



Universidade do Porto
Faculdade de Engenharia
FEUP



Chemical Engineering Department

STUDY AND CHARACTERIZATION OF GRÄTZEL SOLAR CELLS

Luísa Manuela Madureira Andrade

Dissertation presented to obtain the degree of
DOCTOR IN CHEMICAL AND BIOLOGICAL ENGINEERING
by the
UNIVERSITY OF PORTO

SUPERVISORS:

Adélio Miguel Magalhães Mendes, Assistant Professor
Helena Isabel Pereira da Costa Aguilar Ribeiro, Auxiliary Researcher

2010



ciência.Inovação
2010

Programa Operacional Ciência e Inovação 2010
INTERNAÇÃOAL SOLUS L'CONNOIS PLORE



ACKNOWLEDGEMENTS

I am grateful to the Portuguese Foundation for Science and Technology (FCT) for my PhD grant (SFRH/BD/30464/2006). Thankful words to LEPAE, DEQ and FEUP for providing me the conditions to develop my work.

I would like to express my gratitude to Prof. Adélio Mendes and Dr. Helena Aguilar Ribeiro, my supervisors, for the opportunity of working in such interesting topic, for their helpful discussions and for their continuously interest on my work. Many thanks to Prof. Adélio for encouraging me to pursue my dream; thanks Helena for being so generous and comprehensive in the troubled days.

I gratefully acknowledge Prof. Michael Grätzel, who accepted me in his group of research for six profitable months. His guidance and support were fundamental in the development of my work. To all LPI members for welcoming me and promptly help me every time I needed. To Dr. Shaik Zakeeruddin for all the patience, constant availability and for all useful discussions. To Dr. Carole Grätzel for all the positive thoughts and for showing me her love of living. To Dr. Yum Jun-ho for helping me with the transient measurements. I also acknowledge all the facilities and materials provided for the development of the experimental part of my thesis in LPI.

To my friend Paula Sousa for reviewing me the French abstract.

To Celeste, Fernanda and their families for their hospitality during my stays in Lausanne.

Many thanks to my lab mates, for their friendship and support; to the “Solar Group” for the scientific discussions and to Tânia Lopes for the wonderful month spent in Lausanne. Special thanks to Sandra Sá, the journey colleague and friend for the last 9 years. Thank you very much for listening me in the most troubled moments, for your serenity... just for being always there.

I am very thankful to all my friends, for their support, affection and for all the good moments that we spent together. Thank you Su for being there for me...

To my parents for all the love, unconditional support, upbringing, guidance and teachings... for being by my side all days of my life. To my dear sisters, Tecinha and Lausinha, for all the protection, advices and love. Thank you for making me feel your little girl forever...

To my beautiful nephews Beatriz, João and Sofia.

Last but definitely not least, thank you João for all your comprehension, support, attention and love. Thank you for helping me to overcome the difficult moments always with a smile. Thank you for making me feel special...

To my lovely parents and sisters...

PREFACE

The present work was developed in Laboratory for Process, Environmental and Energy Engineering (LEPAE) facilities, in the Chemical Engineering Department of Faculty of Engineering of the University of Porto (FEUP), between 2006 and 2010 and under the grant SFRH/BD/30464/2006.

Part of the studies was also performed in Laboratory of Photonic and Interfaces (LPI) in École Polytechnique Fédéral de Lausanne (EPFL), in Switzerland, under the supervision of Prof. Michael Grätzel (Head of the Laboratory) and Dr. Shaik Zakeeruddin.

This work results from a compilation of 7 scientific papers and 1 book chapter. Each paper represents one independent chapter.

CONTENTS

Abstract	XIII
Sumário	XV
Sommaire	XVII
Figure Captions	XIX
Table Captions	XXVII

PART I: INTRODUCTION

Chapter 1. INTRODUCTION	3
1.1 A brief history of photovoltaics & State of the art	4
1.2 Dye-sensitized Solar Cells	7
1.2.1 Structure and working principles	7
1.2.2 Overview of materials in DSCs devices	12
1.3 Photovoltaic characterisation and electrochemical techniques	18
1.3.1 Current-voltage characteristic	18
1.3.2 Incident photon-to-current conversion efficiency	20
1.3.3 Phototransient measurements	21
1.3.4 Electrochemical impedance spectroscopy	22
1.4 Objectives and outline of this work	36
List of abbreviations and symbols	38
References	42

PART II: DYE-SENSITIZED SOLAR CELLS

Chapter 2. INFLUENCE OF SODIUM CATIONS OF N3 DYE ON THE PHOTOVOLTAIC PERFORMANCE AND STABILITY OF DYE-SENSITIZED SOLAR CELLS	49
Abstract	49
2.1 Introduction	50
2.2 Experimental section	51

2.2.1 Synthesis	51
2.2.2 TiO ₂ electrode preparation	51
2.2.3 Dye-sensitized solar cell fabrication	52
2.2.4 Photovoltaic measurements	52
2.2.5 Electrochemical impedance measurements	53
2.2.6 Photovoltage transient decay	53
2.2.7 Stability Tests	54
2.3 Results and discussion	54
2.3.1 Photovoltaic performance	55
2.3.2 Device stability	58
2.3.3 Electrochemical impedance spectroscopy	61
2.3.4 Photovoltage transient decay	65
2.4 Conclusion	68
Acknowledgments	69
List of abbreviations and symbols	70
References	72

Chapter 3. INFLUENCE OF DIFFERENT CATIONS OF N3 DYES ON THEIR PHOTOVOLTAIC

PERFORMANCE AND STABILITY	75
Abstract	75
3.1 Introduction	76
3.2 Experimental section	77
3.2.1 Dye preparation	77
3.2.2 Composition of electrolyte E1	77
3.2.3 TiO ₂ electrode preparation	77
3.2.4 Dye-sensitized solar cell fabrication	78
3.2.5 Photovoltaic measurements	78
3.2.6 Electrochemical impedance measurements	79
3.2.7 Stability Tests	79
3.3 Results and discussion	79

3.4 Conclusion	87
Acknowledgments	88
List of abbreviations and symbols	89
References	91
Chapter 4. EFFICIENCY ENHANCEMENT OF DYE-SENSITIZED SOLAR CELLS BY COATING THE COUNTER ELECTRODE BACKSIDE WITH A REFLECTIVE COMMERCIAL PAINT	93
Abstract	93
4.1 Introduction	94
4.2 Experimental section	96
4.2.1 Materials	96
4.2.2 Dye-sensitized solar cell fabrication	96
4.2.3 Photovoltaic measurements	97
4.2.4 Electrochemical impedance measurements	98
4.2.5 Reflectance measurements	98
4.3 Results and discussion	99
4.3.1 Light-reflecting performance	99
4.3.2 Photovoltaic performance	100
4.3.3 Electrochemical impedance spectroscopy	102
4.4 Conclusion	108
Acknowledgments	109
List of abbreviations and symbols	110
References	112
Chapter 5. CHARGE-COLLECTION EFFICIENCY IN DYE-SENSITIZED SOLAR CELLS CALCULATED FROM ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY	115
Abstract	115
5.1 Introduction	117
5.2 Experimental section	120
5.2.1 Synthesis	120

5.2.2 Dye-sensitized solar cell fabrication	120
5.2.3 Photovoltaic measurements	121
5.2.4 IPCE measurements	121
5.2.5 Electrochemical impedance measurements	122
5.3 Results and discussion	122
5.3.1 Photovoltaic performance	122
5.3.2 Electrochemical impedance spectroscopy	125
5.3.3 Comparison of η_{col} parameter calculated by IPCE and EIS	132
5.4 Conclusion	133
Acknowledgments	134
List of abbreviations and symbols	135
References	138

Chapter 6. PHENOMENOLOGICAL MODELLING OF DYE-SENSITIZED SOLAR CELLS UNDER TRANSIENT CONDITIONS	141
Abstract	141
6.1 Introduction	143
6.2 Development of the DSC model	144
6.2.1 Electrons	147
6.2.2 Redox species	149
6.2.3 Electrolyte-Platinised contact: Butler-Volmer Equation	151
6.2.4 Dimensionless equations	154
6.2.5 Numerical solution strategy	155
6.3 Results and discussion	156
6.3.1 I - V characteristic	156
6.3.2 EIS spectra	164
6.4 Conclusion	166
Acknowledgments	167
List of abbreviations and symbols	168
References	172

Chapter 7. TRANSIENT PHENOMENOLOGICAL MODELLING OF PHOTOELECTROCHEMICAL CELLS FOR WATER SPLITTING - APPLIED TO UNDOPED HEMATITE ELECTRODES	177
Abstract	177
7.1 Introduction	178
7.2 Development of the PEC cell model	180
7.2.1 Electrons	183
7.2.2 Holes	186
7.2.3 Hydroxyl ions	187
7.2.4 Macroscopic electric field: Poisson equation	190
7.2.5 Electrolyte-Platinum contact: Butler-Volmer Equation	191
7.2.6 Dimensionless equations	196
7.2.7 Numerical solution strategy	197
7.3 Results and discussion	197
7.3.1 <i>I-V</i> characteristic of an undoped hematite electrode based-PEC cell	197
7.3.2 Effect of the electrolyte layer thickness	202
7.3.3 Effect of the hole diffusion length	203
7.3.4 Effect of the Butler-Volmer kinetics	205
7.4 Conclusion	208
Acknowledgments	209
List of abbreviations and symbols	210
References	214
 Chapter 8. IMPEDANCE CHARACTERIZATION OF DYE-SENSITIZED SOLAR CELLS IN A TANDEM ARRANGEMENT FOR HYDROGEN PRODUCTION BY WATER SPLITTING	 217
Abstract	217
8.1 Introduction	218

8.2 Experimental section	221
8.2.1 Synthesis	221
8.2.2 TiO ₂ electrode preparation	222
8.2.3 DSC and PEC cell fabrication	222
8.2.4 <i>I</i> - <i>V</i> measurements	223
8.2.5 Electrochemical impedance spectroscopy of DSCs	224
8.3 Results and discussion	224
8.3.1 DSC characterisation	225
8.3.2 DSC application: tandem cell for water photocleavage	230
8.4 Conclusion	233
Acknowledgments	234
List of abbreviations and symbols	235
References	238

PART IV: FINAL CONCLUSIONS

Chapter 9. GENERAL CONCLUSIONS AND FUTURE WORK SUGGESTIONS	243
---	------------

ABSTRACT

Nowadays, a particular interest in the development of technologies that take advantage of renewable energy sources arises, especially motivated by the need of reducing the dependency on fossil fuel resources and for providing the reduction of the CO₂ emissions. The direct conversion of sunlight into electricity by means of photovoltaic systems has the potential to contribute for the resolution of this problem with a minor environmental impact. Dye-sensitized Solar Cells (DSCs), a type of photoelectrochemical cells, are a new generation of solar cells technology that emerged in the early 1990s, targeting to achieve moderate efficiency devices at very low costs.

The present work aimed the phenomenological understanding of the charge transport in the photoanode and the electron recombination at the semiconductor/electrolyte interface; unsteady-state modelling and simulation of a DSC; improvement and characterisation of different inner-parts of DSCs; and use of the electrochemical impedance spectroscopy (EIS) technique for deeper characterisation of DSCs.

The electron transport and charge recombination in nanocrystalline films were extensively studied mainly using electrochemical impedance spectroscopy. This technique has been widely applied for characterising the electrical behaviour of systems in which the overall performance is determined by a number of coupled processes proceeding at different time rates. Equivalent electrical analogues were used to fit the EIS experimental data, allowing the identification of some of the characteristic parameters of the system; in particular, the infinite transmission line model based on the diffusion-recombination theory was used. However, the interpretation of these phenomena in terms of resistive and capacitive elements is not straightforward due to the complexity inherent to these photoelectrochemical cells. A deeper understanding of the different charge transport processes occurring at DSCs' interfaces is possible if a dynamic phenomenological model is developed. Consequently, a simple dynamic model was for the first time proposed and critically compared to the experimental results.

A new approach based on charge-collection efficiency was used to evaluate the performance of a dye-sensitized solar cell. The charge-collection parameter is related to the competition between recombination of photoinjected electrons with the redox electrolyte and electron transport in the mesoporous semiconductor, independently of the electron recombination kinetics. Electrochemical impedance spectroscopy was used to assess, at specific conditions of bias voltage and illumination, electron transport in the porous semiconductor film and electron recombination in TiO_2 /electrolyte interface. The proposed methodology for collection efficiency calculations based on impedance spectroscopy experiments was validated by incident photon-to-current conversion efficiency measurements performed with front- and rear-side irradiation.

Photoelectrochemical (PEC) cells for water splitting, in particular with an undoped hematite photoanode, were also modelled under transient conditions. This model allowed to study underlying mechanisms of the PEC cell and to assess some of the operation parameters that limit the overall light to chemical energy (hydrogen) conversion. The model results were critically compared with an experimental I - V characteristic, allowing the calculation of the cells' performance parameters.

SUMÁRIO

Actualmente, tem surgido um interesse crescente no desenvolvimento de tecnologias para aproveitar fontes renováveis de energia, especialmente motivado pela necessidade de reduzir a dependência das fontes de combustíveis fósseis e de forma a reduzir as emissões de CO₂. Deste modo, a conversão directa de energia solar em electricidade por via de sistemas fotovoltaicos pode contribuir grandemente para a resolução deste problema sem prejuízo do meio ambiente. As células solares sensibilizadas com corante (DSCs), um tipo de células fotoelectroquímicas, são uma nova geração da tecnologia baseada em células solares, que surgiram no início dos anos 90 e com potencial de originar dispositivos com eficiência moderada e a um baixo custo.

O presente trabalho visa uma compreensão fenomenológica do transporte de carga no fotoânodo e recombinação dos electrões na interface semiconductor/electrólito; modelização e simulação em estado não-estacionário das DSCs; melhoramento e caracterização de diferentes partes constituintes das DSCs; e exploração das potencialidades da técnica de espectroscopia de impedância electroquímica (EIS).

O transporte de electrões e respectiva recombinação nos filmes de semicondutores nanocristalinos foram alvo de intenso estudo, especialmente usando a técnica de espectroscopia de impedância electroquímica. Esta técnica tem sido amplamente usada na caracterização do comportamento eléctrico de vários sistemas nos quais o seu desempenho global é fortemente determinado por um conjunto de fenómenos interligados entre si e que ocorrem a diferentes velocidades. Análogos eléctricos equivalentes são então usados para ajustar os dados experimentais obtidos por EIS, permitindo a identificação de alguns dos parâmetros característicos do sistema; em particular, foi usado o modelo de transmissão em linha baseado na teoria difusão-recombinação. Contudo, a interpretação dos fenómenos acima mencionados apenas com base em elementos resistivos e capacitivos não é simples devido à complexidade inerente às células fotoelectroquímicas. Uma compreensão mais aprofundada dos diferentes processos de transferência de carga que ocorrem nas diferentes interfaces de uma DSC é apenas possível com base num modelo fenomenológico.

Consequentemente, foi desenvolvido um modelo simples em estado transiente e os resultados criticamente comparados com os resultados experimentais.

Para avaliar o desempenho de uma célula solar sensibilizada com corante foi usada também uma nova abordagem que se baseou no parâmetro eficiência de recolha de carga no circuito externo. Este parâmetro de recolha está relacionado com a competição entre recombinação dos electrões fotoinjectados com o par redox presente no electrólito e o transporte de electrões no semiconductor mesoporoso, independentemente da cinética de recombinação. A espectroscopia de impedância electroquímica foi usada uma vez mais para avaliar, em condições específicas de potencial aplicado e iluminação, o transporte de electrões no filme poroso de semiconductor e a recombinação dos electrões na fronteira TiO_2 /electrólito. A metodologia proposta para o cálculo do parâmetro de eficiência de recolha baseado nos resultados de espectroscopia de impedância foi validada através de ensaios de eficiência de conversão de fotão em corrente eléctrica realizados com irradiação pelo lado do fotoeléctrodo e pelo lado do contra-eléctrodo.

Foi desenvolvido um modelo transiente de células fotoeletroquímicas (PEC) para hidrólise da água, em particular com fotoânodo de hematite não dopada. Este modelo permitiu o estudo dos mecanismos subjacentes ao funcionamento de uma célula PEC e avaliar alguns dos parâmetros de operação que limitam a conversão global de energia solar em energia química sobre a forma de hidrogénio. Os resultados obtidos por simulação foram criticamente comparados com a curva I - V experimental do sistema, permitindo o cálculo dos principais parâmetros de desempenho da célula.

SOMMAIRE

De nos jours, il a surgit un crescent intérêt dans le développement de technologies pour profiter des sources renouvelables d'énergie, surtout motivé par le besoin de réduire la dépendance des sources de combustibles fossiles et de manière à réduire les émissions de CO_2 . Ainsi, la conversion directe d'énergie solaire en électricité par moyen de systèmes photovoltaïques peut énormément contribuer à la résolution de ce problème sans porter préjudice à l'environnement. Les cellules solaires sensibilisées par un colorant (DSCs) sont une nouvelle génération de la technologie basée en cellules solaires qui ont émergé au début des années 90 et avec du potentiel de créer des dispositifs d'efficacité modérée et à faible coût.

Ce travail a comme objectif une compréhension phénoménologique du transport de charge dans le semi-conducteur et recombinaison des électrons dans l'interface semi-conducteur/électrolyte ; modélisation et simulation en état non-stationnaire des DSCs ; perfectionnement et caractérisation des différentes parties qui constituent les DSCs ; et exploitation des potentialités de la technique de spectroscopie d'impédance électrochimique (EIS).

Le transport des électrons et respective recombinaison dans les couches de semi-conducteurs nanocristallines ont fait l'objet d'études approfondies, en utilisant surtout la technique de spectroscopie d'impédance électrochimique. Cette technique a été largement utilisée dans la caractérisation du comportement électrique de plusieurs systèmes dans lesquels sa performance globale est fortement déterminée par un ensemble de phénomènes liés entre eux et qui ont lieu dans des vitesses différentes. Des analogues électriques équivalents sont ensuite utilisés pour ajuster les données expérimentales obtenues par EIS, permettant l'identification de quelques paramètres caractéristiques du système ; en particulier, il a été utilisé le modèle de transmission en ligne basée dans la théorie diffusion-recombinaison. Cependant, l'interprétation des phénomènes ci-dessus mentionnés uniquement à partir des éléments résistifs et capacitifs n'est pas simple dû à la complexité inhérente à cellules photoélectrochimiques. Une compréhension plus profonde des différents processus de transfert de charge qui se produisent à différentes interfaces d'un DSC n'est

possible qu'à partir d'un modèle phénoménologique. Par conséquent, il a été développé un modèle simple en régime transitoire et les résultats comparés de façon critique par rapport aux résultats expérimentaux.

Pour évaluer la performance d'une cellule solaire sensibilisée avec du colorant il a été aussi utilisé une nouvelle approche qui est basée sur le paramètre efficacité de collecte de charge dans le circuit extérieur. Ce paramètre de collecte est lié à la compétition entre recombinaison des électrons photoinjectés par le couple redox présent dans l'électrolyte et le transport des électrons dans les semi-conducteurs mésoporeux, indépendamment de la cinétique de recombinaison. La spectroscopie d'impédance électrochimique a été utilisée à nouveau pour évaluer, dans des conditions spécifiques de potentiel appliqué et l'éclairage, le transport des électrons dans les couches poreux de semi-conducteurs et la recombinaison des électrons à la frontière TiO_2 /électrolyte. La méthodologie proposée par le calcul du paramètre d'efficacité de collecte basée sur les résultats de spectroscopie d'impédance électrochimique a été validée par des essais d'efficacité de conversion de photon en courant électrique réalisés avec irradiation du côté photoélectrode et par le côté contre-électrode.

Il a été développé un modèle transitoire de cellules photoélectrochimiques (PEC) pour l'hydrolyse de l'eau, en particulier avec du semi-conducteur de hématite non dopée. Ce modèle a permis l'étude des mécanismes sous-jacents au fonctionnement d'une cellule PEC et d'évaluer certains des paramètres de l'opération qui limitent la conversion globale de l'énergie solaire en énergie chimique sur la forme d'hydrogène. Les résultats obtenus par simulation ont été comparés de façon critique avec la courbe I - V expérimental du système, permettant le calcul des principaux paramètres de performance de la cellule.

FIGURE CAPTIONS

Figure 1.1 - (a) Energy band scheme of a p-n junction solar cell; (b) principle of operation of a dye-sensitized solar cell. E_g - bandgap energy; E_v - valence band energy; E_c - conduction band energy; E_F - semiconductor Fermi energy; e^- - electrons; h^+ - holes; S - ground state of the sensitizer; S^* - excited state of the sensitizer; S^+ - oxidised sensitizer; TCO - transparent conductive oxide. 8

Figure 1.2 - Schematic diagram of the operation kinetics of DSCs: forward electron transfer ($\rightarrow$) and electron loss pathways ($\rightarrow$). The photovoltage, V_{OC} , of the system corresponds to the difference between the TiO_2 Fermi energy, E_F , and the redox energy of the electrolyte, E_{Redox} . 10

Figure 1.3 - Kinetics of the electron transfer processes at the different interfaces in DSCs. CB labels the conduction band edge. 12

Figure 1.4 - Typical I - V curve (solid line) and respective power curve that shows the cell's power output at different voltage bias (dashed line). The full dot in the power curve indicates the maximum-power point (MPP) of the cell. 19

Figure 1.5 - Scheme of the phototransient setup.⁸¹ 22

Figure 1.6 - Sinusoidal voltage perturbation and resulting sinusoidal current response, phase-shifted by φ . V_0 - amplitude of the voltage signal; I_0 - amplitude of the current signal; V_{oc} - open-circuit voltage; I_{oc} - open-circuit current. 24

Figure 1.7 - Typical (a) Bode and (b) Nyquist diagrams for a DSC. 25

Figure 1.8 - Current *versus* voltage curve showing pseudo-linearity. 26

Figure 1.9 - Helmholtz double layer. 28

Figure 1.10 - Circuit diagram and Nyquist plot representing the impedance behaviour of an electrochemical reaction. ω is the radial frequency of the signal perturbation. 29

Figure 1.11 - Circuit diagram and Nyquist plot for a Warburg element used to model diffusion-like mass transport phenomena. ω is the radial frequency of the signal perturbation. 30

Figure 1.12 - Transmission line model used to fit EIS experimental data of DSCs.^{96,100} R_s - series resistance; $R_{TCO/EL}$ - charge transfer resistance at exposed TCO/electrolyte interface; $C_{TCO/EL}$ - double layer capacitance at exposed TCO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_μ - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised TCO; C_{CE} - double layer capacitance at the platinised TCO. 31

Figure 1.13 - Impedance spectra obtained for the diffusion-recombination model when: (a) $R_k \gg R_w$; (b) $R_w \gg R_k$; (c) $R_k \approx R_w$. 34

Figure 1.14 - Simplified circuits of the model presented in Figure 1.13: (a) at very low applied potentials (insulating TiO_2); (b) at high applied potentials (conductive TiO_2).⁹⁶ 36

Figure 2.1 - Molecular structure of the a) $[2Na^+(N3, 2H^+)]$ and b) $[2TBA^+(N3, 2H^+)]$, known as N719 dye. 54

Figure 2.2 - a) Photocurrent intensity-voltage characteristics for devices A to D, measured at AM 1.5 (100 mW cm^{-2}) global sunlight illumination. b) Photocurrent action spectra for the same devices. 57

Figure 2.3 - Evolution of photovoltaic parameters for device A (▲) and device C (■), aged under one sunlight soaking at 50 °C. 59

Figure 2.4 - Evolution of photovoltaic parameters for device B (△) and device D (□), aged under one sunlight soaking at 50 °C. 60

Figure 2.5 - Bode a) and Nyquist b) diagrams obtained for the $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ dye/E1 electrolyte system, before and after 1000 h under thermal/light soaking stress test. In the Nyquist diagram, symbols correspond to the impedance data obtained experimentally in the dark under -0.75 V bias, while solid lines represent the fittings based on the equivalent electrical circuit shown in Figure 2.6.

62

Figure 2.6 - Transmission line model used to fit the EIS experimental data. R_s - series resistance; $R_{\text{FTO/EL}}$ - charge transfer resistance at exposed FTO/electrolyte interface; $C_{\text{FTO/EL}}$ - double layer capacitance at exposed FTO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_μ - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised FTO; C_{CE} - double layer capacitance at the platinised FTO.

63

Figure 2.7 - Open-circuit voltage vs. photogenerated electron densities observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

66

Figure 2.8 - Chemical capacitance vs. open circuit voltage observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

67

Figure 2.9 - Electron lifetimes vs. open-circuit voltage observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

68

Figure 3.1 - a) Photocurrent intensity-voltage characteristics for devices A, B and C, measured at 1 sun (100 mW cm^{-2}), AM 1.5 global sunlight illumination. b) Photocurrent action spectra of the same devices.

80

Figure 3.2 - Evolution of photovoltaic parameters for device A ($\blacktriangle$), device B ($\times$) and device C ($\square$). The cells were kept under one sun visible-light soaking at 50 °C for approximately 1000 h.

82

Figure 3.3 - Bode (a) and Nyquist (b) diagrams obtained for device A before and after 1000 h under thermal/light soaking stress. In the Nyquist diagram, symbols correspond to the impedance data obtained experimentally in the dark under -0.75 V bias, while solid lines represent the fittings according to the equivalent circuit present in Figure 3.4.

84

Figure 3.4 - Transmission line model used to fit the EIS experimental data. R_s - series resistance; $R_{FTO/EL}$ - charge transfer resistance at exposed FTO/electrolyte interface; $C_{FTO/EL}$ - double layer capacitance at exposed FTO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_μ - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised TCO; C_{CE} - double layer capacitance at the platinised TCO.

85

Figure 4.1 - Operating principle of a dye-sensitized solar cell with a reflective layer at the counter electrode side.

96

Figure 4.2 - Reflectance spectra of the paint film in the wavelength range of light absorption by the Z907 sensitizer, with illumination from the paint coated side - "Paint side" - and from the bare glass side - "Glass side".

100

Figure 4.3 - I - V characteristics measured at 1 sun illumination (100 mW cm^{-2} ; AM 1.5G) for devices A (solid line) and B (dashed line). Red - DSC with no reflective material in the CE; green - aluminium foil in the backside of the CE; blue - white paint coated in the backside of the CE.

101

Figure 4.4 - Nyquist diagrams obtained in the dark and under -0.75 V bias for device A. (□) - device with no reflective material; (○) - device with CE backside coated with the reflective paint layer.

103

Figure 4.5 - Electrical analogue used to fit EIS data of DSC devices near the open-circuit voltage.

