Mueller, C. Wang, Low-overpotential electroreduction of carbon monoxide using copper nanowires, *ACS Catal.* 7 (2017) 4467–4472. <https://doi.org/10.1021/acscatal.7b01124>.
- [22] Z. Wang, Y. Zhang, H. Xiong, C. Qin, W. Zhao, X. Liu, Yucca fern shaped CuO nanowires on Cu foam for remitting capacity fading of Li-ion battery anodes, *Sci. Rep.* 8 (2018) 6530. <https://doi.org/10.1038/s41598-018-24963-2>.
- [23] J. Maçaira, L. Andrade, A. Mendes, Highly efficient $\text{SiO}_2/\text{TiO}_2$ composite photoelectrodes for dye-sensitized solar cells, *Sol. Energy.* 158 (2017) 905–916. <https://doi.org/10.1016/j.solener.2017.10.056>.

- [24] L. Zhan, Y. Wang, H. Chang, R. Stehle, J. Xu, L. Gao, W. Zhang, Y. Jia, F. Qing, X. Li, Preparation of ultra-smooth Cu surface for high-quality graphene synthesis, *Nanoscale Res. Lett.* 13 (2018) 340. <https://doi.org/10.1186/s11671-018-2740-x>.
- [25] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, Catalyst coated membrane electrodes for the gas phase CO₂ electroreduction to formate, *Catal. Today*. 346 (2018) 58–64. <https://doi.org/10.1016/j.cattod.2018.11.073>.
- [26] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, CO₂ electroreduction to formate: Continuous single-pass operation in a filter-press reactor at high current densities using Bi gas diffusion electrodes, *J. CO₂ Util.* 34 (2019) 12–19. <https://doi.org/10.1016/j.jcou.2019.05.035>.
- [27] M.C. Biesinger, Advanced analysis of copper X-ray photoelectron spectra, *Surf. Interface Anal.* 49 (2017) 1325–1334. <https://doi.org/10.1002/sia.6239>.
- [28] S. González, M. Pérez, M. Barrera, A.R. González Elipe, R.M. Souto, Mechanism of copper passivation in aqueous sodium carbonate–bicarbonate solution derived from combined X-ray photoelectron spectroscopic and electrochemical data, *J. Phys. Chem. B*. 102 (1998) 5483–5489. <https://doi.org/10.1021/jp981069k>.
- [29] A. Eilert, F. Cavalca, F.S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E.J. Crumlin, H. Ogasawara, D. Friebe, L.G.M. Pettersson, A. Nilsson, Subsurface oxygen in oxide-derived copper electrocatalysts for carbon dioxide reduction, *J. Phys. Chem. Lett.* 8 (2017) 285–290. <https://doi.org/10.1021/acs.jpclett.6b02273>.
- [30] E. Bertheussen, A. Verdager-Casadevall, D. Ravasio, J.H. Montoya, D.B. Trimarco, C. Roy, S. Meier, J. Wendland, J.K. Nørskov, I.E.L. Stephens, I. Chorkendorff, Acetaldehyde as an intermediate in the electroreduction of carbon monoxide to ethanol on oxide-derived copper, *Angew. Chem. Int. Ed.* 55 (2016) 1450–1454. <https://doi.org/10.1002/anie.201508851>.

- [31] J.S. Daubert, G.T. Hill, H.N. Gotsch, A.P. Gremaud, J.S. Ovental, P.S. Williams, C.J. Oldham, G.N. Parsons, Corrosion protection of copper using Al_2O_3 , TiO_2 , ZnO , HfO_2 , and ZrO_2 atomic layer deposition, *ACS Appl. Mater. Interfaces*. 9 (2017) 4192–4201. <https://doi.org/10.1021/acsami.6b13571>.
- [32] A.I. Abdulagatov, Y. Yan, J.R. Cooper, Y. Zhang, Z.M. Gibbs, A.S. Cavanagh, R.G. Yang, Y.C. Lee, S.M. George, Al_2O_3 and TiO_2 atomic layer deposition on copper for water corrosion resistance, *ACS Appl. Mater. Interfaces*. 3 (2011) 4593–4601. <https://doi.org/10.1021/am2009579>.
- [33] S. Min, X. Yang, A.-Y. Lu, C.-C. Tseng, M.N. Hedhili, L.-J. Li, K.-W. Huang, Low overpotential and high current CO_2 reduction with surface reconstructed Cu foam electrodes, *Nano Energy*. 27 (2016) 121–129. <https://doi.org/10.1016/j.nanoen.2016.06.043>.
- [34] M. Le, M. Ren, Z. Zhang, P.T. Sprunger, R.L. Kurtz, J.C. Flake, Electrochemical reduction of CO_2 to CH_3OH at copper oxide surfaces, *J. Electrochem. Soc.* 158 (2011) E45. <https://doi.org/10.1149/1.3561636>.
- [35] D. Yang, Q. Zhu, C. Chen, H. Liu, Z. Liu, Z. Zhao, X. Zhang, S. Liu, B. Han, Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts, *Nat. Commun.* 10 (2019) 677. <https://doi.org/10.1038/s41467-019-08653-9>.
- [36] K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, T.F. Jaramillo, Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces, *J. Am. Chem. Soc.* 136 (2014) 14107–14113. <https://doi.org/10.1021/ja505791r>.
- [37] Y. Peng, T. Wu, L. Sun, J.M. V. Nsanzimana, A.C. Fisher, X. Wang, Selective electrochemical reduction of CO_2 to ethylene on nanopores-modified copper electrodes in aqueous solution, *ACS Appl. Mater. Interfaces*. 9 (2017) 32782–32789. <https://doi.org/10.1021/acsami.7b10421>.

- [38] Y. Chen, M.W. Kanan, Tin oxide dependence of the CO₂ reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts, *J. Am. Chem. Soc.* 134 (2012) 1986–1989. <https://doi.org/10.1021/ja2108799>.
- [39] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C.T. Dinh, F. Fan, C. Cao, F.P.G. de Arquer, T.S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S.O. Kelley, E.H. Sargent, Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration, *Nature*. 537 (2016) 382–386. <https://doi.org/10.1038/nature19060>.
- [40] J. Resasco, L.D. Chen, E. Clark, C. Tsai, C. Hahn, T.F. Jaramillo, K. Chan, A.T. Bell, Promoter effects of alkali metal cations on the electrochemical reduction of carbon dioxide, *J. Am. Chem. Soc.* 139 (2017) 11277–11287. <https://doi.org/10.1021/jacs.7b06765>.
- [41] D. Li, J. Wu, T. Liu, J. Liu, Z. Yan, L. Zhen, Y. Feng, Tuning the pore structure of porous tin foam electrodes for enhanced electrochemical reduction of carbon dioxide to formate, *Chem. Eng. J.* 375 (2019) 122024. <https://doi.org/10.1016/j.cej.2019.122024>.
- [42] S. Zhang, P. Kang, T.J. Meyer, Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate, *J. Am. Chem. Soc.* 136 (2014) 1734–1737. <https://doi.org/10.1021/ja4113885>.
- [43] W. Lv, J. Zhou, F. Kong, H. Fang, W. Wang, Porous tin-based film deposited on copper foil for electrochemical reduction of carbon dioxide to formate, *Int. J. Hydrogen Energy*. 41 (2016) 1585–1591. <https://doi.org/10.1016/j.ijhydene.2015.11.100>.
- [44] D. Li, L. Huang, T. Liu, J. Liu, L. Zhen, J. Wu, Y. Feng, Electrochemical reduction of carbon dioxide to formate via nano-prism assembled CuO microspheres, *Chemosphere*. 237 (2019) 124527. <https://doi.org/10.1016/j.chemosphere.2019.124527>.

- [45] B. Endrődi, G. Bencsik, F. Darvas, R. Jones, K. Rajeshwar, C. Janáky, Continuous-flow electroreduction of carbon dioxide, *Prog. Energy Combust. Sci.* 62 (2017) 133–154. <https://doi.org/10.1016/j.pecs.2017.05.005>.
- [46] J. T. Song, H. Song, B. Kim, J. Oh, Towards Higher Rate Electrochemical CO_2 Conversion: From Liquid-Phase to Gas-Phase Systems, *Catalysts*. 9 (2019) 224. <https://doi.org/10.3390/catal9030224>.

CHAPTER 5

Binary Copper-Bismuth Catalysts for the
Electrochemical Reduction of CO₂: Study on
Surface Properties and Catalytic Activity

Adapted from the article

Azenha, C., Mateos-Pedrero, C., Alvarez-Guerra, M., Irabien, A., Mendes, A., “Binary copper-bismuth catalysts for the electrochemical reduction of CO₂: study on surface properties and catalytic activity”, Chemical Engineering Journal, 2022, 445 (136575).

Binary Copper-Bismuth Catalysts for the Electrochemical Reduction of CO₂: Study on Surface Properties and Catalytic Activity

5.1 Abstract

The CuO NWs electrode, described in Chapter 4, was used as substrate to prepare a series of CuBi catalysts with different Bi loadings, which were tested for the electrochemical reduction of CO₂ (ERCO₂). The developed catalysts were tested in a filter-press cell, and the influence of the catholyte on the catalytic performance was assessed. Catalyst #20C was found to be very selective for formate production, with a faradaic efficiency (FE) of 86.4 % when Cl⁻ ions are present in the catholyte solution. The presence of weak CO₂ adsorption sites on the catalyst surface favors the formation of non-coordinated and monodentate carbonates after CO₂ adsorption, resulting in enhanced formate formation through an outer-sphere mechanism. For catalyst #50C, an unprecedented propane selectivity was recorded (FE of 85.4 %), being the first high-efficiency catalyst for the ERCO₂ to propane ever reported. This remarkable catalytic behavior was attributed to strong CO₂ adsorption sites on the catalyst surface and higher CO₂ and CO adsorption capacity. It is also proposed that a bidentate carbonate is a key intermediate for the ERCO₂ to propane, which is preferably formed when strong Lewis acid and base sites are present on the catalyst surface.

Keywords: CO₂ electroreduction; CuBi catalysts; propane; selectivity; surface properties.

5.2 Introduction

Since the industrial revolution, humanity has become dependent on fossil fuels to meet its increasing energy demands [1,2]. Unfortunately, this reliance on fossil fuels resulted in the rising of the CO₂ atmospheric concentration, already exceeding 417.64 ppm (March 2021) [3], which is considered one of the major causes of climate change [4]. The electrochemical reduction of CO₂ (ERCO₂) represents a promising alternative to help close the anthropogenic carbon cycle and convert intermittent electricity from renewable and clean energy sources (*i.e.*, solar, wind, and hydro) to chemical energy in the form of fuels and feedstock [5–7].

The ERCO₂ was first proposed in 1870 by Royer. However, it is not yet commercially available due to the low price of fossil fuels and significant technological challenges [8,9]. The barriers that prevent the widespread use of this technology include (i) low energy efficiency and sluggish reaction kinetics due to the large energy barrier for CO₂ activation; (ii) low selectivity owing to the relatively similar reduction potentials for all possible reaction products, (iii) the competing hydrogen evolution reaction (HER), which in general is favored under the ERCO₂ working conditions; and, (iv) low catalyst stability over extended operating periods [9,10]. Thus, one of the major challenges in ERCO₂ is the development of high-efficiency ERCO₂ catalysts [10].

The search for suitable ERCO₂ catalysts represents one of the most active areas of current research [11]. Recent works proposed several strategies to improve the efficiency of metal-based ERCO₂ catalysts, namely through the control of particle size, morphology, surface defects, grain boundaries, crystal facets, and electronic properties (bimetallic alloys) [9]. Most catalysts reported so far are powder-based. Thus, the typical preparation of electrodes involves the use of polymer binders, such as Nafion, which makes it difficult to tune the surface properties of the catalyst [2]. Moreover, many active sites are embedded inside and inaccessible for reactants, resulting in decreased activity. Alternative preparation methods that aim to increase the active surface area and long-term stability under electrolysis have been developed. These new preparation routes include the development of self-supported catalysts, where active materials are

grown directly on the surface of conductive substrates [2,11]. Examples of self-supporting catalysts include oxide-derived Au foils, with $> 98\%$ of faradaic efficiency (FE) for CO production and stable current density of -10 mA cm^{-2} for 8 h [12]; and a plasma-activated Cu catalyst, highly selective for the CO_2 reduction to ethylene with a maximum FE of 60% at $-0.9\text{ V}_{\text{RHE}}$ [13]. More recently, De Luna *et al.* used electrochemical deposition techniques to control the morphology and oxidation state of a Cu-based catalyst. The resulting catalyst exhibited a remarkable partial current density for ethylene of -160 mA cm^{-2} at $-1.0\text{ V}_{\text{RHE}}$ [14]. Likewise, Zhong *et al.* demonstrated that bismuth dendrites electrochemically deposited on carbon paper provide higher specific surface area and expose edge sites, resulting in improved catalytic activity and selectivity toward formate [15]. The hydrothermal method was also used to grow CuS nanosheets on the surface of a nickel foam, achieving an FE of 73% for methane production, stable up to 60 h [16].

Chapter 4 described the growth of a CuO nanowires (NWs) catalyst directly on the surface of a commercial copper foam. The developed catalyst proved to be very efficient for the ER CO_2 to methanol, with FE 66.4% at $-0.8\text{ V}_{\text{RHE}}$, while the HER was strongly suppressed. The nanowire structure was identified as the key to lowering the CO_2 adsorption barrier and enhancing the stabilization of the $\text{CO}_2^{\cdot-}$ intermediate, resulting in improved ER CO_2 activity at low applied overpotential [17].

The present chapter studies the effect of bismuth electrodeposition over the CuO NWs. Bi is a non-noble and earth-abundant metal with no known adverse impact on the environment, which has attracted much attention to produce formate through ER CO_2 [18]. In this study, Bi was deposited considering different values of electron charge passed through the substrate. Interestingly, it was found that the physicochemical properties of the catalysts are highly dependent on the charge passed, which in turn controls the product distribution. The performance of the catalysts was tested in a continuous gas diffusion electrode (GDE)-reactor configuration, and different catholyte solutions were evaluated. Formate and propane were produced with high efficiency depending on the catholyte and catalyst used. Besides, by combining electrochemical

measurements with microscopic and spectroscopic characterization techniques, insights into the improved performance and reaction mechanism are provided.

5.3 Experimental

5.3.1 Electrode preparation

The CuO NWs electrodes prepared in Chapter 4 were used as the substrate for bismuth electrodeposition, **Figure 5.1**. An aqueous solution of 0.03 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich, 99.999 %) was prepared with ultrapure water, and HCl (Fluka, 37 %) was added dropwise until the solution became clear [19]. Electrodeposition was carried out at atmospheric conditions, using a three-electrode setup with the CuO NWs as the working electrode and the bismuth solution as the electrolyte. A carbon rod and an Ag/AgCl/Sat. KCl electrode were used as counter and reference electrodes, respectively. A constant current density of 20 mA cm^{-2} was applied until the desired amount of electron charge was passed (5 C, 20 C, and 50 C). The developed catalysts were named according to the electron charge passed through the substrate (#5C, #20C, and #50C).



Figure 5.1. Experimental procedure used for the electrocatalysts preparation.

5.3.2 Electrochemical measurements

All electrochemical measurements were performed at ambient conditions of pressure and temperature in the filter-press cell described in Chapter 4. Experiments were conducted in an experimental setup already described in the literature [20,21] and illustrated in Figure 5.2.

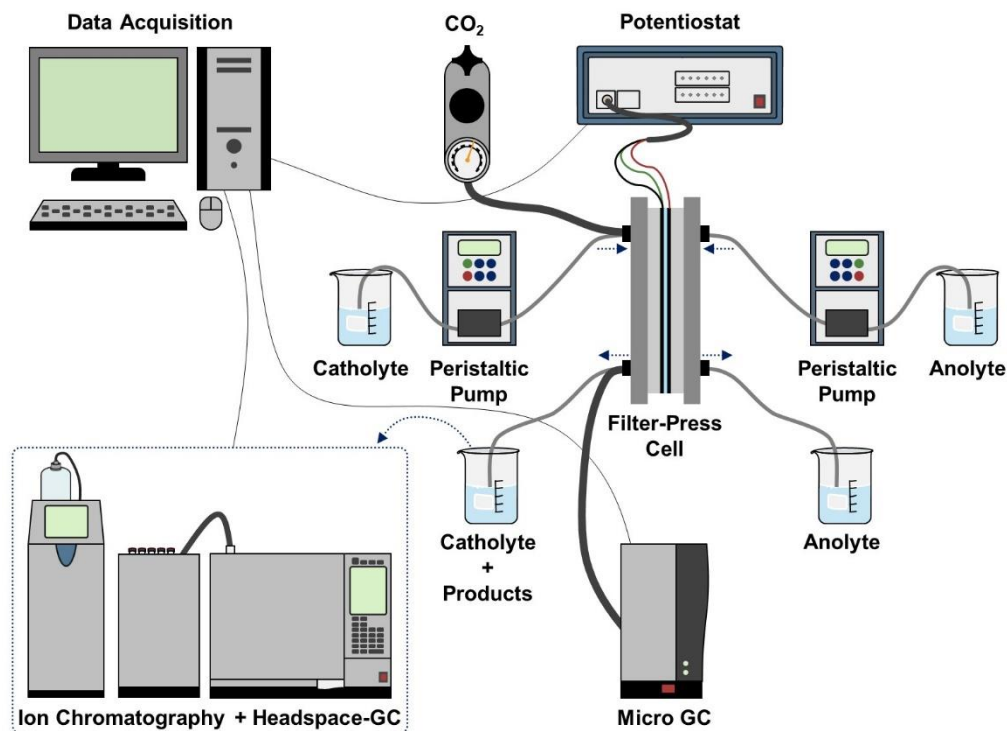


Figure 5.2. Experimental setup.

Following the experimental methodology described in Chapter 4, the geometric electrode surface area was 10 cm², and the cathode and anode compartments were separated with a Nafion 117 cation exchange membrane. A tinned steel mesh was employed as a current collector and a dimensionally stable anode [DSA/O₂ (Ir-MMO (mixed metal oxide) on platinum)] as a counter-electrode. A leak-free Ag/AgCl 3.4 mol L⁻¹ KCl reference electrode was assembled close to the working electrode. An aqueous solution of 1.0 M KOH (PanReac, 85 %) was selected as the anolyte. On the

other hand, two different aqueous solutions were tested as catholyte: 0.1 M KHCO_3 (PanReac, > 99 %), catholyte A; and 0.45 M KHCO_3 + 0.5 M KCl (PanReac, > 99 %), catholyte B. Experiments were conducted at galvanostatic conditions (-45 mA cm^{-2}), with the current supplied by the potentiostat (MSTAT 4, Arbin Instruments). Each test lasted 90 min and was performed on a continuous mode with a single pass of the catholyte and anolyte through the cell at a flow rate of $0.57 \text{ mL min}^{-1} \text{ cm}^{-2}$, using two peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group). Pure gaseous CO_2 was fed to the cell at a flow rate of 200 mL min^{-1} . Each test was conducted in duplicate on different days to ensure the reproducibility of the results.

Gas products were analyzed online every 30 min with a micro gas chromatograph, and liquid samples, collected every 30 min, were analyzed by ion chromatography and headspace-GC.

The faradaic efficiency and product formation rate were determined to evaluate the electrochemical performance of the electrodes.

5.3.3 Physicochemical characterization

The morphology and element distribution were obtained by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, Phenom XL Desktop SEM, and Nova NanoSEM 200). The crystal structure was studied using X-ray diffraction (XRD, PANalytical X'Pert Pro), while X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra HAS) was used to identify the surface chemical composition and valence state, as detailed in Chapter 2.

The CO_2 and CO adsorption was studied by CO_2/CO temperature-programmed desorption combined with mass spectrometry (CO_2/CO -TPD-MS, ChemBET Pulsar TPR/TPD). Samples were pretreated at 120°C for 30 min under He flow, followed by CO_2/CO adsorption at 50°C . Then, the CO_2/CO desorption was monitored using a quadrupole MS (Pfeiffer Vacuum OmniStar GSD 320) in the temperature range of 50°C to 700°C .

CO_2 adsorption was also studied by infrared (IR) spectroscopy (Vertex 70 FTIR, Bruker). IR measurements were performed in transmittance mode using a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. Samples were measured in attenuated total reflectance (ATR) mode using an A225/Q platinum ATR diamond crystal with a single reflection accessory. For each spectrum, 128 scans were accumulated between 4000 cm^{-1} and 700 cm^{-1} at a spectral resolution of 2 cm^{-1} . Before CO_2 adsorption, all samples were treated overnight in a vacuum oven at $80\text{ }^\circ\text{C}$ to remove possible adsorbed contaminants from the catalyst surface, like H_2O . CO_2 adsorption was performed at $50\text{ }^\circ\text{C}$; subsequently, the CO_2 was stepwise desorbed at $150\text{ }^\circ\text{C}$, $250\text{ }^\circ\text{C}$, $350\text{ }^\circ\text{C}$, and $450\text{ }^\circ\text{C}$. IR spectra were acquired after each step. Moreover, the IR spectrum of the bare samples (before CO_2 exposure) was recorded and used as *blank* during spectra interpretation to avoid interference from the characteristic IR absorption of the samples.

5.4 Results and discussion

5.4.1 Physicochemical properties of the catalysts

The morphology of the prepared catalysts was studied by SEM-EDS, **Figure 5.3**. All samples exhibit copper nanowires, indicating that this structure was kept after the electrochemical deposition of bismuth, despite the high acidity of the electrodeposition solution (pH 1). Moreover, after bismuth deposition, the formation of Bi clusters is observed, whose number and size increase with increasing charge passing. Samples #5C and #20C have Bi microclusters with an average diameter of $8.5\text{ }\mu\text{m}$ and $11.5\text{ }\mu\text{m}$, respectively, being these clusters more abundant in sample #20C. The higher number and size of Bi clusters was already expected due to the longer deposition time used when compared to #5C. In turn, sample #50C evidences the formation of even larger Bi clusters, with an average size of $18.0\text{ }\mu\text{m}$.