105

Figure 4.6 - a) Bode and b) Nyquist diagrams of device A obtained at 0.2 sun irradiation and at -0.75 V bias. Open symbols represent the experimental data; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 4.5. 106

Figure 4.7 - a) Bode and b) Nyquist diagrams of device B obtained at 0.2 sun irradiation and at -0.75 V bias. Open symbols represent the experimental data; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 4.5. 107

Figure 5.1 - Competing pathways in a working DSC: electron transport through the mesoporous semiconductor ($\rightarrow$) and electron recombination with electrolyte species ($\leftarrow$). 119

Figure 5.2 - Experimental photovoltaic characteristics of Cells A, B and C with front- (solid line) and rear-side (dashed line) irradiation. (a) I - V curves at 1 sun illumination (AM 1.5G, 100 mW cm^{-2}) and (b) incident photon-to-current-efficiency spectra (20 % light bias). 124

Figure 5.3 - Equivalent circuit used to fit the experimental impedance data in DSCs. The interfacial charge separation across a dye-sensitized heterojunction is represented by a distributed element (DX) shown in the inset. 127

Figure 5.4 - Impedance spectra of cells B and C at different applied potentials: (a) open-circuit potential; (b) maximum power point potential. Symbols correspond to the impedance data obtained experimentally under illumination, while solid lines represent the fittings based on the equivalent electrical circuit shown in Figure 5.3. Inset represents an enlargement of Figure 5.4(b). 128

Figure 5.5 - Electron transport resistance R_w , electron recombination resistance R_k and the capacitance C_μ obtained from impedance data, under 20 % illumination, as a function of the bias potential (corrected from the $I \cdot R$ drop due to series resistance) for (a) cell A, (b) cell B and (c) Cell C. 130

Figure 5.6 - Charge-collection efficiency η_{col} as a function of the bias potential calculated by means of Equation (5.2) for the three devices. 131

Figure 6.1 - Scheme of the modelled DSC. The TiO_2 nanoparticles that form the mesoscopic film are covered with light-absorbing dye molecules. The free volume between $x = 0$ (TCO/ TiO_2 interface) and $x = L$ (electrolyte/platinum interface) is filled with triiodide/iodide electrolyte. Here, TCO stands for transparent coating oxide, typically a fluorine-doped tin oxide film. 145

Figure 6.2 - Detail of the TCO/ TiO_2 interface ($x = 0$), showing the transport of electrons towards the TCO coating and, consequently, to the external circuit. Here, $x = 0^+$ refers to the surface close to the semiconductor; $x = 0^-$ refers to the external surface of the TCO layer. 149

Figure 6.3 - Schematic energy level diagrams of the TCO/ TiO_2 interface and electrolyte/platinised TCO under different operating conditions: (a) under dark equilibrium; (b) under illumination and applied bias lower than V_{oc} ; (c) under illumination at open-circuit conditions. 152

Figure 6.4 - Experimental and simulated I - V characteristics for the system described in Table 6.1, under 1 sun illumination. ($\blacktriangle$) Experimental performance parameters taken from Ref. 11; ($\square$) Simulated maximum power point. Solid and dashed lines correspond to the simulated I - V curve and power output, respectively. 158

Figure 6.5 - Simulated electron density profiles for the system characterised by parameters given in Table 6.1 under 1 sun illumination at short-circuit (SC), open-circuit (OC) and maximum power point (MPP) conditions. 160

Figure 6.6 - Simulated triiodide and iodide concentration profiles for the system characterised by parameters given in Table 6.1 under 1 sun illumination at short-circuit (SC), open-circuit (OC) and maximum power point (MPP) conditions. 160

Figure 6.7 - Transient electron density profiles simulated for the system characterised by parameters given in Table 6.1 under 1 sun illumination and at short-circuit conditions. ϑ is the dimensionless time variable; $\vartheta=1$ corresponds to the steady-state stage. 161

Figure 6.8 - Transient triiodide (solid line) and iodide (dashed line) concentration profiles simulated for the system characterised by parameters given in Table 6.1 under 1 sun illumination and at short-circuit conditions. ϑ is the dimensionless time variable; $\vartheta=1$ corresponds to the steady-state operation. (red - $\vartheta = 0.001$; blue - $\vartheta = 0.01$; green - $\vartheta = 1$) 162

Figure 6.9 - Influence of the dimensionless numbers (a) Da , (b) γ and (c) Φ on the DSCs' photovoltaic performance. 163

Figure 6.10 - Experimental and simulated Nyquist diagrams for the system described in reference 11. The single-frequency voltage perturbation was done at open-circuit conditions (0.638 V) with modulation signal magnitude of 10 mV. The input parameters used in the simulation are presented in Table 6.1. 166

Figure 7.1 - Schematic representation of the modelled PEC cell for photo-assisted water splitting. The TCO/semiconductor interface at $x = 0$ and the electrolyte/platinised TCO at $x = b$ define the limits of the photoanode and the cathode, respectively. The electrolyte solution fills the pores in the photoanode with thickness L and the free volume between $x = L$ and $x = b$. The dimensions of L and b are not in scale since $b \gg L$. 182

Figure 7.2 - Detail of the TCO/semiconductor interface at $x = 0$; $x = 0^+$ denotes the surface close to the semiconductor and $x = 0^-$ refers to the external surface of the TCO layer. 185

Figure 7.3 - Detail of the semiconductor/electrolyte interface at $x = L$. Here, $x = L^-$ and $x = L^+$ denote the limit of the interface semiconductor/electrolyte at the semiconductor and electrolyte sides, respectively. 189

Figure 7.4 - Energy diagram of PEC components with (a) no applied bias E_{Bias} ; (b) applied bias E_{Bias} but not enough for hydrogen evolution and (c) applied bias E_{Bias} enough to produce hydrogen. 194

Figure 7.5 - Experimental (solid line) and simulated (dashed line) I-V characteristic for the system described in Table 7.1 ($\eta_{inj} = 0.93$), under 1 sun back-illumination. The experimental curve was taken from Ref. 35, Figure 6, dashed curve labelled “1’bc no si”. 198

Figure 7.6 - Experimental (solid line) and simulated (dashed line) I-V characteristics for a PEC cell characterised by parameters given in Table 7.1 ($\eta_{inj} = 0.90$), under 1 sun front-side illumination. The experimental curve was taken from Ref. 35, Figure 6, solid curve labelled as “1’ no Si”. 200

Figure 7.7 - Simulated electron density profiles for the system characterised by parameters given in Table 7.1 under 1 sun back-side illumination at 1.23 V. 201

Figure 7.8 - Transient electron density profiles for the system characterized by parameters given in Table 7.1 under 1 sun back-illumination at 1.23 V. Density profiles are presented as a function of dimensionless time ϑ (0.001 -1). 202

Figure 7.9 - Effect of the electrolyte layer thickness in the photocurrent density produced by the PEC cell system under study. The solid curve ($b \approx 10$ mm) is the base case presented in Table 7.1 and in Figure 7.5. 203

Figure 7.10 - Effect of the diffusion length value in the photocurrent density produced by the PEC cell system under study. The solid curve for $L_n = 3$ is the base case presented in Table 7.1 and in Figure 7.5. 204

Figure 7.11 - Relation between the characteristic curves with the correspondent platinum overpotentials at the counter electrode for back- (dashed line) and front-side illumination (solid line). 206

Figure 7.12 - Effect of the transfer coefficient in the photocurrent density produced by the PEC cell system under study. The solid curve for $\beta = 0.5$ is the base case presented in Table 7.1 and in Figure 7.5.	207
Figure 7.13 - Logarithmic representation of the current density <i>versus</i> overpotential for the platinum counter-electrode and for high values of η_{Pt} - Tafel plots.	208
Figure 8.1 - Scheme of a standard DSC/PEC tandem cell configuration.	221
Figure 8.2 - Scheme of the test bench for PEC cell's characterisation.	223
Figure 8.3 - I - V characteristic for the system N719/PMII electrolyte measured at AM 1.5G (100 mW cm^{-2}) global sunlight illumination.	226
Figure 8.4 - a) Bode and magnitude diagrams; b) Nyquist diagram. Open symbols represent experimental data obtained in the dark under 0.75 V bias; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 8.5.	228
Figure 8.5 - Electrical analogue used to fit EIS experimental data, with a simplified transmission line model. ²⁹	230
Figure 8.6 - I - V characteristic for the PEC + DSC tandem cell measured at AM 1.5 (100 mW cm^{-2}) global sunlight illumination.	232
Figure 9.1 - Example of an architectural application of DSCs. ¹	246

TABLE CAPTIONS

Table 2.1 - Systems under study.	56
Table 2.2 - Detailed photovoltaic parameters under various sunlight intensities. The active area of the cell with a metal mask was 0.158 cm^2 .	56
Table 2.3 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 2.6.	64
Table 3.1 - Parameters determined by fitting the EIS experimental data of device A to the equivalent circuit shown in Figure 3.4.	86
Table 4.1 - Photovoltaic parameters for devices A (semitransparent photoanode) and B (double-layered film photoanode), with and without reflective materials (paint or aluminium foil), at 1 sun illumination (100 mW cm^{-2} , AM 1.5G).	101
Table 4.2 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 4.5. Measurements performed under illumination and at open-circuit voltage.	108
Table 5.1 - Collection efficiency values calculated based on IPCE measurements with front- and rear-side irradiation.	125
Table 5.2 - Calculated collection efficiencies based on $\text{IPCE}^{(*)}$ and EIS measurements (at short-circuit conditions) for cells A, B and C. The corresponding efficiency at the maximum power point (MPP) is also presented.	132
Table 6.1 - Simulator input parameters.	157
Table 7.1 - Simulator input and fitting parameters.	199
Table 8.1 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 8.5.	230

PART I:

INTRODUCTION

Chapter 1.

INTRODUCTION

The world power consumption is currently about 13 TW and it is expected that an additional 10 TW will be required in 2050.¹ Moreover, the *Gas Crisis* at the beginning of 2006 has demonstrated that world, and in particular Europe, is still highly vulnerable with respect to its total energy supply. On the other hand, this energetic paradigm is also being hastened by severe climatic consequences of the greenhouse effect caused by fossil fuels combustion and by the environmental effects of several oil spills that have happened in the last years. A possible solution to this quest is the diversification of energy sources including renewable energies, such as thermal solar energy and photovoltaics (PV). In fact, the solar resource in Europe and worldwide is abundant and is the only offering the perspective of a significant cost reduction in the near future. The year of 2008 was a record year for solar PV sales, with an increase of 5.7 GW installed capacity. Actually, since 2003, the total PV production grew in average by almost 50 %, whereas the thin-film PV segment grew in average by over 80 % reaching 400 MW, *i.e.* 10 % of the total PV production in 2007.² The high growth rate of thin-film production clearly shows that this technology is gaining more and more acceptance in the PV worldwide market.² Dye-sensitized solar cells (DSCs) are an important type of thin-film photovoltaics due to their potential for low-cost fabrication and versatile applications, such as flexible or light-weight products.³

The present chapter introduces and reviews the state-of-the-art of photovoltaic technologies and, in particular, of DSCs. The structure and operating mechanisms of dye-sensitized solar cells will be discussed in detail. Finally, the main goals of the present work are addressed.

1.1 A brief history of photovoltaics & State of the art

The history of photovoltaics started in 1839 with the work developed by the French physicist Alexandre Edmond Becquerel, who noticed the generation of an electric current between two platinum electrodes immersed in an illuminated solution containing a metal halide salt.⁴ In 1873, the photovoltaic effect in selenium was observed by Willoughby Smith.⁵ William Grylls Adams and his student Richard Evans Day discovered in 1876 the photovoltaic effect illuminating a junction between selenium and platinum, which resulted in the construction of the first selenium solar cell in 1877.⁶ The American inventor Charles Fritts described this cell in detail for the first time six years later. Despite these photovoltaic cells show less than 1 % conversion of incident light into electric power and age quickly, they are landmarks in the development of this technology. The theory behind the photovoltaic phenomenon was first described by Albert Einstein in 1904, which won him the Nobel Prize in 1921.⁷ During the same year, Wilhelm Hallwachs presented the first prototype of thin-film Schottky barrier devices combining copper and cuprous oxide. In 1916, Robert Millikan provided experimental proofs of the photoelectric effect. Two years later, Jan Czochralski developed the “*Czochralski method*”, a cornerstone of modern materials science, published in a work entitled “*A new method for the measurement of the crystallisation rate of metals*” in 1918.⁸ The photovoltaic effect in cadmium-selenide was observed in 1932.⁹ Some years later, the *Bell Laboratories* used the “*Czochralski method*” to grow single germanium crystals, introducing the use of this method in the production of suitable semiconductors. The first germanium solar cell was produced in 1951.

The “*Solar Age*” began in fact in the 1950’s with the advent of silicon technology by *Bell laboratories*. In 1954, at the *Bell Labs* Daryl Chapin, Calvin Fuller, and Gerald Pearson developed the first high-power silicon PV cell with 6 % efficiency - much more efficient than the first selenium solar cell.¹⁰ Their demonstration inspired in 1954 the New York Times article to predict that solar cells would eventually lead “*to the realisation of one of mankind's most cherished dreams - the harnessing of the almost limitless energy of the sun*”.¹⁰

Until 1970's, important improvements in the silicon PV devices were developed mainly by the *Hoffman Electronics* company. They reported efficiencies of 8 % in 1957, 9 % just one year later, 10 % in 1959 and a record efficiency of about 14 % in 1960. In parallel, the development of a satellite energy supply system using solar cells was initiated. In 1958, *Vanguard I*, the first PV-powered satellite was launched in cooperation with the *U.S. Signal Corp.* The satellite power system operated for 8 years. After *Vanguard I* many progresses in the space field happened: in 1964 the *Nimbus* spacecraft was launched with a 470 W PV array; in 1966 the *Orbiting Astronomical Observatory* was launched with a 1 kW PV array; in 1968 the *OVI-13* satellite was launched with two CdS panels. However, the cost of the photogenerated electricity was so high that this newly born technique became a privilege, only used in extraterrestrial applications. Only in 1970 the research allowed a reduction of about 80 % in the PV cost, enlarging its applications.¹⁰

The energy crisis in the 1970's boosted the research and development of several technologies for producing energy from renewable sources, including photovoltaics. Moreover, some photovoltaic companies were established in the energy market, like *Solar Power Corporation* in 1972, *Solarex Corporation* in 1973 and *Solec International* and *Solar Technology International* in 1975.¹⁰ During this period, the second generation solar cells emerged, solving some of the main problems of the first generation solar cells: these single junction devices involve high energy and labour inputs, which make them rather unviable because of the elevated costs. In opposition, since cadmium telluride (CdTe), copper indium gallium selenide (CIGS), copper indium diselenide (CIS), polycrystalline and amorphous silicon can be applied as thin-films over a substrate such as glass or ceramics, the costs are much lower.

In the 1990's large-scale solar cell producers established in the PV market and the world biggest photovoltaic system was planned. The third generation solar cells technologies, aiming to enhance poor electrical performance of second-generation thin-film technologies, began in this decade. This new generation of solar cells centres on nanotechnology for lowering the costs and includes polymer solar cells, dye-sensitized solar cells and nanocrystalline solar cells.

Progressive efforts pushing photovoltaics to a competitive position in the energy market have allowed an outstanding growth over the last 10 years and it is expected to increase by 25 to 30 % per year in the next decades.¹¹ In fact, in 2004, five manufacturers - *Sharp, Kyocera, Shell Solar, BP Solar* and *RWE SCHOTT Solar* - accounted for 60 % of the PV market. So, while traditional energy sources will become more expensive, PV is becoming much more competitive due not only to technology improvements but also to economies of scale.¹¹

In the early days of photovoltaics, Becquerel's research was in fact motivated by photography. Actually, there is an interesting convergence of photography and photoelectrochemistry since both phenomena are based on a photoinduced charge separation in a liquid-solid interface. However, before being aware of such similarities, and following the experiments developed by Becquerel, Vogel discovered in 1873 that silver halide emulsions sensitized by a dye result in an extended photosensitivity to longer wavelengths.¹² Four years later, J. Moser was the first to report the dye-sensitized photovoltaic effect.¹³ Nevertheless, the modern photoelectrochemistry was only envisaged as an interesting topic for the research community after the works developed by Brattain and Garret¹⁴ and mainly with the first detailed electrochemical and photoelectrochemical studies on the semiconductor-electrolyte interface undertaken by Gerischer.¹⁵ Since then several attempts were made to use dye-sensitized photoelectrochemical cells to convert sunlight into electricity. However, the efficiency of those devices was very low, well below 1 %, mainly due to the poor light harvesting and instability of the dyes employed. In 1991, Brian O'Regan and Michael Grätzel described for the first time a three dimensional (bulk) heterojunction applied to the fabrication of DSCs. This new device was based on the use of semiconductor films consisting of nanometre-sized TiO₂ particles, together with newly developed charge-transfer dyes. These authors report an astonishing efficiency of more than 7 %.¹⁶

Despite the exciting progresses in photoelectrochemistry and particularly in the field of DSCs, so far the conversion of sunlight into electrical power has been widely dominated by solid-state crystalline silicon solar cells. As mentioned before, dye-

sensitized solar cells are a new thin-film generation of photovoltaic devices, differing from the conventional photovoltaic technologies in what concerns the light absorption function, which is separated from the charge carrier transport. Since the work published in 1991,¹⁶ these cells have attracted the interest of the scientific community not only because of their simple and low-cost fabrication process, but also due to their excellent performance under both direct and diffuse light conditions. At present, a certified efficiency of 11.1 % under standard reporting conditions - Air Mass (AM) 1.5 global sunlight, 100 mW cm^{-2} , 298 K - has already been reported, allowing DSCs to become a credible alternative to conventional photovoltaic devices.¹⁷

1.2 Dye-sensitized Solar Cells ¹

1.2.1 Structure and working principles

In a conventional p-n junction photovoltaic cell the semiconductor assumes simultaneously the function of harvesting sunlight to create an electron-hole pair and the transport of charge carriers - Figure 1.1a). On the other hand, in dye-sensitized solar cells the dye is the element responsible for light absorption and charge generation, while charge transport occurs both in the semiconductor and in the electrolyte - Figure 1.1b).

In DSCs, the semiconductor (also named photoelectrode or working electrode - WE) is a mesoporous oxide layer composed of nanometre-sized particles which have been sintered together to allow electronic conduction. Attached to the surface of the oxide is a monolayer of dye molecules (sensitizer), which upon light absorption are promoted into an excited state. As a result, electrons from the valence band (VB) are

¹ Andrade, L.; Ribeiro, H. A.; Mendes, A. (2010) Dye-Sensitized Solar Cells: an Overview, in Energy Production and Storage: Inorganic Chemical Strategies for a Warming World, edited by Robert H. Crabtree. Chichester, UK: John Wiley & Sons, Ltd, pp 53-72.

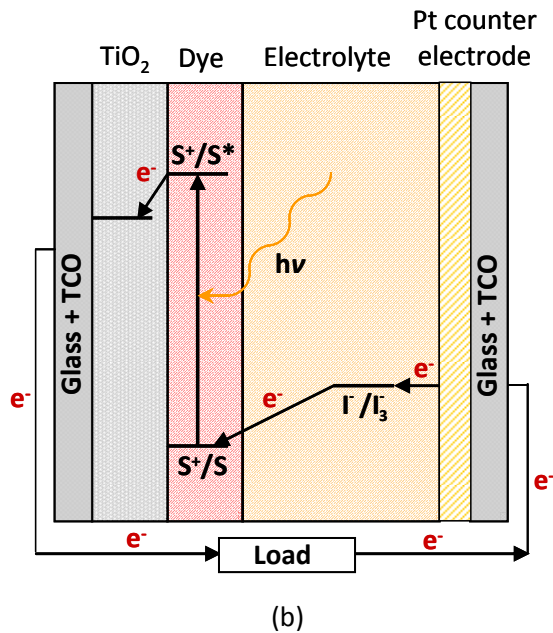
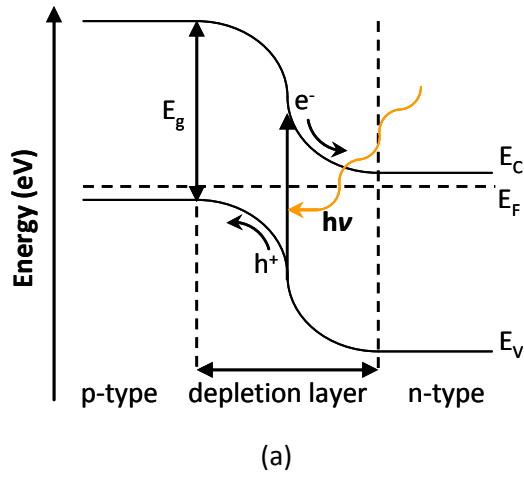


Figure 1.1 - (a) Energy band scheme of a p-n junction solar cell; (b) principle of operation of a dye-sensitized solar cell. E_g - bandgap energy; E_V - valence band energy; E_C - conduction band energy; E_F - semiconductor Fermi energy; e^- - electrons; h^+ - holes; S - ground state of the sensitizer; S^* - excited state of the sensitizer; S^+ - oxidised sensitizer; TCO - transparent conductive oxide.

injected into the conduction band (CB) of the semiconductor, giving rise to formation of excitons (excited electrons) and subsequent charge separation - Figure 1.1b). The free electrons in the conduction band diffuse across the semiconductor towards the external circuit, performing electrical work. Once electrons reach the counter electrode (CE), typically a thin layer of platinum, they react with the electrolyte that fills the space between the two electrodes, usually a solution of an ionic liquid solvent containing a triiodide/iodide redox system. The original state of the oxidized dye is subsequently restored by electron donation from the electrolyte, which is itself regenerated at the platinum counter electrode by reduction of triiodide.¹⁸⁻²¹ The redox electrolyte therefore allows the transport of electrical charge between the two electrodes of the DSC, closing the cycle.

The efficiency of a DSC is strongly determined by the electronic energy levels of the excited state (LUMO) and the ground state (HOMO) of the dye, by the electron Fermi level of the semiconductor and by the redox potential of the electrolyte. Moreover, an operating DSC is largely governed by the relative kinetic rates of several charge transfer processes. Figure 1.2 shows the sequence of the charge transfer processes responsible for the operation of a DSC:²²

1. The photosensitizer, adsorbed on the surface of the semiconductor, absorbs incident sunlight becoming excited from the ground state (S) to the excited state (S*).



2. Excited electrons are injected into the conduction band of the semiconductor, resulting in the oxidation of the sensitizer (S⁺).



3. The oxidised sensitizer (S⁺) is regenerated by accepting electrons from the iodide ion.



4. The triiodide redox mediator diffuses towards the counter electrode and is reduced to iodide.



Additionally to the forward electron transfer and ionic transport processes, several competing electron loss pathways should be considered:

5. Dye excited-state decay to ground state.



6. Recombination of injected electrons with dye cations.



7. Recombination of injected electrons with the triiodide redox mediator.

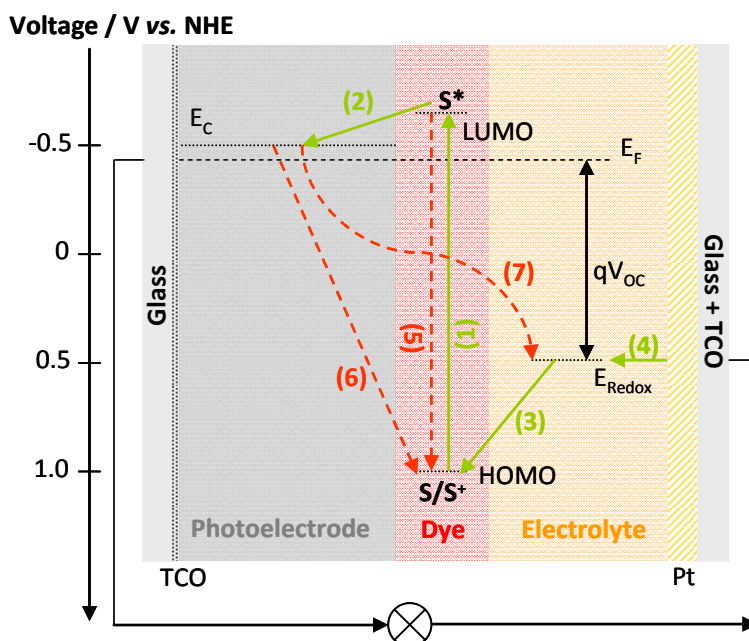


Figure 1.2 - Schematic diagram of the operation kinetics of DSCs: forward electron transfer (—→) and electron loss pathways (---→). The photovoltage, V_{OC} , of the system corresponds to the difference between the TiO_2 Fermi energy, E_F , and the redox energy of the electrolyte, E_{Redox} .

For efficient photoconversion of solar energy into electric current, the charge injection must occur with unit quantum yield (parameter denoting the fraction of photons absorbed by the dye that are converted into conduction band electrons). Thus, the excited state of the dye must lie energetically above the conduction band edge of the semiconductor to guarantee fast electron injection into the semiconductor, before it can fall back to its ground state - reaction (1.5). The rate of electron injection depends on the electronic coupling between the dye LUMO orbital and the accepting states in the semiconductor.²³⁻²⁵ Time-resolved laser spectroscopy measurements are used to study the kinetics of electron injection from sensitizers into the conduction band of the semiconductor. Since typical rates of dye excited-state decay to ground state are in the range 10^7 - 10^{10} s⁻¹ and electron injection rates higher than 10^{12} s⁻¹ have been already reported,²⁶⁻²⁷ efficient electron injection is therefore achieved - Figure 1.3. On the other hand, the oxidised dye must have a more positive potential than the redox couple in the electrolyte. Thus, the regeneration of the dye by the redox electrolyte must be fast in order to prevent recombination of the injected electrons with the oxidised dye - reaction (1.6). This recombination reaction strongly depends on the electrons density in the semiconductor and is naturally undesirable because, instead of electrical current, it simply generates heat. The regeneration reaction is dependent on the iodide concentration, electrolyte viscosity and dye structure.²⁸

The redox electrolyte is responsible for the regeneration of the dye, which becomes oxidised by electron injection to the TiO₂ conduction band, and conducts the positive charges (holes) to the counter electrode, where the redox-couple itself is regenerated. Consequently, for these processes take place, several requirements must be fulfilled. Since the photovoltage of the system corresponds to the difference between the redox potential of the electrolyte and the TiO₂ Fermi level, the redox potential must be as positive as possible in order to guarantee high photovoltages - Figure 1.2. In contrast, the overvoltage required for triiodide reduction at the counter electrode should be small, since it represents a loss in the photovoltage of the cell.

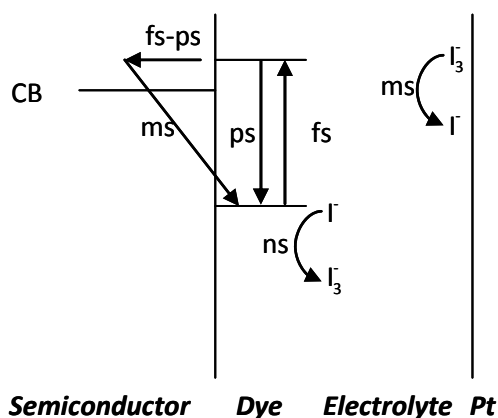


Figure 1.3 - Kinetics of the electron transfer processes at the different interfaces in DSCs. *CB* labels the conduction band edge.

Moreover, to overcome the problem related to possible slow charge-transfer reaction at the counter electrode, a platinum-based catalyst is usually employed.

An efficient DSC also requires that electron transport within the mesoporous semiconductor has to be faster than charge recombination of injected electrons with the redox couple - reaction (1.7). In fact, this is the most predominant loss pathway to be considered in DSCs, hampering the achievement of higher efficiencies - dark current. Dark current often occurs at the semiconductor/electrolyte interface where the sensitizer is not adsorbed. To avoid this phenomenon, pyridine derivatives, such as *tert*-butylpyridine (TBP), are used as coadsorbates on the TiO_2 surface, resulting in the improvement of the photovoltage of the cell.

1.2.2 Overview of materials in DSCs devices

Semiconductor

The semiconductor, typically a metal oxide, is responsible for providing the surface for dye adsorption, for accepting electrons from the excited dye and for conducting them towards the external circuit. This semiconductor layer is typically obtained by applying a paste of metal oxide nanocrystalline particles over a conducting substrate by screen-printing or doctor-blading.²⁹ Its structure plays a crucial role in harvesting

sunlight. The use of high surface area films of nanocrystalline oxide particles, with an average size of about 20 nm, leads to a quite significant surface area available for dye adsorption, responsible for the absorption of a high percentage of the incident sunlight. In contrast, flat electrodes promote very low light harvesting levels due to the small absorption cross section of a monolayer of dye, which results in quite low photovoltaic efficiencies. A suitable degree of porosity is also needed to promote good contact between the dye molecules adsorbed onto the semiconductor nanoparticles and the electrolyte species, ultimately ensuring the regeneration of the dye. Moreover, the porous film must form an interconnected network of nanoparticles to allow the percolation of the injected electrons. In addition, the position of the conduction band edge is also important and must allow charge injection from the excited state of the dye.

Titanium dioxide is the preferred semiconductor for application in DSCs. Although some promising properties exhibited by other semiconducting oxides, like ZnO or SnO₂, TiO₂ is still the cornerstone semiconductor for DSCs' photoelectrodes.³⁰ Two crystalline forms of TiO₂ are normally considered: anatase and rutile. However, the former is preferable since it has a wider bandgap energy of about 3.2 eV and an absorption edge that makes it insensitive to visible light. In fact, this prevents the generation of holes by bandgap excitation which would act as oxidants. In what concerns rutile, it has a lower bandgap (≈ 3.0 eV), higher dark current and absorbs part of the near-UV region, making rutile less chemically stable.³¹⁻³² Furthermore, anatase crystalline form is non-toxic, thermally stable, chemically inert, readily available and cheap.³³⁻³⁴

Bearing in mind that the main loss pathway is the dark current due to reaction of injected electrons with triiodide ions, modified nanocrystalline TiO₂ structures are being developed in order to avoid this recombination pathway. This fact leads to the growing of an emergent and interesting field in DSCs: incorporation of nanotubes,³⁵⁻³⁸ nanowires,³⁹ nanorods⁴⁰⁻⁴¹ and inverse opals⁴²⁻⁴³ in conventional electrodes for dye solar cells. These ordered and oriented structures enhance the electrical conductivity in TiO₂ photoelectrodes, increasing electron percolation through the film.⁴⁴ In

addition, highly ordered nanostructures seem to induce stronger internal light-scattering effects, resulting in higher light harvesting efficiencies. It should be noted however, that defect-mediated recombination may also be promoted in these nanostructures, which means that high crystal quality must be ensured to yield a better performance of the photovoltaic device. Another way to prevent the recapture of photoinjected electrons by triiodide ions is the use of a “blocking layer”, made of semiconductors that have a more negative conduction band than TiO_2 , *e.g.* Al_2O_3 ⁴⁵ or MgO ⁴⁶. The idea is to block the surface with an insulator layer, allowing electron injection but diminishing the interfacial recombination kinetics that limits the overall performance.³ Several surface treatments are also being considered in order to control the unfavourable dark current and increase the photocurrent output. Ito *et al.*⁴⁷ observed that these treatments improve the short-circuit photocurrent density, J_{SC} , by enlarging the surface area of the mesoscopic film. Finally, the use of light-scattering layers is also quite common. It consists of larger titania particles (between 100 and 400 nm) that work as a phototrapping system.⁴⁷⁻⁴⁸ In fact, when using light scattering particles, Koo *et al.*⁴⁹ observed efficiency increments of about 15 %.

Dye

Since in DSCs the function of light absorption is separated from the charge carrier transport, the dye should have a broad absorption spectrum in order to capture solar radiation as much as possible: the ideal dye should absorb light at wavelengths up to 920 nm (equivalent to a semiconductor with a bandgap of approximately 1.4 eV).⁵⁰ To prevent energy losses and to maximise the cell photovoltage, the excited state should be only slightly above the conduction band of the semiconductor but sufficiently above to produce an energetic driving force that ensures electron injection - Figure 1.2. In the same way, the ground state of the dye should be only slightly below the redox potential of the electrolyte to ensure an efficient regeneration process.⁵¹ In addition, the dye should present long stability (it must endure at least 10^8 redox turnovers, corresponding to about 20 years of operation), good adsorption to the

semiconductor's surface, high solubility in the corresponding solvent and no toxicity.^{18,34}

Up to now, sensitizers based on bipyridyl complexes of ruthenium have been widely used due to their advantageous spectral properties, photostability in the final device and high energy conversion efficiencies.⁵²⁻⁵⁵ An example of high performance ruthenium polypyridine complexes is the cis-dithiocyanato bis (4, 4'-dicarboxylic acid - 2, 2'-bipyridine) ruthenium(II), commonly known as the N3 dye. The carboxylate groups in N3 dye confer a strong binding to the TiO₂ surface, explaining its excellent stability, while the isothiocyanato (NCS) groups enhance its response to visible light. For an N3-based dye-sensitized solar cell, the measured incident photon-to-current conversion efficiency (IPCE) values exceeds 80 % in the wavelength range between 480 and 600 nm, reaching 85-90 % between 510 and 570 nm.^{39,56-58} Since the development of the N3 dye in 1993,⁵⁶ its tetrabutylammonium (TBA) salt N719 has been used as the standard red dye because of its unmatched performance.⁵⁹ This dye is derived from the N3 form by substituting two protons with two TBA cations. Based on intensive efforts to enhance spectral response in the red and near-IR region, the dye tris(cyanato)-2,2',2''-terpyridyl-4,4',4''-tricarboxylate) Ru(II), also called black dye, was developed. TiO₂/black dye-based DSCs show IPCE values around 80 % over a broad wavelength range extending from 400 to 700 nm.⁶⁰ More recently, the amphiphilic ruthenium dye Z907⁶¹ and the high molar extinction coefficient dye K19⁶² have attracted researchers' attention.

Although high efficiency and stability have been achieved with ruthenium-based dyes, alternatives should also be considered. In fact, due to its scarcity, ruthenium is a very expensive metal. Organic dyes, such as porphyrins, phthalocyanines, cyanines and merocyanines, can be a promising alternative since they are much cheaper than ruthenium compounds.⁶³⁻⁶⁴ However, the efficiency and stability achieved with these compounds is still very low.⁶⁵

Semiconductor quantum dots are another attractive option. Quantum dots are a non-traditional type of semiconductors with limitless applications due to their particle sizes that are small enough to produce quantum confinement effects. By changing the

particle size, different absorption spectra is obtained. Furthermore, quantum dots have a very high extinction coefficient when compared with conventional dyes, allowing the use of thinner mesoporous oxide films. The main disadvantage is the possibility of photocorrosion when the junction contact is a liquid electrolyte, mainly due to the aggressive nature of the electrolyte employed.⁶⁶

Despite all efforts made up to now concerning the improvement on photovoltaic performance and stability, it is still mandatory to find novel efficient and stable sensitizers.

Electrolyte

The redox couple in the electrolyte has the function of regenerating the dye after electron injection into the conduction band of the semiconductor, as well as to transport the positive charges (holes) towards the counter electrode. The most used liquid electrolyte in DSCs is based on the charge mediator I_3^-/I^- redox couple in acetonitrile, a low-viscosity volatile solvent. In fact, its redox potential is energetically favourable with respect to redox potential of several oxidised ruthenium-based dyes and fully organic sensitizers, which contributes for maximising the cell voltage.⁶⁷ The electrolyte mediator should not absorb in the visible range to prevent competition with the sensitizer. Since the maximum photovoltage of the cell is determined by the redox potential edge of the electrolyte, it should be as positive as possible to provide high photovoltages. While in the counter electrode the redox couple must be reversible, in the semiconductor it should be inert. The redox couple should be highly soluble in the solvent to ensure high concentration of charge carriers in the electrolyte. Additionally, the solvent should allow fast diffusion of the charge carriers and should not contribute to desorption of the dye from the surface of the semiconductor.

The electrolyte characteristics strongly affect the overall operation of the DSC mainly due to its influence in the mass transport of charge carriers. In fact, the electrolyte participates in the electron transfer kinetics at the counter electrode (the maximum current density is normally achieved when the reduction of I_3^- occurs as fast

as it can be supplied by diffusion to the counter electrode); strongly controls the dark current reactions and determines the charge transport in the pores of the film semiconductor and in solution (dependent not only on the viscosity of the electrolyte but also on the structure of the semiconductor). The photovoltage can also be affected by non-electroactive species in the electrolyte, particularly by cations that can adsorb onto the surface of the TiO_2 electrode, shifting its conduction band edge to a lower energy level. This can lower the photovoltage, but enhance the efficiency of interfacial charge injection, increasing the photocurrent and the efficiency of the DSC.⁶⁸

Despite solid and quasi-solid state electrolytes have recently been developed and improved, liquid electrolytes are still the most commonly used. However, the latter require efficient encapsulation of the DSC, necessary to prevent the loss of electrolyte by leakage and/or evaporation of the solvent. This is in fact the major drawback for long-term stability of DSCs, with important consequences to the market implementation of the technology. Bearing this in mind, several efforts have been developed in order to overcome this problem: TiO_2 DSCs assembled with non-volatile electrolytes based on ionic liquids (commonly known as robust electrolytes) instead of the typical organic solvents seems to be a good solution. In fact, ionic liquids have good chemical and thermal stability, negligible vapour pressure, nonflammability, high ionic conductivity and high solubility for organic or inorganic materials.²¹ Despite the recent advancements⁶⁹⁻⁷¹ the high viscosity of the common electrolytes limit their applications, ultimately reducing the efficiency of the cells.

Counter electrode

At the CE the reduction of triiodide to iodide takes place - reaction (1.4). However, to ensure fast reaction kinetics and to overcome the high activation energy of the two-electron transfer, a catalyst is needed. Platinum is traditionally used as the most efficient catalyst not only because it provides high exchange current densities, but also because it is transparent. The deposition method of the platinum catalyst onto the TCO substrate influences its performance. In fact, it has been found that platinum

become unstable in the presence of the iodide electrolyte when coated electrochemically or by vapour deposition.⁷²⁻⁷³ Since platinum is very expensive some other cheaper alternatives are also being studied. Among other materials, carbon,⁷⁴ carbon black,⁷⁵ graphite,⁷⁶ activated carbon⁷⁷ or single-wall carbon nanotubes⁷⁸ and conductive polymers⁷⁷ have been used as counter electrodes in DSCs. Moreover, the CE is normally chosen bearing in mind the final application of the DSC. For instance, for DSCs incorporated in power-producing windows, a transparent CE should be employed; for inexpensive DSCs, a low cost material like a carbon catalyst should be used; or for very efficient cells, a material with the lowest possible sheet resistance and with high rate of redox electrolyte reduction should be considered.⁷⁵

1.3 Photovoltaic characterisation and electrochemical techniques²

1.3.1 Current-voltage characteristic

An experimental I - V curve is shown in Figure 1.4, together with the respective power curve. The overall conversion efficiency (η_{global}) of a dye-sensitized solar cell is determined by the photocurrent density measured under short-circuit conditions (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF) and the intensity of incident light (I_s):

$$\eta_{global} = \frac{J_{sc} V_{oc}}{I_s} FF \quad (1.8)$$

Under full sunlight (1 sun, AM 1.5 global) the incident light intensity I_s is 100 mW cm^{-2} .

The power curve is calculated as the product of current density by voltage and the maximum-power point (MPP) is labelled with a dot in Figure 1.4. At this point, the device delivers the highest power output with voltage V_{MPP} and current I_{MPP} . The fill

² Andrade, L.; Ribeiro, H. A.; Mendes, A. (2010) Dye-Sensitized Solar Cells: an Overview, in Energy Production and Storage: Inorganic Chemical Strategies for a Warming World, edited by Robert H. Crabtree. Chichester, UK: John Wiley & Sons, Ltd, pp 53-72.

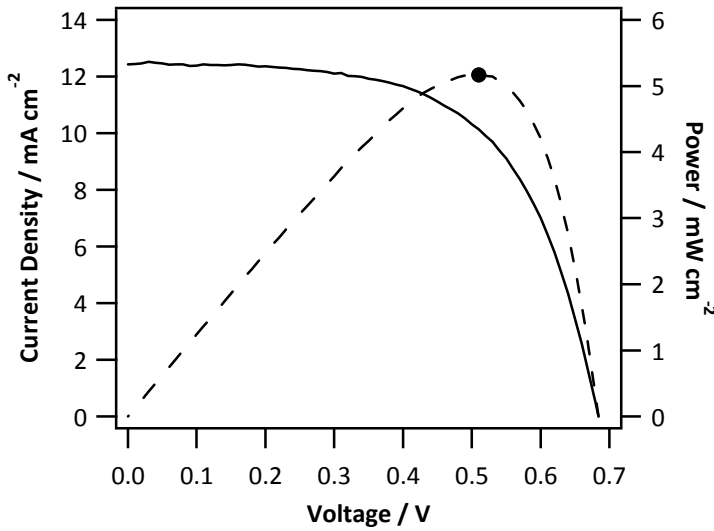


Figure 1.4 - Typical I - V curve (solid line) and respective power curve that shows the cell's power output at different voltage bias (dashed line). The full dot in the power curve indicates the maximum-power point (MPP) of the cell.

factor is the ratio of solar cell's actual power to that obtained from its I_{sc} and V_{oc} :

$$FF = \frac{I_{MPP} V_{MPP}}{I_{sc} V_{oc}} \quad (1.9)$$

The I - V characteristic determines the current voltage response of the device in the dark and under different light conditions. The behaviour of the cell under different operating conditions should be considered: at maximum-power point, at dark equilibrium, at open-circuit and at short-circuit conditions. The power output from a DSC operating at its maximum-power point requires not only efficient charge collection and subsequent electric current generation, but also setting-up a photovoltage corresponding to the difference between the quasi-Fermi level of electrons in the semiconductor and the redox energy of the electrolyte. On the other hand, in the dark, there is neither voltage nor current generation. The Fermi level energy of electrons in the conduction band equilibrates with the redox energy of the electrolyte. When the cell operates under illumination and at open-circuit conditions, there is no current flowing through the external circuit. In this case, the injection and recombination rates are in equilibrium in the TiO_2 mesoporous structure.

Consequently, all injected electrons are recaptured by triiodide ions, the oxidised dye is regenerated by iodide and there is no electron transfer from the platinum counter electrode to the triiodide ions.⁷⁹ On the other hand, under short-circuit conditions the current generated by the cell is measured at an applied potential of zero volts. The short-circuit current is a function of the illumination intensity.

1.3.2 Incident photon-to-current conversion efficiency

The incident photon-to-current conversion efficiency (IPCE) is defined as the ratio of the number of photogenerated electrons flowing in the external circuit ($N_{electrons}$) to the number of incident photons with a given wavelength ($N_{photons}$):

$$IPCE(\lambda) = \frac{N_{electrons}}{N_{photons}} \quad (1.10)$$

Substituting now the photocurrent definition as the amount of electrical charge transferred per time unit ($I_{sc} = qN_{electrons}/t$) in the previous equation, the IPCE is therefore defined as:

$$IPCE(\lambda) = \frac{N_{electrons}}{N_{photons}} = \frac{qN_{electrons}/t}{qN_{photons}/t} = \frac{I_{sc}}{qN_{photons}/t} \quad (1.11)$$

where q is the elementary charge, I_{sc} is the photocurrent and t is the time.

The number of incident photons with a given wavelength relates to the power of the incident light (P_{inc}) by Equation (1.12):

$$P_{inc} = \frac{N_{photons}}{t} h\nu = \frac{N_{photons}}{t} h \frac{c_0}{\lambda} \quad (1.12)$$

where h is the Planck constant, ν is the frequency, c_0 is the speed of light and λ is the wavelength. Substituting Equation (1.12) into Equation (1.11), the IPCE value can be rewritten as:

$$IPCE(\lambda) = \frac{I_{sc}}{q\lambda P_{inc} / hc_0} = \frac{I_{sc} hc_0}{P_{inc} q\lambda} = \frac{I_{sc}}{P_{inc}} \frac{1240}{\lambda} \times 100\% \quad (1.13)$$

Finally, the photon-to-current conversion efficiency may be expressed as a function of three efficiency parameters:

$$IPCE(\lambda) = \eta_{abs}(\lambda) \eta_{inj}(\lambda) \eta_{col}(\lambda) \quad (1.14)$$

where η_{abs} is the light absorption efficiency of the dye, η_{inj} is the quantum yield of electron injection and η_{col} is the efficiency of collecting the injected electrons at the conducting glass substrate.⁸⁰ High efficient cells can achieve very high IPCE values over a broad range of the visible spectrum, which implies that injection and collection efficiencies are close to 100 % after taking into account reflection losses at the glass surface.⁵⁶

1.3.3 Phototransient measurements

Phototransient measurements can be used to determine the recombination rate constants. In a transient photoelectrical decay experiment, a light transient of small amplitude is used to probe the device that is under equilibrium and monitor the decay kinetics. Two diodes are used in phototransient measurements: a red light diode to generate a voltage perturbation near the open-circuit photovoltage (V_{oc}) of the cell and a white bias light produced by an array of white light emitting diodes. Figure 1.5 sketches a phototransient setup.⁸¹

Electron transport properties and electron lifetime in DSCs have been modelled taking into account the influence of intraband charge traps, *i.e.* assuming that the majority of photoinjected electrons are localised in trap states and that they are conducted towards the external circuit by means of trapping/detrapping events.⁸²⁻⁸⁴ For mesoporous TiO_2 , the electron diffusion coefficient, the electron lifetime and the chemical capacitance are significantly influenced by traps. It is therefore important to infer the trapping conditions for the system under study in order to assess its influence on the photovoltaic performance. On the basis of the trapping/detrapping model, longer electron lifetimes and smaller capacitances can be interpreted as higher trap densities and/or different trap distributions.⁸⁵

Normally, the transient signals follow a mono-exponential decay, thus the recombination rate constant k_e^- can be extracted from the slope of the semi-logarithmic plot. The chemical capacitance (C_μ) of the TiO_2 /electrolyte interface and

density of states at the V_{oc} are calculated by $C_{\mu} = \Delta Q / \Delta V$, where ΔV is the peak of the photovoltage transient and ΔQ is the number of electrons injected during the red light flash step of the photoelectrical decay experiment. ΔQ is obtained by integrating the transient of a short-circuit photocurrent generated from an identical red-light pulse.⁸⁶ Moreover, the electron density in the titania film irradiated with a white light of a given intensity is measured by the charge extraction method.⁸⁷

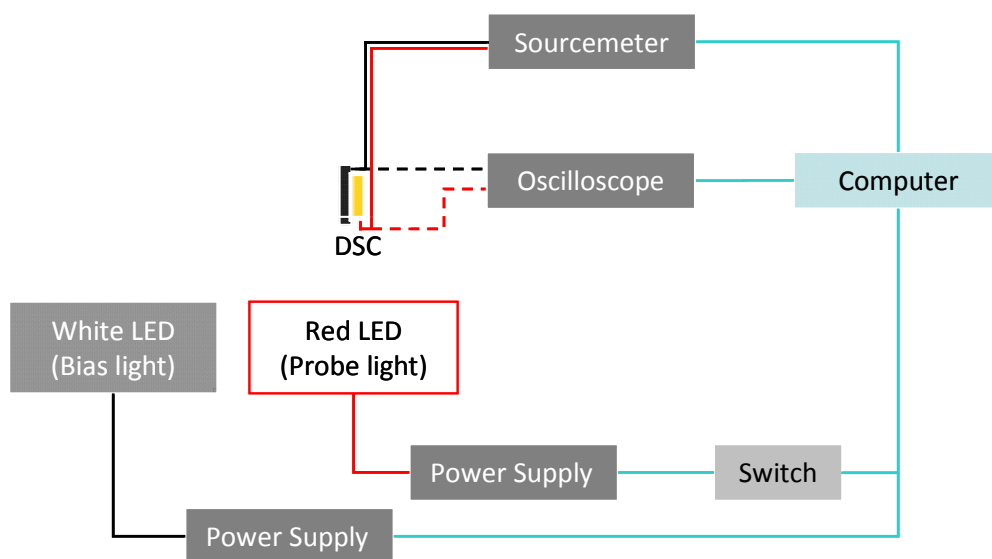


Figure 1.5 - Scheme of the phototransient setup.⁸¹

1.3.4 Electrochemical impedance spectroscopy

The steady-state I - V characteristic gives the performance parameters of the cell, such as the I_{sc} , V_{oc} and FF . Nevertheless, more detailed properties cannot be extracted from steady-state measurements and so dynamic techniques should be considered. These techniques allow the investigation of the charge transfer kinetics, mainly characterised by diffusion coefficients and lifetime of the different charge carriers. One of the most powerful characterisation techniques of DSCs involving transient probing is Electrochemical Impedance Spectroscopy (EIS).

EIS is a dynamic technique that has many advantages, not only because it is user-friendly, but also due to its sensitivity and ability to separate different complex processes as those occurring in a DSC.⁸⁸⁻⁹⁰ However, working in the linear response range of the system has to be ensured.

Despite being a relatively easy method to apply in the study of electrochemical systems, the results may sometimes be difficult to interpret. The use of equivalent electrical analogues to fit the EIS experimental data is a useful tool in this respect, as it helps to identify and interpret some of the characteristic parameters of the system, such for instance the internal resistances of a DSC.

EIS Fundamentals

EIS is a technique widely used for characterising the electrical behaviour of systems in which the overall performance is determined by a number of strongly coupled processes, each proceeding at a different rate. The most common and standard procedure in impedance measurements consists of applying a small voltage sinusoidal perturbation and monitoring the resulting current response of the system at the corresponding frequency (Figure 1.6). An EIS measurement can be performed under any bias illumination and at any working condition of the solar cell. Nevertheless, the single-frequency voltage perturbation is usually done at open-circuit conditions with a modulation signal of magnitude V_0 :

$$V(t) = V_{oc} + V_0 \cos(\omega t) \quad (1.15)$$

The response in current has the same period as the voltage perturbation but will be phase-shifted by φ :

$$I(t) = I_{oc} + I_0 \cos(\omega t - \varphi) \quad (1.16)$$

V_0 and I_0 are the amplitudes of voltage and current signals, respectively, and $\omega (= 2\pi f)$ is the radial frequency in radians per second; the open-circuit current I_{oc} is zero.

Similar to resistance, impedance is a measure of the ability of a system to impede the flow of electrical current. Thus, impedance is the ratio of a time-dependent voltage to a time-dependent current defined by Equations (1.15) and (1.16):

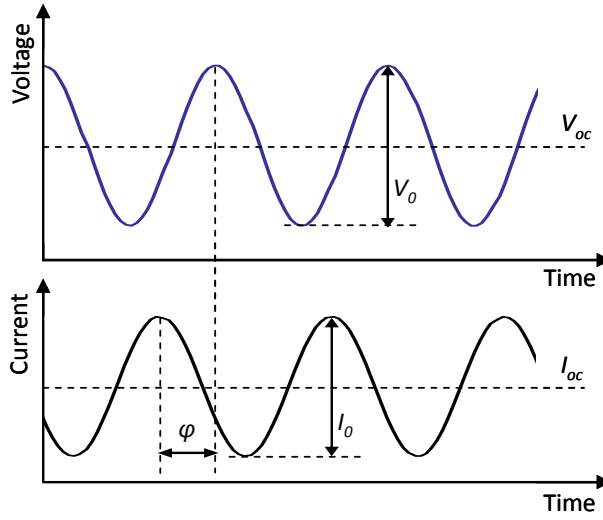


Figure 1.6 - Sinusoidal voltage perturbation and resulting sinusoidal current response, phase-shifted by φ . V_0 - amplitude of the voltage signal; I_0 - amplitude of the current signal; V_{oc} - open-circuit voltage; I_{oc} - open-circuit current.

$$Z = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \varphi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \varphi)} \quad (1.17)$$

The impedance is therefore expressed in terms of a magnitude, Z_0 , and a phase shift, φ . Applying complex notation, the impedance response of a system can be described in terms of real and imaginary components, as follows: ⁹¹

$$Z = Z_0 \frac{\exp(j\omega t)}{\exp(j\omega t - j\varphi)} = Z_0 (\cos \varphi + j \sin \varphi) \quad (1.18)$$

Knowing the real Z' ($Z' = Z_0 \cos \varphi$) and the imaginary Z'' ($Z'' = Z_0 \sin \varphi$) parts of the impedance, as well as the phase angle φ , the Nyquist and Bode diagrams can be plotted. The former is the representation of the $-Z''$ vs. Z' , while the Bode diagram is the representation in a semi-logarithmic plot of the symmetric value of the phase angle φ vs. frequency.

A typical EIS spectrum for a DSC under illumination exhibits three semicircles in the Nyquist plot and three frequency peaks in the Bode phase diagram - Figure 1.7. The phenomena involved at these characteristic frequencies, from low to high frequencies (from right to left in Figure 1.7b), are: the Nernst diffusion of ionic species within the

electrolyte, electron transfer at the TiO_2 /electrolyte interface and the redox reaction at the platinum counter electrode. In some cases two peaks might overlap, in particular, the low-frequency peak often vanishes underneath the mid-frequency peak.⁹²

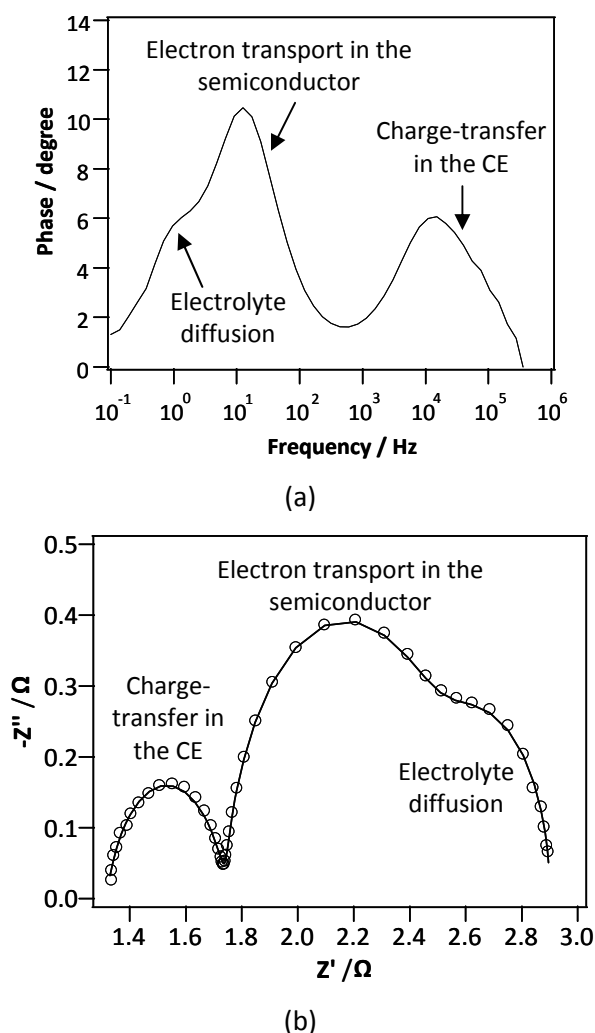


Figure 1.7 - Typical (a) Bode and (b) Nyquist diagrams for a DSC.