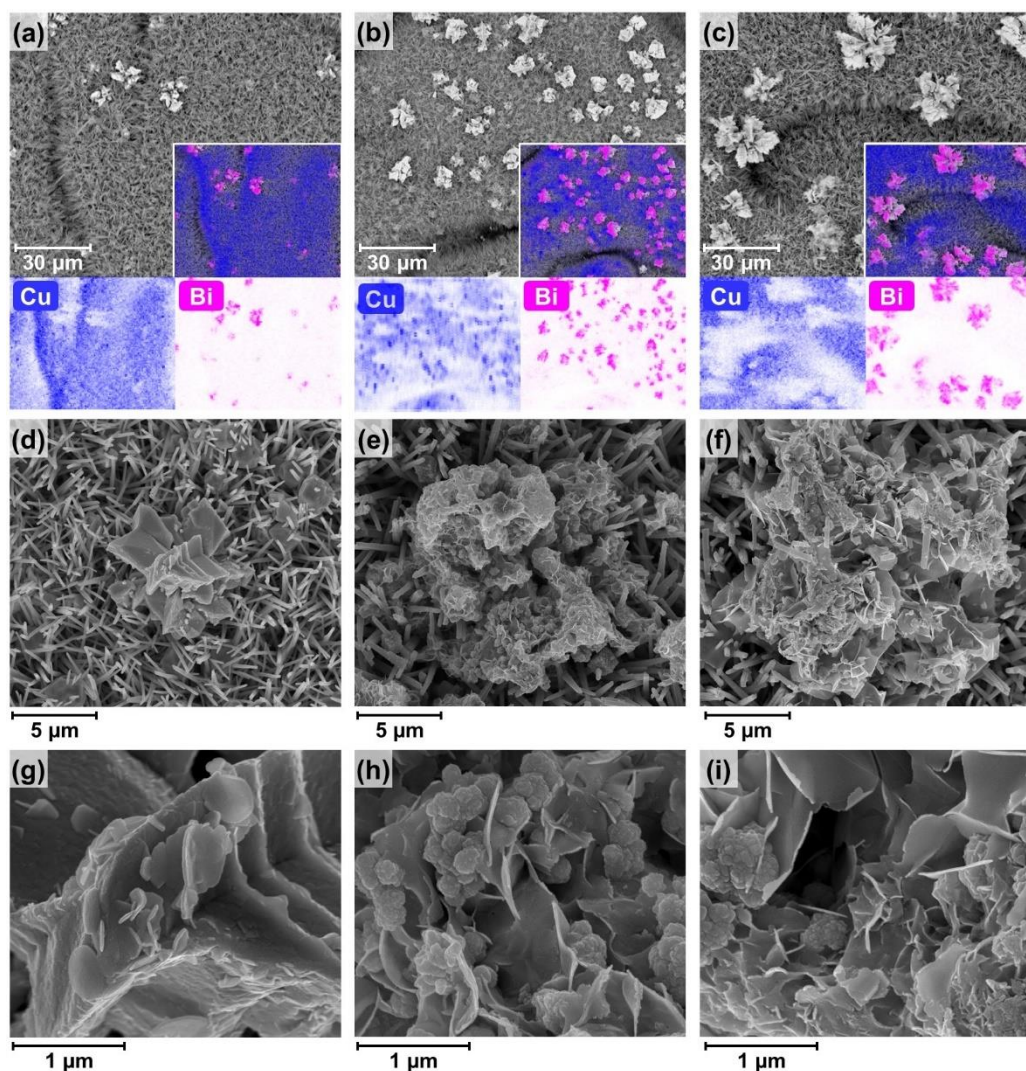


Figure 5.3. (a-c) Low and (d-i) high-magnification SEM images with elemental mapping of Cu and Bi for catalysts (a, d, g) #5C, (b, e, h) #20C, and (c, f, i) #50C.

A closer look also indicates that the morphology of the Bi particles changes with the charge passing. Sample #5C shows small Bi grains with smooth surfaces and sharp edges and corners (**Figure 5.3d**). In addition, **Figure 5.3g** shows the formation of small platelet-like structures on the surface of the Bi grains. On the other hand, samples #20C and #50C are rougher and more heterogeneous (**Figures 5.3e and f**). **Figures 5.3h and i** also indicate that the previously formed platelet-like structures grew in radius. Thus, it

is observed that the Bi grains evolve to flower-like structures with the increasing charge passing, following the evolution trend of the Bi clusters during the electrodeposition already well-illustrated by Liu *et al.* [22].

The crystalline structure of the as-prepared catalysts was characterized by XRD, **Figure 5.4**. All samples exhibit the main diffraction lines of Cu^0 at 43.5° (111), 50.6° (200), and 74.2° (220), ascribed to the bulk structure of the copper foam substrate. The main diffraction peak of the Cu_2O crystalline phase is also observed at 36.5° (111), denoting that the CuO NWs are reduced to Cu_2O NWs during electrodeposition. This reduction occurs because, during electrodeposition, CuO is subjected to a potential close to the standard potential for Cu^{2+} reduction to Cu^+ (*ca.* $-0.15 \text{ V}_{\text{RHE}}$).

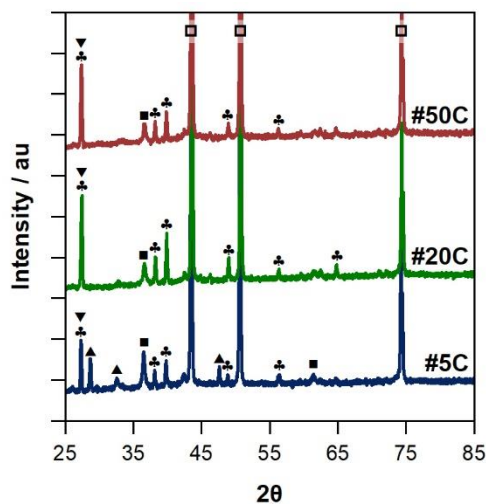


Figure 5.4. XRD pattern of the developed catalysts. $\square$ Cu^0 (JCPDS card no. 04-0836), $\blacksquare$ Cu_2O (JCPDS card no. 05-0667), $\clubsuit$ Bi^0 (JCPDS card no. 85-1329), $\blacktriangledown$ monoclinic $\alpha\text{-Bi}_2\text{O}_3$ (JCPDS card no. 41-1449), and $\blacktriangle$ cubic $\delta\text{-Bi}_2\text{O}_3$ (JCPDS no. 76-2478).

The characteristic diffraction lines of the Bi^0 phase are detected at 27.3° (012), 38.1° (104), 39.8° (110), 48.8° (202), and 56.3° (205). Overlapping Bi^0 (012), the main peak of the $\alpha\text{-Bi}_2\text{O}_3$ phase (120) is observed at 27.3° . The appearance of additional XRD features of $\alpha\text{-Bi}_2\text{O}_3$ at 26.9° (111) and 33.1° (-122) confirms the presence of this phase. Sample #5C also displays diffraction peaks ascribed to cubic $\delta\text{-Bi}_2\text{O}_3$ at 28.7° (111),

32.6° (200), and 47.6° (220), in agreement with the mechanism of bismuth electrodeposition proposed by Liu *et al.* [22]. According to these authors, the flower-like bismuth structures are produced following three stages: (i) growth of hexagonal Bi grains, (ii) nucleation of Bi₂O₃, and (iii) growth of Bi₂O₃ flowers. Initially, hexagonal Bi grains grow on the surface of the Cu substrate. The high curvature of the edges and corners of the Bi grains induces a strong electric field, guiding the migration of Bi³⁺ ions from the electrolyte solution. As a result, cubic Bi₂O₃ platelet nucleates on the edges and corners of the hexagonal grains. The platelet then grows along its edges, forming a nanopetal. As the radius of the nanopetals increases, the electric field near the edges decreases, eventually stopping the particle growth. Based on the characterization results, the same mechanism was observed in the present work. However, unlike the work of Liu *et al.*, which reports the production of body-centered cubic (bcc) Bi₂O₃ phase, in the present study, face-centered cubic (fcc) structures were developed.

Table 5.1. Results of XRD analysis.

Sample	Phase	Crystallite size (nm)	% (v/v) ^a
#5C	Cu ⁰	21.3 ± 5.0	81.8
	Cu ₂ O	16.0 ± 0.5	10.1
	Bi ⁰	8.4 ± 5.0	4.0
	α-Bi ₂ O ₃	23.9 ± 0.1	1.8
	δ- Bi ₂ O ₃	24.7 ± 5.0	2.3
#20C	Cu ⁰	30.4 ± 5.0	81.8
	Cu ₂ O	8.8 ± 0.5	9.0
	Bi ⁰	33.3 ± 5.0	5.6
	α-Bi ₂ O ₃	6.3 ± 0.1	3.6
#50C	Cu ⁰	24.6 ± 5.0	87.1
	Cu ₂ O	11.0 ± 0.5	6.2
	Bi ⁰	46.9 ± 5.0	3.9
	α-Bi ₂ O ₃	4.2 ± 0.1	2.8

^a: volume concentration.

The $\delta\text{-Bi}_2\text{O}_3$ Bragg peaks vanish as the charge passing increases, being absent for samples #20C and #50C. It is well known that $\alpha\text{-Bi}_2\text{O}_3$ is more stable than fcc $\delta\text{-Bi}_2\text{O}_3$ [23], which may explain why $\alpha\text{-Bi}_2\text{O}_3$ is the only bismuth oxide phase present for longer electrodeposition times. Another effect of the increasing charge passing is the increase in Bi^0 crystallite size, from 8.4 nm of sample #5C to 46.9 nm of #50C (Table 5.1), following SEM results and literature [19].

Surface atomic composition and valence state of the main elements were analyzed by XPS. CuO NWs sample was also evaluated for comparison purposes (Table 5.2). All samples show the Bi 4f region of the spectrum dominated by $4f_{7/2}$ and $4f_{5/2}$ components, which were deconvoluted into two sets of peaks, Figure 5.5a. According to the literature, the XPS peaks at binding energies (BE) of *ca.* 159.3 eV and *ca.* 164.7 eV, with a doublet separation of 5.3 eV, are ascribed to Bi^{3+} in Bi_2O_3 [24,25]. The lower BE peaks at 157.8 eV and 163.1 eV are assigned to Bi^0 [23]. This result indicates that the as-prepared catalysts contain Bi_2O_3 and Bi^0 , in good agreement with XRD.

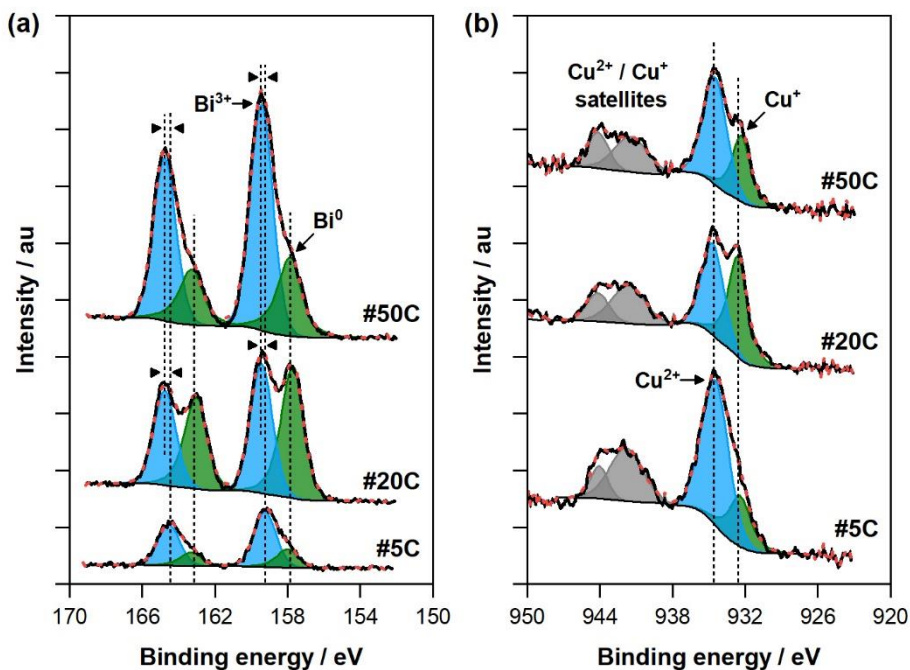


Figure 5.5. (a) Bi 4f, and (b) Cu 2p_{3/2} spectra of the developed catalysts.

Table 5.2. Bi 4f_{7/2}, Cu 2p_{3/2}, Cu LMM, and modified Auger parameter values for the prepared electrodes; CuO NWs is also included for comparison purposes.

Sample	Compound	BE ^a (eV)	FWHM ^b (eV)	KE ^c (eV)	FWHM (eV)	α' (eV)	At. % ^d
CuO NWs	CuO	933.6	2.40	917.4	2.10	1851.0	100.0
#5C	Cu ₂ O	932.4	2.12	916.7	2.10	1849.1	18.6
	CuO	934.5	2.62	917.7	2.10	1852.2	59.0
	Bi ⁰	157.9	1.43	--	--	--	5.7
	Bi ₂ O ₃	159.2	1.43	--	--	--	16.7
#20C	Cu ₂ O	932.6	1.87	916.5	2.10	1849.1	22.4
	CuO	934.7	2.14	917.9	2.10	1852.6	21.1
	Bi ⁰	157.6	1.26	--	--	--	29.7
	Bi ₂ O ₃	159.3	1.42	--	--	--	26.8
#50C	Cu ₂ O	932.3	1.82	916.6	2.10	1848.9	13.1
	CuO	934.5	2.31	917.8	2.10	1852.3	24.5
	Bi ⁰	157.8	1.48	--	--	--	19.3
	Bi ₂ O ₃	159.3	1.43	--	--	--	43.1

^a: binding energy; ^b: full width at half maximum; ^c: kinetic energy; α' : modified Auger parameter;

^d: calculated according to Cu 2p_{3/2} and Bi 4f_{7/2}.

With the increasing deposition time, the core level of Bi₂O₃ shifts toward high BE, which is attributed to the transition from δ - to α -Bi₂O₃, already identified by XRD. The δ phase of Bi₂O₃ adopts a defective fluorite structure with two oxygen vacancies per unit cell, whose vacancy alignment strongly impacts the electronic structure of the oxide [26]. Thus, δ - and α -Bi₂O₃ present a slightly different electronic density. While the BE of Bi³⁺ matches the typical reported values for Bi(III) oxides (159.0 eV to 159.8 eV) [24,25], a positive shift of *ca.* 0.7 eV is observed for Bi⁰ when compared to reported values for metal bismuth (157.1 eV) [15,23,24]. The higher BE suggests that the electron density around Bi⁰ decreased, possibly because the electron cloud was attracted to the Cu atoms due to a strong interaction between Bi and Cu [27]. It is worth mentioning that the intensity of Bi 4f peaks increases with increasing deposition time, suggesting higher Bi

loading, as expected. Moreover, **Table 5.3** indicates that the Bi/Cu XPS ratio increases for longer deposition times, indicating surface enrichment with Bi and/or larger particle size.

The peak-fit of the Cu 2p_{3/2} core level denotes the presence of two copper valences, **Figure 5.5b**. The high BE peak centered at *ca.* 934.6 eV is ascribed to Cu²⁺ [28], possibly due to surface reoxidation upon air exposure. On the other hand, the low BE peak at *ca.* 932.4 eV can be attributed to Cu⁺ and/or Cu⁰; thus, chemical state differentiation was based on the Cu LMM Auger peak [28,29], **Table 5.2**. The Auger peak at *ca.* 916.6 eV suggests that Cu⁺ is present, which is confirmed by the modified Auger parameter of *ca.* 1849.0 eV [28]. XPS does not detect the Cu⁰ bulk structure of the copper foam; therefore, it can be stated that the surface of the copper foam is evenly covered with Cu₂O NWs and bismuth particles. The intensity of Cu 2p peaks decreases with increasing deposition time, in contrast to that observed for Bi 4f. Once again, it shows that the copper surface is enriched with bismuth during the electrodeposition process.

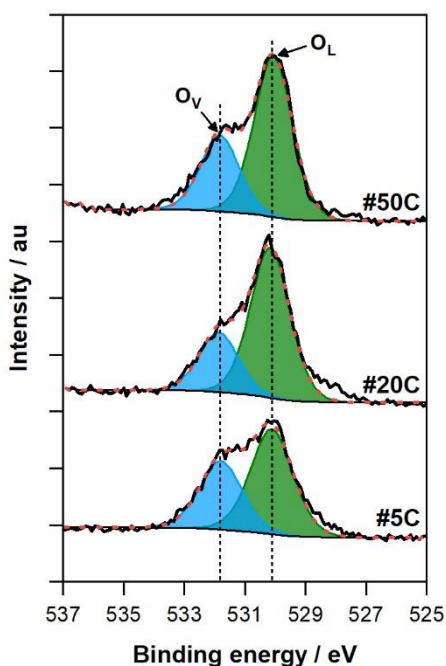


Figure 5.6. O 1s XPS spectra of the developed catalysts.

The O 1s peak shows two main contributions: lattice oxygen (low BE peak, O_L) and surface oxygen defects in the metal oxides (high BE peak, O_V) [30,31], **Figure 5.6**. The peak area ratios are summarized in **Table 5.3**, revealing that #5C is the sample with more oxygen defects, possibly due to the presence of δ - Bi_2O_3 . Oxygen vacancies can also be formed to compensate for the charge imbalance caused by the strong interaction between Bi and Cu, as reported for Cr_2O_3 [32]. This seems to be a rational explanation since the $O_V/(O_V+O_L)$ ratio follows the same trend of the upward shift in the BE of Bi^0 , increasing in the following order #20C < #50C < #5C, **Tables 5.2 and 5.3**.

Table 5.3. Surface atomic ratio determined by XPS.

Sample	$O_V/(O_V+O_L)$	$O_L/(O_V+O_L)$	Bi/Cu	Cu^+/Cu total	Bi^0/Bi total
#5C	0.39	0.61	0.24	0.2	0.3
#20C	0.28	0.72	1.07	0.4	0.5
#50C	0.32	0.68	1.26	0.2	0.3

O_V : oxygen vacancy; O_L : lattice oxygen

5.4.2 ER CO_2 activity

The catalytic activity of the developed catalysts for CO_2 electroreduction was evaluated using a filter-press cell working at a constant current density of -45 mA cm^{-2} , as reported in previous works [20,21]. All tests were carried out at atmospheric conditions on a continuous mode, with a single pass of the catholyte and anolyte through the cell. Experiments were performed using either 0.1 M $KHCO_3$ (catholyte A) or 0.45 M $KHCO_3$ + 0.5 M KCl (catholyte B) to assess the influence of the catholyte. All samples were tested at least in duplicate on different days to ensure the reproducibility of the results.

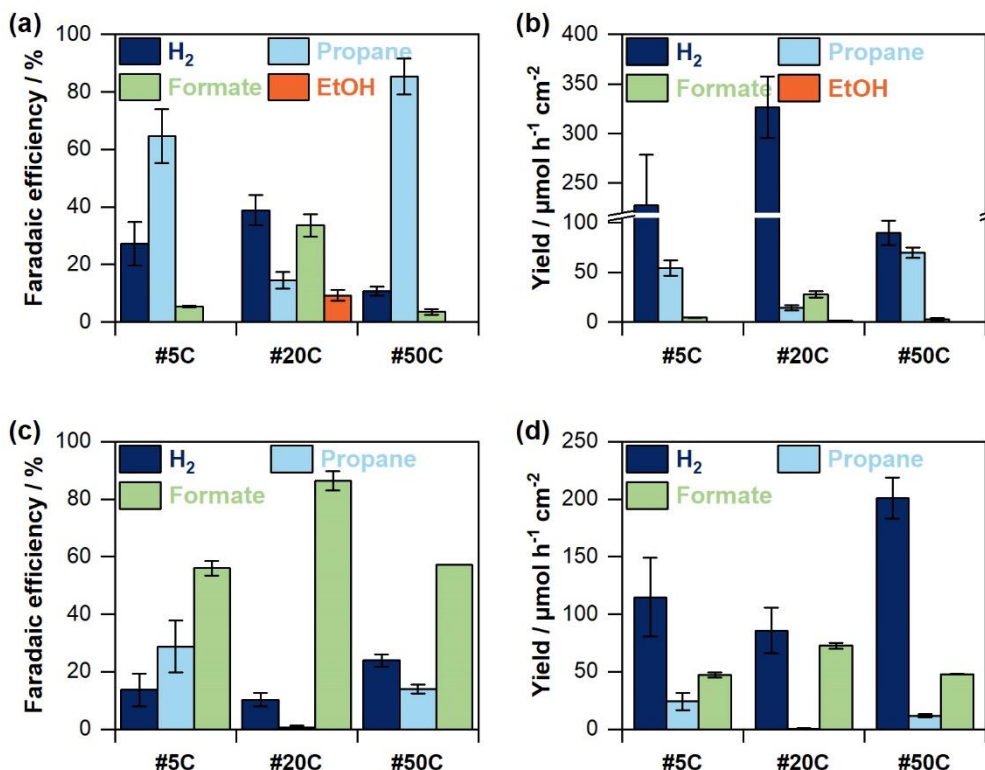


Figure 5.7. (a, c) Faradaic efficiencies and (b, d) production yield for the developed catalysts. Tests were performed on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell at a current density of -45 mA cm^{-2} . (a, b) Catholyte A: 0.1 M KHCO_3 ; (c, d) catholyte B: 0.45 M KHCO_3 + 0.5 M KCl .

Figures 5.7a and b illustrate the results obtained with catholyte A. As observed, for catalyst #20C, formate was the main ER CO_2 product with an FE of 33.6 % and production yield of $28.2 \mu\text{mol h}^{-1} \text{cm}^{-2}$. The achieved values are quite low compared to other Bi-containing catalysts, reported as highly selective and active for the ER CO_2 to formate [33]. For instance, Bi-based catalysts prepared by electrodeposition on carbon paper achieved a maximum formate FE of 96.4 % and a partial current density of -15.2 mA cm^{-2} at *ca.* $-1.13 \text{ V}_{\text{RHE}}$ in 0.5 M NaHCO_3 [15]. Hoffman *et al.* reported an FE up to 90 % at $-0.8 \text{ V}_{\text{RHE}}$ with a dendritic Cu-Bi catalyst [34]; while Wen *et al.* described a Bi-Sn catalyst displaying an FE of 96 % and a production rate of

740 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ at $-1.1 V_{\text{RHE}}$ [19]. Moreover, a remarkable production rate of 3949 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ with FE of 70.6 % was recently reported by Díaz-Sainz *et al.* using carbon-supported Bi nanoparticles. Tests were performed at -300 mA cm^{-2} in a filter-press cell [21]. The high partial formate current density of -210 mA cm^{-2} satisfies the commercial standards ($> 200 \text{ mA cm}^{-2}$) [33].