It is important to holdback that impedance analysis is based on the assumption that the system under study behaves linearly. Since linear systems typically exhibit features and properties that are much simpler than the general nonlinear cases, the analysis tends less complex. A system is linear if it complies with both homogeneity and additivity principles, which state that: i) when a perturbation is imposed to a system, the response will be proportional and of the same type as the input signal (for instance, if a tensile strength applied to a sample increases two fold, the corresponding strain will double); ii) if the perturbation imposed to a system consists of the weighted sum of several input signals, then, the output is simply the weighted sum of the system's responses to each input signal. Mathematically, let us consider $y_1(t)$ the response of a continuous time system $x_1(t)$ and $y_2(t)$ the output corresponding to the input $x_2(t)$. Then the system is linear if:

i) **Principle of homogeneity:** the response to $a \cdot x_1(t)$ is $a \cdot y_1(t)$

ii) **Principle of additivity:** The response to $x_1(t) + x_2(t)$ is $y_1(t) + y_2(t)$

Attempting on the system under study, *i.e.* a dye-sensitized solar cell and its I - V characteristic (Figure 1.4), it is clear that the response to a voltage input signal is not linear. The way to circumvent this situation is to consider only a small portion of the cell's current *versus* voltage curve, which appears to be linear - Figure 1.8. In practice, for EIS measurements a small voltage perturbation (1-20 mV) is applied to the cell, ensuring that the response is in the pseudo-linear range.⁹³

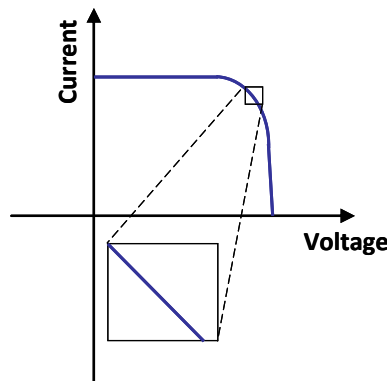


Figure 1.8 - Current *versus* voltage curve showing pseudo-linearity.

Electrical analogues

General EIS data is commonly analysed by means of equivalent electrical circuit models, which may consist of resistors, capacitors, inductors and more complex elements, assembled in series or in parallel. In particular, fitting the experimental data to specific arrangements of electrical elements can provide relevant information concerning reaction kinetics, ohmic conduction processes and even mass transfer phenomena occurring in electrochemical systems such as DSCs. The most common circuit elements used to describe electrochemical cells behaviour are briefly described hereafter. However, complementary knowledge about standard circuit elements is strongly encouraged.⁹¹

Ohmic Resistance. The equivalent analogue for an ohmic conduction process is a simple resistor, which according to the Ohm's law represents the resistance to electric charge transfer. The impedance of an ohmic resistance Z_R is simply defined as:

$$Z_R = R \quad (1.19)$$

Notice that the impedance of a resistor (R) is independent of frequency and has no imaginary component.

Double Layer Capacitance. An electrical double layer exists at the interface between an electrode and its surrounding electrolyte. This double layer is formed due to the charge separation that occurs across the interface: an excess of ions of opposite charge to that on the electrode will be found on the electrolyte phase boundary. A simple way to understand the double layer behaviour is to imagine that ions at each side of the interface approach the electrode surface as closely as possible, originating two parallel layers of equal and opposite charge, one on the electrode side and the other on the electrolyte side - Figure 1.9. This double-layer will act as a charge storage device,⁹⁴ i.e. a capacitor (C) with an impedance response Z_C defined as follows:

$$Z_C = \frac{1}{j\omega C} \quad (1.20)$$

where j is the imaginary number and ω is the radial frequency.

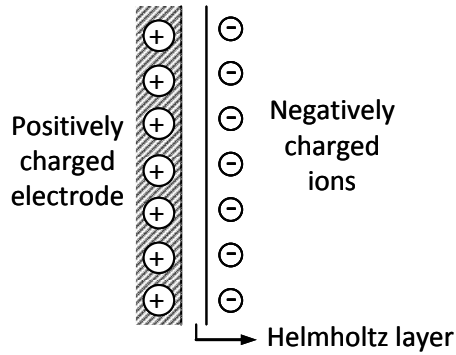


Figure 1.9 - Helmholtz double layer.

In real cells formed by nanoporous semiconductors, the double layer capacitor does not behave ideally. Instead it acts like a constant phase element (CPE), a non-ideal capacitance with a non-uniform distribution of current in the heterogeneous material. In this case, the impedance of the double layer capacitance is defined as:

$$Z_{CPE} = \frac{1}{j\omega C^n} \quad (1.21)$$

where n ($0 < n < 1$) is an empirical constant with no real physical meaning; for ideal capacitors $n = 1$.⁹¹

Electrochemical Reaction. The impedance behaviour of an electrochemical reaction can be well represented by a parallel assembling of a resistor, R , and a capacitor, C . While the resistor models the kinetics of the electrochemical reaction, the capacitor describes the charge separation across the interface.⁹⁵

Components of an electrical circuit can be connected in series or in parallel. The net impedance of a system with elements assembled in series is the sum of the impedances of the circuit elements, whereas the total impedance combined in parallel is given by:

$$\frac{1}{Z_{parallel}} = \frac{1}{Z_1} + \dots + \frac{1}{Z_i} \quad (1.22)$$

being i the number of circuit elements. Thus, for an electrochemical reaction the total impedance may be defined as:

$$Z = \frac{1}{1/R + j\omega C} \quad (1.23)$$

The corresponding Nyquist diagram, presented in Figure 1.10, shows a semicircle with diameter R . The extension of the semicircle, therefore, provides useful information concerning the reaction kinetics of the system: facile reaction kinetics will show a small diameter, while a blocking electrode will be characterised by a huge semicircle. Finally, the time constant of the reaction kinetics, τ , is given by:

$$\omega_{\max} = \frac{1}{\tau} = \frac{1}{RC} \quad (1.24)$$

where $\omega_{\max}$ is the radial frequency at the semicircle maximum (Figure 1.10).

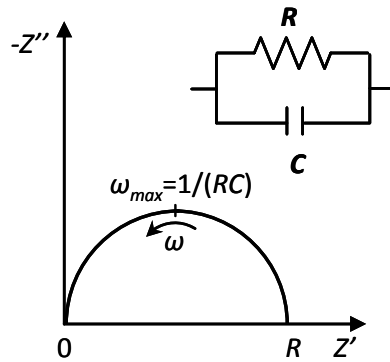


Figure 1.10 - Circuit diagram and Nyquist plot representing the impedance behaviour of an electrochemical reaction. ω is the radial frequency of the signal perturbation.

Mass Transport. In most electrochemical systems mass transport is based on diffusion processes that can be modelled by a Warburg circuit element. At high frequencies the Warburg impedance is small since diffusing reactants do not have to move very far. At low frequencies the reactants have to diffuse farther, increasing the Warburg-impedance. In this case, an infinite thickness diffusion layer may be assumed, which leads to the definition of the “infinite” Warburg impedance, Z_w :

$$Z_w = \frac{\sigma_i}{\sqrt{\omega}}(1 - j) \quad (1.25)$$

where σ_i is the Warburg coefficient for species i and is given by:

$$\sigma_i = \frac{RT}{(nF)^2 A \sqrt{2}} \left(\frac{1}{c_i \sqrt{D_i}} \right) \quad (1.26)$$

A is the electrode area, n is the number of electrons transferred in the electrode reaction (see Equation (1.4)), c_i is the bulk concentration of the reactant species i and D_i is the respective diffusion coefficient, R is the ideal gas constant, T is the absolute temperature and F is the Faraday constant. On a Nyquist plot the Warburg impedance appears as a 45° diagonal line - Figure 1.11.

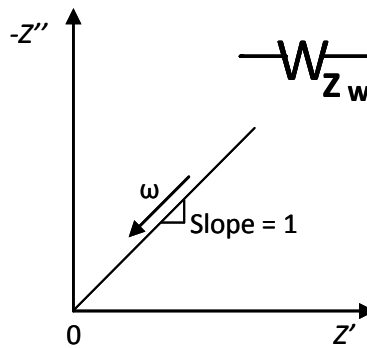


Figure 1.11 - Circuit diagram and Nyquist plot for a Warburg element used to model diffusion-like mass transport phenomena. ω is the radial frequency of the signal perturbation.

After this brief description of the most common and simple electrical elements, the following paragraphs will attempt on more complex analogues, namely those used in the analysis of DSCs. Recently, several models based on electrical analogues have been developed in an effort to understand all the complex charge-transfer phenomena that take place at the interfaces of DSCs.^{83,88-89,96-98} However, the interpretation of these phenomena in terms of resistive and capacitive elements is not straightforward due to the complexity inherent to these photoelectrochemical cells. The electron transport, accumulation and charge recombination in nanocrystalline TiO_2 films have been widely studied by Bisquert *et al.*,⁹⁹ who suggested an infinite transmission line model based on the diffusion-recombination theory - Figure 1.12.

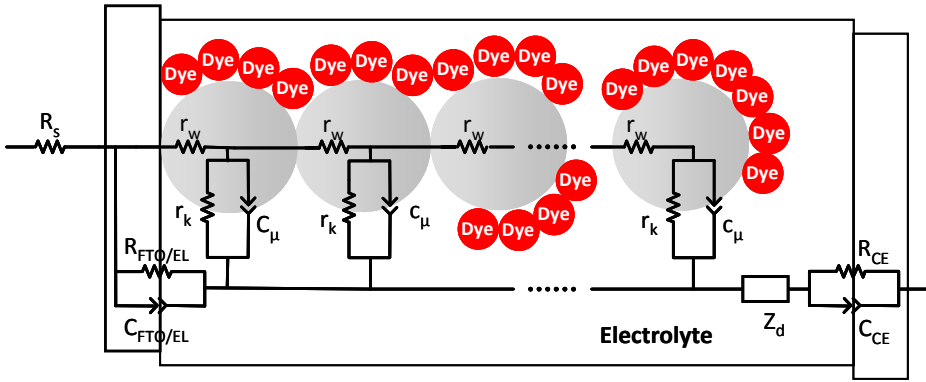


Figure 1.12 - Transmission line model used to fit EIS experimental data of DSCs.^{96,100} R_s - series resistance; $R_{TCO/EL}$ - charge transfer resistance at exposed TCO/electrolyte interface; $C_{TCO/EL}$ - double layer capacitance at exposed TCO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_μ - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised TCO; C_{CE} - double layer capacitance at the platinised TCO.

This model describes the whole mesoscopic TiO_2 film as an interconnected network of nanoparticles. In an EIS measurement electrons are injected into the TiO_2 film, which in its turn is charged by electron percolation through the individual particles of the film. This charge transfer process is characterised by a resistance R_w . Then, some of the injected electrons may recombine with the oxidised species in the electrolyte and the remaining electrons are then recaptured by the TCO current collector during the opposite phase of the sinusoidal voltage modulation (see Figure 1.6). The recombination phenomenon is characterised by a charge transfer resistance, R_k , and a capacitance, C_μ . If L is the thickness of the mesoscopic TiO_2 film, the electron transport resistance is defined as $R_w = r_w L$, while the interfacial charge recombination resistance is $R_k = r_k / L$. Note that the lowercase letters refer to the circuit element properties per unit length L since they are distributed in a repetitive arrangement throughout the entire semiconductor of thickness L . The chemical capacitance, $C_\mu = c_\mu L$, reflects the change of electron density at the TiO_2 /electrolyte interface upon a small variation of the chemical potential. This $r_w(r_k C_\mu)$ electrical analogue, representing the two pathways for electron transfer at the semiconductor, is

assembled in series with a diffusion-like element Z_d , which characterises the Nernst diffusion impedance of I_3^- ions in the electrolyte. Regeneration of I_3^- at the counter electrode is characterised by R_{CE} and C_{CE} , which are the charge transfer resistance and double layer capacitance at the platinised TCO, respectively. R_s is the series resistance, including the sheet resistance of the TCO glass and the contact resistance of the cell.⁹⁰ $R_{TCO/EL}$ and $C_{TCO/EL}$ stand for the charge transfer resistance and the corresponding double layer capacitance at exposed TCO/electrolyte interface.

Fitting EIS experimental data of the DSC to the transmission line model described above, parameters R_k , R_w and C_μ allow the calculation of the electron lifetime, τ_n , and the effective electron diffusion length, L_n :

$$\tau_n = R_k C_\mu \quad (1.27)$$

$$L_n = L \sqrt{R_k / R_w} \quad (1.28)$$

$$L_n = \sqrt{D_n \tau_n} \quad (1.29)$$

Combining Equations (1.27), (1.28) and (1.29) the effective diffusion coefficient of electrons in the TiO_2 semiconductor, D_n ($D_n = L_n^2 / \tau_n$), can also be obtained.¹⁰¹

The impedance model described above is valid for a homogeneous distribution of electrons in the semiconductor, yielding to constant resistive and capacitive elements in the transmission line model - Figure 1.12. The impedance function of the diffusion-recombination model in nanostructured electrodes is described by the following equation:⁹⁹

$$Z = \left(\frac{R_w R_k}{1 + j\omega / \omega_k} \right)^{1/2} \coth \left[\left(\frac{\omega_k}{\omega_d} \right)^{1/2} \left(1 + \frac{j\omega}{\omega_k} \right)^{1/2} \right] \quad (1.30)$$

where ω_d is the characteristic frequency of diffusion; ω_k is the characteristic frequency of recombination; ω is the angular frequency of the perturbation and j is the imaginary number. Note that ω_d and ω_k are related to the transit time τ_{tr} and lifetime τ_n , as defined in Equation (1.24):

$$\omega_d = \frac{D_n}{L^2} = \frac{1}{\tau_{tr}} \quad (1.31)$$

$$\omega_k = \frac{1}{R_k C_\mu} = \frac{1}{\tau_n} \quad (1.32)$$

From this diffusion-recombination model, three particular physical situations should be considered, as illustrated in Figure 1.13.⁹⁶ The first case corresponds to the situation where the charge-transfer resistance associated to recombination of electrons at the $\text{TiO}_2/\text{electrolyte}$ interface is much higher than the electron transport resistance through the semiconductor ($R_k \gg R_w$). This means that the electron lifetime is much higher than the transit time and the respective diffusion length will be larger than the thickness of the cell, an essential requirement for efficient cells ($L_n \gg L$). At low frequencies Equation (1.30) reduces to the expression of a semi-circle defined as:

$$Z = \frac{1}{3}R_w + \frac{R_k}{1 + j\omega / \omega_k} \quad (1.33)$$

while at high frequencies the impedance function is defined by a straight line with slope 1:

$$Z = R_w \left(\frac{j\omega}{\omega_d} \right)^{1/2} \quad (1.34)$$

As a result, the impedance spectrum in Figure 1.13(a) shows a small Warburg diffusion impedance at high frequencies, *i.e.* a straight line with slope 1, followed by a large arc with characteristic frequency ω_k due to the recombination process. The total impedance is in fact largely dominated by the high recombination resistance, the second term in Equation (1.33). On the other hand, if electrons tend to recombine with the I_3^- ions in the electrolyte, a low recombination resistance will be observed together with a high resistance to electron diffusion through the semiconductor film ($R_w \gg R_k$). As a consequence, $L_n \ll L$ and the impedance spectrum in Figure 1.13(b) exhibits a Gerischer impedance at low frequencies:

$$Z = \left(\frac{R_w R_k}{1 + j\omega / \omega_k} \right)^{1/2} \quad (1.35)$$

As in the previous case, at high frequencies the impedance spectrum shows a diffusion line with slope 1, defined by Equation (1.34). Finally, Figure 1.13(c) illustrates

the intermediate situation, where $R_w \approx R_k$. In this case, the time constants are similar and thus $L_n \approx L$.

Note that the model defined by Equation (1.30), illustrated in Figure 1.13 and based on the considerations made until this moment, describes only the behaviour of the semiconductor and do not take into account the effects of the TCO layer, the platinum counter-electrode or the diffusion of the redox species in the electrolyte.

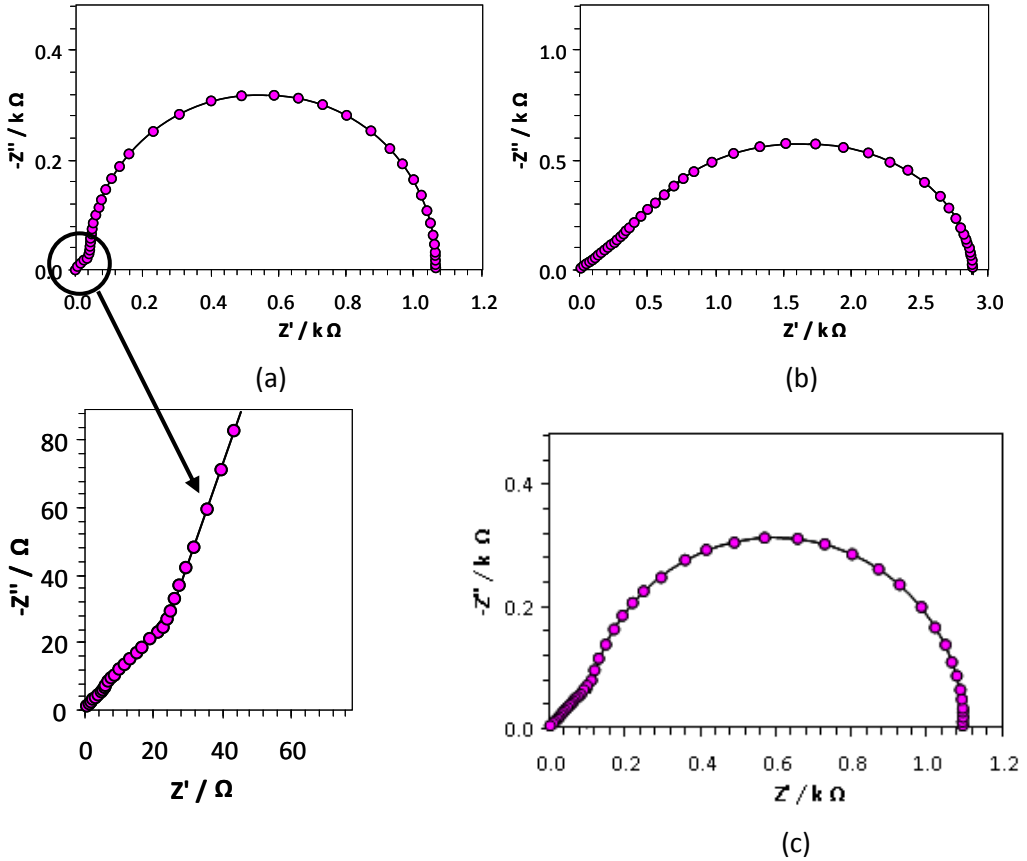


Figure 1.13 - Impedance spectra obtained for the diffusion-recombination model when: (a) $R_k \gg R_w$; (b) $R_w \gg R_k$; (c) $R_k \approx R_w$.

The shape of the impedance spectra is also strongly affected by the light intensity and the potential applied to the system, and therefore this should be taken into account when performing impedance measurements. Increasing the illumination at

constant voltage, the recombination resistance decreases significantly with respect to its value measured in the dark. In what concerns the applied voltage, varying its value implies a variation in the electron Fermi level of the injected electrons in the semiconductor and, consequently, a variation in the capacitance. Changing the operating conditions may therefore allow the extraction of important information about the processes occurring in DSCs. In fact, at very low applied potentials, the impedance spectrum has only one semicircle displaced from the origin by R_s . Since at low potentials the TiO_2 behaves like an insulator, this semicircle is due to the parallel contributions of the charge transfer resistance and the corresponding double layer capacitance at exposed TCO/electrolyte interface, $R_{\text{TCO/EL}}$ and $C_{\text{TCO/EL}}$, respectively. At high frequencies, a smooth deformation in this single semicircle can be detected, arising from the contribution of the platinised counter electrode (R_{CE} in parallel with C_{CE}). Moreover, as the current flow at these potentials is very low the diffusion element in the electrolyte, Z_d , can be neglected and the corresponding electric analogue is reduced to that shown in Figure 1.14(a). As the voltage increases, the TiO_2 becomes more conductive and the transport resistance becomes negligible. At very high potentials, the chemical capacitance C_μ , which reflects the change of electron density, dominates over the double layer capacitance at the TCO/electrolyte interface ($C_\mu \gg C_{\text{TCO/EL}}$), and the impedance spectrum assumes the typical shape of a DSC Nyquist plot as shown in Figure 1.7. The transmission line model reduces to that shown in Figure 1.14(b) where a single parallel arrangement of R_k and C_μ is assembled in series with an ohmic resistance R_s , the counter electrode contribution (R_{CE} and C_{CE}) and the diffusion in the electrolyte (Z_d).

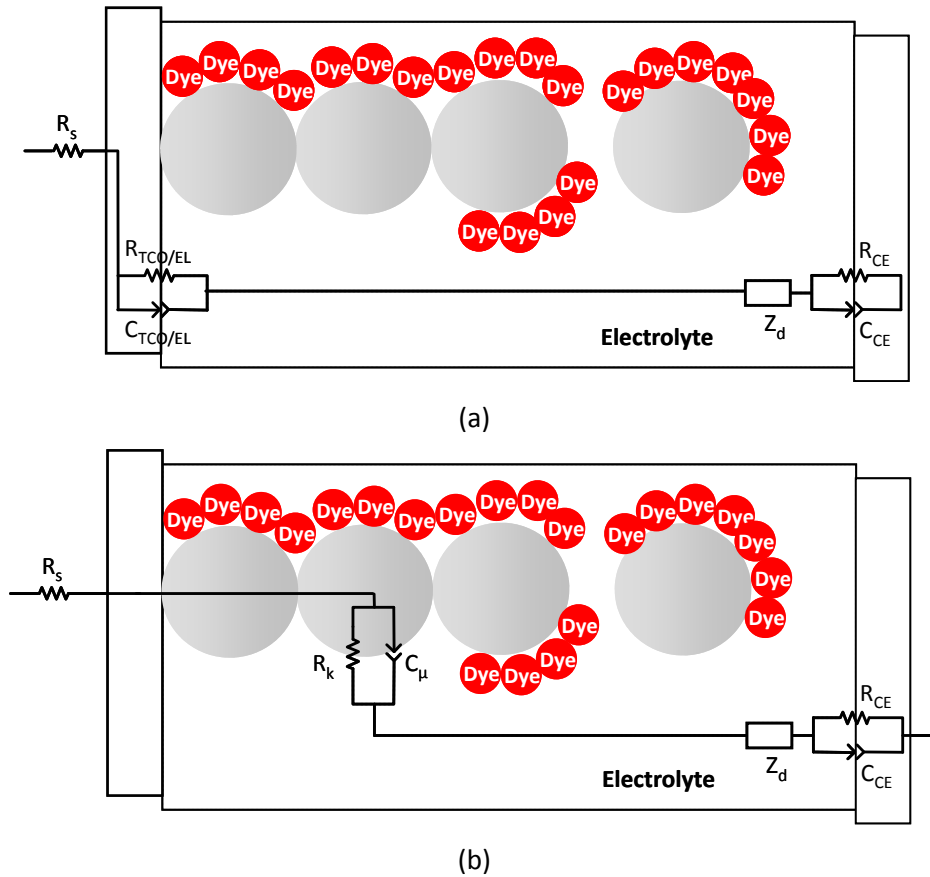


Figure 1.14 - Simplified circuits of the model presented in Figure 1.13: (a) at very low applied potentials (insulating TiO_2); (b) at high applied potentials (conductive TiO_2).⁹⁶

1.4 Objectives and outline of this work

In the last years, research on DSC technology has been growing quite fast and remarkable developments on various aspects have been achieved. Nevertheless, many other improvements should be considered in the various fields of DSCs to surpass the record efficiency of approximately 11 % obtained in laboratory-scale cells. Thus, this thesis aims to contribute to the insightful study and characterisation of DSCs.

This work is divided into four parts. **Part I (Chapter 1)** introduces the photovoltaic cells giving emphasis to DSCs. It discusses important aspects of the working

mechanisms of DSCs and their materials. An overview on photovoltaic characterisation and on electrochemical techniques is also presented, stressing the electrochemical impedance spectroscopy technique and the corresponding interpretation based on electrical analogues. **Part II (Chapter 2 to Chapter 6)** focuses on the development of more efficient and stable DSC systems; different techniques were used to characterise those cells. **Chapter 2** and **Chapter 3** concern the study of modified dyes coupled with different electrolytes, targeting a higher stability. An innovative approach for improving the overall efficiency of DSCs is given in **Chapter 4**. **Chapter 5** and **Chapter 6** study the phenomena occurring in DSCs. In particular, in **Chapter 6** is developed a transient phenomenological model: the steady-state approach allows the construction of the I - V characteristic, giving important informations about the main factors that influence the performance of DSCs; the transient approach is an important tool to relate the phenomenological behaviour of DSCs with certain dynamic techniques, such as EIS. Following the photoelectrochemical study performed for DSCs, **Part III** studies another photoelectrochemical device (**Chapter 7 and Chapter 8**): photoelectrochemical cells for water splitting. A transient phenomenological model of PEC cells for water splitting using undoped hematite photoanode is presented in **Chapter 7**. In **Chapter 8**, two DSCs are coupled to a PEC cell in a tandem arrangement, illustrating a practical use of DSCs devices to supply the external bias needed by the hematite-based PEC cell for hydrogen evolution. Finally, in **Part IV** the main conclusions and for future work suggestions are presented.

List of abbreviations and symbols

Abbreviations	Definition	Units
A	Electrode area	cm^2
AM	Air mass	
c_0	Speed of light	cm s^{-1}
c_i	Bulk concentration of the reactant species i	mol dm^{-3}
C	Capacitor	F
C_{CE}	Double-layer capacitance at the platinised TCO	F
$C_{TCO/EL}$	Double-layer capacitance at exposed TCO/electrolyte interface	F
C_μ	Chemical capacitance	F
CB	Conduction band	
CE	Counter electrode	
CPE	Constant phase element	
D_i	Diffusion coefficient of the reactant species i	$\text{cm}^2 \text{s}^{-1}$
D_n	Diffusion coefficient of electrons in the TiO_2 semiconductor	$\text{cm}^2 \text{s}^{-1}$
DOS	Density of states	
DSCs	Dye-sensitized Solar Cells	
e^-	Electrons	
E_C	Conduction band energy	J
E_F	Semiconductor Fermi energy	J
E_g	Bandgap energy	J
E_{Redox}	Redox energy of the electrolyte	J
E_V	Valence band energy	J
EIS	Electrochemical impedance spectroscopy	
f	Frequency	Hz
F	Faraday constant ($F = 96\,485,3399(24) \text{ C mol}^{-1}$)	C mol^{-1}
FF	Fill factor	

h	Planck constant ($h = 6.62606896(33) \times 10^{-34}$ J s)	J s
h^+	Holes	
HOMO	Highest occupied molecular orbital	
$I(t)$	Current response	mA
I_{oc}	Open-circuit current	mA
I_{MPP}	Current in the maximum-power point	mA
I_s	Incident light intensity	mW cm ⁻²
I_{sc}	Short-circuit current	mA
I_0	Amplitude of the current signal	mA
IPCE	Incident photon-to-current conversion efficiency	%
IR	Infrared	
j	Imaginary number	
J_{sc}	Short-circuit photocurrent density	mA cm ⁻²
k_{e-}	Recombination rate constant	s ⁻¹
L	Thickness of the semiconductor film	μm
L_n	Electron diffusion length	μm
LUMO	Lowest unoccupied molecular orbital	
MPN	3-Methoxypropionitrile	
MPP	Maximum-power point	
n	Empirical constant in constant phase elements or the number of electrons transferred in a reaction	
$N_{electrons}$	Number of light-generated electrons	
$N_{photons}$	Number of incident photons at a given wavelength	
NBB	1-Butyl-1H-benzimidazole	
NCS	Isothiocyanato group	
NHE	Normal hydrogen electrode	
NMR	Nuclear magnetic resonance	
P_{inc}	Incident power	mW
PMII	1-Propyl-3-methylimidazolium iodide	

PMITFSI	1-Propyl-3-methyl Imidazolium trifluoro methyl sulfonamide	
PV	Photovoltaics	
q	Elementary charge ($q = 1.60217646 \times 10^{-19}$ C)	C
R	Ideal gas constant ($R = 8.314472(15)$ J K ⁻¹ mol ⁻¹) or a resistor (Ω)	J K ⁻¹ mol ⁻¹ Ω
R_{CE}	Charge-transfer resistance at the platinised TCO	Ω
R_k	Recombination resistance	Ω
R_s	Series resistance	Ω
$R_{TCO/EL}$	Charge transfer resistance at exposed TCO/electrolyte interface	Ω
R_w	Electron transport resistance	Ω
S	Ground state of the sensitizer	
S^*	Excited state of the sensitizer	
S^+	Oxidised sensitizer	
t	Time	s
T	Absolute temperature	K
TBA	Tetrabutylammonium	
TBP	<i>Tert</i> -butylpyridine	
TCO	Transparent conductive oxide	
UV	Ultraviolet	
$V(t)$	Voltage perturbation	V
V_{MPP}	Voltage in the maximum-power point	V
V_{oc}	Open-circuit photovoltage	V
V_0	Amplitude of the voltage signal	V
VB	Valence band	
WE	Working electrode	
$Z(t)$	Impedance	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

Z_C	Impedance of a capacitor	Ω
Z_{CPE}	Impedance of a constant phase element	Ω
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z_R	Impedance of an ohmic resistance	Ω
Z_w	Impedance of a Warburg element	Ω
Z_0	Ratio of the amplitude of the voltage signal and the amplitude of the current signal	Ω

Greek symbols	Definition	Units
γ -BL	γ -butyrolactone	
ΔQ	Number of electron injected during the red light flash	C
ΔV	Peak of the photovoltage transient	V
η_{abs}	Absorption efficiency	%
η_{col}	Collection efficiency	%
η_{global}	Global efficiency of a DSC	%
η_{inj}	Injection efficiency	%
λ	Wavelength	nm
ν	Frequency	Hz
σ_i	Warburg coefficient for species i	$\Omega s^{-1/2}$
τ	Time constant	s
τ_n	Electron lifetime	s
τ_{tr}	Transit time	s
φ	Phase angle	degree
ω	Radial frequency	$rad s^{-1}$
ω_d	Characteristic radial frequency of diffusion	$rad s^{-1}$
ω_k	Characteristic radial frequency of recombination	$rad s^{-1}$
ω_{max}	Radial frequency at the semicircle maximum	$rad s^{-1}$

References

- (1) Key World Energy Statistics, *International Energy Agency*, **2008**.
- (2) Jäger-Waldau, A. *PV Status Report 2008: Research, Solar Cell Production and Market Implementation of Photovoltaics*, **2008**.
- (3) Lenzmann, F. O.; Kroon, J. M. *Adv. OptoElectron.* **2007**, 2007, ID 65073.
- (4) Becquerel, E. C. *R. Acad. Sci. Paris* **1839**, 9, 561.
- (5) Smith, W. *Nature* **1873**, 7, 303.
- (6) Adams, W. G.; Day, R. E. *Proc. R. Soc. Lond. A* **1877**, 25, 113.
- (7) Einstein, A. *Ann. Phys.* **1905**, 17, 132.
- (8) Czocharalski, J. *Z. Phys. Chem.* **1918**, 92, 219.
- (9) Audubert, R.; Stora, C. *Compt. rend.* **1932**, 194, 1124.
- (10) <http://www.pvresources.com/en/history.php> (09/07/2010)
- (11) Hoffmann, W. *Sol. Energy Mater. Sol. Cells* **2006**, 90, 3285.
- (12) Vogel., H. W. *Ber. Dtsch. Chem. Ges.* **1873**, 6, 1730.
- (13) Moser, J. *Monatsh. Chem.* **1887**, 8, 373.
- (14) W. H. Brattain, C. G. B. G. *Bell Syst. Tech. J.* **1955**, **34**, 129.
- (15) Gerischer, H. *J. Electrochem. Soc.* **1966**, 113, 1174.
- (16) O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737.
- (17) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jap. J. Appl. Phys., Part 2: Letters* **2006**, 45, L638.
- (18) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, 33, 269.
- (19) Grätzel, M. *C. R. Chim.* **2006**, 9, 578.
- (20) Grätzel, M. *J. Photochem. Photobiol. A* **2004**, 164, 3.
- (21) Kong, F.; Dai, S.; Wang, K. *Adv. OptoElectron.* **2007**, 2007, 75384.
- (22) Peter, L. *J. Electroanal. Chem.* **2007**, 599, 233.
- (23) Tachibana, Y.; Moser, J. E.; Gratzel, M.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem.* **1996**, 100, 20056.
- (24) Cherepy, N.; Smestad, G.; Grätzel, M.; Zhang, J. *J. Phys. Chem. B* **1997**, 101, 9342.

-
- (25) Willis, R. L.; Olson, C.; O'Regan, B.; Lutz, T.; Nelson, J.; Durrant, J. R. *J. Phys. Chem. B* **2002**, *106*, 7605.
- (26) Anderson, N.; Lian, T. *Annu. Rev. Phys. Chem.* **2005**, *56*, 491.
- (27) Durrant, J. R.; Haque, S. A.; Palomares, E. *Chem. Commun.* **2006**, 3279.
- (28) Grätzel, M.; Durrant, J. R. In *Nanostructured and photoelectrochemical systems for solar photon conversion*; Imperial College Press: London, **2008**.
- (29) Li, Y.; Hagen, J.; Schaffrath, W.; Otschik, P.; Haarer, D. *Sol. Energy Mater. Sol. Cells* **1998**, *56*, 167.
- (30) Sayama, K.; Sugihara, H.; Arakawa, H. *Chem. Mater.* **1998**, *10*, 3825.
- (31) Deb, S. *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 1.
- (32) Park, N.; Lagemaat, J.; Frank, A. *J. Phys. Chem. B* **2000**, *104*, 8989.
- (33) Kalyanasundaram, K.; Grätzel, M. *Coord. Chem. Rev.* **1998**, *177*, 347.
- (34) Gonçalves, L. M.; Bermudez, V. d. Z.; Ribeiro, H. A.; Mendes, A. M. *Energy Environ. Sci.* **2008**, *1*, 655.
- (35) Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2006**, *6*, 215.
- (36) Zhu, K.; Neale, N.; Miedaner, A.; Frank, A. *Nano Lett.* **2007**, *7*, 69.
- (37) Wei, M.; Konishi, Y.; Zhou, H.; Sugihara, H.; Arakawa, H. *J. Electrochem. Soc.* **2006**, *153*, A1232.
- (38) Park, J.; Lee, T.; Kang, M. *Chem. Commun.* **2008**, 2867.
- (39) Adachi, M.; Murata, Y.; Takao, J.; Jiu, J.; Sakamoto, M.; Wang, F. *J. Am. Chem. Soc.* **2004**, *126*, 14943.
- (40) Jiu, J.; Isoda, S.; Wang, F.; Adachi, M. *J. Phys. Chem. B* **2006**, *110*, 2087.
- (41) Greene, L.; Yuhas, B.; Law, M.; Zitoun, D.; Yang, P. *Inorg. Chem.* **2006**, *45*, 7535.
- (42) Huisman, C.; Schoonman, J.; Goossens, A. *Sol. Energy Mater. Sol. Cells* **2005**, *85*, 115.
- (43) Kuo, C.; Lu, S. *Nanotechnology* **2008**, *19*, 095705.
- (44) Longo, C.; Paoli, M. *J. Braz. Chem. Soc.* **2003**, *14*, 889.
- (45) Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. *Chem. Commun.* **2002**, 1464.

- (46) Kay, A.; Grätzel, M. *Chem. Mater.* **2002**, *14*, 2930.
- (47) Ito, S.; Murakami, T.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M.; Grätzel, M. *Thin Solid Films* **2008**, *516*, 4613.
- (48) Wang, Z.; Kawauchi, H.; Kashima, T.; Arakawa, H. *Coord. Chem. Rev.* **2004**, *248*, 1381.
- (49) Koo, H.; Park, J.; Yoo, B.; Yoo, K.; Kim, K.; Park, N. *Inorg. Chim. Acta* **2008**, *361*, 677.
- (50) Grätzel, M. *Prog. Photovoltaics Res. Appl.* **2000**, *8*, 171.
- (51) Kelly, C.; Meyer, G. *Coord. Chem. Rev.* **2001**, *211*, 295.
- (52) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988.
- (53) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216.
- (54) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.
- (55) Kohle, O.; Ruile, S.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 4779.
- (56) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- (57) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218.
- (58) Wang, Z.-S.; Yamaguchi, T.; Sugihara, H.; Arakawa, H. *Langmuir* **2005**, *21*, 4272.
- (59) Nazeeruddin, M.; DeAngelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
- (60) Nazeeruddin, M.; Péchy, P.; Grätzel, M. *Chem. Commun.* **1997**, 1705.
- (61) Wang, P.; Zakeeruddin, S.; Moser, J.; Nazeeruddin, M.; Sekiguchi, T.; Grätzel, M. *Nat. Mater.* **2003**, *2*, 402.
- (62) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, M.; Grätzel, M. *Appl. Phys. Lett.* **2005**, *86*, 123508.
- (63) Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. *Chem. Commun.* **2009**, 2198.

-
- (64) Wang, M.; Xu, M.; Shi, D.; Li, R.; Gao, F.; Zhang, G.; Yi, Z.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Mat.* **2008**, *20*, 4460.
- (65) Choi, H.; Lee, J.; Song, K.; Kang, S.; Ko, J. *Tetrahedron* **2007**, *63*, 3115.
- (66) Plass, R.; Pelet, S.; Krueger, J.; Grätzel, M.; Bach, U. *J. Phys. Chem. B* **2002**, *106*, 7578.
- (67) Wolfbauer, G.; Bond, A. M.; Eklund, J. C.; MacFarlane, D. R. *Sol. Energy Mater. Sol. Cells* **2001**, *70*, 85.
- (68) Kalaighan, G. P.; Kang, Y. S. *J. Photochem. Photobiol C* **2006**, *7*, 17.
- (69) Bai, Y.; Cao, Y.; Zhang, J.; Wang, M.; Li, R.; Wang, P.; Zakeeruddin, S.; Grätzel, M. *Nat. Mater.* **2008**, *7*, 626.
- (70) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (71) Kuang, D.; Klein, C.; Zhang, Z.; Ito, S.; Moser, J.; Zakeeruddin, S.; Grätzel, M. *Small* **2007**, *3*, 2094.
- (72) Papageorgiou, N.; Maier, W.; Grätzel, M. *J. Electrochem. Soc.* **1997**, *144*, 876.
- (73) Olsen, E.; Hagen, G.; Lindquist, S. *Sol. Energy Mater. Sol. Cells* **2000**, *63*, 267.
- (74) Kitamura, T.; Maitani, M.; Matsuda, M.; Wada, Y.; Yanagida, S. *Chem. Lett.* **2001**, *30*, 1054.
- (75) Murakami, T.; Grätzel, M. *Inorg. Chim. Acta* **2008**, *361*, 572.
- (76) Kay, A.; Grätzel, M. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 99.
- (77) Imoto, K.; Takahashi, K.; Yamaguchi, T.; Komura, T.; Nakamura, J.; Murata, K. *Sol. Energy Mater. Sol. Cells* **2003**, *79*, 459.
- (78) Suzuki, K.; Yamaguchi, M.; Kumagai, M.; Yanagida, S. *Chem. Lett.* **2003**, *32*, 28.
- (79) Rodriguez, J. A.; Fernández, M. *Synthesis, Properties, and Applications of Oxide Nanomaterials*; John Willey & Sons. Inc, **2007**.
- (80) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.
- (81) Zang, Z. PhD, EPFL, Lausanne, **2008**.
- (82) Nelson, J.; Haque, S. A.; Klug, D. R.; Durrant, J. R. *Phys. Rev. B* **2001**, *63*, 205321.
- (83) Bisquert, J.; Zaban, A.; Greenshtein, M.; Mora-Sero, I. *J. Am. Chem. Soc.* **2004**, *126*, 13550.

-
- (84) Bisquert, J.; Vikhrenko, V. S. *J. Phys. Chem. B* **2004**, *108*, 2313.
- (85) Fukai, Y.; Kondo, Y.; Mori, S.; Suzuki, E. *Electrochem. Commun.* **2007**, *9*, 1439.
- (86) O'Regan, B. C.; Lenzmann, F. J. *J. Phys. Chem. B* **2004**, *108*, 4342.
- (87) Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. *J. Phys. Chem. B* **2000**, *104*, 8916.
- (88) Wang, Q.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. B* **2005**, *109*, 14945.
- (89) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.
- (90) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. J. *J. Phys. Chem. B* **2002**, *106*, 334.
- (91) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, **2005**.
- (92) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (93) *Modern Aspects Of Electrochemistry*, No. 32; Kluwer Academic Publishers, **2002**.
- (94) Bard, A. J.; Faulkner, L. R. *ELECTROCHEMICAL METHODS: Fundamentals and Applications*; Second ed.; John Wiley & Sons, Inc.: USA, **2001**.
- (95) O'Hayre, R.; Cha, S.-W.; Colella, W.; Prinz, F. B. *Fuel Cells Fundamentals*; John Wiley & Sons, Inc.: New York, **2006**.
- (96) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.
- (97) Bisquert, J. *J. Phys. Chem. Chem. Phys.* **2003**, *5*, 5360.
- (98) Lagemaat, J.; Park, N. G.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 2044.
- (99) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. *J. Phys. Chem. B* **2000**, *104*, 2287.
- (100) Andrade, L.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Ribeiro, H. A.; Mendes, A.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 1117.
- (101) Wang, Q.; Ito, S.; Grätzel, M.; Fabregat-Santiago, F.; Mora-Sero, I.; Bisquert, J.; Bessho, T.; Imai, H. *J. Phys. Chem. B* **2006**, *110*, 25210.

PART II:

DYE-SENSITIZED SOLAR CELLS

Chapter 2.

INFLUENCE OF SODIUM CATIONS OF N3 DYE ON THE PHOTOVOLTAIC PERFORMANCE AND STABILITY OF DYE-SENSITIZED SOLAR CELLS

Luísa Andrade, Shaik M. Zakeeruddin, Mohammad K. Nazeeruddin, Helena Aguilar Ribeiro, Adélio Mendes and Michael Grätzel

(ChemPhysChem 2009, 10, 1117-1124)

Abstract

We report on the effect of substituting the two tetrabutyl ammonium counter ions of the standard N719 dye by sodium ions on the performance and stability of dye-sensitized solar cells. The di-sodium analogue of N719 in conjunction with a non-volatile electrolyte gave a conversion efficiency of 7.6 % under standard global AM 1.5 sunlight. Devices maintained 99 % of their initial performance after 1000 h under full sunlight aging at 50 °C. Electrochemical impedance spectroscopy and photovoltage transient decay studies revealed the evolution of the solar cell parameters during aging. Remarkably, a decrease in the rate of electron back reaction with the triiodide ions across the TiO₂/electrolyte interface appeared upon aging as well as enhanced electronic conduction in the TiO₂ film.

Keywords: Dyes, electrochemical impedance spectroscopy, electron transport, photovoltage transient decay, solar cells.

2.1 Introduction

In Dye-sensitized Solar Cells (DSCs), the dye is a major player in the quest for high overall photoelectric conversion efficiencies. To be suitable for application in DSCs, the dye must fulfil several requirements. Ideally, the sensitizer should absorb all incident light in a large wavelength range (from the UV to visible and near-IR regions). It should be strongly bound to the semiconductor surface via its ligands and inject electrons to its conduction band with a quantum yield of unity.¹ The energy level of the excited state of the dye must be more negative than that of the semiconductor's conduction band to allow electron injection. Moreover, the oxidation potential of the oxidised dye has to be more positive than the oxidation potential of the redox couple in the electrolyte, so that fast dye regeneration can take place. The dye should also be stable enough to sustain 10^8 redox cycles under illumination without noticeable loss of photovoltaic performance of the DSC.²⁻³

Up to now, ruthenium complexes have been widely used as sensitizers due to their advantageous spectral properties, photostability in the final device and high conversion efficiency.⁴⁻⁹ An example of high performance ruthenium polypyridine complexes is the *cis*-di(thiocyanato)bis (4, 4'- dicarboxylic acid - 2, 2'- bipyridine) Ruthenium(II), commonly known as the N3 dye.¹⁰⁻¹⁵ Since the development of the N3 dye in 1993,¹⁰ its tetrabutylammonium salt N719 has been used as the standard red dye because of its unmatched performance.¹⁶ This dye is derived from N3 by substituting two protons with two TBA (tetrabutylammonium) cations. Despite all efforts made up to now concerning the improvement on photovoltaic performance and stability, it is still mandatory to find novel efficient sensitizers as well as stable and low-volatile electrolytes.

In the present work, we modified the N719 dye by substituting the two TBA cations with sodium ions. The modified dye was subsequently incorporated in solar cells, which were then submitted to accelerated thermal/light soaking aging tests for device performance and stability evaluation. This new sensitizer is coded as $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ hereafter. The results were then compared with those obtained for a DSC with the standard sensitizer N719 ($[2\text{TBA}^+(\text{N3}, 2\text{H}^+)]$). Additionally, these two dyes were tested

in combination with two different electrolytes (E1 and E2) derived from an imidazolium salt, both having low volatility with negligible vapour pressure and high electric conductivity at room temperature.

2.2 Experimental section

All chemicals used were of purest quality. 3-Methoxypropionitrile (MPN) and γ -butyrolactone (γ -BL) were obtained from Fluka and distilled before use. 1-Propyl-3-methylimidazolium iodide (PMII), 1-Butyl-3-methylimidazolium iodide (BMII) and 1-Propyl-3-methylimidazoliumtrifluoromethylsulfonamide (PMITFSI) ionic liquids were prepared according to literature methods and the purity was confirmed by ^1H NMR (nuclear magnetic resonance) spectra.¹⁷ Guanidinium thiocyanate (GuNCS) was purchased from Fluka. 1-Butyl-1H-benzimidazole (NBB) was synthesised as reported.¹⁸

2.2.1 Synthesis

N719 dye was synthesised as reported earlier.¹⁹ The di-sodium $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ dye was prepared as follows. First N719 dye was dissolved in acetonitrile solvent and to this an excess amount of sodium triflate in acetonitrile was added. Immediately the respective counter ion containing complex was precipitated, filtered and washed with acetonitrile and dried under vacuum. Electrolyte E1 contains PMII (1.0 M), iodine (0.15 M), GuNCS (0.1 M) and NBB (0.5 M) in 3-methoxypropionitrile. Electrolyte E2 contains iodine (0.1 M), N-methylbenzimidazole (0.5 M) in a mixture of BMII; PMITFSI; γ -BL (2; 3 ;1) vol/vol.

2.2.2 TiO_2 electrode preparation

A screen-printed double layer film of interconnected TiO_2 particles was used as mesoporous photoelectrode. A 7 μm -thick film of 20 nm-sized TiO_2 particles was first printed on the fluorine-doped SnO_2 conducting glass electrode (FTO) and further coated by a 5 μm -thick second layer of 400 nm-sized light scattering anatase particles.

The detailed preparation procedures of TiO₂ nanocrystals, pastes for screen-printing and double-layer nanostructured TiO₂ film have been reported elsewhere.²⁰

2.2.3 Dye-sensitized solar cell fabrication

The working electrode, described above, was sealed with a 25 µm-thick transparent Surlyn ring (from DuPont) at 130 °C for 15 s to the counter electrode (FTO glass - 15 Ω/square - coated with a platinum solution chemically deposited at 450 °C for 15 min). The cells were filled with an electrolyte solution through a pre-drilled hole done in the counter electrode. The hole was then sealed with a Bynel disc and a thin glass to avoid leakage of the electrolyte.

2.2.4 Photovoltaic measurements

A 450 W xenon light source (Oriel, USA) was used to give a simulated irradiance of 100 mW cm⁻² (the equivalent of one sun at air mass 1.5) at the surface of solar cells. The spectral output of the lamp was matched in the region of 350-750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra. Various incident light intensities were regulated with wavelength neutral wire mesh attenuators. The current-voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). This process was fully automated using Wavemetrics software. A similar data acquisition system was used to control the incident photon-to-current conversion efficiency measurement. Under full computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the *IPCE* (λ) as defined by $IPCE(\lambda) = 124000(J_{sc}/\lambda\phi)$, where λ is the wavelength (nm), J_{sc} is the short-circuit photocurrent density (mA cm⁻²) and ϕ is the incident radiative flux (mW cm⁻²).

Photovoltaic performance was measured by using a metal mask with an aperture area of 0.158 cm².

2.2.5 Electrochemical impedance measurements

Electrochemical impedance spectroscopy (EIS) experiments were carried out with a computer-controlled potentiostat (EG&G M273) equipped with a frequency response analyser (EG&G M1025). The frequency range was 0.005 Hz - 100 kHz and the magnitude of the modulation signal was 10 mV. All the measurements were performed at room temperature in the dark at -0.75 V. The EIS spectra were fitted to an appropriate electrical analogue by means of the ZView software (v2.5b, Scribner Associates Inc.).

2.2.6 Photovoltage transient decay

In the transient photoelectrical decay experiment, different steady-state lights were supplied with a home-made white light-emitting diode array by tuning the driving voltage and a red light-emitting diode array controlled with a fast solid-state switch was used to generate a perturbing pulse with a width of 200 ms. The pulsed red light and steady-state white light were both incident on the photoanode side of a testing cell. The red pulse was carefully controlled by the driving potential of diodes to keep the modulated photovoltage below 5 mV. We used red light as a probe to generate a photovoltage perturbation near the open-circuit photovoltage (V_{oc}) of the cell under the white light and measured the voltage decay process thereafter. Normally, the transient signals follow a mono-exponential decay, thus the recombination rate constant, k_e , can be extracted from the slope of the semi-logarithmic plot. The capacitance (C_μ) of the TiO₂/electrolyte interface and density of states (DOS) at the V_{oc} are calculated by $C_\mu = \Delta Q / \Delta V$, where ΔV is the peak of the photovoltage transient and ΔQ is the number of electron injected during the red light flash. The latter is obtained by integrating the transient of a short-circuit photocurrent generated from an identical red-light pulse. This method may underestimate the actual injected

electrons by the fraction that is lost due to recombination during the electron collection. The error is thought to be less than 30 % in the worst case. More critically, it does not affect the shape of the calculated capacitance *versus* potential but only the magnitude. The electron density in the titania film under a given white light intensity was measured by the charge extraction method.²¹

2.2.7 Stability Tests

Hermetically sealed cells were used to check the long-term stability under visible light soaking at 50 °C. The light soaking experiments employed a polyester film of 50 µm-thickness (Preservation Equipment Ltd, UK) as a 400 nm UV cut-off filter. Cells were irradiated at open-circuit with a Suntest CPS lamp (ATLAS GMBH, 100 mW cm⁻², 50 °C) over a period of 1000 h. The cells were taken out at regular intervals to record the photocurrent-voltage curve. These measurements were carried out at room temperature after allowing the cells to cool down and equilibrate during 2 h.

2.3 Results and discussion

The molecular structure of the $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ dye is shown in Figure 2.1 together with that of N719 dye for comparison. All the information related to the synthesis of both dyes was given in the Experimental section 2.2.1.

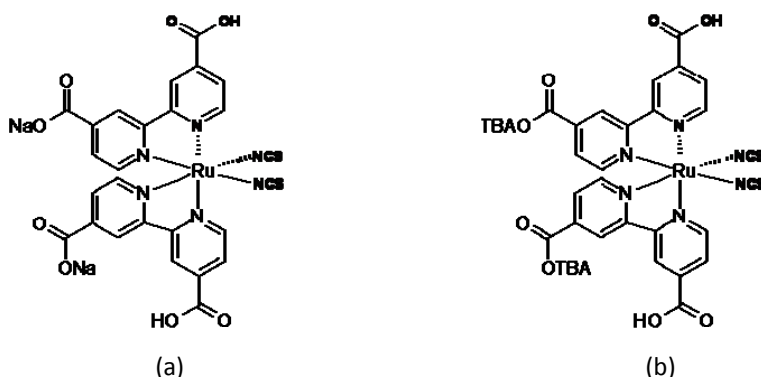


Figure 2.1 - Molecular structure of the a) $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ and b) $[2\text{TBA}^+(\text{N3}, 2\text{H}^+)]$, known as N719 dye.

2.3.1 Photovoltaic performance

The anchoring groups of dye immobilise it on the nanocrystalline TiO_2 surface allowing high quantum yields of the excited state electron transfer process.²² The anchoring group of the adsorbed dye transfers most of its protons to the semiconductor surface, charging it positively. This change in the TiO_2 surface enhances the adsorption of the anionic ruthenium complexes creating a dipole that favours electron injection from the excited state of the dye into the conduction band of the semiconductor, therefore inducing high photocurrents. Nevertheless, this positive shift of the Fermi level induced by surface protonation lowers the open-circuit potential. If the sensitizer carries fewer protons, it is expected to obtain high open-circuit potential and the opposite trend is observed if the sensitizer is fully protonated. So, an optimal degree of protonation of the sensitizer should be considered to reach maximum overall conversion efficiency. Thus, the TBA-based dye was prepared bearing in mind the protonation effect on the photovoltaic performance of DSCs.^{7,19,22-23} Herein, we study the effect of replacing the TBA ions by sodium ions on the DSC performance and stability.