As described above, sample #20C exhibited low selectivity toward formate, along with an excessive H_2 output from the competitive HER (FE of 38.9 %). Thus, knowing that the electrolyte plays a major role in the ERCO_2 product distribution [35–37], with the addition of specific anions and cations providing ways to tune the selectivity of the reaction [38], catholyte B was tested [20,21]. As illustrated in **Figure 5.7c**, the formate selectivity increased for all samples. In particular, sample #20C exhibited a 2.6-fold increment in formate FE, from 33.6 % (catholyte A, pH 7.25) to 86.4 % (catholyte B, pH 6.82). The obtained FE is more consistent with the literature values previously discussed; however, the production yield of $72.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$ remains very low. To increase the formate yield, catalyst #20C was tested under the same electrolysis conditions but considering a higher current density (-90 mA cm^{-2}), **Figure 5.8**.

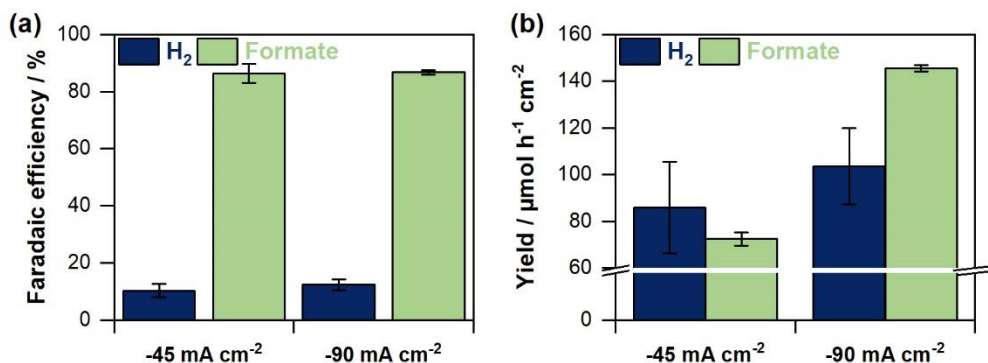


Figure 5.8. (a) Faradaic efficiency and (b) production yield for catalyst #20C, working on a continuous mode with a single pass of the catholyte and anolyte through the electrochemical cell, at a current density of -45 mA cm^{-2} or -90 mA cm^{-2} . An aqueous solution of $0.45 \text{ M KHCO}_3 + 0.5 \text{ M KCl}$ was used as catholyte (catholyte B).

As evidenced, no loss in the FE was detected, and the formate yield improved by 2-fold, reaching $145.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$. This result suggests that the developed catalyst is robust; it allows working at higher current densities while maintaining the high selectivity and stability toward formate, which is critical for increasing the system energy efficiency and, thus, the economic competitiveness of the reaction.

Figure 5.7 shows that the catholyte is a critical factor in controlling H_2 production from the competitive HER, which is hindered when catholyte B is used. For sample #20C, the H_2 FE decreased from 38.9 % (electrolyte A) to 10.2 % (electrolyte B), representing a 3.8-fold reduction in HER activity. Catalyst #5C shows a lighter suppression of the HER when tested with electrolyte B; nevertheless, the H_2 production decreased by 2.0-times. It is well accepted that changes in the electrolyte pH can alter the reaction pathway [35,38]. However, no significant pH deviations are noticed in the present study (**Table 5.4**). Still, it is important to distinguish between bulk electrolyte pH and local pH at the catalyst surface. During the ER CO_2 , both the CO_2 reduction and the HER produce hydroxide anions (OH^-), raising the local pH. As previously reported, increasing the local pH suppresses the hydrogen evolution (pH-dependent reaction) and enhances the selectivity toward multi-carbon products [39]. Thus, electrolytes with higher ionic strength (*i.e.*, stronger buffer effect) would theoretically promote H_2 production by lowering the local pH [38,39]. Despite that, in the present study, the HER was inhibited when an electrolyte with a higher bicarbonate concentration was used (catholyte B). Therefore, attention must be paid to the effect of adding a halide salt (KCl) to the electrolyte solution. According to the literature, strong hydrogen bonds can be formed between hydrogen atoms and Cl^- ions [38], which may explain the inhibition of the HER when KCl is present (catholyte B). Moreover, computational and experimental studies demonstrated that Cl^- ions conveniently block active sites for proton reduction, remarkably decreasing the side reaction activity at the reaction interface. Additionally, Cl^- is considered an electron donor, which facilitates the electron transfer process to the vacant orbital of inert CO_2 and thus stabilizes the key $\text{CO}_2^{\cdot-}$ radical [40].

Table 5.4. Details of the ER CO_2 testing.

Catalyst	Bismuth loading (mg cm^{-2})		Catholyte ^c	Cathode pH ^d	Current density (mA cm^{-2})	Cathodic potential (V_{RHE})	Cell voltage (V)
	Theoretical ^a	Real ^b					
#5C	0.2	0.21 ± 0.04	A	11	-45	-0.9 ± 0.3	4.6 ± 0.3
#20C	0.7	0.68 ± 0.07	A	11	-45	-1.0 ± 0.8	4.2 ± 0.8
#50C	2.1	2.17 ± 0.06	A	11	-45	-1.1 ± 0.5	4.7 ± 0.2
#5C	0.2	0.21 ± 0.04	B	10	-45	-0.6 ± 0.3	2.5 ± 0.1
#20C	0.7	0.68 ± 0.07	B	10	-45	-1.3 ± 0.3	2.8 ± 0.1
#50C	2.1	2.17 ± 0.06	B	10	-45	-0.8 ± 0.2	2.5 ± 0.2
#20C	0.7	0.68 ± 0.07	B	10	-90	-0.6 ± 0.1	3.1 ± 0.1

^a: bismuth loading determined according to the total charge passed during the electrodeposition;

^b: bismuth loading determined by weighting the CuO NWs substrate before and after bismuth electrodeposition; ^c: catholyte A, 0.1 M KHCO_3 (pH of 7.25 and conductivity of 14.15 mS cm^{-1} after CO_2 saturation), and catholyte B, 0.45 M KHCO_3 + 0.5 M KCl (pH of 6.82 and conductivity of 85.8 mS cm^{-1} , after CO_2 saturation); ^d: measured with pH test strips after the ER CO_2 testing.

Notwithstanding that the catholyte is crucial in determining the product selectivity, a finding already reported by several authors [35–37], the most interesting and remarkable result of this study concerns the propane production. A throughout search of the relevant literature suggests that the CO_2 reduction to propane with high efficiency was not reported so far. Usually, propane is detected as an ER CO_2 product only in trace amounts. For instance, a faradaic efficiency of *ca.* 0.20 % was reported for a Pd-Au catalyst at $-1.5 \text{ V}_{\text{RHE}}$ [41]. Moreover, Hara *et al.* proposed that products with more than two carbons (C_{2+}) are preferentially formed at small current densities ($< -10 \text{ mA cm}^{-2}$). The authors also suggested that C_{2+} selectivity increases with increasing pressure, with a maximum propane FE of 0.41 % recorded at 30 atm, for an applied potential of *ca.* $-0.8 \text{ V}_{\text{RHE}}$ and current density of -5 mA cm^{-2} [42,43]. Meanwhile, as depicted in **Figure 5.7a**, in the present study, propane was selectively produced at atmospheric conditions of temperature and pressure, with a total current density of -45 mA cm^{-2} . When tested with catholyte A, catalysts #5C and #50C showed a propane FE of 64.6 %

and 85.3 %, respectively. Notably, catalyst #50C achieved a propane production yield of $70 \mu\text{mol h}^{-1} \text{cm}^{-2}$, with an FE for H_2 production of only 10.7 %, making it the first high-efficiency catalyst for the ER CO_2 to propane ever reported.

5.4.3 CO_2 and CO adsorption behavior

To understand the exceptional selectivity toward propane production and the influence of the catholyte, temperature-programmed desorption (TPD) experiments were carried out using CO_2 and CO as probe gas.

The strength of the CO_2 adsorption sites, *i.e.*, weak, intermediate, strong, and very strong, was estimated according to the literature from the area under the corresponding CO_2 desorption pattern for the temperature ranges of 50–200 °C, 200–400 °C, 400–650 °C and > 650 °C, respectively [44].

As reported, the dominant product is dependent on the correlation between the binding energy of key intermediates and the catalyst surface [45]. Therefore, tuning the binding energies of the reaction intermediates has long been considered a strategy to improve the selectivity of target products and the energy efficiency of CO_2 electroreduction. According to Sabatier's principle, the best catalyst should feature an appropriate interaction between reaction intermediates and the surface of catalysts, neither too strong nor too weak for maximum activity [46,47]. As a result, the absence of very strong chemisorption sites, as illustrated in **Figure 5.9**, is a positive feature of the developed catalysts. Too strong chemisorption leads to catalyst poisoning by CO_2 [48].

Figure 5.9 shows no significant difference in CO_2 adsorption before and after electrolysis with catholyte A, suggesting that catholyte A has no effect on the CO_2 adsorption capacity of the developed catalysts. As observed in **Figures 5.9a** and **b**, catalyst #20C is dominated by intermediate CO_2 adsorption sites, whereas strong adsorption predominates in samples #5C and #50C. Thus, combining this information with the obtained FE, it is possible to infer that intermediate CO_2 adsorption strength is related to high selectivity to formate and H_2 . At the same time, strong chemisorption

appears to promote propane production. According to the literature, formate or formic acid is produced through an outer-sphere mechanism [46]. As initially established by Hori *et al.*, the formate production is initiated by the formation of free or weakly adsorbed CO_2^* , followed by a proton attack to the carbon atom [49]. More recently, quantum mechanics calculations carried out by Chen *et al.* predicted an alternative route for formate formation, in which a surface H^* (being $*$ an adsorption site) reacts with physisorbed CO_2 . This reaction pathway suggests that the CO_2 does not need to be first activated by the metal surface; instead, the physisorbed CO_2 reacts directly with surface H^* , along with the transfer of one electron, to form HCOO^- [50]. Both mechanisms denote that poor CO_2 adsorption is the key to format production, in good agreement with the present results.

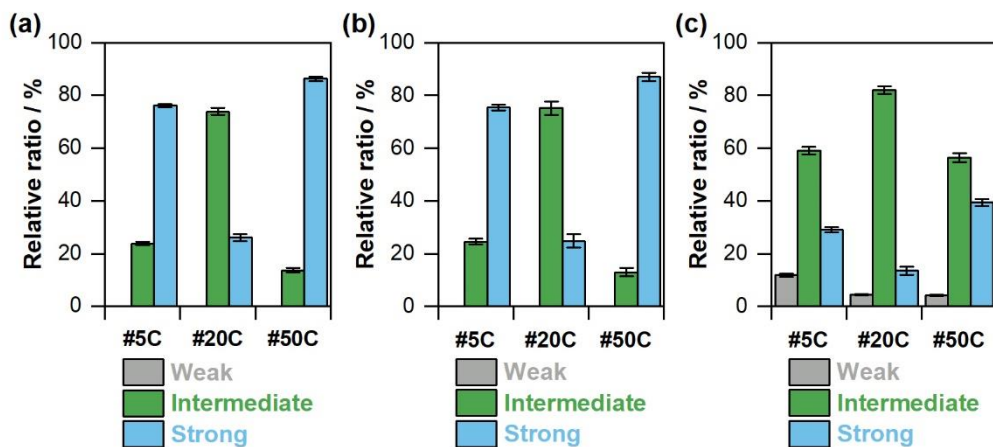


Figure 5.9. Relative ratio and strength of the CO_2 adsorption sites (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B. The error bar relates to the standard deviation of three independent reads.

Catalysts #5C and #50C showed unprecedented selectivity to propane production, which is attributed to stronger adsorption and stabilization of CO_2 , allowing its conversion to fully reduced products. According to the characterization results, a higher degree of interaction between copper and bismuth species appears to facilitate CO_2 adsorption. XPS results, summarized in **Table 5.2**, show that for samples #5C and #50C, the BE of

Cu_2O is negatively shifted by *ca.* 0.3 eV, compared to #20C. In contrast, the BE of Bi^0 shifted to higher energies by *ca.* 0.3 eV. Thus, XPS results suggest that an electron transfer from Bi^0 to Cu_2O occurred, increasing the interaction between both elements [27].

The CO_2 activation, not essential for the formate production, is also believed to be promoted by the higher number of oxygen vacancies present in #5C and #50C, similarly to that reported for ZnO nanosheets [51]. The presence of this type of defect results in highly stable adsorption configurations with stronger activation of the C=O bonds; in addition, it acts as trap centers to transform CO_2 into CO_2^- by a one-electron transfer process [52–54].

Although catalysts #5C and #50C are both highly selective for CO_2 conversion to propane, the highest value of propane FE was recorded for #50C (FE of 85.3 %). By comparing the CO_2 desorption pattern of both catalysts, it is possible to observe that the intensity of the desorption peaks is higher for sample #50C, **Figures 5.10a and b**. This result suggests a greater CO_2 adsorption capacity, which may be related to the higher selectivity for propane production of #50C compared to #5C. Moreover, results indicate that the bismuth particle size, morphology, and loading influence the CO_2 adsorption and, thus, the propane selectivity. Accordingly, the Bi-rich surface with large flower-like particles observed for #50C is assumed to enhance the CO_2 conversion to propane.

As discussed before and endorsed by several authors, the electrolyte has a critical influence on the ER CO_2 product distribution. Halide ions are usually considered to participate or influence the electrochemical reactions due to the nature of their strong adsorption on the surface of electrodes (anion coverage) [35,37]. The halide effect on cubic Cu_2O structures was accessed by Varela *et al.*, showing enhanced selectivity toward CO in the presence of Cl^- and Br^- , while CH_4 production was favored by I^- [36]. According to the authors, the different selectivity is due to the ability of the halide to donate more negative charge, creating surface dipoles [37]. Density functional theory (DFT) calculations confirmed the adsorption of Cl^- , Br^- , and I^- on Cu surfaces at potentials where CO_2 reduction occurs [35,55]. Thus, the developed electrodes were subjected to 30 min of electrolysis at -0.8 V_{RHE} with catholyte B and then analyzed by

CO₂-TPD, **Figure 5.9c**. Compared with TPD results acquired before and after electrolysis with catholyte A (**Figures 5.9a and b**), **Figure 5.9c** shows that the strength of the CO₂ adsorption decreased for all samples when catholyte B was used. With catholyte B, all samples are dominated by intermediate CO₂ adsorption sites (82 % for #20C and 58 % for #5C and #50C). Moreover, some weak adsorption spots are noticed. The reduction of the CO₂ binding affinity to the catalyst surface explains the massive increase in formate FE when catholyte B was used, in agreement with the reaction mechanism previously described. Also, the lower amount of strong CO₂ adsorption sites can be related to the drastic decrease in propane formation. For instance, for sample #50C, a decrease in propane FE by 6.1-fold was observed when catholyte B was employed. This result indicates that when catholyte B is used, some strong adsorption sites are blocked by Cl⁻. Therefore, it is proposed that the catholyte actively controls the ERCO₂ selectivity by modifying the CO₂ adsorption capacity and, thus, the reaction pathway.

Besides CO₂, understanding the binding strength of the *CO intermediate is equally essential, as its subsequent conversion via proton-electron transfer on the catalyst surface determines whether H₂, CO, or more reduced products are formed [7]. Thus, CO-TPD experiments were carried out under the same conditions (*e.g.*, attenuation) as CO₂-TPD. The obtained signal intensity is much lower than the CO₂-TPD (Figure A.20, Appendix A), making it difficult to accurately integrate the desorption peaks due to noise and/or poorly resolved peaks. However, the acquired results provide useful information.

As observed for CO₂ adsorption, results presented in **Figure 5.11** suggest that catholyte A does not affect the CO adsorption capacity of the developed catalyst. **Figure 5.11** also shows that no weak CO adsorption signal was recorded, regardless of the catalyst and catholyte used, explaining why CO was not detected as an ERCO₂ product. The binding energy of CO on the catalyst surface is high enough to prevent the formed CO from being readily desorbed, leaving this reaction intermediate stabilized and ready for further reduction. Catalyst #20C has the lowest CO adsorption capacity, being almost null when catholyte B is used. This result is consistent with the high formate selectivity recorded for this catalyst and the previously discussed outer-sphere

mechanism for formate production. On the other hand, catalysts #5C and #50C show higher adsorption capacity. Nevertheless, in all cases, the CO adsorption decreased when catholyte B was used, in line with that observed for CO_2 and the higher selectivity for formate production.

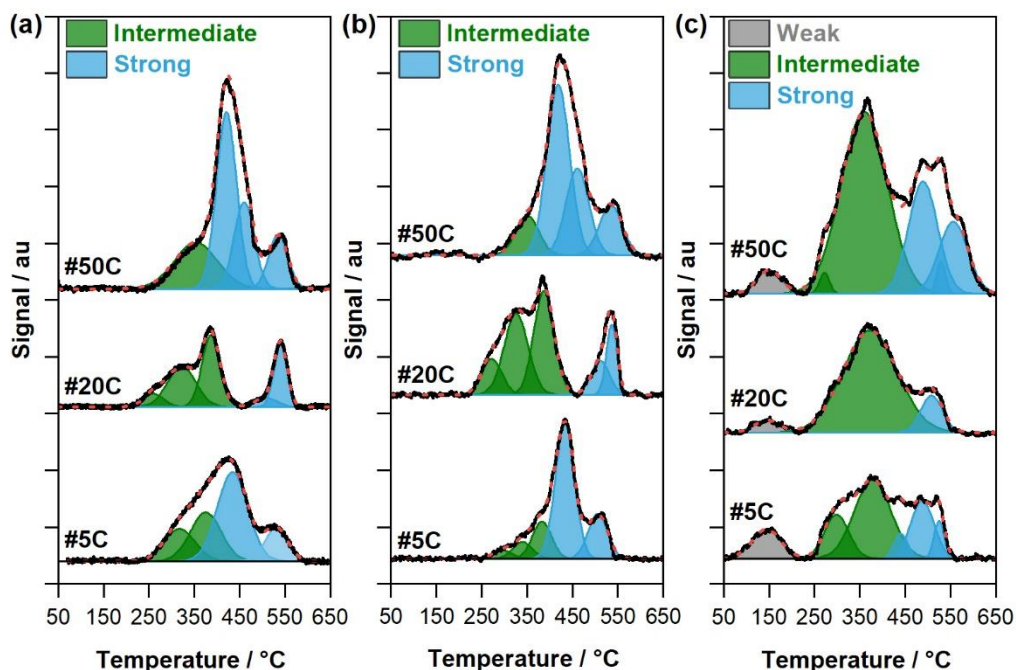


Figure 5.10. Representative CO_2 desorption pattern obtained (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B.

The Lewis basicity and acidity of the developed catalysts can also be evaluated according to the CO_2 - and CO-TPD results, respectively. According to **Figure 5.10a**, all samples present strong Lewis basic sites. On the other hand, **Figure 5.11a** show that high-temperature CO-TPD peaks are almost absent for sample #20C, suggesting the absence of strong Lewis acidity. Thus, the results indicate that #20C has a more moderate Lewis acidity strength. In contrast, catalysts #5C and #50C show strong Lewis acidity. The role of surface basic and acid Lewis sites in CO_2 adsorption was already documented in the literature [56,57]. In particular, Bhattacharyya *et al.* studied the adsorption of CO_2 on TiO_2 nanotubes. The authors identified that differences in the Lewis acidity and

basicity might be related to the preferential formation of carbonates and bicarbonates species after CO₂ adsorption [56]. Details are discussed in the next section.

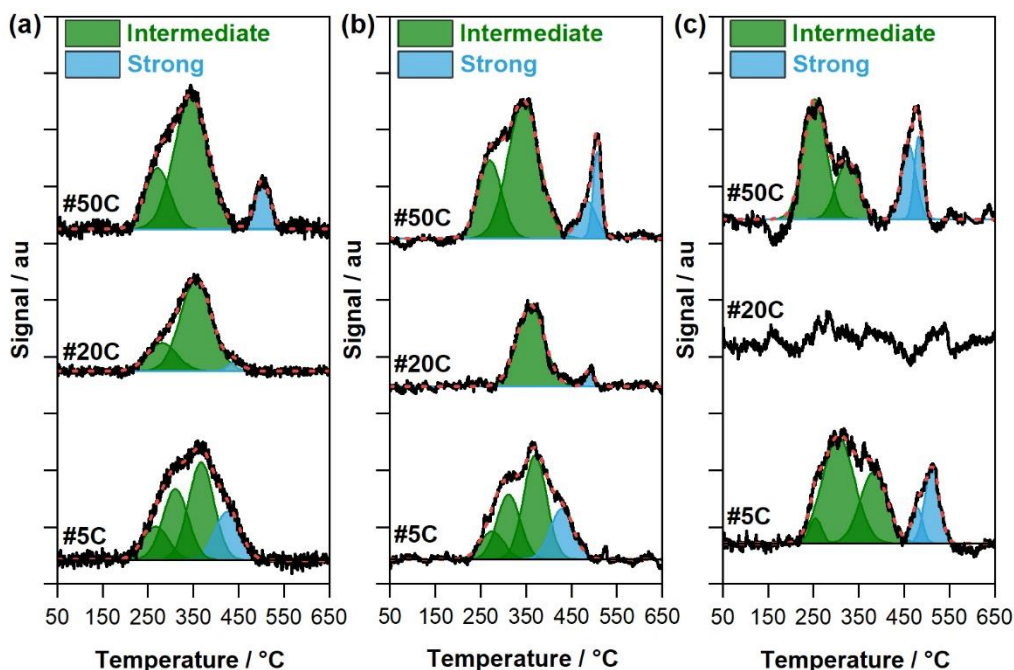


Figure 5.11. Representative CO desorption pattern obtained (a) before and after 30 min of electrolysis with (b) catholyte A and (c) catholyte B.

5.4.4 CO₂ coordination

IR experiments were carried out to identify the species formed on the surface of the developed catalysts after CO₂ adsorption, which might be relevant mechanistically in the CO₂ reduction process. **Figure 5.12** shows the IR spectra obtained between 700 cm⁻¹ and 2000 cm⁻¹ since the only visible changes were detected in this region. No peaks were noticed for the bare samples (before CO₂ adsorption); thus, all IR bands are attributed to species formed following the CO₂ adsorption process. Moreover, the peaks observed are due to stretching and bending vibrations of bonds between carbon and oxygen atoms, and their assignment is summarized in **Table 5.5**.