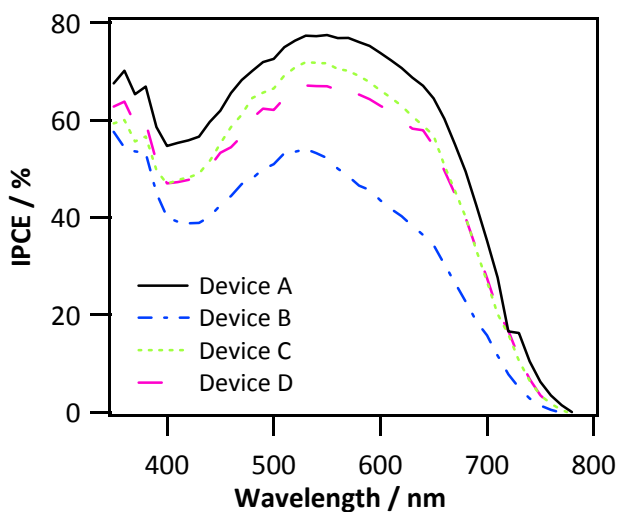
Figure 2.2a) shows the photocurrent density as a function of voltage of four DSCs prepared with $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ and N719 dyes, both in combination with electrolytes E1 and E2 (see Table 2.1). The corresponding photovoltaic parameters of these fresh cells (short-circuit current density, J_{sc} ; open-circuit voltage, V_{oc} ; fill factor, FF and efficiency, η) are presented in Table 2.2 as a function of light intensity. The highest overall power conversion efficiency was obtained for the system N719 dye/E1 electrolyte (device C) due to the higher values of V_{oc} and FF . However, the sodium-based dye in combination with the same electrolyte (device A) presented the highest photocurrent density at all light intensities. Table 2.2 shows that the effect of cation substitution depends on the electrolyte composition. The MPN-based electrolyte E1 produces better efficiencies than E2, containing γ -BL as a solvent, maximum efficiency values being 8.51 ± 0.01 % (0.1 sun) for device A and 8.8 ± 0.1 % (0.1 sun) for device C.

Table 2.1 - Systems under study.

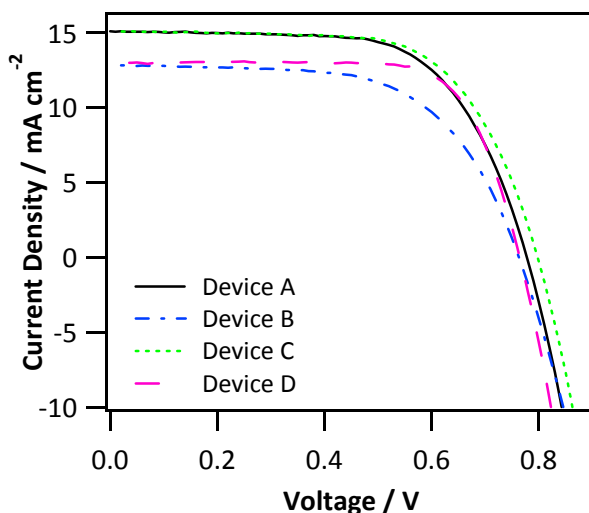
Device	Dye	Electrolyte
A	[2Na ⁺ (N3, 2H ⁺)]	E1
B	[2Na ⁺ (N3, 2H ⁺)]	E2
C	N719	E1
D	N719	E2

Table 2.2 - Detailed photovoltaic parameters under various sunlight intensities. The active area of the cell with a metal mask was 0.158 cm².

Device	Light intensity	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / mV	FF	$\eta / \%$
A	1 sun	15.10±0.01	777±1	0.66±0.01	7.6±0.2
	0.5 sun	8.15±0.04	759.7±0.8	0.70±0.01	8.21±0.06
	0.1 sun	1.51±0.01	710.3±0.6	0.754±0.001	8.51±0.01
B	1 sun	12.75±0.07	773±15	0.60±0.02	5.9±0.1
	0.5 sun	7.0±0.2	766±20	0.67±0.02	6.8±0.2
	0.1 sun	1.33±0.04	702±21	0.756±0.004	7.39±0.06
C	1 sun	14.9±0.1	797±6	0.712±0.005	8.45±0.06
	0.5 sun	8.00±0.06	779±5	0.750±0.004	8.80±0.08
	0.1 sun	1.47±0.01	728±5	0.783±0.001	8.8±0.1
D	1 sun	13.00±0.01	767±4	0.74±0.01	7.35±0.08
	0.5 sun	7.01±0.01	746±5	0.76±0.01	7.5±0.1
	0.1 sun	1.29±0.02	685±5	0.77±0.01	7.30±0.01



(a)



(b)

Figure 2.2 - a) Photocurrent intensity-voltage characteristics for devices A to D, measured at AM 1.5 (100 mW cm^{-2}) global sunlight illumination. b) Photocurrent action spectra for the same devices.

The better performance of devices A and C, based on E1 electrolyte, is also reflected in the IPCE spectra presented in Figure 2.2b). Devices A and C reach a maximum of approximately 72 % at 530 nm and 78 % at 550 nm, respectively. On the other hand,

the photocurrent action spectra for the E2-based systems show lower IPCE values at 530 nm: maximum of 54 % for device B and 67 % for device D. The highest IPCE obtained with device C is therefore in line with its better photovoltaic performance.

2.3.2 Device stability

Besides efficiency, the long-term stability is also a key requirement for practical implementation of the photovoltaic technology. The four cells were subjected to light soaking at 50 °C for 1000 h. The evolution of the photovoltaic performance throughout the aging process is presented in Figure 2.3 and Figure 2.4. Device A, employing sensitizer $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ along with E1 electrolyte, shows an excellent stability with a drop of less than 1 % in efficiency (7.59 % to 7.54 %) during 1000 h aging. The small decrease in the J_{sc} was compensated by an increase in FF and V_{oc} . By contrast, device C suffered a decrease in the power conversion efficiency during the aging process, from 8.40 % to 7.11 %. A drop of all the photovoltaic parameters occurred during the aging time. Thus, in spite of the excellent initial performance exhibited by this system, it showed poor stability as observed in previous studies.²⁴ Moreover, combining the N719 dye with the E2 electrolyte renders the system even less stable. After 1000 h of light soaking, there was a drop of about 25 % in efficiency, ascribed to major losses in all photovoltaic parameters. The same behaviour was observed for device B, suggesting that E2 electrolyte renders these devices unstable probably due to desorption of dye in this electrolyte. The nature of the counter ion has a great impact on the solubility of these ruthenium sensitizers in commonly used organic solvents. Replacing the two TBA ions of N719 with two sodium ions makes complex less soluble than N719 dye. This will explain for the better stability of devices with di-sodium salt dye.

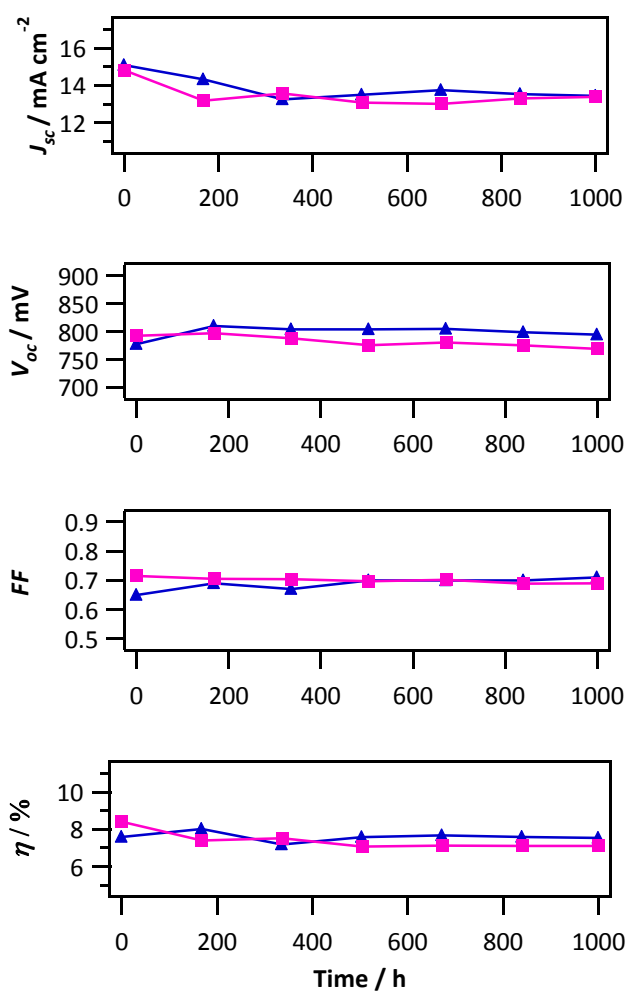


Figure 2.3 - Evolution of photovoltaic parameters for device A (▲) and device C (■), aged under one sunlight soaking at 50 °C.

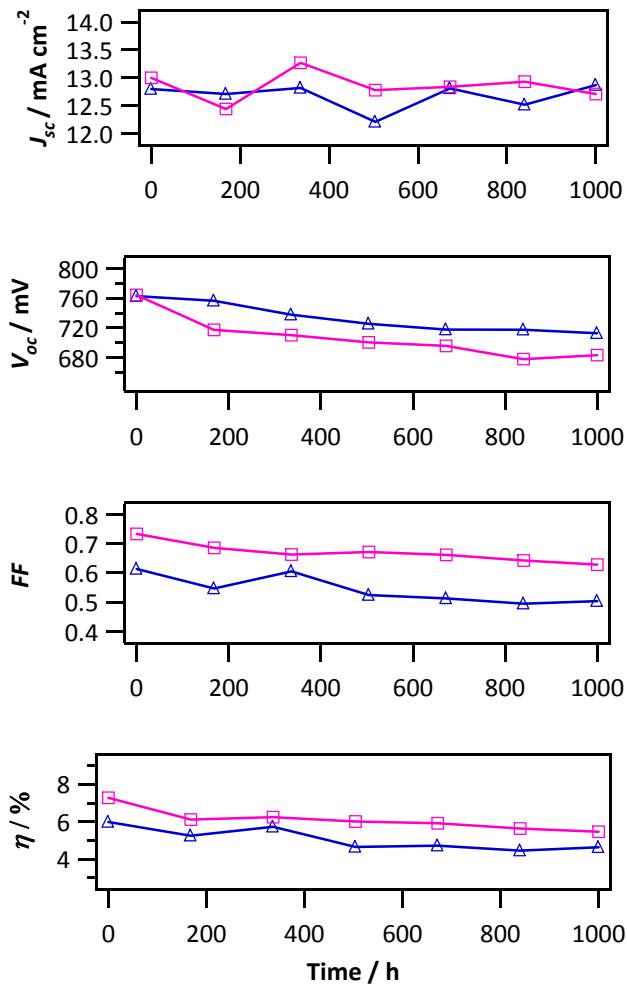


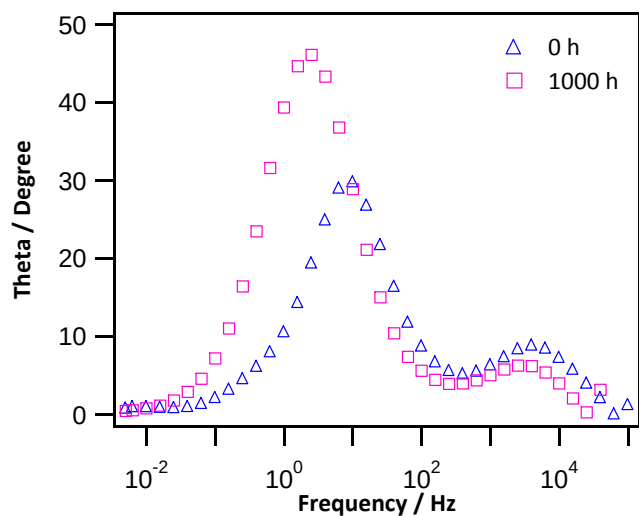
Figure 2.4 - Evolution of photovoltaic parameters for device B (Δ) and device D ($\square$), aged under one sunlight soaking at 50 °C.

Considering the promising results in terms of performance/long-term stability of sodium-based DSCs in combination with E1 electrolyte, a more detailed characterisation of these cells was performed - Sections 2.3.3 and 2.3.4.

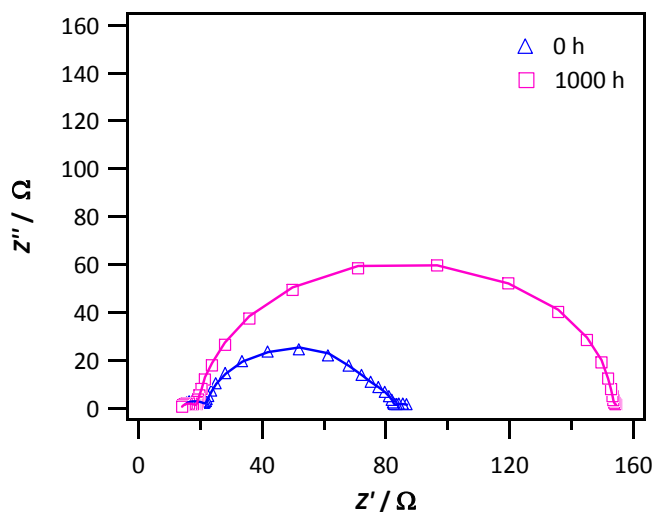
2.3.3 Electrochemical impedance spectroscopy

The effect of the aging process on the overall performance of device A was analysed by means of electrochemical impedance spectroscopy. This technique allows to determine the charge-transfer resistances at the platinum counter electrode and at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, as well as to determine the Nernstian diffusion within the electrolyte.²⁵ The Bode and Nyquist plots (Z'' - imaginary part of impedance *versus* Z' - real part of impedance) for the sodium-based system, before and after the aging process, are shown in Figure 2.5.

Recently, electrical equivalent circuits have been developed in order to rationalise the charge-transfer and transport phenomena that take place in DSCs.²⁶⁻³¹ However, the interpretation of these phenomena in terms of resistive and capacitive elements is not straightforward due to the complexity inherent to these photoelectrochemical cells. The electron transport and charge recombination in nanocrystalline TiO_2 films have been widely studied by Bisquert *et al.*,³² who suggested a transmission line model to describe the kinetic processes of DSCs, considering the whole mesoscopic TiO_2 film as an interconnected network. Under forward bias, electrons are transferred from the FTO substrate into the TiO_2 film, allowing electron propagation through its individual particles with a resistance R_w . A part of the injected electrons may be lost by reaction with I_3^- in the electrolyte. The recombination phenomenon is characterised by a charge transfer resistance, R_k , and a chemical capacitance, C_μ . If L is the thickness of the mesoscopic TiO_2 film, the electron transport resistance is defined as $R_w = r_w L$, while the interfacial charge recombination resistance is $R_k = r_k / L$. The chemical capacitance $C_\mu (= c_\mu L)$ reflects the change of electron density upon a small variation of the chemical potential. It is important to emphasise that the recombination phenomenon considered in the present study is only related to electron transfer by back reaction with the electrolyte - known as dark current.



(a)



(b)

Figure 2.5 - Bode a) and Nyquist b) diagrams obtained for the $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ dye/E1 electrolyte system, before and after 1000 h under thermal/light soaking stress test. In the Nyquist diagram, symbols correspond to the impedance data obtained experimentally in the dark under -0.75 V bias, while solid lines represent the fittings based on the equivalent electrical circuit shown in Figure 2.6.

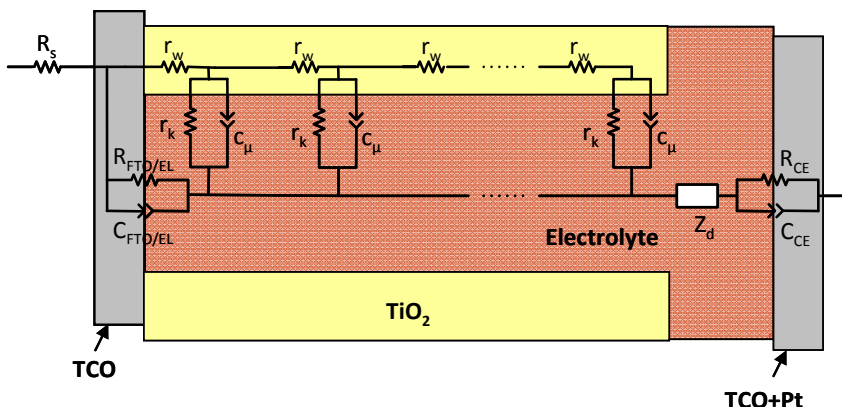


Figure 2.6 - Transmission line model used to fit the EIS experimental data. R_s - series resistance; $R_{FTO/EL}$ - charge transfer resistance at exposed FTO/electrolyte interface; $C_{FTO/EL}$ - double layer capacitance at exposed FTO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_μ - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised FTO; C_{CE} - double layer capacitance at the platinised FTO.

In addition to the circuit elements described above, the transmission line model comprises other elements that describe the additional processes occurring in the DSCs. Regeneration of I_3^- at the counter electrode is characterised by R_{CE} and C_{CE} , which are the charge transfer resistance and the double-layer capacitance at the platinised FTO, respectively. $R_{FTO/EL}$ and $C_{FTO/EL}$ are the charge transfer resistance and the corresponding double-layer capacitance at exposed FTO/electrolyte interface. R_s is the series resistance, including the sheet resistance of the FTO glass and the contact resistance of the cell. Finally, Z_d is the Warburg element showing the Nernst diffusion of I_3^- in the electrolyte. The fitting of the experimental data was accomplished with the ZView software using the equivalent circuit presented in Figure 2.6. For better fitting, all capacitor elements were replaced by constant phase elements (CPE), non-ideal capacitances associated with a non-uniform distribution of current in the heterogeneous TiO_2 film.³³

Besides the determination of R_k and R_w , the electron lifetime τ_n ($\tau_n = R_k C_\mu$), the effective electron diffusion length L_n ($L_n = L \sqrt{R_k / R_w}$) and the diffusion coefficient of

electrons in the TiO_2 semiconductor D_n ($D_n = L_n^2 / \tau_n$) can also be obtained.³⁴ The impedance spectra in Figure 2.5 clearly show the ideal characteristics of the diffusion-recombination model: the charge-transfer resistance associated to recombination of electrons at the TiO_2 /electrolyte interface (R_k) is much higher than the electron transport resistance through the semiconductor (R_w), meaning that the cell exhibits carrier collection efficiency near unity.³⁴ Moreover, the correspondent values obtained by fitting show that R_k/R_w is much higher than unity for both fresh and aged cells (Table 2.3). This fact can also be explained by the L_n values that are much higher than the film thickness, indicating the excellent transport properties. The increased ratio R_k/R_w obtained for the aged cell is ascribed to a major increase in R_k and to a slight decrease in R_w . This means that electron recombination with the electrolyte is inhibited upon aging and the transport properties in the TiO_2 film are enhanced. This analysis of R_w is in line with the increased diffusion coefficient presented in Table 2.3, probably due to the positive shift of the conduction band energy level edge with respect to the redox potential of electrolyte. The same conclusions can be drawn from the significant increase of the intermediate semicircle in Figure 2.5, which corresponds to a higher value of the charge-transfer resistance at this interface (mainly ascribed to R_k).

Table 2.3 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 2.6.

Exposure time / h	R_k / Ω	R_w / Ω	R_k/R_w	$L_n / \mu\text{m}$	τ_n / ms	$D_n / \text{cm}^2 \text{s}^{-1}$
0	61.8	3.0	20.6	31.8	20.2	5.01×10^{-4}
1000	130.7	2.2	59.4	54.0	40.7	7.16×10^{-4}

The fitting results also allow the calculation of the electron lifetime, yielding a larger τ_n (40.7 ms) for the aged device than for the fresh one (20.2 ms). These results are supported by the Bode-phase diagram in Figure 2.5a), where a slight left-shift of the middle-frequency peak (corresponding to the TiO_2 /dye/electrolyte interface) is noticed after 1000 h accelerated aging. This reveals an increase in the electron

lifetime in the semiconductor at the same bias voltage, which is in line with the values in Table 2.3. The increase of electron lifetime explains the higher V_{oc} observed in aged devices, since this parameter is strongly affected by the balance between the electron injection in TiO_2 and the recombination with I_3^- in the electrolyte.

Finally, a decrease in the redox charge transfer resistance at the platinum counter electrode was observed upon aging, which explains the decrease of the left-hand side semicircle in the Nyquist diagram (Figure 2.5b). This semicircle corresponds to the high-frequency peak in the Bode plot, which has moved towards larger values (meaning lower electron lifetimes and shorter redox reaction times). This situation is consistent with the improvement of FF over the same aging period (from 0.647 to 0.706), fact that can be attributed to the activation or better contact between the electrolyte and the platinum catalyst.³⁵

2.3.4 Photovoltage transient decay

To further elucidate the underlying mechanisms connected to the aging process, photovoltage transient decay measurements were performed.³⁶⁻³⁷ Electron transport and lifetime in DSCs have been modeled taking into account the influence of intra-band charge traps, *i.e.*, considering that the majority of photoinjected electrons are localised in trap states and they are conducted towards the external circuit by means of trapping/detrapping events.³⁸⁻³⁹ For mesoporous TiO_2 , the electron diffusion coefficient and lifetime and the chemical capacitance are significantly influenced by traps. It is therefore important to infer on the trapping conditions for the system under study, in order to assess its influence on the photovoltaic performance. On the basis of the trapping/detrapping model, longer electron lifetimes and smaller capacitances can be interpreted as higher trap densities and/or different trap distributions.⁴⁰

In Figure 2.7, the V_{oc} of both fresh and aged cells is plotted as a function of the photogenerated charge density. Similar trends are observed for both cells since slopes of 168 and 177 mV/decade were obtained for fresh and aged cells, respectively, suggesting a high density of traps in the semiconductor.⁴⁰ However, at a given charge

density the fresh and aged samples show different V_{oc} , indicating that the conduction band edge positively shifted about 20 mV for the aged sample. In fact, this positive shift of the conduction band after aging explains the increase in photovoltage.

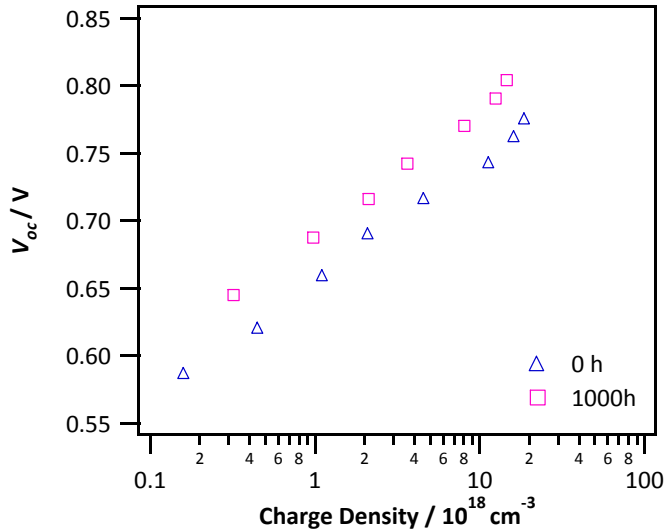


Figure 2.7 - Open-circuit voltage vs. photogenerated electron densities observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

In addition, the film capacitance plotted against V_{oc} (Figure 2.8) shows a very similar trend for the two periods, indicating that the recombination rates are comparable. The chemical capacitance is related to trap states, which accumulates and releases the electrons. Actually, since fresh and aged cells show similar photovoltaic performances, the density of traps in the photoelectrodes are expected to be the same. Moreover, the slight difference observed in Figure 2.8 is in line with the ratio R_k/R_w obtained previously by fitting: the aging process lowers the film capacitance reducing the number of recombination centers available at a given cell potential. This is confirmed by the higher electron recombination resistance, R_k , obtained for the aged cell.

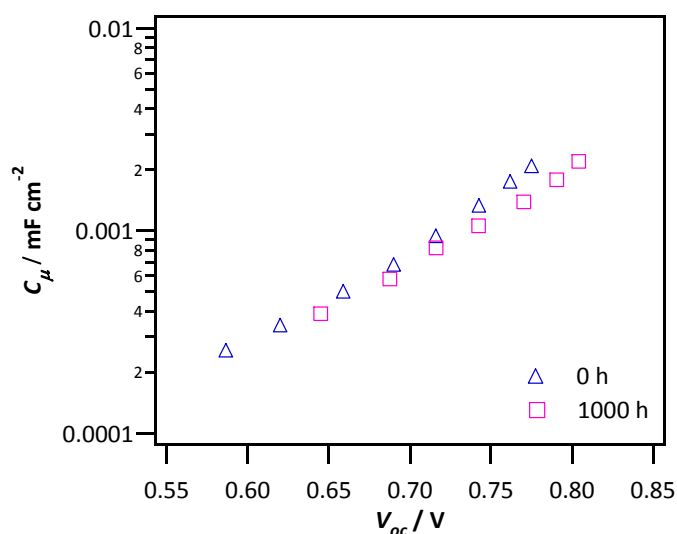


Figure 2.8 - Chemical capacitance vs. open circuit voltage observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

Finally, Figure 2.9 shows the evolution of the electron lifetime, determined by the photovoltage transient decay method, upon aging of the $2Na^+[N3.2H^+]$ dye/E1 electrolyte system. Once again, these results confirm the electron lifetime increase during the aging process. This behaviour allows us to conclude that the stability of this system during the aging process is responsible for the photovoltage and photovoltaic performance enhancement.

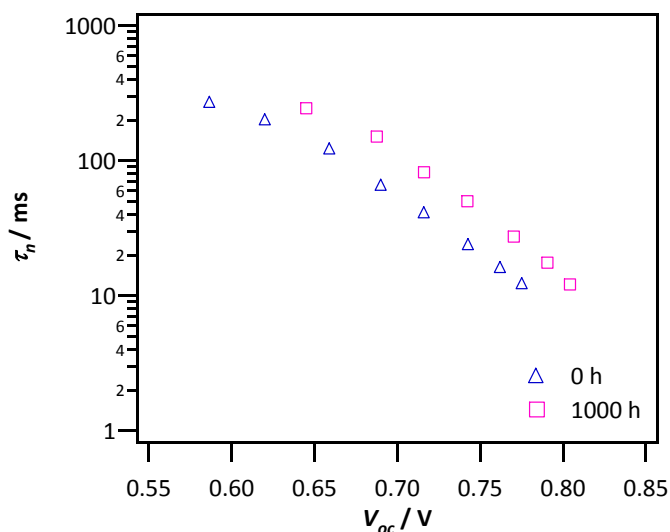


Figure 2.9 - Electron lifetimes vs. open-circuit voltage observed for fresh and aged devices (1000 h under 50 °C/light soaking stress).