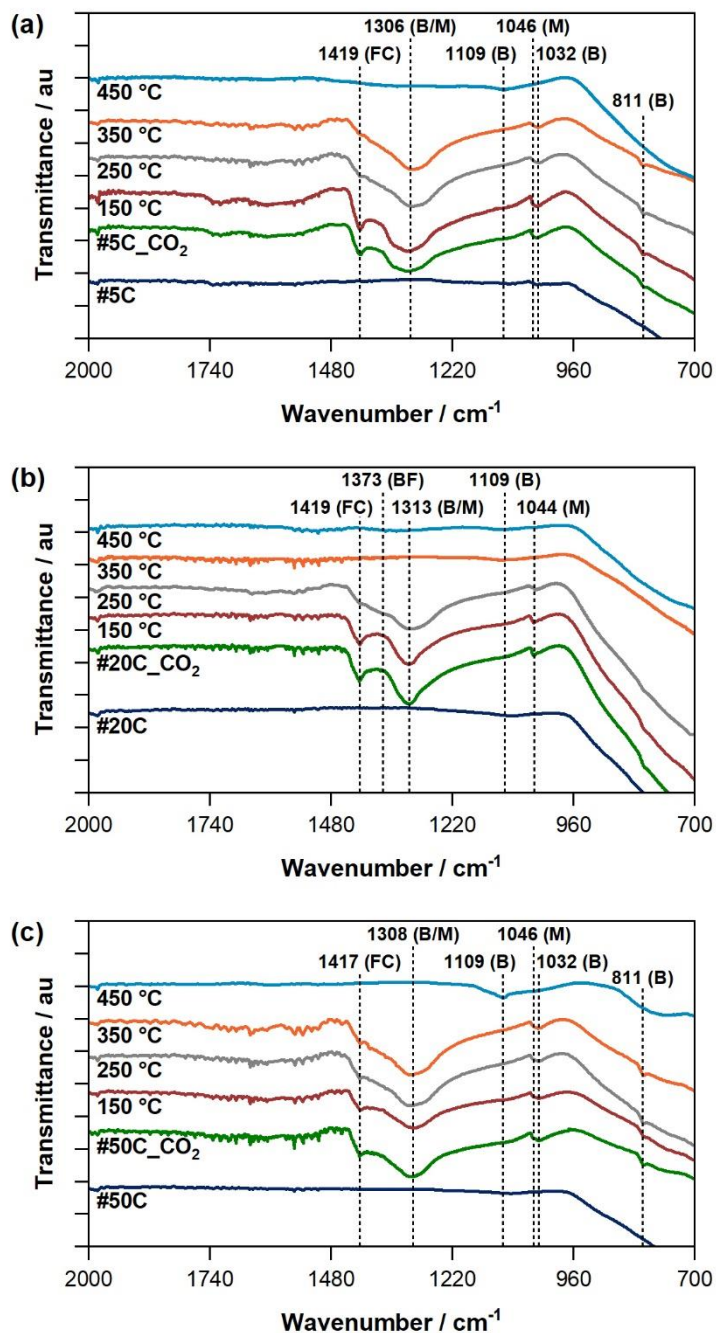


Figure 5.12. Infrared spectra collected over catalysts (a) #5C, (b) #20C, and (c) #50C, as prepared, after CO_2 adsorption, and during the stepwise CO_2 desorption at 150 °C, 250 °C, 350 °C, and 450 °C.

As observed in **Figure 5.12**, a series of carbonate-like or strongly perturbed CO₂ species (*i.e.*, no more linear) are formed after CO₂ adsorption at 50 °C. Furthermore, **Figure 5.12** promptly evidences significant differences between sample #20C and samples #5C and #50C. Catalyst #20C shows no IR absorption bands above 250 °C, suggesting that all carbonate species are desorbed after evacuation at 350 °C. This finding is in good agreement with the CO₂-TPD results (**Figure 5.9a**), which showed that catalyst #20C is dominated by sites of intermediate CO₂ adsorption strength. On the other hand, for catalysts #5C and #50C, IR signals were recorded even at 450 °C. This result suggests a higher CO₂ adsorption affinity for these samples, as previously evidenced by the CO₂-TPD measurements.

In detail, all samples present an IR band at *ca.* 1419 cm⁻¹ assigned to non-coordinated CO₃ [58,59], which is not strongly adsorbed and can be mostly removed after evacuation at 250 °C. The absorption band located at *ca.* 1045 cm⁻¹ (shoulder at 1046 cm⁻¹ for #5C and #50C samples) suggests the presence of monodentate carbonate species [58,60]. At the same time, the IR peaks at 1109 cm⁻¹, 1032 cm⁻¹, and 811 cm⁻¹ are attributed to bidentate CO₃, with the last two signals only observed for catalysts #5C and #50C [58,61–63]. Overall, the IR spectral signal of monodentate CO₃ at *ca.* 1045 cm⁻¹ is not noticed above 250 °C. On the other hand, the peaks ascribed to bidentate CO₃ are observed even after evacuation at 350 °C. Notably, for sample #50C, the 1109 cm⁻¹ band is still present with strong intensity at 450 °C. This result suggests a higher binding affinity of the bidentate structure over the monodentate.

According to the literature, the peak at *ca.* 1306-1313 cm⁻¹ can be ascribed to the symmetric stretching vibrations of mono- or bidentate CO₃ [6,64,65]. This peak would typically be accompanied by its asymmetric counterpart at 1400/1600 cm⁻¹, and the $\Delta\nu_3$ splitting could be used to identify the type of coordination [61,66]. However, in the present work, no peaks were observed in this region of the IR spectrum. Still, an assignment attempt can be made considering the thermal stability of the different carbonate species [61]. As previously stated, for all catalysts, monodentate IR signatures are absent above 250 °C, while bidentate signals are recorded even after evacuation at 350 °C. From this perspective, monodentate CO₃ is most likely present in catalyst #20C,

while bidentate CO_3 is formed after CO_2 adsorption on the surface of samples #5C and #50C. Moreover, considering the temperature dependence of each species, it is assumed that the stepwise CO_2 desorption observed in the CO_2 -TPD analysis (**Figure 5.10a**) resulted from the desorption of non-coordinated and monodentate carbonates, species absorbed with intermediate strength, followed by the desorption of strongly adsorbed bidentate carbonates.

A closer look at **Figure 5.12b** reveals that, after thermal treatment at 250 °C, catalyst #20C has a shoulder at 1373 cm^{-1} . This peak can be attributed to bidentate formate species [67,68], which are typically detected after CO_2 hydrogenation on metal oxides and have already been identified as ER CO_2 intermediate [1,69]. The presence of this intermediate is likely related to the higher faradaic efficiency toward formate production recorded for catalyst #20C (**Figure 5.7a**). Koh *et al.* investigated three possible pathways for the CO_2 reduction to formate [1]. Using DFT calculations, the authors showed that the formation of a bidentate formate intermediate ($^*\text{OCOH}$) is the most energetically favorable route. In turn, high-index Bi ^{0} planes at 27.3° (012), 39.8° (110), and 38.1° (104), preferentially developed in sample #20C (as shown in the XRD pattern in **Figure 5.4**), efficiently stabilize the $^*\text{OCOH}$ intermediate and contribute to the superior CO_2 reduction to formate.

In general, it is considered that basic centers contribute to the improvement of acidic CO_2 chemisorption [57]. However, Bhattacharyya *et al.* reported that an interplay between Lewis acid and base sites is needed. Moreover, the different acid-base character of the catalyst surface controls the species formed during CO_2 adsorption. The presence of strong Lewis acid and base sites in close proximity provides optimum conditions for the formation of bidentate carbonate species. On the other hand, weak Lewis acid sites near strong Lewis base sites favor monodentate carbonate formation. According to the literature, it is proposed that the C atom in CO_2 first coordinates to the strong Lewis base site, increasing the electron density around the oxygen atoms in the bound CO_2 . As a result, the O atoms will preferably coordinate with less electron-rich sites (strong Lewis acid centers), producing bidentate carbonates. If only weak Lewis acid centers are

available, the electron-rich O atoms will not coordinate, resulting in the formation of monodentate carbonates [56].

As discussed, catalyst #20C presents strong Lewis basicity and moderate Lewis acidity, resulting in the preferential formation of monodentate CO_3 species. On the other hand, samples #5C and #50C show strong Lewis acidity and basicity, promoting the formation of bidentate species. Thus, the results of the present study are in agreement with the literature.

Table 5.5. Summary of the IR absorption frequencies (cm^{-1}) for the various adsorbed CO_2 species.

Surface Species ^a	Structure	Wavenumber (cm^{-1})	Assignment ^b	Literature Values
Free carbonate (FC)		1417; 1419	$\nu_{\text{as}}(\text{CO})$	1410 [58]; 1415 [61]
Monodentate carbonate (M)		1313; 1308; 1306	$\nu_{\text{s}}(\text{CO}_3)$	1370-1300 [6,65]; 1389 [64]
		1044; 1046	$\nu(\text{CO})$	1048 [58]; 1046 [60]
		1313; 1308; 1306	$\nu_{\text{s}}(\text{CO}_2)$	1312 [64]; 1325 [70]
Bidentate carbonate (B)		1109	$\nu(\text{CO})$	1090 [61]; 1100 [58]
		1032	$\nu(\text{CO})$	1050-980 [62]; 1011 [63]
		811	$\delta(\text{CO}_2)$	887 [58]; 830 [62]
Bidentate formate (BF)		1373	$\nu_{\text{s}}(\text{CO}_2)$	1380 [67]; 1372 [68]

^a: symbols in Figure 5.12; ^b: ν – stretching mode, ν_{s} – symmetric stretching, ν_{as} – antisymmetric stretching, δ – bending mode.

As mentioned earlier, the surface of catalyst #20C is dominated by intermediate CO_2 adsorption sites, which is favorable for enhanced formate production, according to the reaction mechanisms proposed by several authors [46,49,50]. Moreover, sample #20C presents moderate Lewis acid sites and strong Lewis base sites. Based on the IR analysis, non-coordinated and monodentate carbonates are the main species formed when CO_2 is

adsorbed on this type of sites. These species are then selectively reduced to formate. On the other hand, the presence of a large number of oxygen defects and a synergetic effect between Cu^+ and Bi^0 results in the predominance of strong adsorption sites on the surface of catalysts #5C and #50C. These catalysts are also characterized by the presence of strong Lewis acid and base sites. CO_2 is strongly absorbed on these sites, and bidentate carbonates are formed. Therefore, it is proposed that this bidentate intermediate is the key to the selective ER CO_2 to propane.

5.5 Conclusions

In this work, CuBi catalysts with different Bi loadings were developed for the ER CO_2 , following a simple electrodeposition approach. The performance of the developed catalysts was evaluated in a continuous-gas diffusion electrode (continuous-GDE) reactor configuration, working at galvanostatic conditions at -45 mA cm^{-2} . Formate and propane were produced with high efficiency depending on the catholyte and catalyst used. When Cl^- ions were present in the catholyte solution, formate was selectively produced using catalyst #20C, with an FE of 86.4 % and production rate of $75.2 \mu\text{mol h}^{-1} \text{ cm}^{-2}$. Preliminary results indicated that it is possible to enhance the formate yield by increasing the current density without compromising the FE, confirming the robustness of the developed materials. The high formate selectivity was attributed to the presence of weak CO_2 adsorption sites on the catalyst surface, which favors the outer-sphere mechanism of ER CO_2 to formate. In addition, when halide ions (*e.g.*, Cl^-) are present in the electrolyte, the CO_2 adsorption strength decreases, enhancing formate production. It is proposed that Cl^- ions are adsorbed on the catalyst surface, possibly hindering strong CO_2 adsorption sites.

An unprecedented high selectivity for propane production was recorded for catalyst #50C, with FE of 85.3 % and partial current density of -38.4 mA cm^{-2} . This remarkable catalytic behavior was ascribed to the higher CO_2 and CO adsorption capacity and the presence of strong CO_2 adsorption sites on the catalyst surface. Moreover, catalyst #50C

presents strong Lewis acid and base sites, which promotes the formation of bidentate carbonates, following the CO₂ adsorption. Thus, it is proposed that the bidentate carbonate is a crucial intermediate for the selective ERCO₂ to propane. Lastly, the characterization results suggest that a strong interaction between copper and bismuth and a higher number of oxygen defects are the key to the enhanced CO₂ binding affinity and, therefore, high performance for ERCO₂ to propane.

Acknowledgments

Azenha, C., is grateful to the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant (reference SFRH/BD/128768/2017). This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); and was performed under the project “SunStorage - Harvesting and storage of solar energy”, POCI-01-0145-FEDER-016387, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. The authors also acknowledge P. Tavares from UME-UTAD for the XRD analyses, CEMUP for the XPS analyses, and SEMAT for the SEM analysis. J. Capitão (LEPABE/ALiCE) is acknowledged for performing the TiO₂ depositions by ALD.

Nomenclature

Abbreviation	Definition
ATR	Attenuated total reflectance mode
bcc	Body-centered cubic
BE	Binding energy
CO ₂ -TPD-MS	Carbon dioxide temperature-programmed desorption combined with mass spectrometry
CO-TPD-MS	Carbon monoxide temperature-programmed desorption combined with mass spectrometry
DAS	Dimensionally stable anode
DFT	Density functional theory
ERCO ₂	Electrochemical reduction of CO ₂
fcc	Face-centered cubic
FE	Faradaic efficiency
FTIR	Fourier-transform infrared spectroscopy
FWHM	Full width at half maximum
GDE	Gas diffusion electrode
HER	Hydrogen evolution reaction
IR	Infrared
JCPDS	Joint committee on powder diffraction standards
KE	Kinetic energy
MCT	Mercury cadmium telluride detector
MMO	Mixed metal oxide
NWs	Nanowires
O _L	Lattice oxygen
O _V	Oxygen vacancy
RHE	Reversible hydrogen electrode
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
TPD	Temperature-programmed desorption
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Greek Symbol	Definition	Unit
α'	Modified Auger parameter	eV
δ	Bending mode	
$\Delta\nu_3$	Splitting of the stretching vibration	
ν	Stretching mode	
ν_{as}	Antisymmetric stretching	
ν_{s}	Symmetric stretching	

References

- [1] J.H. Koh, D.H. Won, T. Eom, N.-K. Kim, K.D. Jung, H. Kim, Y.J. Hwang, B.K. Min, Facile CO_2 electro-reduction to formate via oxygen bidentate intermediate stabilized by high-index planes of Bi dendrite catalyst, *ACS Catal.* 7 (2017) 5071–5077. <https://doi.org/10.1021/acscatal.7b00707>.
- [2] H. Yang, X. Wang, Q. Hu, X. Chai, X. Ren, Q. Zhang, J. Liu, C. He, Recent progress in self-supported catalysts for CO_2 electrochemical reduction, *Small Methods*. (2020) 1900826. <https://doi.org/10.1002/smt.201900826>.
- [3] Pro Oxygen, The World's CO_2 Home Page, (2021). <https://www.co2.earth/> (accessed October 25, 2021).
- [4] C. Song, Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing, *Catal. Today*. 115 (2006) 2–32. <https://doi.org/10.1016/j.cattod.2006.02.029>.
- [5] R.G. Grim, Z. Huang, M.T. Guarnieri, J.R. Ferrell, L. Tao, J.A. Schaidle, Transforming the carbon economy: Challenges and opportunities in the convergence of low-cost electricity and reductive CO_2 utilization, *Energy Environ. Sci.* 13 (2020) 472–494. <https://doi.org/10.1039/C9EE02410G>.
- [6] M.F. Baruch, J.E. Pander, J.L. White, A.B. Bocarsly, Mechanistic insights into the reduction of CO_2 on tin electrodes using in situ ATR-IR spectroscopy, *ACS Catal.* 5 (2015) 3148–3156. <https://doi.org/10.1021/acscatal.5b00402>.
- [7] D. Gao, R.M. Arán-Ais, H.S. Jeon, B. Roldan Cuenya, Rational catalyst and electrolyte design for CO_2 electroreduction towards multicarbon products, *Nat. Catal.* 2 (2019) 198–210. <https://doi.org/10.1038/s41929-019-0235-5>.
- [8] P.R. Yaashikaa, P. Senthil Kumar, S.J. Varjani, A. Saravanan, A review on photochemical, biochemical and electrochemical transformation of CO_2 into value-added products, *J. CO_2 Util.* 33 (2019) 131–147. <https://doi.org/10.1016/j.jcou.2019.05.017>.

- [9] V.C. Hoang, V.G. Gomes, N. Kornienko, Metal-based nanomaterials for efficient CO₂ electroreduction: Recent advances in mechanism, material design and selectivity, *Nano Energy*. 78 (2020) 105311. <https://doi.org/10.1016/j.nanoen.2020.105311>.
- [10] S. Garg, M. Li, A.Z. Weber, L. Ge, L. Li, V. Rudolph, G. Wang, T.E. Rufford, Advances and challenges in electrochemical CO₂ reduction processes: An engineering and design perspective looking beyond new catalyst materials, *J. Mater. Chem. A*. 8 (2020) 1511–1544. <https://doi.org/10.1039/C9TA13298H>.
- [11] H. Wang, J. Jia, P. Song, Q. Wang, D. Li, S. Min, C. Qian, L. Wang, Y.F. Li, C. Ma, T. Wu, J. Yuan, M. Antonietti, G.A. Ozin, Efficient electrocatalytic reduction of CO₂ by nitrogen-doped nanoporous carbon/carbon nanotube membranes: A step towards the electrochemical CO₂ refinery, *Angew. Chem. Int. Ed.* 56 (2017) 7847–7852. <https://doi.org/10.1002/anie.201703720>.
- [12] Y. Chen, C.W. Li, M.W. Kanan, Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles, *J. Am. Chem. Soc.* 134 (2012) 19969–19972. <https://doi.org/10.1021/ja309317u>.
- [13] H. Mistry, A.S. Varela, C.S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E.A. Stach, J.C. Yang, P. Strasser, B.R. Cuenya, Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene, *Nat. Commun.* 7 (2016) 12123. <https://doi.org/10.1038/ncomms12123>.
- [14] P. De Luna, R. Quintero-Bermudez, C.-T. Dinh, M.B. Ross, O.S. Bushuyev, P. Todorović, T. Regier, S.O. Kelley, P. Yang, E.H. Sargent, Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction, *Nat. Catal.* 1 (2018) 103–110. <https://doi.org/10.1038/s41929-017-0018-9>.
- [15] H. Zhong, Y. Qiu, T. Zhang, X. Li, H. Zhang, X. Chen, Bismuth nanodendrites as a high performance electrocatalyst for selective conversion of CO₂ to formate, *J. Mater. Chem. A*. 4 (2016) 13746–13753. <https://doi.org/10.1039/C6TA06202D>.

- [16] Z. Zhao, X. Peng, X. Liu, X. Sun, J. Shi, L. Han, G. Li, J. Luo, Efficient and stable electroreduction of CO_2 to CH_4 on CuS nanosheet arrays, *J. Mater. Chem. A*. 5 (2017) 20239–20243. <https://doi.org/10.1039/C7TA05507B>.
- [17] C. Azenha, C. Mateos-Pedrero, M. Alvarez-Guerra, A. Irabien, A. Mendes, Enhancement of the electrochemical reduction of CO_2 to methanol and suppression of H_2 evolution over CuO nanowires, *Electrochim. Acta*. 363 (2020) 137207. <https://doi.org/10.1016/j.electacta.2020.137207>.
- [18] M. Fan, S. Prabhudev, S. Garbarino, J. Qiao, G.A. Botton, D.A. Harrington, A.C. Tavares, D. Guay, Uncovering the nature of electroactive sites in nano architected dendritic Bi for highly efficient CO_2 electroreduction to formate, *Appl. Catal. B Environ.* 274 (2020) 119031. <https://doi.org/10.1016/j.apcatb.2020.119031>.
- [19] G. Wen, D.U. Lee, B. Ren, F.M. Hassan, G. Jiang, Z.P. Cano, J. Gostick, E. Croiset, Z. Bai, L. Yang, Z. Chen, Orbital interactions in Bi-Sn bimetallic electrocatalysts for highly selective electrochemical CO_2 reduction toward formate production, *Adv. Energy Mater.* 8 (2018) 1802427. <https://doi.org/10.1002/aenm.201802427>.
- [20] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, Catalyst coated membrane electrodes for the gas phase CO_2 electroreduction to formate, *Catal. Today*. 346 (2018) 58–64. <https://doi.org/10.1016/j.cattod.2018.11.073>.
- [21] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, CO_2 electroreduction to formate: Continuous single-pass operation in a filter-press reactor at high current densities using Bi gas diffusion electrodes, *J. CO_2 Util.* 34 (2019) 12–19. <https://doi.org/10.1016/j.jcou.2019.05.035>.
- [22] X.-Y. Liu, P. Sun, S. Ren, L.-S. Wen, Electrodeposition of high-pressure-stable bcc phase bismuth flowerlike micro/nanocomposite architectures at room temperature without surfactant, *Electrochem. Commun.* 10 (2008) 136–140. <https://doi.org/10.1016/j.elecom.2007.11.013>.

- [23] W. Zuo, W. Zhu, D. Zhao, Y. Sun, Y. Li, J. Liu, X.W. (David) Lou, Bismuth oxide: a versatile high-capacity electrode material for rechargeable aqueous metal-ion batteries, *Energy Environ. Sci.* 9 (2016) 2881–2891. <https://doi.org/10.1039/C6EE01871H>.
- [24] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data*, 1992. <https://doi.org/9780962702624>.
- [25] F.E. Oropeza, I.J. Villar-Garcia, R.G. Palgrave, D.J. Payne, A solution chemistry approach to epitaxial growth and stabilisation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ films, *J. Mater. Chem. A* 2 (2014) 18241–18245. <https://doi.org/10.1039/C4TA04352A>.
- [26] A. Walsh, G.W. Watson, D.J. Payne, R.G. Edgell, J. Guo, P.-A. Glans, T. Learmonth, K.E. Smith, Electronic structure of the α and δ phases of Bi_2O_3 : A combined ab initio and X-ray spectroscopy study, *Phys. Rev. B* 73 (2006) 235104. <https://doi.org/10.1103/PhysRevB.73.235104>.
- [27] Z. Xie, X. Zhou, H. Wu, L. Chen, H. Zhao, Y. Liu, L. Pan, H. Chen, One-pot hydrothermal synthesis of CuBi co-doped mesoporous zeolite Beta for the removal of NO_x by selective catalytic reduction with ammonia, *Sci. Rep.* 6 (2016) 30132. <https://doi.org/10.1038/srep30132>.
- [28] M.C. Biesinger, Advanced analysis of copper X-ray photoelectron spectra, *Surf. Interface Anal.* 49 (2017) 1325–1334. <https://doi.org/10.1002/sia.6239>.
- [29] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.* 257 (2010) 887–898. <https://doi.org/10.1016/j.apsusc.2010.07.086>.

- [30] A.K.R. Police, S.V.P. Vattikuti, K.K. Mandari, M. Chennaiahgari, P.Sharma M.V., D.K. Valluri, C. Byon, Bismuth oxide cocatalyst and copper oxide sensitizer in $\text{Cu}_2\text{O}/\text{TiO}_2/\text{Bi}_2\text{O}_3$ ternary photocatalyst for efficient hydrogen production under solar light irradiation, *Ceram. Int.* 44 (2018) 11783–11791. <https://doi.org/10.1016/j.ceramint.2018.03.262>.
- [31] T. Qin, X. Zhang, D. Wang, T. Deng, H. Wang, X. Liu, X. Shi, Z. Li, H. Chen, X. Meng, W. Zhang, W. Zheng, Oxygen vacancies boost $\delta\text{-Bi}_2\text{O}_3$ as a high-performance electrode for rechargeable aqueous batteries, *ACS Appl. Mater. Interfaces.* 11 (2019) 2103–2111. <https://doi.org/10.1021/acsami.8b19575>.
- [32] J.J. Carey, M. Legesse, M. Nolan, Low valence cation doping of bulk Cr_2O_3 : charge compensation and oxygen vacancy formation, *J. Phys. Chem. C.* 120 (2016) 19160–19174. <https://doi.org/10.1021/acs.jpcc.6b05575>.
- [33] Z. Yang, F.E. Oropeza, K.H.L. Zhang, p-block metal-based (Sn, In, Bi, Pb) electrocatalysts for selective reduction of CO_2 to formate, *APL Mater.* 8 (2020) 060901. <https://doi.org/10.1063/5.0004194>.
- [34] Z.B. Hoffman, T.S. Gray, Y. Xu, Q. Lin, T.B. Gunnoe, G. Zangari, High selectivity towards formate production by electrochemical reduction of carbon dioxide at copper–bismuth dendrites, *ChemSusChem.* 12 (2019) 231–239. <https://doi.org/10.1002/cssc.201801708>.
- [35] D. Gao, F. Scholten, B. Roldan Cuenya, Improved CO_2 electroreduction performance on plasma-activated Cu catalysts via electrolyte design: Halide Effect, *ACS Catal.* 7 (2017) 5112–5120. <https://doi.org/10.1021/acscatal.7b01416>.
- [36] A.S. Varela, W. Ju, T. Reier, P. Strasser, Tuning the catalytic activity and selectivity of Cu for CO_2 electroreduction in the presence of halides, *ACS Catal.* 6 (2016) 2136–2144. <https://doi.org/10.1021/acscatal.5b02550>.

- [37] P. Sebastián-Pascual, S. Mezzavilla, I.E.L. Stephens, M. Escudero-Escribano, Structure-sensitivity and electrolyte effects in CO₂ electroreduction: From model studies to applications, *ChemCatChem*. 11 (2019) 3626–3645. <https://doi.org/10.1002/cctc.201900552>.
- [38] M. Moura de Salles Pupo, R. Kortlever, Electrolyte effects on the electrochemical reduction of CO₂, *ChemPhysChem*. 20 (2019) 2926–2935. <https://doi.org/10.1002/cphc.201900680>.
- [39] D. Raciti, M. Mao, J.H. Park, C. Wang, Local pH effect in the CO₂ reduction reaction on high-surface-area copper electrocatalysts, *J. Electrochem. Soc.* 165 (2018) F799–F804. <https://doi.org/10.1149/2.0521810jes>.
- [40] M. Zhao, H. Tang, Q. Yang, Y. Gu, H. Zhu, S. Yan, Z. Zou, Inhibiting hydrogen evolution using a chloride adlayer for efficient electrochemical CO₂ reduction on Zn electrodes, *ACS Appl. Mater. Interfaces*. 12 (2020) 4565–4571. <https://doi.org/10.1021/acsami.9b22811>.
- [41] R. Kortlever, I. Peters, C. Balemans, R. Kas, Y. Kwon, G. Mul, M.T.M. Koper, Palladium–gold catalyst for the electrochemical reduction of CO₂ to C₁–C₅ hydrocarbons, *Chem. Commun.* 52 (2016) 10229–10232. <https://doi.org/10.1039/C6CC03717H>.
- [42] K. Hara, A. Kudo, T. Sakata, Electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous electrolyte, *J. Electroanal. Chem.* 391 (1995) 141–147. [https://doi.org/10.1016/0022-0728\(95\)03935-A](https://doi.org/10.1016/0022-0728(95)03935-A).
- [43] K. Hara, A. Kudo, T. Sakata, Electrochemical CO₂ reduction on a glassy carbon electrode under high pressure, *J. Electroanal. Chem.* 421 (1997) 1–4. [https://doi.org/10.1016/S0022-0728\(96\)01028-5](https://doi.org/10.1016/S0022-0728(96)01028-5).
- [44] M.A. Naeem, A.S. Al-Fatesh, W.U. Khan, A.E. Abasaheed, A.H. Fakeeha, Syngas production from dry reforming of methane over nano Ni polyol catalysts, *Int. J. Chem. Eng. Appl.* 4 (2013) 315–320. <https://doi.org/10.7763/IJCEA.2013.V4.317>.

- [45] W. Yang, K. Dastafkan, C. Jia, C. Zhao, Design of electrocatalysts and electrochemical cells for carbon dioxide reduction reactions, *Adv. Mater. Technol.* 3 (2018) 1700377. <https://doi.org/10.1002/admt.201700377>.
- [46] D.D. Zhu, J.L. Liu, S.Z. Qiao, Recent advances in inorganic heterogeneous electrocatalysts for reduction of carbon dioxide, *Adv. Mater.* 28 (2016) 3423–3452. <https://doi.org/10.1002/adma.201504766>.
- [47] J.T. Feaster, C. Shi, E.R. Cave, T. Hatsukade, D.N. Abram, K.P. Kuhl, C. Hahn, J.K. Nørskov, T.F. Jaramillo, Understanding selectivity for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide on metal electrodes, *ACS Catal.* 7 (2017) 4822–4827. <https://doi.org/10.1021/acscatal.7b00687>.
- [48] R. Arrigo, M.E. Schuster, S. Wrabetz, F. Girgsdies, J.-P. Tessonnier, G. Centi, S. Perathoner, D.S. Su, R. Schlögl, New insights from microcalorimetry on the FeOx/CNT-based electrocatalysts active in the conversion of CO_2 to fuels, *ChemSusChem*. 5 (2012) 577–586. <https://doi.org/10.1002/cssc.201100641>.
- [49] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrocatalytic process of CO selectivity in electrochemical reduction of CO_2 at metal electrodes in aqueous media, *Electrochim. Acta.* 39 (1994) 1833–1839. [https://doi.org/10.1016/0013-4686\(94\)85172-7](https://doi.org/10.1016/0013-4686(94)85172-7).
- [50] T. Cheng, H. Xiao, W.A. Goddard, Reaction mechanisms for the electrochemical reduction of CO_2 to CO and formate on the Cu(100) surface at 298 K from quantum mechanics free energy calculations with explicit water, *J. Am. Chem. Soc.* 138 (2016) 13802–13805. <https://doi.org/10.1021/jacs.6b08534>.
- [51] Z. Geng, X. Kong, W. Chen, H. Su, Y. Liu, F. Cai, G. Wang, J. Zeng, Oxygen vacancies in ZnO nanosheets enhance CO_2 electrochemical reduction to CO, *Angew. Chem. Int. Ed.* 57 (2018) 6054–6059. <https://doi.org/10.1002/anie.201711255>.

- [52] S. Huygh, A. Bogaerts, E.C. Neyts, How oxygen vacancies activate CO₂ dissociation on TiO₂ anatase (001), *J. Phys. Chem. C*. 120 (2016) 21659–21669. <https://doi.org/10.1021/acs.jpcc.6b07459>.
- [53] L. Zhang, W. Wang, D. Jiang, E. Gao, S. Sun, Photoreduction of CO₂ on BiOCl nanoplates with the assistance of photoinduced oxygen vacancies, *Nano Res.* 8 (2015) 821–831. <https://doi.org/10.1007/s12274-014-0564-2>.
- [54] L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang, Y. Li, Engineering coexposed {001} and {101} facets in oxygen-deficient TiO₂ nanocrystals for enhanced CO₂ photoreduction under visible light, *ACS Catal.* 6 (2016) 1097–1108. <https://doi.org/10.1021/acscatal.5b02098>.
- [55] I.T. McCrum, S.A. Akhade, M.J. Janik, Electrochemical specific adsorption of halides on Cu 111 , 100 , and 211: A Density Functional Theory study, *Electrochim. Acta*. 173 (2015) 302–309. <https://doi.org/10.1016/j.electacta.2015.05.036>.
- [56] K. Bhattacharyya, A. Danon, B. K. Vijayan, K.A. Gray, P.C. Stair, E. Weitz, Role of the surface lewis acid and base sites in the adsorption of CO₂ on titania nanotubes and platinized titania nanotubes: An in situ FT-IR study, *J. Phys. Chem. C*. 117 (2013) 12661–12678. <https://doi.org/10.1021/jp402979m>.
- [57] M.A.A. Aziz, A.A. Jalil, S. Wongsakulphasatch, D.-V.N. Vo, Understanding the role of surface basic sites of catalysts in CO₂ activation in dry reforming of methane: A short review, *Catal. Sci. Technol.* 10 (2020) 35–45. <https://doi.org/10.1039/C9CY01519A>.
- [58] W.N.R.W. Isahak, Z.A.C. Ramli, M.W. Ismail, K. Ismail, R.M. Yusop, M.W.M. Hisham, M.A. Yarmo, Adsorption–desorption of CO₂ on different type of copper oxides surfaces: Physical and chemical attractions studies, *J. CO₂ Util.* 2 (2013) 8–15. <https://doi.org/10.1016/j.jcou.2013.06.002>.
- [59] J. Szanyi, J.H. Kwak, Dissecting the steps of CO₂ reduction: 1. The interaction of CO and CO₂ with γ -Al₂O₃: An in situ FTIR study, *Phys. Chem. Chem. Phys.* 16 (2014) 15117–15125. <https://doi.org/10.1039/C4CP00616J>.

- [60] Z. Li, M. Chen, X. Li, Z. Lei, J. Qu, P. Huang, Q. Zhang, F. Saito, Surface modification of basic copper carbonate by mechanochemical processing with sulfur and ammonium sulfate, *Adv. Powder Technol.* 28 (2017) 1877–1881. <https://doi.org/10.1016/j.appt.2017.04.017>.
- [61] K. Coenen, F. Gallucci, B. Mezari, E. Hensen, M. van Sint Annaland, An in-situ IR study on the adsorption of CO_2 and H_2O on hydrotalcites, *J. CO_2 Util.* 24 (2018) 228–239. <https://doi.org/10.1016/j.jcou.2018.01.008>.
- [62] V.F. Kiselev, O. V. Krylov, Adsorption and catalysis on transition metals and their oxides, Springer-Verlag: New York, 1989. <https://doi.org/10.1007/978-3-642-73887-6>.
- [63] K. Yoshikawa, H. Sato, M. Kaneeda, J.N. Kondo, Synthesis and analysis of CO_2 adsorbents based on cerium oxide, *J. CO_2 Util.* 8 (2014) 34–38. <https://doi.org/10.1016/j.jcou.2014.10.001>.
- [64] R.J. Walker, A. Pougin, F.E. Oropeza, I.J. Villar-Garcia, M.P. Ryan, J. Strunk, D.J. Payne, Surface termination and CO_2 adsorption onto bismuth pyrochlore oxides, *Chem. Mater.* 28 (2016) 90–96. <https://doi.org/10.1021/acs.chemmater.5b03232>.
- [65] M. Piumetti, S. Bensaid, D. Fino, N. Russo, Nanostructured ceria-zirconia catalysts for CO oxidation: Study on surface properties and reactivity, *Appl. Catal. B: Environ.* 197 (2016) 35–46. <https://doi.org/10.1016/j.apcatb.2016.02.023>.
- [66] G. Busca, V. Lorenzelli, Infrared spectroscopic identification of species arising from reactive adsorption of carbon oxides on metal oxide surfaces, *Mater. Chem.* 7 (1982) 89–126. [https://doi.org/10.1016/0390-6035\(82\)90059-1](https://doi.org/10.1016/0390-6035(82)90059-1).
- [67] A. Guerrero-Ruiz, I. Rodriguez-Ramos, J.L.G. Fierro, Dehydrogenation of methanol to methyl formate over supported copper catalysts, *Appl. Catal.* 72 (1991) 119–137. [https://doi.org/10.1016/0166-9834\(91\)85033-R](https://doi.org/10.1016/0166-9834(91)85033-R).

- [68] L. Lin, S. Yao, Z. Liu, F. Zhang, N. Li, D. Vovchok, A. Martínez-Arias, R. Castañeda, J. Lin, S.D. Senanayake, D. Su, D. Ma, J.A. Rodriguez, In situ characterization of Cu/CeO₂ nanocatalysts for CO₂ hydrogenation: morphological effects of nanostructured ceria on the catalytic activity, *J. Phys. Chem. C*. 122 (2018) 12934–12943. <https://doi.org/10.1021/acs.jpcc.8b03596>.
- [69] J. Albo, M. Alvarez-Guerra, P. Castaño, A. Irabien, Towards the electrochemical conversion of carbon dioxide into methanol, *Green Chem.* 17 (2015) 2304–2324. <https://doi.org/10.1039/C4GC02453B>.
- [70] S.E. Collins, M.A. Baltanás, A.L. Bonivardi, Infrared spectroscopic study of the carbon dioxide adsorption on the surface of Ga₂O₃ polymorphs, *J. Phys. Chem. B*. 110 (2006) 5498–5507. <https://doi.org/10.1021/jp055594c>.

CHAPTER 6

General Conclusions and Outlook

General Conclusions and Outlook

6.1 Conclusions

The present work studied copper-based catalysts for the electrochemical reduction of CO₂ (ERCO₂). A complete structural, morphological and electrochemical characterization was performed to accomplish the proposed objectives.

Initially, a bimetallic CuZn oxide catalyst was synthesized following a solvothermal route, a simple and low-cost technique suitable for scale-up. It was observed that this synthetic route results in the production of two shelled hollow spheres, with a copper-rich inner shell and a mixed copper-zinc oxide outer shell. However, the structure of the resulting material is strongly influenced by the synthesis time, *i.e.*, shorter synthesis results in the production of mainly amorphous material, while more complex systems (core-shell) are obtained when increasing synthesis time. Moreover, longer syntheses promote the reduction of Cu²⁺ species to Cu⁺ and Cu⁰, and strengthen the interaction between copper and zinc. As a result, the electrocatalytic behavior for CO₂ reduction is strongly dependent on the synthesis time. In short, with the increasing synthesis time, the number of reaction products obtained decreases primarily due to the strengthening of the copper-zinc interaction. As reported, when a bimetallic CuZn structure is formed, a shift in the *d*-band center of Cu occurs, resulting in lower CO binding strength. Thus, copper loses the functionality to reduce CO₂ to hydrocarbons and alcohols, and CO emerges as the main ERCO₂ product. The catalysts prepared with 15 h of synthesis showed the best results regarding the catalytic stability under electrolysis conditions. Thus, this sample was selected for studying different post-synthesis treatments.

According to the results presented in Chapter 3, the different post-synthesis treatments studied either resulted in severe structural modifications (*ex situ* conditioning) or minor

surface rearrangement (*in situ* conditioning). *Ex situ* reduction under H₂ atmosphere was responsible for increasing the crystallite size and reducing the copper oxidation state to metallic copper. As a result, the overall catalytic activity increased due to a massive increase in the hydrogen evolution reaction (HER) activity. On the other hand, the application of *in situ* potential cycling before the electrochemical measurements slightly rearranged the catalytic surface. In particular, starting the potential cycling by the anodic scan promotes an electron transfer from zinc to copper species, increasing the interaction and synergetic effect. As a result, Cu⁺ species on the catalyst surface are stabilized, and the number of oxygen defects increases, boosting the CO₂-to-CO conversion. Moreover, the synergetic effect between copper and zinc was studied. Therefore, it was proposed that Cu-Zn in intimate contact are the active centers for the ERCO₂. The particular electronic structure of these active centers is responsible for stabilizing key reaction intermediates. Geometric effects can also be present, overcoming the scaling relation typical of monometallic systems.

As an alternative to *conventional* powder-based catalysts, self-supported catalysts were also studied. In general, powder catalysts require time-consuming electrode fabrication through coating procedures with the assistance of polymeric binders, *e.g.*, Nafion. As a result, uncontrolled microstructures are obtained, with limited active surface areas and many dead volumes. In turn, self-supported catalysts, where the active materials are grown directly on specific conductive substrates, present several advantages. This class of catalysts enables the production of 3D porous structures with controlled nanostructures. Thus, this strategy outperforms the conventional planar catalyst coatings by increasing the catalytically active surface area, resulting in better exposure and utilization of active sites. In the present work, self-supported catalysts were produced by anodizing a commercial copper foam. It was concluded that the particular morphology of the resulting material (*i.e.*, nanowires) improves the ERCO₂ activity while suppressing the parasitic HER reaction. As a result, the developed catalyst (CuO NWs) proved to be highly active for methanol production, outperforming the single metal Cu-catalysts reported so far. The enhanced activity of CuO NWs was attributed to the nanowire structure that enhances the electron transfer to form CO₂^{•-}. Moreover, the network of

pores created after anodization drives the CO₂ to the active sites, decreasing the diffusion resistance. The developed material also proved to be suitable for use in a continuous gas diffusion electrode (GDE)-cell configuration.

Using the developed CuO NWs catalyst as starting material, a series of CuBi catalysts were prepared with different Bi loadings. The developed catalysts were tested on a GDE-cell configuration, and the influence of the catholyte and bismuth loading on the catalytic performance was assessed. According to the obtained results, the presence of Cl⁻ ions in the catholyte solution decreases the CO₂ adsorption strength, favoring the formation of non-coordinated and monodentate carbonates after CO₂ adsorption, which enhances the production of formate. Interestingly, an unprecedented propane selectivity was recorded using the catalyst with the highest bismuth loading, being the first high-efficiency catalyst for the ERCO₂ to propane ever reported (faradaic efficiency of 85.4 %). This unique catalytic behavior was attributed to the presence of strong CO₂ adsorption sites on the catalyst surface and higher CO₂ and CO adsorption capacity. Infrared spectroscopy experiments also suggested that a bidentate carbonate is a crucial intermediate for the ERCO₂ to propane, which is preferably formed when strong Lewis acid and base sites are present on the catalyst surface.

6.2 Outlook

Aside from the development of improved ERCO₂ catalysts, a major challenge for the industrial implementation of this technology is upscaling, which requires the improvement of reactor design. So far, the most common reactor in academic studies (this thesis included) is the three-electrode cell configuration due to its ease of operation under ambient conditions. Nevertheless, these systems rely on aqueous electrolytes, showing several drawbacks for industrial application, *e.g.*, limited scalability and low CO₂ solubility hindering high productivity, consumption of alkali reactants, electrolyte replacement, complex products separation, and recirculation pumps requirement. Thereby, reactor designs based on membrane electrode assembly (MEA) were proposed

to overcome the identified limitations. Combined with gas diffusion electrodes, these systems increase the CO₂ diffusivity and concentration at the electrode interface, boosting the current density and productivity. In this context, our research group has been developing an electrochemical cell based on the technology employed in proton-exchange membrane fuel cells (PEMFC). Thus, as future work, it would be important to test the developed catalysts in this cell configuration. As a result, it would be possible to determine whether the catalytic performance in aqueous systems translates to the more commercially relevant reaction designs, which is crucial for improving the catalyst design.

The present work already proposed a possible reaction mechanism (Chapter 3) and identified potential reaction intermediates (Chapter 5). However, proper real-time monitoring of the nature and strength of adsorbed species on the catalyst surface and solution species involved in the ERCO₂ process is only possible using *in situ*/operando techniques. Thus, future work should also focus on using *in situ*/operando techniques to gain a better understanding of the Cu-Zn synergetic effect and the processes behind the catalytic surface rearrangement observed during the *in situ* conditioning (Chapter 3). Finally, since the present work describes the first high-performing catalyst for propane production, it would be interesting to explore the reaction mechanism for the ERCO₂ to propane. This information is critical for the successful future development of catalysts.

APPENDIX A

Supplementary Figures and Tables

Supplementary Figures and Tables

A.1 Supplementary figures and tables to Chapter 2

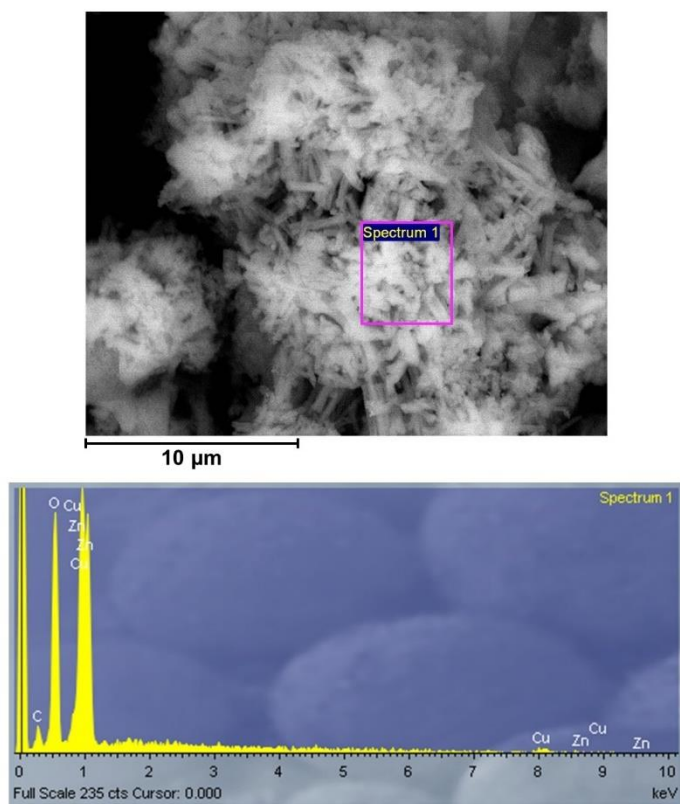


Figure A.1. SEM-EDX analysis of CuZn_5. Accelerating voltage of 10 kV.