2.4 Conclusion

The number of protons and the nature of cations of the dye influence the open-circuit potential and the short-circuit current of dye-sensitized solar cells. Thus, a new dye was synthesised by substituting two TBA cations of the N719 dye with sodium ions. In combination with a low-volatile electrolyte (E1), this new sensitizer gave a photovoltaic power conversion efficiency of 7.6 % at 100 mW cm^{-2} , AM 1.5 simulated sunlight conditions. Moreover, this system revealed a striking stability when submitted to full sunlight soaking at 50 °C. The $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]/\text{E1}$ system retained almost 99 % of its initial photovoltaic performance. The open-circuit voltage had an increase of about 20 mV, while the FF enhanced its initial value in 8 %. These observations are in line with the results obtained by electrochemical impedance spectroscopy, which show a higher recombination resistance at the $\text{TiO}_2/\text{electrolyte}$ interface compared to electron diffusion resistance in the TiO_2 film. This remained valid for the aged cell. Photovoltage transient measurements also confirmed the stability of the system. Our work shows that selection of counter ions for N3 type

sensitizers offers an attractive option to enhance the stability of dye sensitized solar cells.

Acknowledgments

We thank Dr. Minkui Wang for the discussions. L. Andrade and H. Aguilar Ribeiro are grateful to the Portuguese Foundation for Science and Technology (FCT) for their PhD and Post-doc grants (reference: SFRH/BD/30464/2006 and SFRH/BPD/36992/2007, respectively). S. M. Zakeeruddin, Md. K. Nazeeruddin and M. Grätzel thank the Swiss National Science Foundation for financial support.

List of abbreviations and symbols

Abbreviations	Definition	Units
AM	Air mass	
BMI	1-Butyl-3-methylimidazolium iodide	
C_{CE}	Double-layer capacitance at the platinised FTO	F
$C_{FTO/EL}$	Double-layer capacitance at exposed FTO/electrolyte interface	F
C_{μ}	Chemical capacitance	F
CPE	Constant phase element	
D_n	Diffusion coefficient of electrons in the TiO_2 semiconductor	$cm^2 s^{-1}$
DOS	Density of states	
DSC	Dye-sensitized Solar Cell	
EIS	Electrochemical impedance spectroscopy	
FF	Fill factor	
FTO	Fluorine-doped SnO_2 conducting glass electrode	
I	Current	mA
IPCE	Incident photon-to-current conversion efficiency	%
IR	Infrared	
J_{sc}	Short-circuit photocurrent density	$mA cm^{-2}$
k_{e^-}	Recombination rate constant	s^{-1}
L	Thickness of the semiconductor film	μm
L_n	Electron diffusion length	μm
MPN	3-Methoxypropionitrile	
NBB	1-Butyl-1H-benzimidazole	
NCS	Isothiocyanato group	
NMR	Nuclear magnetic resonance	
PMI	1-Propyl-3-methylimidazolium iodide	

PMITFSI	1-Propyl-3-methyl Imidazolium trifluoro methyl sulfonamide	
R_{CE}	Charge-transfer resistance at the platinised FTO	Ω
$R_{FTO/EL}$	Charge transfer resistance at exposed FTO/electrolyte interface	Ω
R_k	Recombination resistance	Ω
R_s	Series resistance	Ω
R_w	Electron transport resistance	Ω
TBA	Tetrabutylammonium	
UV	Ultraviolet	
V	Voltage	V
V_{oc}	Open-circuit photovoltage	V
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

Greek symbols	Definition	Units
γ -BL	γ -butyrolactone	
ΔQ	Number of electrons injected during the red light flash	C
ΔV	Peak of the photovoltage transient	V
η	Global efficiency of a DSC	%
λ	Wavelength	nm
τ_n	Electron lifetime	ms
φ	Incident light intensity	mW cm ⁻²

References

- (1) Grätzel, M. *Pure Appl. Chem.* **2001**, 73, 459.
- (2) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, 33, 269.
- (3) Kelly, C.; Meyer, G. *Coord. Chem. Rev.* **2001**, 211, 295.
- (4) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, 107, 2988.
- (5) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, 110, 1216.
- (6) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, 33, 5741.
- (7) Kohle, O.; Ruile, S.; Gratzel, M. *Inorg. Chem.* **1996**, 35, 4779.
- (8) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, 112, 7099.
- (9) Ruile, S.; Kohle, O.; Péchy, P.; Grätzel, M. *Inorg. Chim. Acta* **1997**, 261, 129.
- (10) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, 115, 6382.
- (11) Adachi, M.; Murata, Y.; Takao, J.; Jiu, J.; Sakamoto, M.; Wang, F. *J. Am. Chem. Soc.* **2004**, 126, 14943.
- (12) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, 126, 12218.
- (13) Wang, Z.-S.; Yamaguchi, T.; Sugihara, H.; Arakawa, H. *Langmuir* **2005**, 21, 4272.
- (14) Ushiroda, S.; Ruzyski, N.; Lu, Y.; Spitler, M. T.; Parkinson, B. A. *J. Am. Chem. Soc.* **2005**, 127, 5158.
- (15) Nazeeruddin, M.; Pechy, P.; Renouard, T.; Zakeeruddin, S.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G.; Bignozzi, C.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, 123, 1613.
- (16) Nazeeruddin, M.; Klein, C.; Liska, P.; Gratzel, M. *Coord. Chem. Rev.* **2005**, 249, 1460.
- (17) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, 35, 1168.

- (18) Kuang, D.; Klein, C.; Ito, S.; Moser, J. E.; Humphry-Baker, R.; Evans, N.; Duriaux, F.; Grätzel, C.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Mater.* **2007**, *19*, 1133.
- (19) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C. H.; Gratzel, M. *Inorg. Chem.* **1999**, *38*, 6298.
- (20) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (21) Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. *J. Phys. Chem. B* **2000**, *104*, 8916.
- (22) Nazeeruddin, M.; Humphry-Baker, R.; Liska, P.; Gratzel, M. *J. Phys. Chem. B* **2003**, *107*, 8981.
- (23) Pelet, S.; Moser, J.-E.; Gratzel, M. *J. Phys. Chem. B* **2000**, *104*, 1791.
- (24) Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. *Nat. Mater.* **2003**, *2*, 229.
- (25) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (26) Wang, Q.; Moser, J.-E.; Gratzel, M. *J. Phys. Chem. B* **2005**, *109*, 14945.
- (27) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.
- (28) Bisquert, J.; Zaban, A.; Greenshtein, M.; Mora-Sero, I. *J. Am. Chem. Soc.* **2004**, *126*, 13550.
- (29) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.
- (30) Bisquert, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5360.
- (31) Lagemaat, J.; Park, N. G.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 2044.
- (32) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. *J. Phys. Chem. B* **2000**, *104*, 2287.
- (33) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, 2005.
- (34) Wang, Q.; Ito, S.; Gratzel, M.; Fabregat-Santiago, F.; Mora-Sero, I.; Bisquert, J.; Bessho, T.; Imai, H. *J. Phys. Chem. B* **2006**, *110*, 25210.

- (35) Toivola, M.; Peltokorpi, L.; Halme, J.; Lund, P. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1733.
- (36) Peter, L. M. *J. Phys. Chem. C* **2007**, *111*, 6601.
- (37) Kopidakis, N.; Neale, N. R.; Frank, A. J. *J. Phys. Chem. B* **2006**, *110*, 12485.
- (38) Nelson, J.; Haque, S. A.; Klug, D. R.; Durrant, J. R. *Phys. Rev. B* **2001**, *63*, 205321.
- (39) van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2001**, *105*, 11194.
- (40) Fukai, Y.; Kondo, Y.; Mori, S.; Suzuki, E. *Electrochem. Commun.* **2007**, *9*, 1439.

Chapter 3.

INFLUENCE OF DIFFERENT CATIONS OF N3 DYES ON THEIR PHOTOVOLTAIC PERFORMANCE AND STABILITY

Luísa Andrade, Shaik M. Zakeeruddin, Mohammad K. Nazeeruddin, Helena Aguilar Ribeiro, Adélio Mendes and Michael Grätzel

(International Journal of Chemical Engineering 2009, Article ID 563420, 7 pages)

Abstract

In the present work the N3 dye was modified by substituting two of its protons by potassium or sodium cations. The performance and stability of dye-sensitized solar cells incorporating the new dyes were evaluated under light soaking (100 mW cm^{-2}) at 50°C . Photocurrent measurements demonstrated that proton substitution by potassium cations renders the system more stable. Further characterisation of the potassium-based devices was performed by electrochemical impedance spectroscopy to investigate the charge transfer phenomena occurring at the different interfaces of the cells.

Keywords: dye-sensitized solar cells, proton substitution, stability, electrochemical impedance spectroscopy.

3.1 Introduction

In Dye-sensitized Solar Cells (DSCs), the dye is a crucial component to achieve high overall photoelectric conversion efficiency. Up to now, ruthenium complexes have been widely investigated due to their advantageous spectral properties, device photostability and high conversion efficiency.¹⁻³ An example of these ruthenium polypyridine complexes with better performance as sensitizer is the cis-di(thiocyanato)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II), commonly known as N3.⁴ Since the development of the N3 dye in 1993,⁴ its tetrabutylammonium (TBA) salt N719 has been used as the standard red dye because of its unmatched performances. Similarly to the N719 dye, new dyes were developed bearing in mind that the number of protons in the dye influences the open-circuit potential and the short circuit current of a DSC.⁵ In this work we modified the N3 dye by partially substituting its protons with different cations, namely, sodium and potassium. The modified dyes were subsequently incorporated in final DSC devices, which were then submitted to accelerated thermal/light soaking aging tests for performance and stability evaluation. The cells were subjected to full sunlight irradiation at 50 °C for about 1000 hours, during which time their photovoltaic parameters were periodically monitored.

Electrochemical impedance spectroscopy (EIS) was used to investigate the charge transfer phenomena occurring at the different interfaces of the DSCs. This technique has been widely used for the characterisation of several electrochemical systems and, in particular, to analyse internal resistances in the DSCs.⁶⁻¹⁵ In 2000 Bisquert *et al.*¹² applied their models in the analysis of the mechanisms of electron recombination in nanoporous TiO₂ dye-sensitized solar cells.¹² After this first approach, EIS became more and more useful, playing a crucial role in what concerns modelling and understanding the complex charge phenomena occurring in DSCs.⁶⁻¹⁵ The charge-transfer resistance at the transparent conductive layer (TCO), the charge-transfer resistance at the counter electrode/electrolyte interface and the charge-transfer resistance at TiO₂/dye/electrolyte interface can therefore be obtained by fitting the EIS results to appropriate equivalent electrical circuits.¹⁶

3.2 Experimental section

All chemicals used in the present work were of purest quality. γ -butyrolactone (γ -BL) was obtained from Fluka and distilled before use. 1-Butyl-3-methylimidazolium iodide (BMII) and 1-Propyl-3-methylimidazoliumtrifluoromethylsulfonamide (PMITFSI) ionic liquids were prepared according to literature methods and the purity was confirmed by ^1H NMR (nuclear magnetic resonance) spectra.¹⁷

3.2.1 Dye preparation

N719 dye was synthesised as reported earlier.¹⁸ The dipotassium [$2\text{K}^+(\text{N3}, 2\text{H}^+)$] and disodium [$2\text{Na}^+(\text{N3}, 2\text{H}^+)$] dyes were prepared as follows. First, N719 dye was dissolved in acetonitrile solvent and to this an excess amount of potassium triflate or sodium triflate in acetonitrile was added. Immediately, the triflate counter ion was precipitated, filtered and washed with acetonitrile and dried under vacuum.

3.2.2 Composition of electrolyte E1

0.1 M iodine, 0.5 M N-methylbenzimidazole in a mixture of BMII; PMITFSI; γ -BL (2; 3; 1) vol/vol.

3.2.3 TiO_2 electrode preparation

A screen-printed double-layer film of interconnected TiO_2 particles was used as mesoporous photoelectrode. A 7 μm -thick film of 20 nm-sized TiO_2 particles was first printed on the fluorine doped SnO_2 conducting glass electrode (FTO) and further coated by a 5 μm -thick second layer of 400 nm-sized light scattering anatase particles. The detailed preparation procedures of TiO_2 nanocrystals, pastes for screen-printing and double-layer nanostructured TiO_2 film have been reported elsewhere.¹⁹

3.2.4 Dye-sensitized solar cell fabrication

The working electrode, described above, was sealed to the counter electrode (CE) by means of a 25 μm -thick transparent Surlyn ring (from DuPont) at 130 $^{\circ}\text{C}$ for 15 seconds. The CE is a fluorine-doped SnO_2 conducting glass electrode (FTO) - 15 Ω/square - coated with a platinum solution chemically deposited at 450 $^{\circ}\text{C}$ for 15 minutes. The cells were filled with the electrolyte solution through a pre-drilled hole in the counter electrode. The hole was then sealed with a Bynel disc and a thin glass to avoid leakage of the electrolyte.

3.2.5 Photovoltaic measurements

All photovoltaic measurements were performed under a 450 W xenon light source able to provide 100 mW cm^{-2} sunlight Air Mass (AM) 1.5. The spectral output of the lamp was matched in the region of 350-750nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Iserlohn, Germany) so as to reduce the mismatch between the simulated and true solar spectra. Various incident light intensities were regulated with wavelength neutral wire mesh attenuators. I - V curves were obtained by applying an external bias to the cells and measuring the respective photocurrent response with a digital source meter (Keithley Instruments Inc., Ohio, USA Model 2400). The incident photon-to-current conversion efficiency (IPCE) was recorded by a data-collecting system as a function of excitation wavelength. The incident light from a 300 W xenon lamp (ILC Technology, CA, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon., UK) onto the cell under test. The monochromator output was incremented through the visible spectrum to generate the $IPCE(\lambda)$ as defined by $IPCE(\lambda) = 124000(J_{sc}/\lambda\phi)$, where λ is the wavelength (nm), J_{sc} is short-circuit photocurrent density (mA cm^{-2}), and ϕ is the incident radiative flux (mW cm^{-2}). Photovoltaic performance was determined for an active area of 0.158 cm^2 defined by a metal mask.

3.2.6 Electrochemical Impedance Measurements

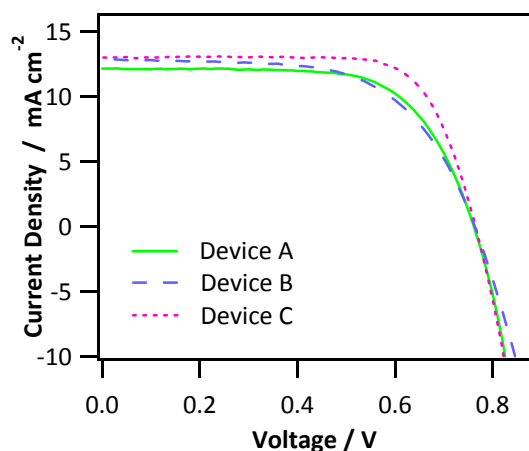
Impedance experiments were carried out with a computer-controlled potentiostat (EG&G M273) equipped with a frequency response analyser (EG&G M1025). The frequency range was 0.005 Hz - 100 kHz and the magnitude of the modulation signal was 10 mV. All the measurements were performed at room temperature in the dark at -0.75 V bias. The EIS spectra were fitted to an appropriate electrical analogue by means of the ZView software (v2.5b, Scribner Associates Inc, NC, USA).

3.2.7 Stability Tests

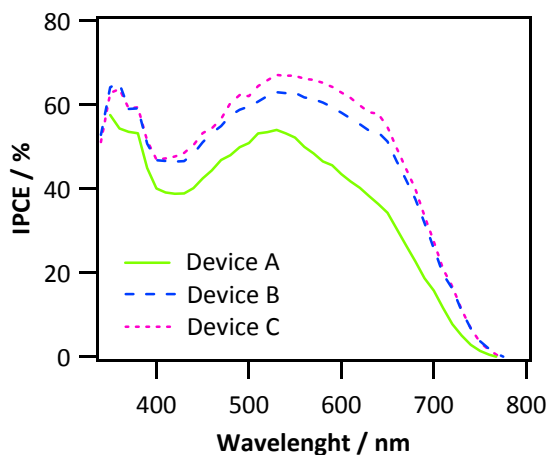
Hermetically sealed cells were used to check the long-term stability under visible light soaking at 50 °C. The light soaking experiments employed a polymer film of 50 μm -thickness (Preservation Equipment Ltd, UK) as a 400 nm UV cut-off filter. Two cells of each type with matched photovoltaic performances were exposed at open circuit to a Suntest CPS lamp (ATLAS Material Testing Solutions, GMBH, 100 mW cm^{-2} , 50 °C) over a period of 1000 hours. The cells were taken out at regular intervals to record the photocurrent-voltage curve.

3.3 Results and discussion

Figure 3.1a) shows the photocurrent density-voltage curves obtained under AM 1.5 simulated sunlight (100 mW cm^{-2}) for DSCs prepared with $[2\text{K}^+(\text{N3}, 2\text{H}^+)]$, $[2\text{Na}^+(\text{N3}, 2\text{H}^+)]$ and N719 dyes in association with electrolyte E1. The cells were labelled as device A, B and C, respectively. For simplicity, the results for one single cell of each type are presented hereafter.



(a)



(b)

Figure 3.1 - a) Photocurrent intensity-voltage characteristics for devices A, B and C, measured at 1 sun (100 mW cm^{-2}), AM 1.5 global sunlight illumination. b) Photocurrent action spectra of the same devices.

Comparing the three systems under study, device C shows the best initial photovoltaic performance. In fact, it is already known by its unmatched performance. On the basis of cations' substitution in the N3 dye, the anchoring groups of the adsorbed sensitizer transfer most of its protons to the semiconductor surface, charging it positively. This change in the TiO_2 surface enhances the adsorption of the

anionic ruthenium complexes and favours electron injection from the excited state of the dye into the conduction band of the semiconductor, resulting in higher photocurrents. Nevertheless, this positive shift of the Fermi level induced by surface protonation leads to a low open-circuit potential. In fact, if the sensitizer has less protons, it is expected to obtain high open-circuit potential and low photocurrents, and the other way round if the sensitizer is fully protonated. So, an optimal degree of protonation of the sensitizer should be considered to reach maximum overall conversion efficiency.⁵ In this study we observed that the sodium-based system (device B) presents higher values of short-circuit current, J_{sc} , and open-circuit voltage, V_{oc} , than cells with the potassium based system (device A) - Figure 3.1a). However, the latter system has higher overall power conversion efficiency, η , due to a higher value of the fill factor, FF . This fact is explained by a reduction in the series resistance of the cell with potassium salt dye.

In Figure 3.1b) the IPCE for devices A, B, and C can be compared. The IPCE is plotted as a function of the excitation wavelength. In line with the better photovoltaic performance, device C shows the highest IPCE: maximum of about 67 % at 530 nm. At the same wavelength, device A reaches a maximum of 54 %, while device B reaches approximately 63 %.

Apart from efficiency, the long-term stability is also a key issue regarding the industrial development and commercialisation of DSCs. Thus, an intimate relation between photovoltaic performances and stability should be achieved. The evolution of the photovoltaic performances throughout the aging process of the three systems under study is presented in Figure 3.2. Device A reveals a better stability when compared with the two other systems. Actually, this device kept close to 90 % of its initial performance after 1000 hours of light soaking at 50 °C. In contrast, devices B and C showed a drop in efficiency of about 23 % and 25 %, respectively. The higher stability of device A is mainly due to an increase in the photocurrent (6 %) during the first week of aging, which was then maintained at the same level for the rest of the aging period. Additionally, this system shows a quite stable evolution of the FF values, indicating constancy in series resistance during the aging process. Despite its high photovoltaic performance as a fresh cell, the N719 system was unstable, exhibiting a

marked decrease in J_{sc} and V_{oc} soon after the first week. This may be due to desorption of dye from the TiO_2 surface. Moreover, the sodium salt containing device B does not rend the system very stable, as suggested by the strong oscillation in all its photovoltaic parameters.

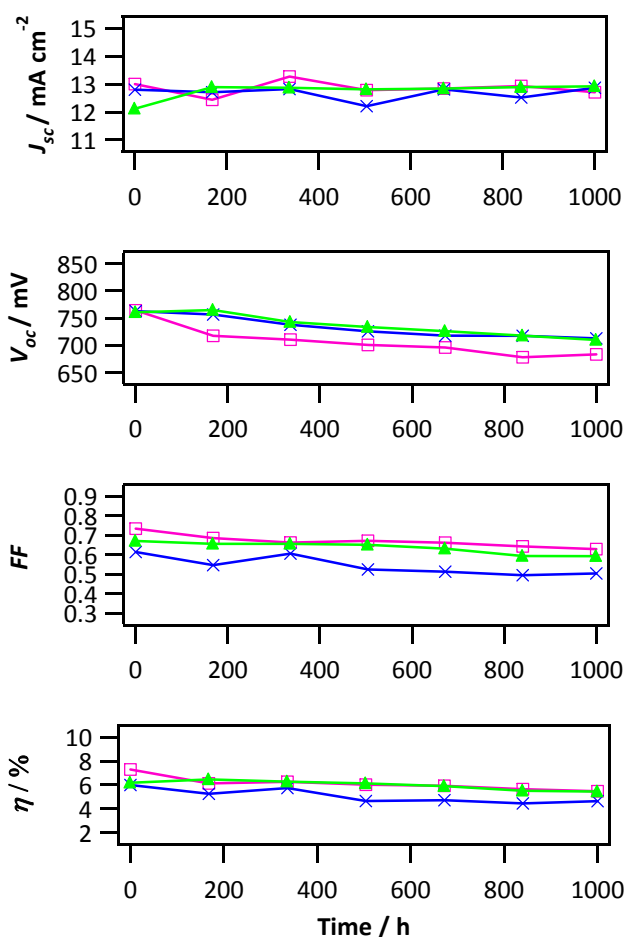


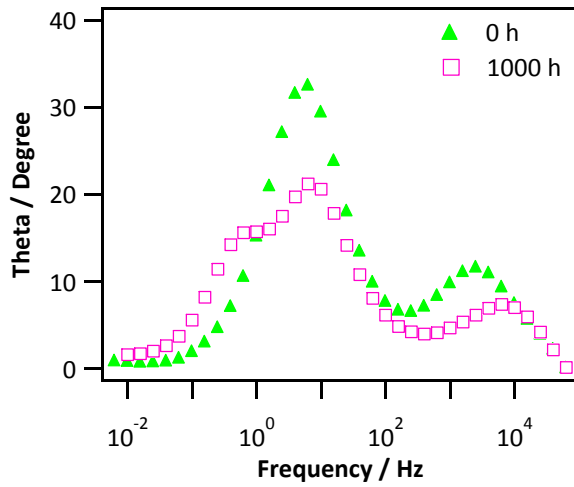
Figure 3.2 - Evolution of photovoltaic parameters for device A ($\blacktriangle$), device B ($\times$) and device C ($\square$). The cells were kept under one sun visible-light soaking at 50 °C for approximately 1000 h.

The stability tests allow us to conclude that the number and type of substituting cations will strongly influence the photovoltaic performances of the devices. Considering the ionic potentials of the cations we can realise how strongly they will be electrostatically attracted to ions of opposite charge and to what extent the cations

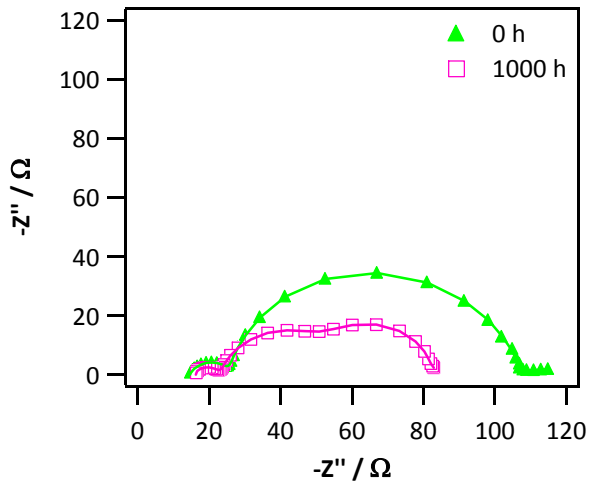
will repel other ions of like-charge. As the sodium cation has higher ionic potential than the potassium cation, we may be induced to say that the stability is improved when substituting the N3 protons by sodium cations. However, this conclusion is not straightforward since we have to consider the DSC system with all its components. The present work proves this fact since potassium substitution renders a better stability. The positive shift of the Fermi level upon adsorption of the dye decreases the gap between the redox couple and the Fermi level. This fact will strongly influence the TiO_2 /dye/electrolyte interaction, which is not totally understood.

Bearing in mind the promising results in terms of performance and long-term stability of the potassium based DSC, a deeper characterisation of the system was performed. In this sense, the effect of the aging process in the overall performance of device A was analysed by means of electrochemical impedance spectroscopy. This technique allows us to determine the charge-transfer resistances at the platinum counter electrode and at the TiO_2 /dye/electrolyte interface as well as to determine the Nernstian diffusion of I^-/I_3^- ions within the electrolyte.^{6,16} The Bode and Nyquist (Z'' - imaginary part of impedance *versus* Z' - real part of impedance) plots for the potassium-based system, before and after the aging process, are shown in Figure 3.3.

Several physical models have been developed in an effort to understand all the complex charge-transfer processes that take place in DSCs.^{9,12,20} These works employ the diffusion-recombination model to study the electronic processes taking place at the semiconductor, whereas the electron transfer phenomena at the electrolyte and contact interfaces are described by simple RC electrical arrangements (resistor in parallel with a capacitor). Actually, the electron transport and charge recombination in nanocrystalline TiO_2 films have been widely studied by Bisquert *et al.*,¹² who suggested an infinite transmission line model to describe the charge transfer phenomena occurring at the mesoscopic TiO_2 film, as presented in Figure 3.4.



(a)



(b)

Figure 3.3 - Bode (a) and Nyquist (b) diagrams obtained for device A before and after 1000 h under thermal/light soaking stress. In the Nyquist diagram, symbols correspond to the impedance data obtained experimentally in the dark under -0.75 V bias, while solid lines represent the fittings according to the equivalent circuit present in Figure 3.4.

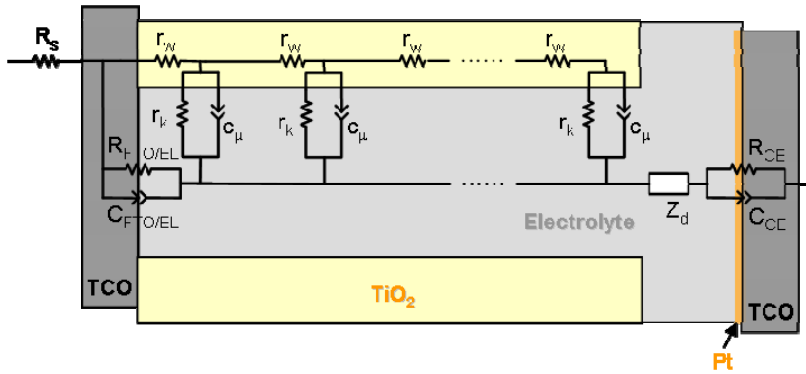


Figure 3.4 - Transmission line model used to fit the EIS experimental data. R_s - series resistance; $R_{FTO/EL}$ - charge transfer resistance at exposed FTO/electrolyte interface; $C_{FTO/EL}$ - double layer capacitance at exposed FTO/electrolyte interface; r_k - recombination resistance; r_w - transport resistance; c_{μ} - chemical capacitance; Z_d - Nernst diffusion within electrolyte; R_{CE} - charge transfer resistance at the platinised TCO; C_{CE} - double layer capacitance at the platinised TCO.