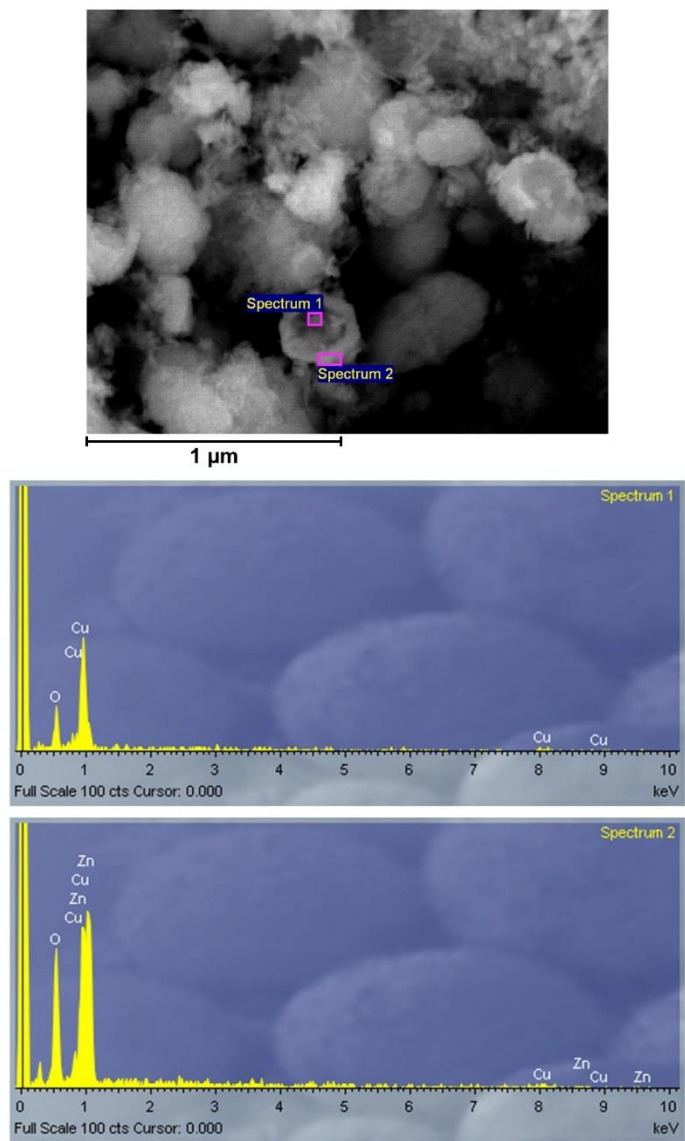


Figure A.2. SEM-EDX analysis of CuZn₁₅. Accelerating voltage of 10 kV.

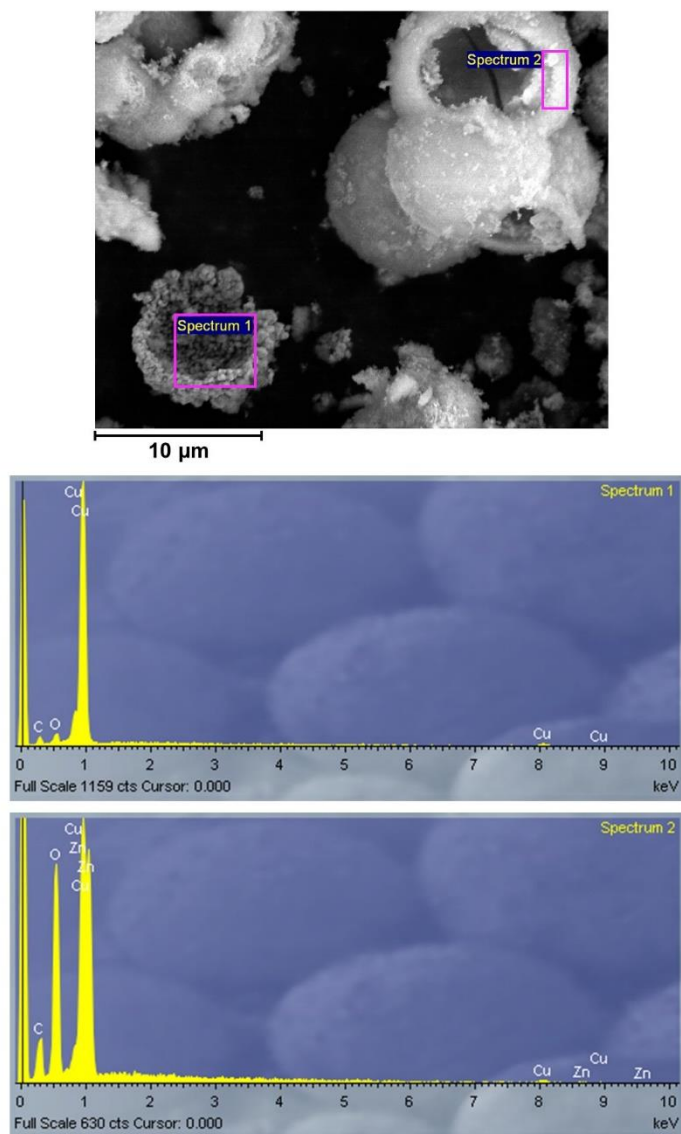


Figure A.3. SEM-EDX analysis of CuZn₂₅. Accelerating voltage of 10 kV.

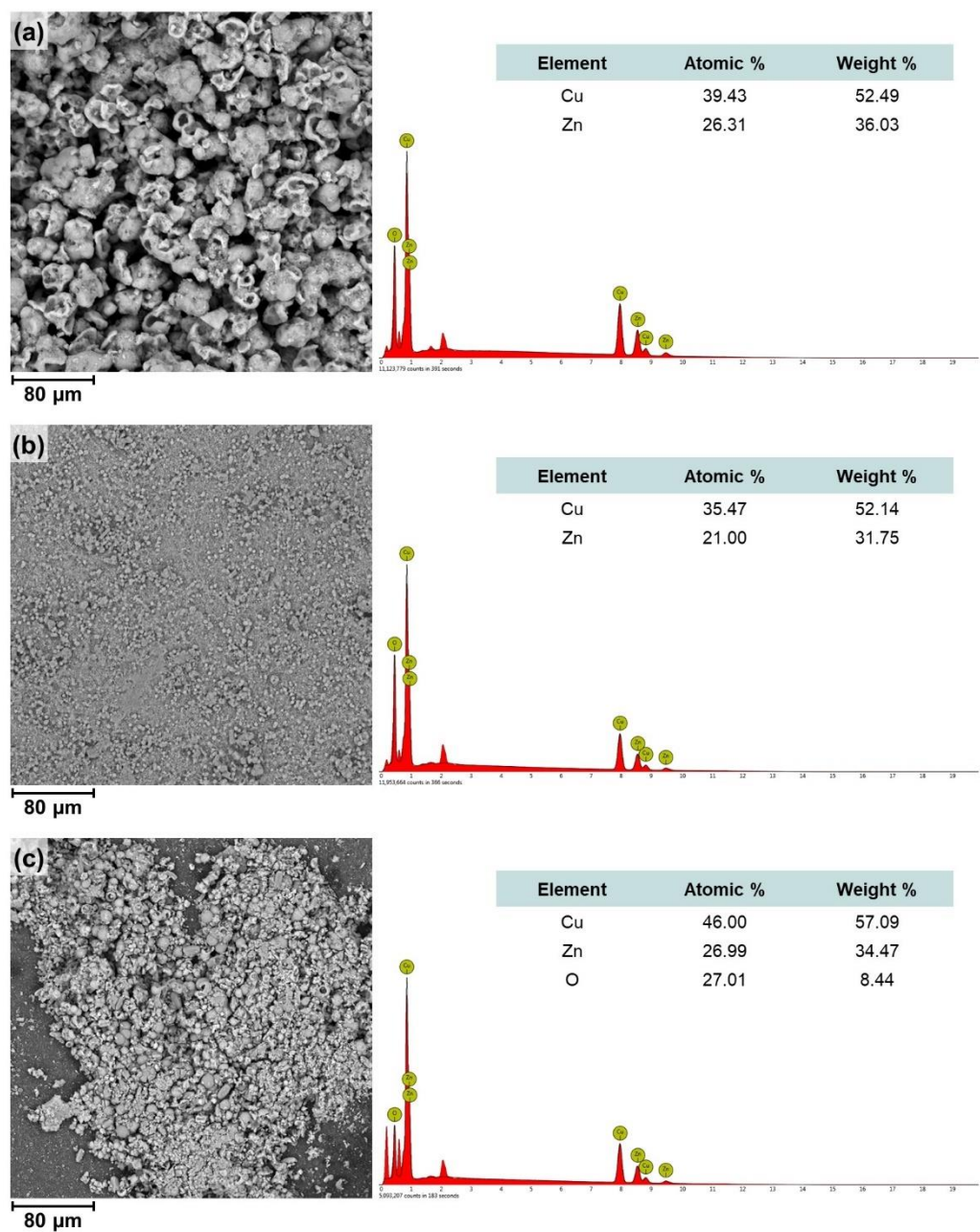


Figure A.4. SEM-EDX analysis of the electrodes produced with the CuZn catalysts: (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25. Accelerating voltage of 15 kV.

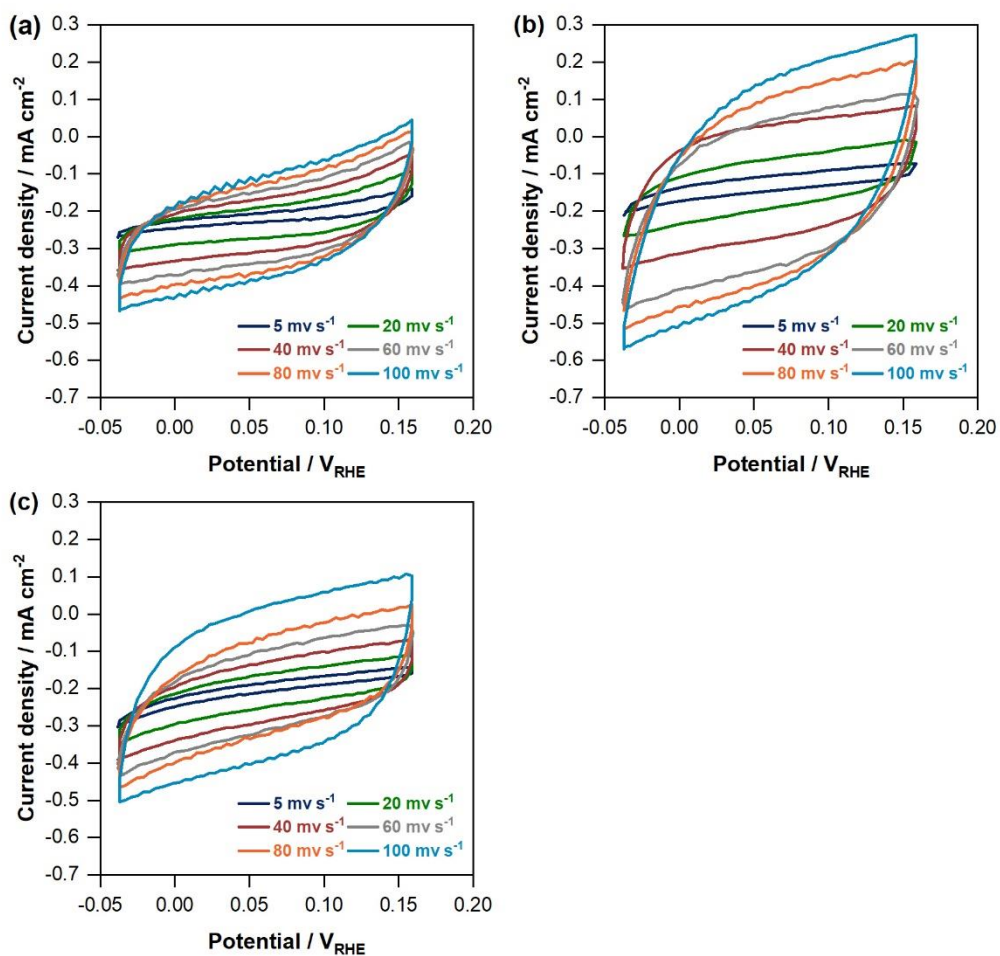


Figure A.5. Cyclic voltammograms in the non-faradaic region of (a) CuZn₅, (b) CuZn₁₅, (c) CuZn₂₅, and (d) polycrystalline Cu foil.

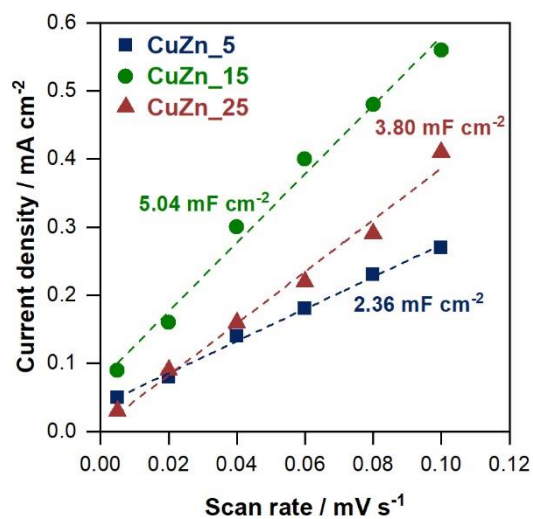


Figure A.6. Double-layer capacitance of the electrodes prepared with the developed CuZn catalysts.

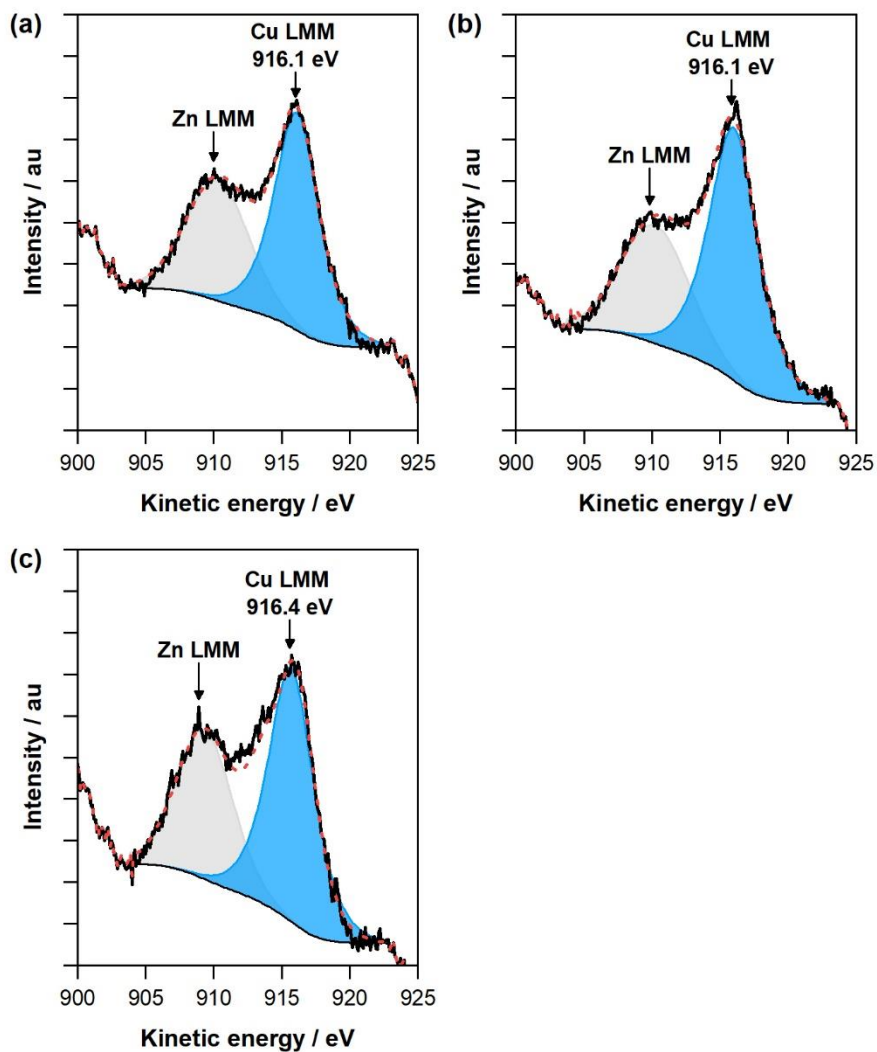


Figure A.7. Cu Auger LMM spectra for (a) CuZn_5, (b) CuZn_15, and (c) CuZn_25.

Table A.1. ER CO_2 results for CuZn_5 electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.7	-0.8	-0.9	-1.0	-1.1	-1.2	-1.3	-1.4
$J_{\text{total}}^{\text{a}}$ (mA cm^{-2})		2.4	3.4	5.6	7.6	10.3	11.6	12.5	15.2
H_2	FE (%)	85.5	89.5	81.2	80.1	81.7	83.0	66.4	65.6
	j_{x}^{b} (mA cm^{-2})	2.1	3.0	4.5	6.1	8.4	9.6	8.3	10.0
	k^{c} ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	42.1	61.3	92.7	124.4	172.2	196.3	170.1	203.5
CO	FE (%)	14.9	9.3	13.9	19.9	16.0	13.3	30.5	33.1
	j_{x} (mA cm^{-2})	0.4	0.3	0.8	1.5	1.6	1.5	3.8	5.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	7.3	6.4	15.9	30.8	33.7	31.4	78.2	102.5
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	3.0	2.3	2.1	0.0	0.0	0.0	1.8	0.0
	j_{x} (mA cm^{-2})	0.1	0.1	0.1	0.0	0.0	0.0	0.2	0.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.2	0.2	0.4	0.0	0.0	0.0	0.7	0.0
CH_3OH	FE (%)	0.0	0.0	1.6	0.0	0.0	0.0	1.6	0.0
	j_{x} (mA cm^{-2})	0.0	0.0	0.1	0.0	0.0	0.0	0.2	0.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	0.6	0.0	0.0	0.0	1.3	0.0
$\text{C}_3\text{H}_8\text{O}$ (2-Propanol)	FE (%)	0.0	0.0	2.5	0.0	1.7	1.4	1.3	0.0
	j_{x} (mA cm^{-2})	0.0	0.0	0.1	0.0	0.2	0.2	0.2	0.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	0.3	0.0	0.4	0.3	0.4	0.0
Total FE (%)		103.3	101.1	101.4	100.0	99.4	97.6	101.7	98.7

^a: total current density; ^b: partial current density; ^c: product formation rate.

Table A.2. ER CO_2 results for CuZn_15 electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.7	-0.8	-0.9	-1.0	-1.1	-1.2	-1.3	-1.4
J_{total} (mA cm^{-2})		2.0	2.7	4.1	7.4	9.1	11.3	13.8	15.2
H_2	FE (%)	58.0	67.0	76.1	66.0	84.3	82.3	77.2	64.4
	j_x (mA cm^{-2})	1.2	1.8	3.1	4.9	7.6	9.3	10.6	9.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	24.0	37.0	63.5	100.3	156.4	190.7	231.6	200.2
CO	FE (%)	46.7	27.7	14.2	28.6	14.1	17.2	19.4	35.4
	j_x (mA cm^{-2})	0.9	0.7	0.6	2.1	1.3	1.9	2.7	5.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	19.3	15.3	11.8	43.4	26.2	39.8	57.6	110.3
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	0.0	2.7	2.5	6.2	1.0	3.1	2.5	1.6
	j_x (mA cm^{-2})	0.0	0.1	0.1	0.5	0.1	0.3	0.3	0.2
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.2	0.3	1.4	0.3	1.1	1.1	0.8
CH_4	FE (%)	0.0	0.0	7.2	1.8	0.0	0.0	0.0	0.0
	j_x (mA cm^{-2})	0.0	0.0	0.3	0.1	0.0	0.0	0.0	0.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	1.5	0.7	0.0	0.0	0.0	0.0
Total FE (%)		104.7	97.4	99.9	102.6	99.4	102.5	99.1	101.4

Table A.3. ER CO_2 results for CuZn_25 electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.7	-0.8	-0.9	-1.0	-1.1	-1.2	-1.3	-1.4
J_{total} (mA cm^{-2})		2.2	3.6	5.4	7.2	10.2	11.3	13.2	15.2
H_2	FE (%)	87.3	86.6	74.5	79.3	80.7	78.3	85.1	76.5
	j_x (mA cm^{-2})	1.9	3.1	4.0	5.7	8.2	8.9	11.2	11.6
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	38.5	63.4	82.4	116.9	167.9	181.5	229.9	237.0
CO	FE (%)	12.2	16.7	23.1	20.2	16.6	19.0	15.1	21.8
	j_x (mA cm^{-2})	0.3	0.6	1.2	1.5	1.7	2.2	2.0	3.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	5.4	12.2	25.5	29.9	34.4	44.1	40.8	67.5
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	0.0	0.0	0.0	1.7	0.9	0.0	0.9	1.0
	j_x (mA cm^{-2})	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	0.0	0.4	0.3	0.0	0.4	0.5
Total FE (%)		99.6	103.2	97.2	101.2	98.2	97.4	101.1	99.2

A.2 Supplementary figures and tables to Chapter 3

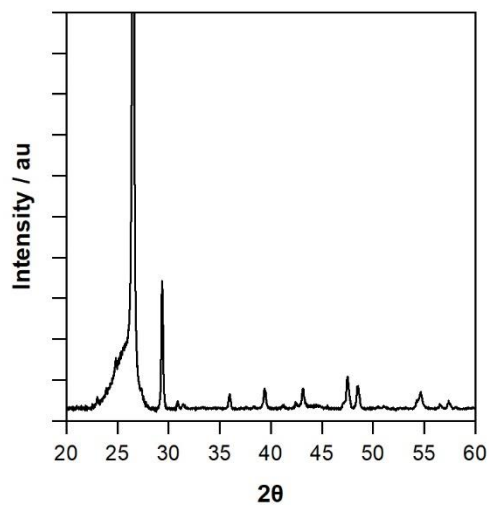


Figure A.8. XRD pattern of the gas diffusion layer (GDL, Sigracet 35BC, SGL Group) used for electrode preparation.

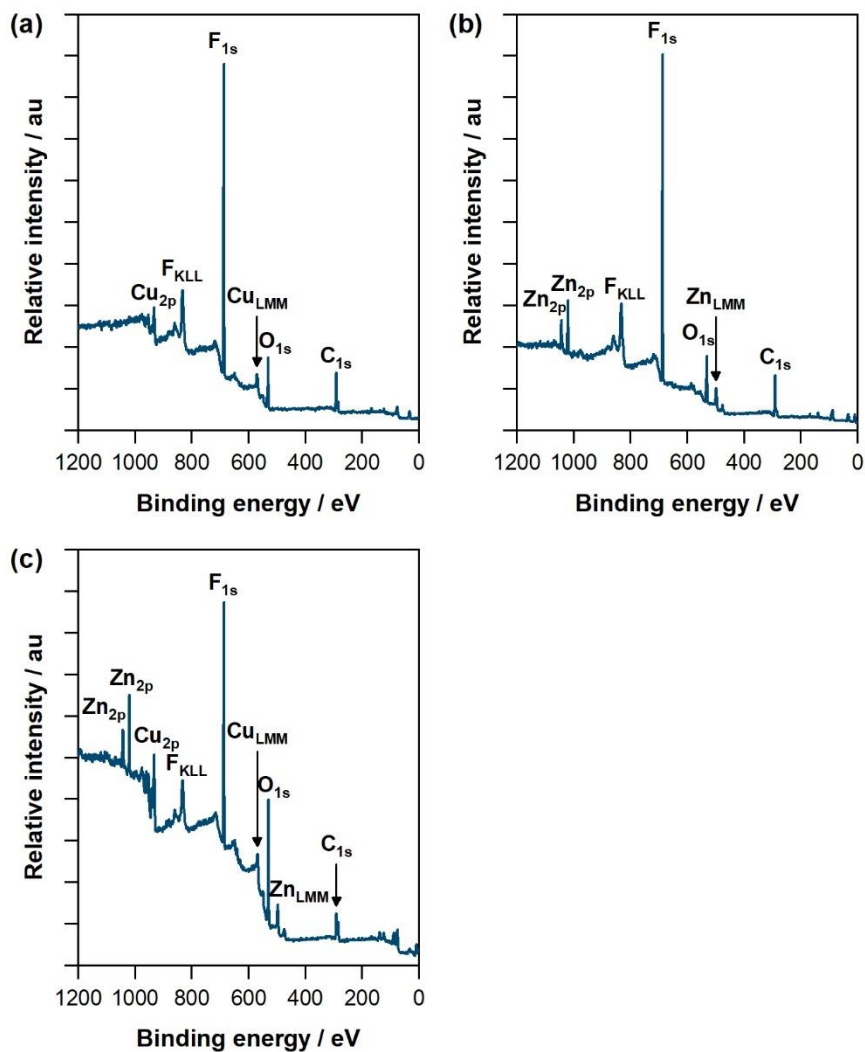


Figure A.9. XPS survey spectra of (a) Cu, (b) Zn, and (c) CuZn samples.

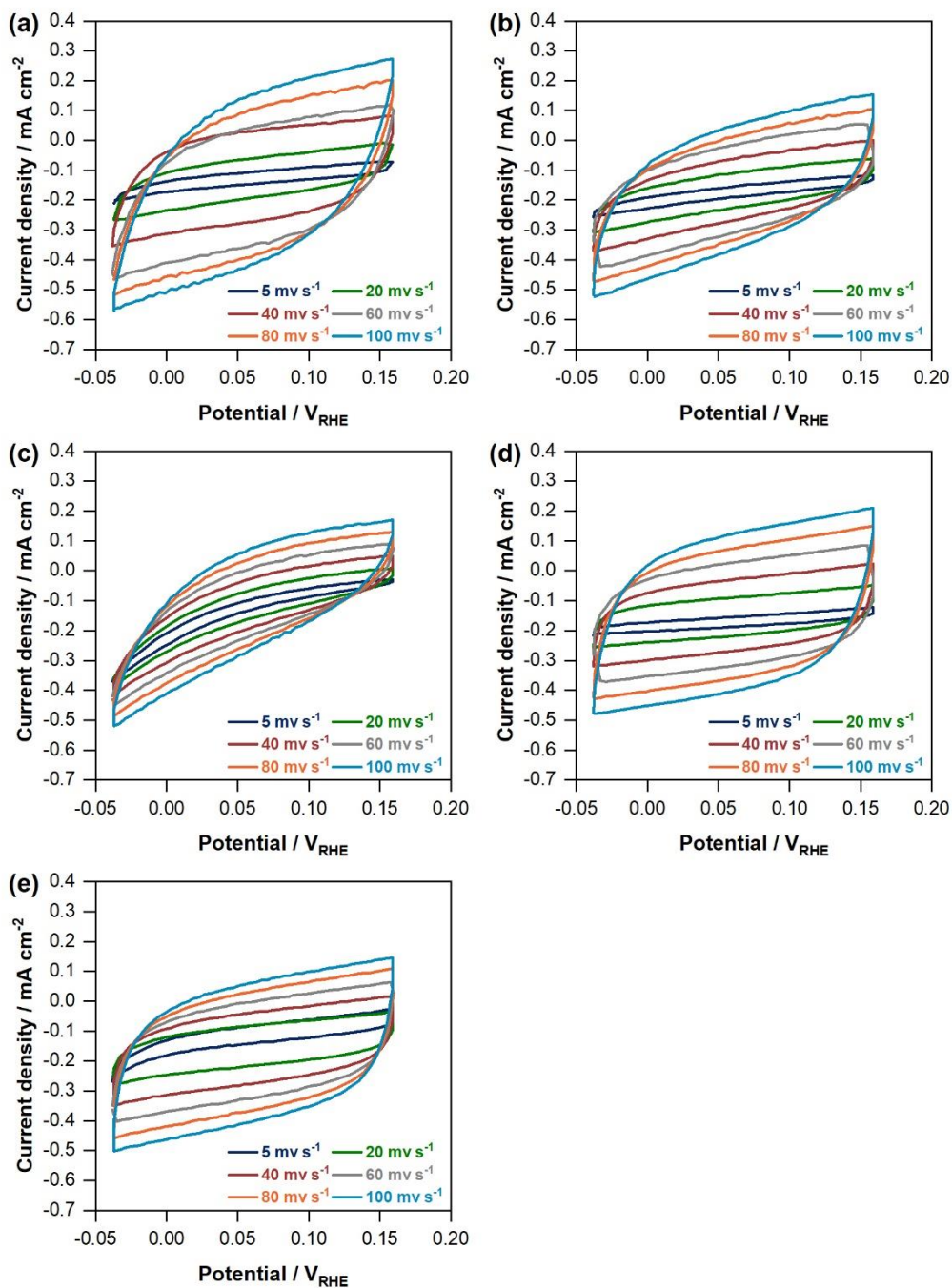


Figure A.10. Cyclic voltammograms of (a) CuZn, (b) CuZn₂₄₀, (c) CuZn₃₀₀, (d) CuZn_{AS}, and (e) CuZn_{CS}, obtained for a non-faradaic potential range.

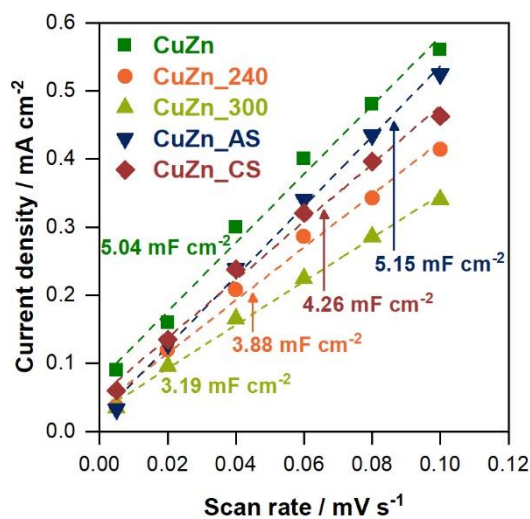


Figure A.11. Double-layer capacitance of the CuZn electrodes.

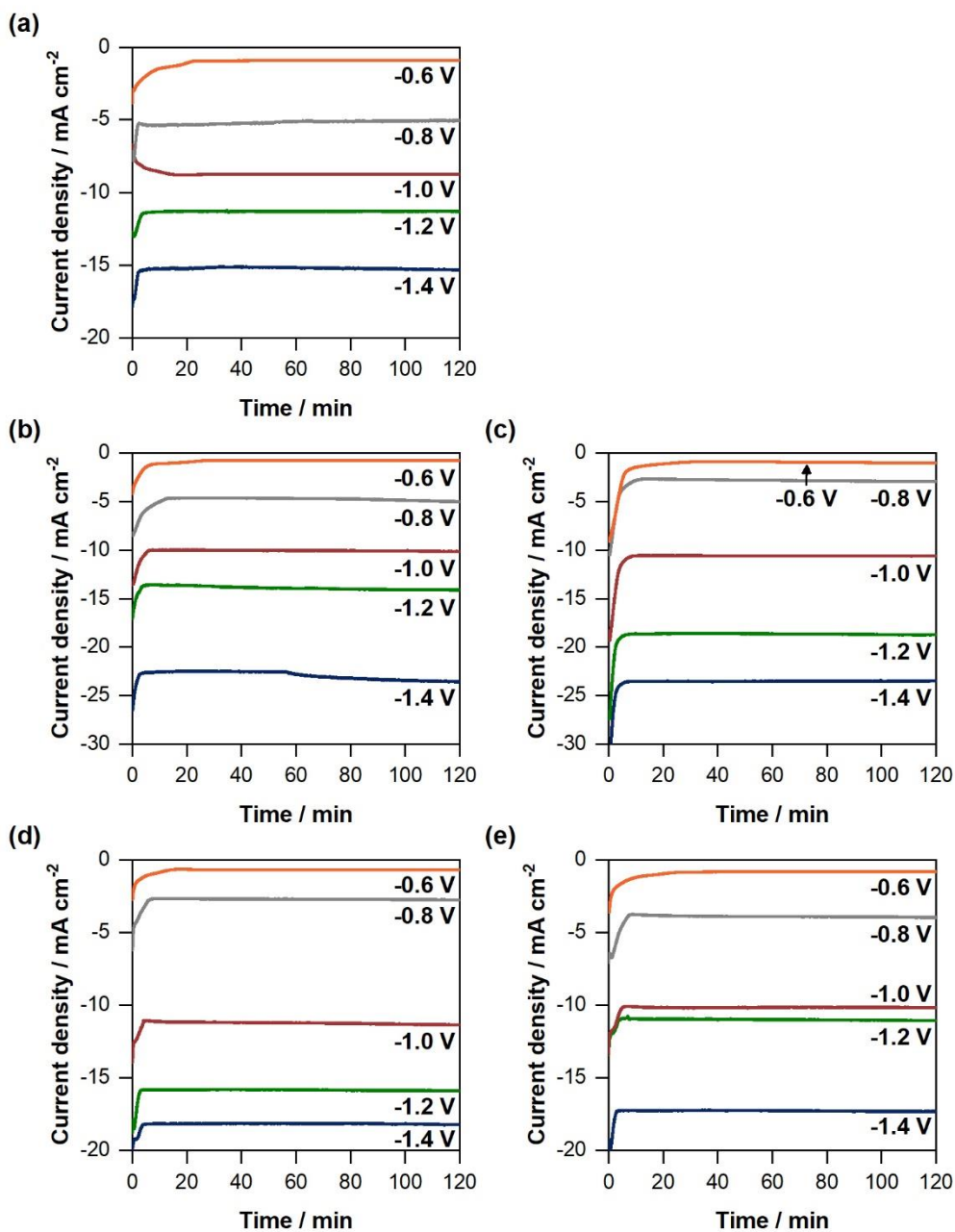


Figure A.12. Chronoamperometric curves at various potentials for CO_2 reduction in CO_2 -saturated 0.1 M KHCO_3 for (a) CuZn, (b) CuZn_240, (c) CuZn_300, (d) CuZn_AS, and (e) CuZn_CS.

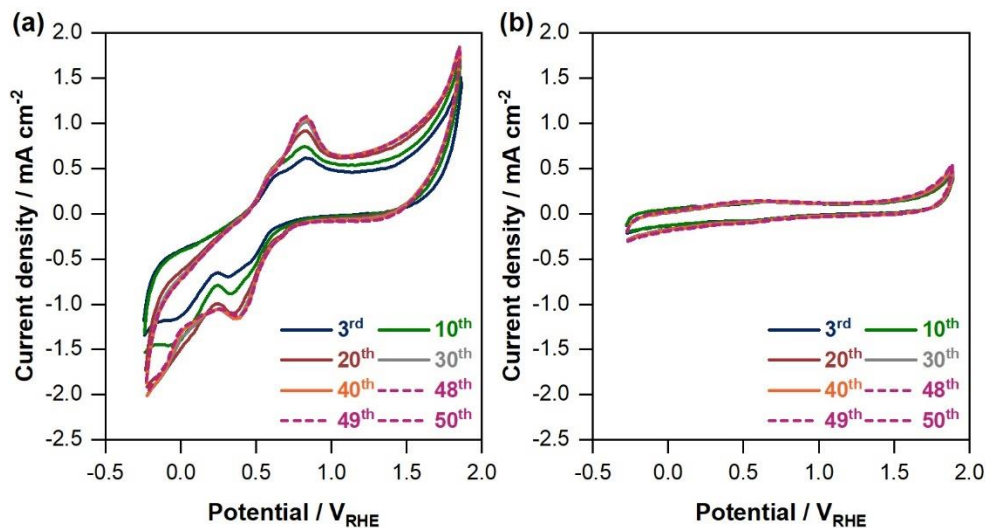


Figure A.13. IR-corrected CVs in N_2 -saturated 0.1 M $KHCO_3$, starting with the anodic scan (AS), for (a) Cu and (b) Zn single-element catalysts.

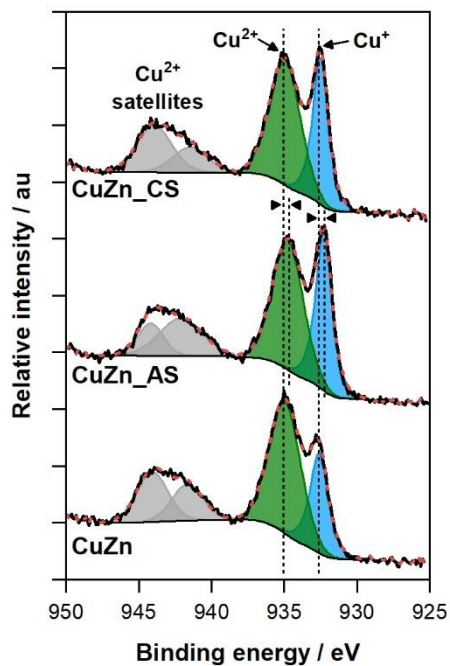


Figure A.14. Cu $2p_{3/2}$ XPS spectra of CuZn, CuZn_AS, and CuZn_CS.

Table A.4. ER CO_2 results for CuZn electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		1.2	5.2	8.7	11.3	15.2
H_2	FE (%)	98.1	70.7	66.3	82.3	64.3
	j_x (mA cm^{-2})	1.2	3.7	5.8	9.3	9.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	24.1	75.3	118.0	190.7	200.2
CO	FE (%)	0.0	28.2	26.1	17.2	35.4
	j_x (mA cm^{-2})	0.0	1.5	2.3	1.9	5.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	30.1	46.4	39.8	110.3
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	0.0	1.4	4.7	3.1	1.6
	j_x (mA cm^{-2})	0.0	0.1	0.4	0.3	0.2
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.2	1.3	1.1	0.8
CH_4	FE (%)	0.0	0.0	1.8	0.0	0.0
	j_x (mA cm^{-2})	0.0	0.0	0.2	0.0	0.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	0.8	0.0	0.0
Total FE (%)		98.1	100.4	98.9	102.5	101.4

Table A.5. ER CO_2 results for CuZn_240 electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		1.1	4.8	10.0	13.9	23.0
H_2	FE (%)	96.3	84.2	76.7	65.8	65.9
	j_{x} (mA cm^{-2})	1.1	4.0	7.7	9.2	15.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	22.2	82.1	157.3	187.2	309.6
CO	FE (%)	0.0	13.2	23.6	31.9	34.3
	j_{x} (mA cm^{-2})	0.0	0.6	2.4	4.4	7.9
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	12.9	48.3	90.7	161.0
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	4.1	0.9	0.8	0.0	0.4
	j_{x} (mA cm^{-2})	0.0	0.0	0.1	0.0	0.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.1	0.1	0.3	0.0	0.3
Total FE (%)		100.4	98.3	101.2	97.7	100.5

Table A.6. ER CO_2 results for CuZn_300 electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		1.2	2.8	10.6	18.7	23.5
H_2	FE (%)	98.7	68.5	74.2	64.4	61.4
	j_x (mA cm^{-2})	1.2	1.9	7.8	12.1	14.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	25.0	39.3	160.5	246.8	295.4
CO	FE (%)	0.0	16.3	23.9	31.8	33.2
	j_x (mA cm^{-2})	0.0	0.5	2.5	6.0	7.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	9.4	51.7	121.9	159.8
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	3.4	4.4	1.8	2.1	2.4
	j_x (mA cm^{-2})	0.0	0.1	0.2	0.4	0.6
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.1	0.4	0.6	1.2	1.8
CH_3OH	FE (%)	0.0	9.3	1.3	1.5	1.4
	j_x (mA cm^{-2})	0.0	0.3	0.1	0.3	0.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	1.6	0.9	1.8	2.0
Total FE (%)		102.1	98.2	101.2	99.9	97.9

Table A.7. ER CO_2 results for CuZn_AS electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		1.0	2.7	11.2	15.9	18.2
H_2	FE (%)	95.0	75.2	38.5	38.1	33.3
	j_{x} (mA cm^{-2})	1.0	2.0	4.3	6.0	6.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	16.3	41.9	87.9	123.7	123.8
CO	FE (%)	0.0	19.7	57.4	59.2	65.7
	j_{x} (mA cm^{-2})	0.0	0.5	6.4	9.4	11.9
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	10.9	130.8	192.2	244.1
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	6.5	5.3	1.2	1.4	0.6
	j_{x} (mA cm^{-2})	0.1	0.1	0.1	0.2	0.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.2	0.4	0.4	0.7	0.4
Total FE (%)		101.5	100.2	97.1	98.6	99.7

Table A.8. ER CO_2 results for CuZn_CS electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		1.1	4.0	10.2	10.9	17.4
H₂	FE (%)	95.2	79.3	81.0	75.7	69.9
	j_{x} (mA cm^{-2})	1.1	3.1	8.2	8.2	12.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	22.2	64.4	168.4	168.6	248.4
CO	FE (%)	0.0	15.9	16.3	23.9	28.2
	j_{x} (mA cm^{-2})	0.0	0.6	1.7	2.6	4.9
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	12.9	33.9	53.3	100.1
C₂H₅OH	FE (%)	6.4	0.6	0.4	0.9	0.6
	j_{x} (mA cm^{-2})	0.1	0.0	0.0	0.1	0.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.2	0.1	0.1	0.3	0.3
Total FE (%)		101.6	95.7	97.8	100.6	98.7

Table A.9. ER CO_2 results for Cu electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		7.9	10.7	16.9
H_2	FE (%)	53.9	62.7	66.2
	j_{x} (mA cm^{-2})	4.3	6.7	11.2
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	86.9	137.1	228.7
CO	FE (%)	17.9	9.8	14.0
	j_{x} (mA cm^{-2})	1.4	1.0	2.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	28.9	21.3	48.5
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	20.5	16.7	7.4
	j_{x} (mA cm^{-2})	1.6	1.8	1.2
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	5.0	5.5	3.9
CH_4	FE (%)	6.2	9.7	13.8
	j_{x} (mA cm^{-2})	0.5	1.0	2.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	2.5	5.3	11.9
Total FE (%)		98.5	98.8	101.4

Table A.10. ER CO_2 results for Cu_AS electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		6.1	12.1	14.0
H_2	FE (%)	50.9	61.2	48.6
	j_{x} (mA cm^{-2})	3.1	7.4	6.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	63.6	150.8	138.7
CO	FE (%)	8.2	11.9	19.5
	j_{x} (mA cm^{-2})	0.5	1.4	2.7
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	10.2	29.2	55.5
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	35.3	22.9	24.8
	j_{x} (mA cm^{-2})	2.2	2.8	3.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	6.7	8.6	10.8
CH_4	FE (%)	4.4	5.5	3.5
	j_{x} (mA cm^{-2})	0.3	0.7	0.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	1.4	3.4	2.5
Total FE (%)		98.7	101.5	96.4

Table A.11. ER CO_2 results for Zn electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		2.0	5.4	9.2
H_2	FE (%)	21.5	13.9	16.5
	j_{x} (mA cm^{-2})	0.4	0.7	1.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	8.7	15.3	31.1
CO	FE (%)	77.0	80.7	80.8
	j_{x} (mA cm^{-2})	1.5	4.3	7.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	31.0	88.6	152.6
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	3.3	3.9	3.2
	j_{x} (mA cm^{-2})	0.1	0.2	0.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.2	0.7	0.9
Total FE (%)		101.8	98.5	100.4

Table A.12. ER CO_2 results for Zn_AS electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		2.0	5.1	8.6
H_2	FE (%)	19.3	15.8	16.0
	j_{x} (mA cm^{-2})	0.4	0.8	1.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	7.9	16.6	28.0
CO	FE (%)	80.4	82.0	80.6
	j_{x} (mA cm^{-2})	1.6	4.2	6.9
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	33.3	86.2	141.3
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	2.2	1.4	1.0
	j_{x} (mA cm^{-2})	0.0	0.1	0.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.1	0.2	0.3
Total FE (%)		101.9	99.1	98.0

Table A.13. ER CO_2 results for CuZn_{mix} electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		6.4	10.1	15.1
H_2	FE (%)	55.1	59.8	64.8
	j_{x} (mA cm^{-2})	3.5	6.0	9.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	72.5	123.6	199.8
CO	FE (%)	25.1	18.6	25.8
	j_{x} (mA cm^{-2})	1.6	1.9	3.9
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	33.0	38.4	79.5
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	12.6	17.3	4.9
	j_{x} (mA cm^{-2})	0.8	1.8	0.7
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	2.5	5.4	2.3
CH_4	FE (%)	5.3	4.8	3.2
	j_{x} (mA cm^{-2})	0.3	0.5	0.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	1.8	2.5	2.5
Total FE (%)		98.1	100.4	98.7

Table A.14. ER CO_2 results for CuZn_{mix}_AS electrode. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-1.0	-1.2	-1.4
J_{total} (mA cm^{-2})		7.0	10.6	14.8
H₂	FE (%)	54.1	57.9	57.0
	j_{x} (mA cm^{-2})	3.8	6.1	8.4
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	77.5	125.0	172.1
CO	FE (%)	26.0	18.5	28.6
	j_{x} (mA cm^{-2})	1.8	2.0	4.2
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	37.2	40.0	81.2
C₂H₅OH	FE (%)	17.1	21.0	10.7
	j_{x} (mA cm^{-2})	1.2	2.2	1.6
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	3.7	6.9	4.9
CH₄	FE (%)	3.3	1.3	2.0
	j_{x} (mA cm^{-2})	0.2	0.1	0.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	1.2	0.7	1.5
Total FE (%)		100.6	98.7	98.2

A.3 Supplementary figures and tables to Chapter 4

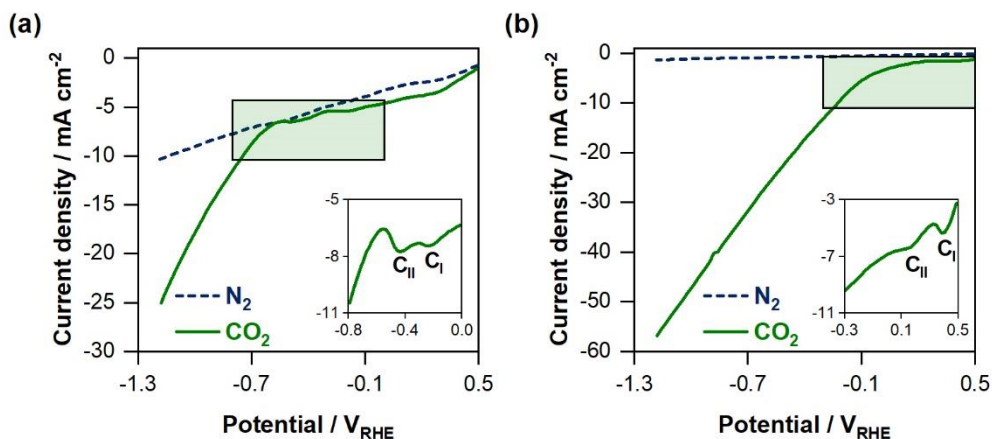


Figure A.15. LSV curves at cathodic potentials in N₂ (dashed lines) and CO₂-saturated (full lines) 0.1 M KHCO₃ for (a) Cu(OH)₂ NWs and (b) CuO NWs, showing a magnification of the lower potential region. Scan rate, 20 mV s⁻¹.

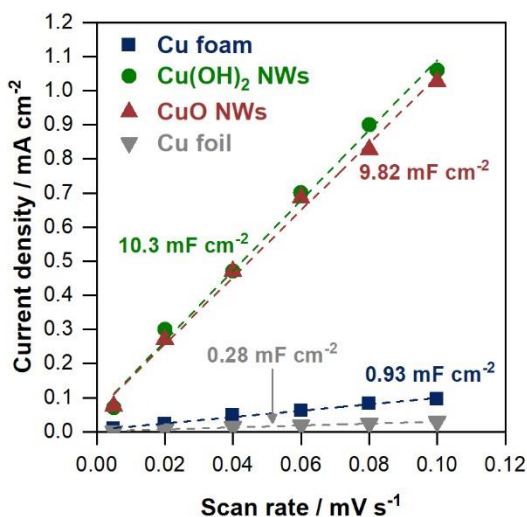


Figure A.16. Double-layer capacitance of the developed electrodes and polycrystalline copper foil.

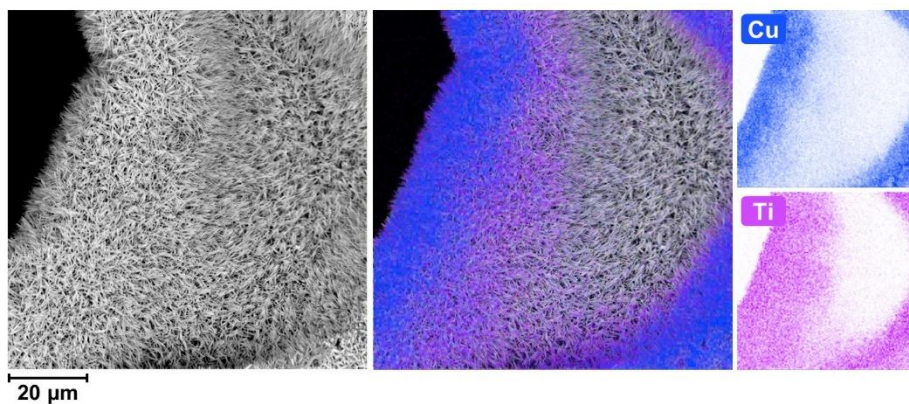


Figure A.17. SEM-EDS elemental mapping of Cu and Ti for CuO NWs electrode after TiO₂ deposition by ALD.

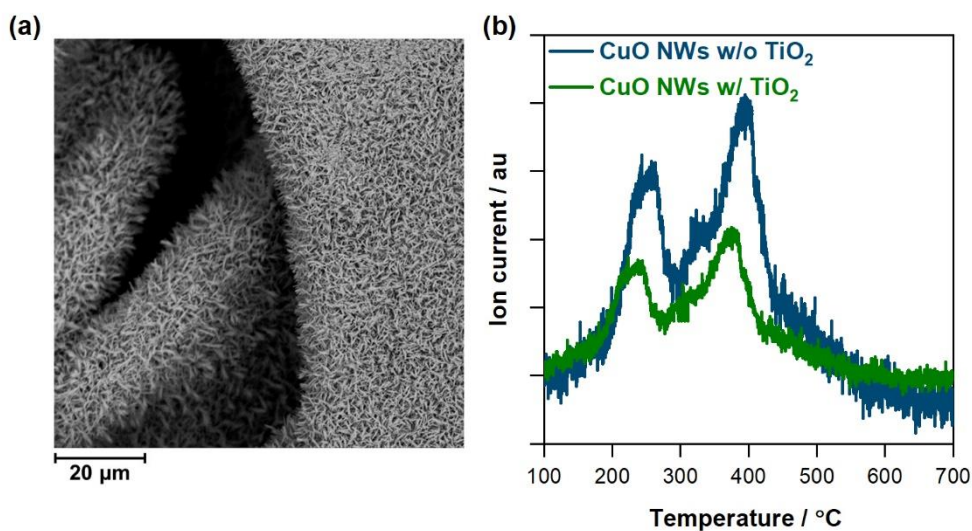


Figure A.18. (a) SEM image of the CuO NWs electrode coated with a protective TiO₂ layer after 2 h electrolysis; and (b) CO₂-TPD-MS profile of CuO NWs electrode with (green curve) and without TiO₂ (blue curve).

SEM-EDS mapping evidences a good coverage of the TiO_2 layer, with some Ti-rich regions being observed (**Figure A.17**). CO_2 -TPD-MS profiles of CuO NWs with and without TiO_2 show two broad desorption regions in the low-temperature range ($230\text{ }^\circ\text{C}$ - $260\text{ }^\circ\text{C}$) and high-temperature range ($380\text{ }^\circ\text{C}$ - $390\text{ }^\circ\text{C}$) (**Figure A.18b**). The CuO NWs with TiO_2 clearly show a significantly lower peak intensity, suggesting that the CO_2 adsorption capacity decreases after TiO_2 deposition. Thus, it can be assumed that CuO centers are covered by TiO_2 , which reduces the number of exposed sites for CO_2 adsorption, resulting in lower CO_2 adsorption and ERCO_2 activity.

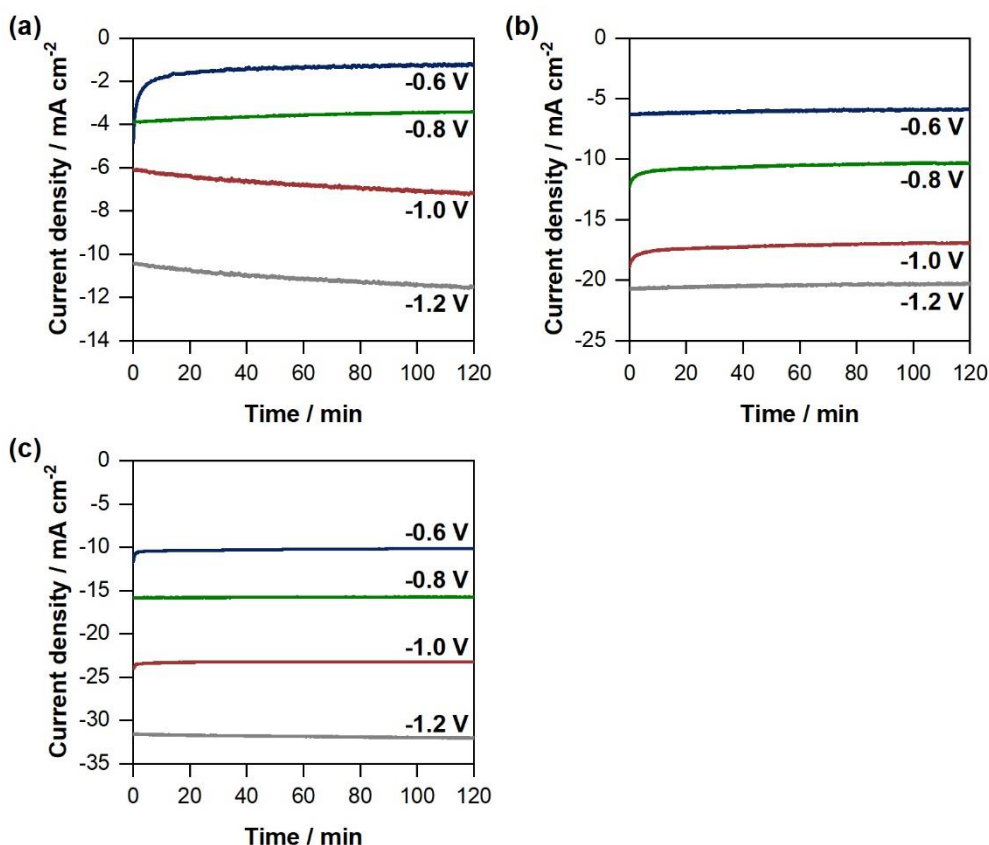


Figure A.19. Chronoamperometric curves at various potentials for CO_2 reduction in CO_2 -saturated 0.1 M KHCO_3 for (a) Cu foam, (b) CuO(OH)_2 NWs, and (c) CuO NWs.

Table A.15. Cell voltage (V), measured between the working and counter electrodes, for each catalyst and applied cathodic potential.

Cathodic potential (V_{RHE})	Cell voltage (V)		
	Cu foam	Cu(OH) ₂ NWs	CuO NWs
-1.2	-3.45	-3.53	-3.30
-1.0	-3.12	-2.82	-2.97
-0.8	-2.79	-2.47	-2.65
-0.6	-2.43	-2.17	-2.36

Table A.16. Cell energy efficiency (EE) for CO₂ reduction to methanol.

Cathodic potential (V_{RHE})	EE Methanol (%)		
	Cu foam	Cu(OH) ₂ NWs	CuO
-1.2	2.58	2.78	18.8
-1.0	4.18	4.71	24.4
-0.8	3.44	7.59	31.2
-0.6	5.18	8.73	32.7

Table A.17. ER CO_2 results for Cu foam. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2
J_{total} (mA cm^{-2})		1.3	3.4	7.2	11.5
H_2	FE (%)	78.0	83.0	81.9	85.2
	j_x (mA cm^{-2})	1.0	2.8	5.9	9.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	20.7	57.7	120.6	200.4
CO	FE (%)	0.0	3.4	4.3	4.7
	j_x (mA cm^{-2})	0.0	0.1	0.3	0.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	2.4	6.3	11.1
CH_3OH	FE (%)	10.1	7.7	10.5	7.2
	j_x (mA cm^{-2})	0.1	0.3	0.8	0.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.8	1.6	4.7	5.1
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	4.4	3.5	4.2	2.5
	j_x (mA cm^{-2})	0.1	0.1	0.3	0.3
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.2	0.4	0.9	0.9
Total FE (%)		92.5	97.6	100.9	99.6

Table A.18. ER CO_2 results for $\text{Cu}(\text{OH})_2$ NWs. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2
J_{total} (mA cm^{-2})		5.9	10.0	16.8	20.0
H_2	FE (%)	35.5	41.3	42.6	54.9
	j_x (mA cm^{-2})	2.1	4.1	7.2	11.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	42.8	84.6	146.5	224.6
CO	FE (%)	37.4	38.4	40.4	32.6
	j_x (mA cm^{-2})	2.2	3.8	6.8	6.5
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	45.2	78.6	139.0	133.5
CH_3OH	FE (%)	15.2	15.1	10.7	7.9
	j_x (mA cm^{-2})	0.9	1.5	1.8	1.6
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	5.6	9.4	11.2	9.8
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	4.9	6.1	6.0	5.6
	j_x (mA cm^{-2})	0.3	0.6	1.0	1.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.9	1.9	3.1	3.5
Total FE (%)		93.0	100.8	99.7	101.0

Table A.19. ER CO_2 results for CuO NWs. Tests were performed using step-potential electrolysis in CO_2 -saturated 0.5 M KHCO_3 (the current density was noted without a minus sign here).

Potential (V_{RHE})		-0.6	-0.8	-1.0	-1.2
J_{total} (mA cm^{-2})		10.1	15.7	23.3	26.1
H_2	FE (%)	13.7	14.1	13.5	18.6
	j_x (mA cm^{-2})	1.4	2.2	3.1	4.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	28.2	45.2	64.4	99.2
CO	FE (%)	0.0	0.0	0.0	10.9
	j_x (mA cm^{-2})	0.0	0.0	0.0	2.8
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	0.0	0.0	0.0	58.1
CH_3OH	FE (%)	62.2	66.4	58.3	49.9
	j_x (mA cm^{-2})	6.3	10.4	13.6	13.0
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	39.1	64.9	84.3	80.9
$\text{C}_2\text{H}_5\text{OH}$	FE (%)	15.4	16.3	21.6	23.5
	j_x (mA cm^{-2})	1.6	2.6	5.0	6.1
	k ($\mu\text{mol h}^{-1} \text{cm}^{-2}$)	4.8	8.0	15.6	19.0
Total FE (%)		91.4	96.8	93.4	102.9

Table A.20. Faradaic efficiency and production rate of the ER CO_2 products determined using the filter-press cell, working at a current density of -45 mA cm^{-2} (the current density was noted without a minus sign here).

		Catalyst	
		Cu foam	CuO NWs
H₂	FE (%)	47.9	14.7
	j_x (mA cm^{-2})	21.6	6.6
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	402.0	123.2
CO	FE (%)	N/D ^a	0.6
	j_x (mA cm^{-2})	N/D	0.3
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	N/D	4.8
CH₃OH	FE (%)	0.7	66.1
	j_x (mA cm^{-2})	0.3	29.7
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	0.2	18.5
C₂H₅OH	FE (%)	19.9	3.2
	j_x (mA cm^{-2})	8.9	1.5
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	2.8	0.5
C₃H₈	FE (%)	18.1	N/D
	j_x (mA cm^{-2})	8.1	N/D
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	15.2	N/D
HCOO⁻	FE (%)	11.1	14.9
	j_x (mA cm^{-2})	5.0	6.7
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	9.3	12.5
Total FE (%)		97.6	99.5

^a: N/D, not detected.

A.4 Supplementary figures and tables to Chapter 5

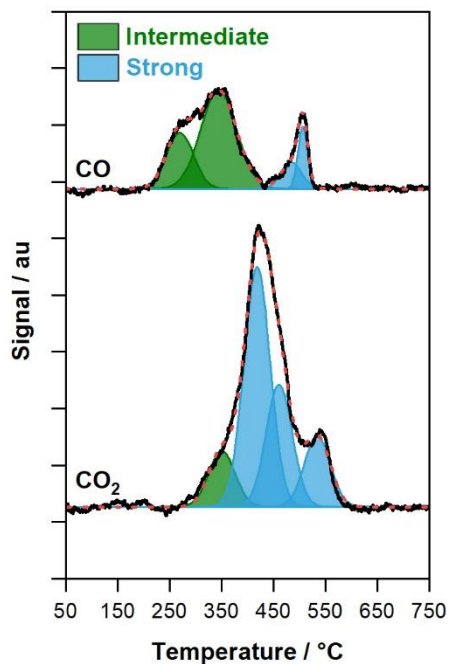


Figure A.20. Comparison between CO₂ and CO desorption profile obtained for catalyst #50C, after electrolysis with catholyte A. CO₂ and CO-TPD experiments were performed under the same operating conditions (*e.g.*, attenuation, adsorbate flow rate, heating ramp, catalyst mass).

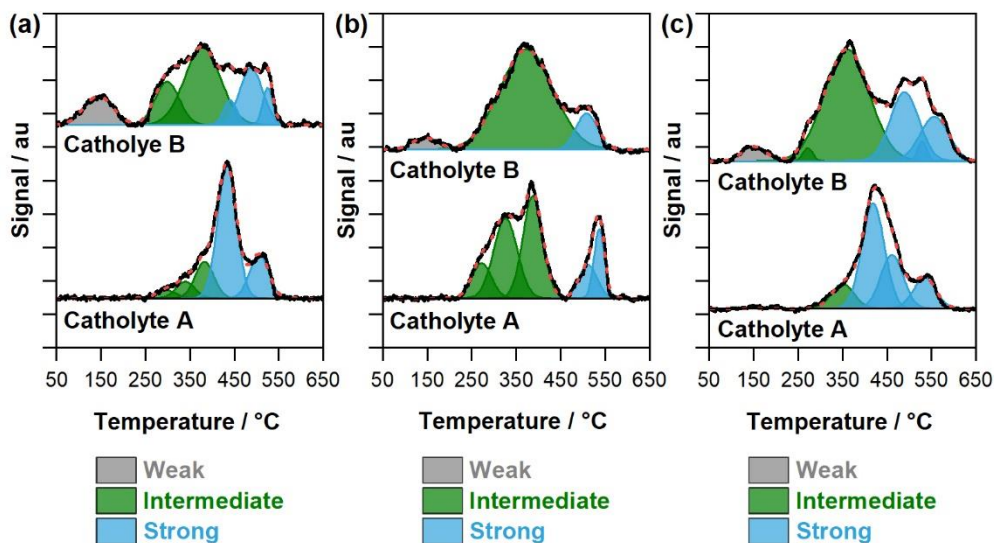


Figure A.21. Comparison of CO₂ desorption pattern obtained with catholyte A and catholyte B for catalysts (a) #5C, (b) #20C, and (c) #50C.

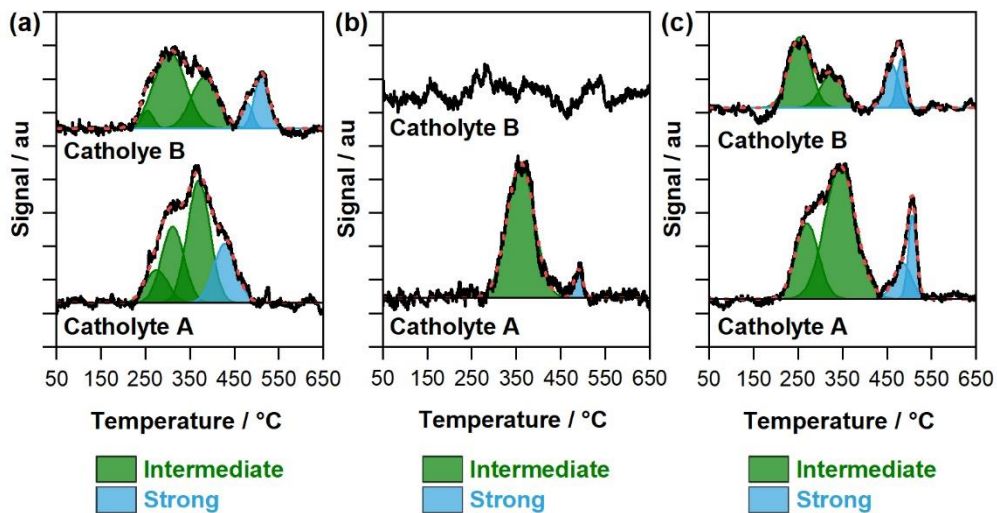


Figure A.22. Comparison of CO desorption pattern obtained with catholyte A and catholyte B for catalysts (a) #5C, (b) #20C, and (c) #50C.

Table A.21. Faradaic efficiency and production rate of the ER CO_2 products determined using the filter-press cell, working at a current density of -45 mA cm^{-2} , using catholyte A: 0.1 M KHCO_3 (the current density was noted without a minus sign here).

		Catalyst		
		#5C	#20C	#50C
H₂	FE (%)	27.1	38.9	10.7
	j_x (mA cm^{-2})	12.2	17.5	4.8
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	227.9	326.5	90.1
C₃H₈	FE (%)	64.6	14.6	85.3
	j_x (mA cm^{-2})	29.1	6.6	38.4
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	54.2	14.4	70.0
HCOO⁻	FE (%)	5.3	33.6	3.5
	j_x (mA cm^{-2})	2.4	15.1	1.6
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	4.5	28.2	3.0
C₂H₅OH	FE (%)	N/D	9.3	N/D
	j_x (mA cm^{-2})	N/D	4.2	N/D
	k ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$)	N/D	1.3	N/D
Total FE (%)		97.1	96.4	99.6

Table A.22. Faradaic efficiency and production rate of the ER CO_2 products determined using the filter-press cell, working at a current density of -45 mA cm^{-2} , using catholyte B: $0.45 \text{ M KHCO}_3 + 0.5 \text{ M KCl}$ (the current density was noted without a minus sign here).

		Catalyst		
		#5C	#20C	#50C
H₂	FE (%)	13.7	10.2	23.9
	$j_x \text{ (mA cm}^{-2}\text{)}$	6.2	4.6	10.8
	$k \text{ (}\mu\text{mol h}^{-1} \text{ cm}^{-2}\text{)}$	114.8	85.9	200.9
C₃H₈	FE (%)	28.8	0.5	14.0
	$j_x \text{ (mA cm}^{-2}\text{)}$	13.0	0.2	6.3
	$k \text{ (}\mu\text{mol h}^{-1} \text{ cm}^{-2}\text{)}$	24.2	0.5	11.8
HCOO⁻	FE (%)	56.0	86.4	57.2
	$j_x \text{ (mA cm}^{-2}\text{)}$	25.2	38.9	25.7
	$k \text{ (}\mu\text{mol h}^{-1} \text{ cm}^{-2}\text{)}$	47.0	72.5	48.0
C₂H₅OH	FE (%)	N/D	N/D	N/D
	$j_x \text{ (mA cm}^{-2}\text{)}$	N/D	N/D	N/D
	$k \text{ (}\mu\text{mol h}^{-1} \text{ cm}^{-2}\text{)}$	N/D	N/D	N/D
Total FE (%)		98.5	97.2	95.1