The transmission line model assumes the TiO_2 photoanode as an interconnected network where electrons, after excitation, can diffuse towards the external circuit with a resistance R_w or recombine at the TiO_2 /electrolyte interface. Assuming that the recombination phenomenon is only related to electron transfer by back reaction with the electrolyte (dark current), it can be described by a charge transfer resistance, R_k , and a chemical capacitance, C_{μ} . If L is the thickness of the mesoscopic TiO_2 film, the electron transport resistance through the semiconductor is defined as $R_w = r_w L$, while the interfacial charge recombination resistance and the chemical capacitance at the interface are, respectively, $R_k = r_k / L$ and $C_{\mu} = c_{\mu} L$.

The other charge-transfer processes occurring in DSCs are also considered in the electrical analogue, as shown in Figure 3.4. Regeneration of I_3^- at the counter electrode is characterised by R_{CE} and C_{CE} , which represent the charge transfer resistance and the double-layer capacitance at the platinised FTO glass, respectively. Finally, the ZView software was used to fit the experimental data to the equivalent circuit presented in Figure 3.4. For better fitting, all capacitor elements were replaced

by constant phase elements (CPE), non-ideal capacitances associated with a non-uniform distribution of current in the heterogeneous TiO_2 film.²¹

Table 3.1 presents some parameters useful to understand the underlying mechanisms related to the aging process. Besides R_k and R_w , the electron lifetime τ_n ($\tau_n = R_k C_\mu$), the effective electron diffusion length L_n ($L_n = L\sqrt{R_k / R_w}$), and the effective diffusion coefficient of electrons in the TiO_2 semiconductor D_n ($D_n = L_n^2 / \tau_n$) can also be obtained.²⁰ According to the diffusion-recombination model, the ratio R_k/R_w (>1) clearly shows that the charge-transfer resistance associated to recombination of electrons at the TiO_2 /electrolyte interface (R_k) is much higher than the electron transport resistance through the semiconductor (R_w). This means that the cell exhibits carrier collection efficiency near unity.²⁰

Table 3.1 - Parameters determined by fitting the EIS experimental data of device A to the equivalent circuit shown in Figure 3.4.

Exposure time / h	R_k / Ω	R_w / Ω	R_k / R_w	$L_n / \mu\text{m}$	τ_n / ms	$D_n / \text{cm}^2 \text{s}^{-1}$
0	67.2	5.1	13.3	25.5	11.1	5.90×10^{-4}
1000	32.3	1.8	18.4	30.0	4.5	2.00×10^{-3}

Moreover, Table 3.1 shows that L_n is much higher than the thickness of the mesoscopic TiO_2 film ($L \approx 12 \mu\text{m}$) in both fresh and aged cells, confirming the excellent transport properties. The increased J_{sc} for the aged sample can be attributed to the longer electron diffusion length compared to the fresh sample ($J_{sc}^{0 \text{ hours}} = 12.1 \text{ mA cm}^{-2}$ and $J_{sc}^{1000 \text{ hours}} = 12.9 \text{ mA cm}^{-2}$). As shown in Figure 3.3a), the middle frequency peak position of the aged sample was slightly shifted to higher frequencies, revealing a decrease in the electron lifetime. The decreased electron lifetime is mainly ascribed to a major decrease in R_k (in Table 3.1) for the aged sample compared to the fresh one. This means that electrons recombine more easily with the electrolyte upon aging. A faster electron recapture taking place in the aged device prevents the electron accumulation in the TiO_2 nanoparticles from reaching the same density as for

the fresh devices. As a result, the drop of V_{oc} was observed in aged devices (Figure 3.2). The same conclusions can be drawn from the significant decrease of the intermediate semicircle in Figure 3.3b), which corresponds to a lower value of the charge-transfer resistance (R_k) at this interface. The increased electron diffusion coefficient was probably due to the positive shift of the conduction band energy level edge.

A decrease in the redox charge-transfer resistance at the platinum counter electrode was observed upon aging ($R_{CE}^{0 \text{ hours}} = 9.1 \, \Omega$ and $R_{CE}^{1000 \text{ hours}} = 5.5 \, \Omega$). This explains the decrease of the left-hand side semicircle in the Nyquist diagram. This semicircle corresponds to the high-frequency peak in the Bode plot, which has moved toward larger values. Additionally, an overlap between the photoelectrode impedance (middle semicircle) and that related to the Nernstian diffusion within the electrolyte (right hand semicircle) can be noticed. This was probably due to a larger overpotential for the I^-/I_3^- redox reaction on the platinum electrode of the aged sample, accompanied with a fill factor problem (FF decreases from 0.67 to 0.59 upon aging).

3.4 Conclusion

Two N3-based dyes were synthesised bearing in mind that the number of protons in the sensitizer influences the open-circuit potential and the short-circuit current of the DSC. Potassium and sodium cations were used to substitute two protons of the N3 dye and the resulting dyes were compared with the well-known N719 dye that contains two TBA cations. Despite presenting the highest initial photovoltaic performance, the N719 system was rather unstable, exhibiting a strong decrease in J_{sc} and V_{oc} upon aging, which might be due to dye desorption. In addition, sodium substitution in place of TBA does not help to enhance the stability of devices, whereas substitution with potassium salt revealed better stability compared to the other two systems. In fact, this system kept close to 90 % of its initial performance after 1000 hours of light soaking at 50 °C.

Acknowledgments

L. Andrade and H. Aguilar Ribeiro are grateful to the Portuguese Foundation for Science and Technology (FCT) for their PhD and post-doc grants (SFRH/BD/30464/2006 and SFRH/BPD/36992/2007, respectively).

List of abbreviations and symbols

Abbreviations	Definition	Units
AM	Air mass	
BMIl	1-Butyl-3-methylimidazolium iodide	
C	Capacitor	F
C_{CE}	Double-layer capacitance at the platinised FTO	F
$C_{FTO/EL}$	Double-layer capacitance at exposed FTO/electrolyte interface	F
CPE	Constant phase element	
C_{μ}	Chemical capacitance	F
D_n	Diffusion coefficient of electrons in the TiO_2 semiconductor	$cm^2 s^{-1}$
DSCs	Dye-sensitized solar cells	
EIS	Electrochemical impedance spectroscopy	
FF	Fill factor	
FTO	Fluorine-doped SnO_2 conducting glass electrode	
I	Current	mA
IPCE	Incident photon-to-current conversion efficiency	%
J_{sc}	Short-circuit photocurrent density	$mA cm^{-2}$
L	Thickness of the semiconductor film	μm
L_n	Electron diffusion length	μm
NMR	Nuclear magnetic resonance	
PMITFSI	1-Propyl-3-methyl Imidazolium trifluoro methyl sulfonamide	
R	Resistor	Ω
R_{CE}	Charge-transfer resistance at the platinised FTO	Ω
$R_{FTO/EL}$	Charge transfer resistance at exposed FTO/electrolyte interface	Ω
R_k	Recombination resistance	Ω

R_s	Series resistance	Ω
R_w	Electron transport resistance	Ω
TBA	Tetrabutylammonium	
TCO	Transparent conductive oxide	
UV	Ultraviolet	
V	Voltage	V
V_{oc}	Open-circuit photovoltage	V
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

<i>Greek symbols</i>	Definition	Units
γ -BL	γ -butyrolactone	
η	Global efficiency of a DSC	%
λ	Wavelength	nm
τ_n	Electron lifetime	ms
φ	Incident light intensity	mW cm ⁻²

References

- (1) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099.
- (2) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.
- (3) Ruile, S.; Kohle, O.; Péchy, P.; Grätzel, M. *Inorg. Chim. Acta* **1997**, *261*, 129.
- (4) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- (5) Nazeeruddin, M.; Humphry-Baker, R.; Liska, P.; Gratzel, M. *J. Phys. Chem. B* **2003**, *107*, 8981.
- (6) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (7) Green, A. N. M.; Palomares, E.; Haque, S. A.; Kroon, J. M.; Durrant, J. R. *J. Phys. Chem. B* **2005**, *109*, 12525.
- (8) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.
- (9) Adachi, M.; Sakamoto, M.; Jiu, J.; Ogata, Y.; Isoda, S. *J. Phys. Chem. B* **2006**, *110*, 13872.
- (10) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.
- (11) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 334.
- (12) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. *J. Phys. Chem. B* **2000**, *104*, 2287.
- (13) Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 8774.
- (14) Han, L. Y.; Koide, N.; Chiba, Y.; Mitate, T. *Appl. Phys. Lett.* **2004**, *84*, 2433.
- (15) Han, L.; Koide, N.; Chiba, Y.; Islam, A.; Komiyama, R.; Fuke, N.; Fukui, A.; Yamanaka, R. *Appl. Phys. Lett.* **2005**, *86*, 213501.
- (16) Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Gratzel, M. *J. Phys. Chem. C* **2007**, *111*, 6550.

- (17) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
- (18) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C. H.; Gratzel, M. *Inorg. Chem.* **1999**, *38*, 6298.
- (19) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (20) Wang, Q.; Ito, S.; Gratzel, M.; Fabregat-Santiago, F.; Mora-Sero, I.; Bisquert, J.; Bessho, T.; Imai, H. *J. Phys. Chem. B* **2006**, *110*, 25210.
- (21) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, 2005.

Chapter 4.

EFFICIENCY ENHANCEMENT OF DYE-SENSITIZED SOLAR CELLS BY COATING THE COUNTER ELECTRODE BACKSIDE WITH A REFLECTIVE COMMERCIAL PAINT

Luísa Andrade, Rui Cruz, Shaik M. Zakeeruddin, Helena Aguilar Ribeiro, Michael Grätzel and Adélio Mendes

(to be submitted, 2010)

Abstract

The efficiency of dye-sensitized solar cells was improved by inducing secondary light absorption at the photoelectrode. The conventional structure of dye-sensitized solar cells was modified by coating the counter electrode backside with a reflective paint layer in order to reflect back to the semiconductor the portion of light that crosses the photoanode and reaches the counter electrode. By doing so the photocurrent of the cell was increased. Moreover, there was no negative effect of this layer in the inner components of the cell. The material of choice was a cheap commercially available paint. Two systems differing in the photoanode were considered to validate the results. The performance of the new device configuration increased by almost 10 % for a semitransparent TiO_2 photoanode and 6 % for a double-layered TiO_2 photoanode. The photovoltaic performance of the semitransparent cell with the backside of its counter electrode coated with the reflective paint was compared with the results obtained when an aluminium foil material was used. The comparison allowed to conclude that the use of a reflective paint film is a low-cost and an effective way to increase the photocurrent density of a dye-sensitized solar cell.

Keywords: Dye-sensitized solar cells, counter electrode, efficiency, reflective materials, electrochemical impedance spectroscopy.

4.1 Introduction

Despite the initial success of more than 11 % solar energy conversion efficiency,¹ further efforts are needed to improve dye-sensitized solar cells' (DSCs) performance and stability. The overall conversion efficiency of a DSC, η , is determined by the integral photocurrent density measured under short-circuit conditions (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF) and the intensity of the incident light (I_s):

$$\eta = \frac{J_{sc} V_{oc}}{I_s} FF \quad (4.1)$$

Under full sunlight (1 sun, air mass AM 1.5 global intensity, $I_s = 100 \text{ mW cm}^{-2}$) short circuit photocurrents of $16\text{-}22 \text{ mA cm}^{-2}$ can be achieved with the most efficient ruthenium sensitizers, *e.g.* red and black dyes,² while V_{oc} and FF values are in the range of $0.70\text{-}0.80 \text{ V}$ and $0.65\text{-}0.75$, respectively. Actually, higher values of open-circuit voltage were achieved with the N719 dye (cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4''-dicarboxylato) ruthenium(II) bis (tetrabutylammonium)) in combination with a self-assembly facilitating adsorbent, such as guanidinium thiocyanate (GuSCN), which appears to reduce the recombination rate of the conduction band electrons with triiodide ions (dark current). An open-circuit voltage of about 0.86 V has been reported.³ Another way of improving the solar to current conversion efficiency is by enhancing light harvesting in the photoelectrode. In fact, increased absorption would result directly in increased current outputs and higher efficiencies. This can be achieved by means of light scattering structures composed of metal oxide large particles with diameter of several hundred nanometres, which enable the increase of the optical path length in the semiconductor.⁴ However, while larger particles are needed for effective light scattering, they provide lower effective surface area for dye adsorption, as reported by Ferber *et al.*⁵ who presented a computer optimisation of the TiO_2 particles size. This is in fact a very important feature to be considered when designing DSCs for architectural applications where transparency and colour is required. Fine tuning of these properties may be achieved by engineering particle size, film thickness, semiconductor oxide layer structure and dye cocktail

components, but at the cost of effective photocurrent losses. This occurs because a larger fraction of the light striking the photoelectrode crosses it without being absorbed by the dye, finally reaching the surface of the counter electrode (CE). Therefore, by coating the counter electrode backside with a reflective layer, part of this non-absorbed light will be reflected back to the semiconductor, enabling its absorbance by the dye this time - Figure 4.1. Indirectly, the counter electrode reflectance is increased without changing the inner components of the DSC. In fact, the main idea is to incorporate a reflective film in the DSCs' structure that ultimately acts as a mirror. The use of a silver reflection coating has already been reported,⁶ with the disadvantages of being an expensive material that needs to be protected from atmospheric corrosion (oxidation). This approach was also used in large DSC modules in which the backside of the counter electrodes was sputtered with a thin metallic Ag film allowing secondary dye-absorption. In addition, the thickness of the platinum and electrolyte layers was optimised to increase the number of photons absorbed by the dye molecules when the cells were irradiated from the CE side. The overall efficiency of the modules was increased by 1 %.⁷

In the present work the material of choice for the reflection film was very cheap and easy to apply: a commercial paint with different possibilities of colour. Typically, paint formulations are composed of TiO_2 in rutile form due to its high refractive index. As mentioned before, this is the underneath reason for using scattering layers at the photoanode. Besides enhancing light harvesting inside the semiconductor layer, the scattering layers promote electrical insulation between the two electrodes of the DSC while letting the redox electrolyte species diffuse freely among them. However, harvesting the maximum amount of reflected light would require very thick TiO_2 insulating layers. Consequently, voltage losses in the electrolyte would be expected due to the increased resistance of the redox species to diffuse through the porous insulating layer. Again, by incorporating the paint reflective layer in the backside of a DSC, there is no negative effect of this layer in the overall efficiency of the device. In addition, for applications where the cell's transparency is not an essential requirement, this structure is an alternative way to achieve higher efficiencies without increasing significantly the total cost of the devices.

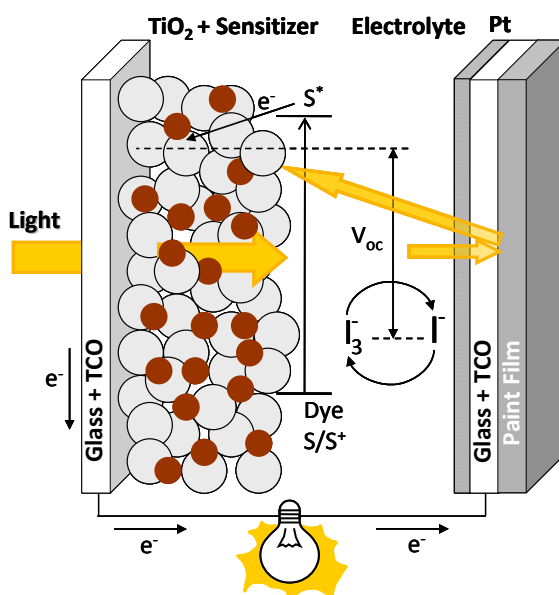


Figure 4.1 - Operating principle of a dye-sensitized solar cell with a reflective layer at the counter electrode side.

4.2 Experimental section

4.2.1 Materials

The Z907 dye was synthesised as reported earlier⁸ and the composition of Z959 electrolyte is 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I_2 , 0.1 M guanidinium thiocyanate and 0.5 M *ter*-butylpyridine in acetonitrile and valeronitrile solvent mixture.

An exterior water-base, white mate paint (CIN, Portugal) with a total solar reflectance of 90 % was used as reflective layer.

4.2.2 Dye-sensitized solar cell fabrication

Screen-printed semitransparent and double-layered films of interconnected TiO_2 particles were used as photoanodes (active area 0.28 cm^2). The cells with semitransparent photoanode and with the double-layered film are denoted hereafter

as devices A and B, respectively. For the semitransparent layer, an 8.3 μm -thick film of 20 nm-sized TiO_2 particles was printed onto the fluorine-doped SnO_2 conducting glass electrode (FTO). For the double-layered film, a 7 μm -thick film of 20 nm-sized TiO_2 particles was first printed onto the glass substrate and further coated by a 5 μm -thick second layer composed of 400 nm-sized light-scattering anatase TiO_2 particles. The detailed preparation procedures of TiO_2 pastes for screen-printing have been reported elsewhere.⁹ The TiO_2 film electrodes were dipped into a 0.3 mM $\text{NaRu}(\text{4-carboxylic acid-4'-carboxylate} - 2, 2' - \text{bipyridine})$, (4, 4' - dinonyl-2, 2' bipyridine) (NCS)₂ dye solution at room temperature for 10 minutes to adsorb the dye and then washed with acetonitrile and dried by air flow. The working and counter electrodes were sealed with a 25 μm -thick transparent Surlyn ring (from DuPont) at 130 $^\circ\text{C}$ for 15 s. The counter electrode was prepared by chemical deposition of a platinum solution onto a similar conducting substrate used for the TiO_2 electrode (FTO glass, 15 Ω per square). The annealing step was performed at 450 $^\circ\text{C}$ for 15 min to activate the platinum catalyst. After sealing, the cells were filled with the electrolyte solution through a pre-drilled hole done in the counter electrode side. Finally, the hole was sealed with a melted Surlyn disc covered by a thin glass lamella to avoid leakage of the electrolyte. Finally, after characterisation of this set of cells by means of electrochemical methods, a layer of reflective paint (double coated) was applied at the counter electrodes backside. In order to compare the performance of the reflective paint to that of an aluminium material, device A was characterised also with an aluminium foil in the backside of the counter electrode to induce light reflection.

4.2.3 Photovoltaic measurements

A full spectrum, collimated, ozone free, 450 W xenon light source (Oriel, USA) was used to give an irradiance of 100 mW cm^{-2} (1 sunlight intensity, 1.5 AM Global) at the front surface of the DSCs devices. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra. Under these conditions, the current-voltage characteristics of

the cells were obtained by imposing an external potential and measuring the generated photocurrent using an electronic load (Keithley, model 2400 series). The devices were masked to have an illuminated active area of 0.159 cm^2 .

4.2.4 Electrochemical impedance measurements

Electrochemical impedance measurements of DSCs were performed with an Autolab Frequency Analyser setup consisting of the Autolab PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) and the Frequency Response Analyser (FRA) module. The obtained impedance spectra were fitted with the ZView software (v2.8b, Scribner Associates Inc.). The measurements were performed under dark and at 20 % light intensity (white LED light radiation), at various forward bias voltages (from -0.80 V to 0 V) in the frequency range of 0.05 Hz - 1 MHz, with oscillation potential amplitudes of 10 mV and at 20 °C. The photoanode was connected to the working electrode of the electrochemical station and the counter electrode was connected to the auxiliary and the reference electrodes (two-electrode configuration).

4.2.5 Reflectance measurements

To measure the paint's reflectance, a double-coated layer was applied to an identical glass surface as the one used in the DSC counter electrode. Reflectance measurements were carried out using an ultraviolet/visible/near infrared (UV/VIS/NIR) spectrometer (Lambda 750, Perkin Elmer) equipped with a 60 mm integration sphere and Spectralon as reflectance standard. Two types of measurements were performed: with light illuminating the paint coated side and light illuminating the bare glass side (in order to simulate the real case).

4.3 Results and discussion

4.3.1 Light-reflecting performance

Devices A and B were prepared with the amphiphilic ruthenium sensitizer NaRu (4 - carboxylic acid - 4' - carboxylate - 2, 2' - bipyridine), (4, 4' - dinonyl - 2, 2' bipyridine), (NCS)₂ also known as Z907. It is a hydrophobic dye able to sensitize very efficiently wide bandgap oxide semiconductors like titanium dioxide, up to a wavelength of 750 nm, and has a proved enhanced stability in DSCs. So far, dye-sensitized solar cells have been plagued by performance degradation at temperatures between 80 and 85 °C.¹⁰⁻¹² Its incident photon-to-current conversion efficiency (IPCE), defined as the number of electrons generated by light in the external circuit divided by the number of incident photons, exceeds 70 % in the wavelength range near the absorption peak, *ca.* 520 nm, with a measured molar extinction coefficient of $12.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 521 nm.¹⁰

Considering the wavelength range of 400 nm to 800 nm, the spectral region where light is absorbed by the Z907 sensitizer, the paint reflection film used in the present work showed a reflectance above 90 % when illuminated from the coated side and around 40 % to 60 % when illuminated from the bare glass side - Figure 4.2. This is comparable to a silver film applied on the backside of a DSC's counter electrode, where it was observed a reflectance of approximately 80 % in the same wavelength range.¹³

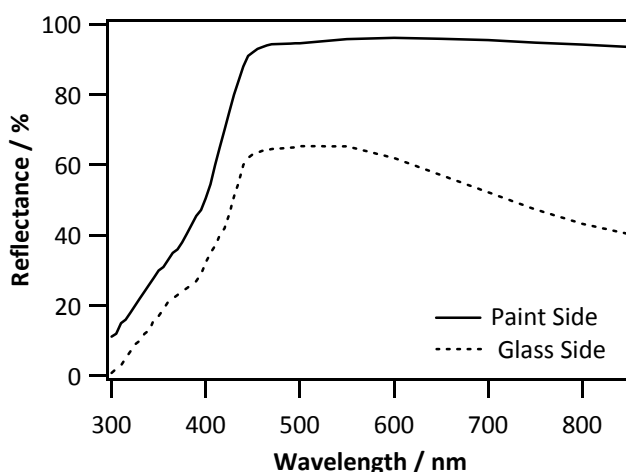


Figure 4.2 - Reflectance spectra of the paint film in the wavelength range of light absorption by the Z907 sensitizer, with illumination from the paint coated side - “Paint side” - and from the bare glass side - “Glass side”.

4.3.2 Photovoltaic performance

Figure 4.3 shows the I - V characteristic curves obtained for devices A and B. For comparison, I - V curves obtained for the two devices with a paint reflection layer coated onto the DSCs’ counter electrodes are also plotted. Device A, a DSC with a semitransparent photoanode, was also characterised with an aluminium foil in the backside of its counter electrode. Thus, the effect of these materials on the overall efficiency of the cells can be evaluated. Considering the three cases under study (DSC with no reflective material, use of an aluminium foil and a reflective paint, noted hereafter as *DSC*, *DSC + Al* and *DSC + Paint*, respectively), the reflective paint arrangement represents the most favourable cell design in terms of light back reflection. The corresponding photovoltaic parameters (short-circuit current density, J_{sc} ; open-circuit voltage, V_{oc} ; fill factor, FF ; and efficiency, η) and the relative increase percentages of the overall conversion efficiency, $\Delta\eta$, are presented in Table 4.1.

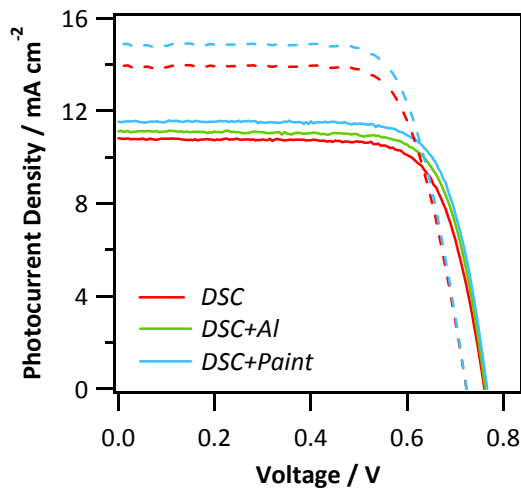


Figure 4.3 - *I-V* characteristics measured at 1 sun illumination (100 mW cm^{-2} ; AM 1.5G) for devices A (solid line) and B (dashed line). Red - DSC with no reflective material in the CE; green - aluminium foil in the backside of the CE; blue - white paint coated in the backside of the CE.

Table 4.1 - Photovoltaic parameters for devices A (semitransparent photoanode) and B (double-layered film photoanode), with and without reflective materials (paint or aluminium foil), at 1 sun illumination (100 mW cm^{-2} , AM 1.5G).

	Device	V_{oc} / V	$J_{sc} / \text{mA cm}^{-2}$	FF	$\eta / \%$	$\Delta\eta / \%$
A	<i>DSC</i>	0.761	10.82	0.740	6.09	---
	<i>DSC + Al</i>	0.762	11.11	0.751	6.36	4.4
	<i>DSC + Paint</i>	0.766	11.53	0.753	6.65	9.2
B	<i>DSC</i>	0.723	13.85	0.727	7.28	---
	<i>DSC + Paint</i>	0.721	14.77	0.729	7.77	6.7

The results presented in Table 4.1 clearly show that there is a conversion efficiency increase when both types of reflective surfaces are used – paint film or aluminium foil. As expected, there was no significant changes in the open-circuit voltage and in the fill factor values since the effect of the reflective layer should only be noticed in the photocurrent density value. In fact, the open-circuit voltage of a DSC arises from the energy difference between the electrons' Fermi level in the TiO_2 electrode and the

redox potential of ions in the electrolyte.¹⁴ Likewise, the fill factor is influenced by the resident resistances, such as the series and shunt resistances,¹⁵ meaning that the use of the same internal structure of the cell would not result in resistance variations. In fact, different fill factor values are observed for devices A and B due to the semiconductor layered structure. Since the reflective structure was applied at the outer surface of the DSC, there was no interference in any of its inner elements. This means that the enhanced efficiency was only due to the increase in photocurrent density, resulting in a much higher J_{sc} value. This arises from the fact that some of the incident light is not initially absorbed by the dye and crosses the semiconductor, striking the CE and the reflective layer (paint film or aluminium foil) behind it. Light is then reflected back, towards the photoelectrode giving rise to secondary photon absorption by the dye molecules. Therefore, the amount of injected electrons is increased and, consequently, the photocurrent also increases.¹⁴ The DSCs coated with the paint layer show a conversion efficiency enhancement of almost 7 % for the opaque film and more than 9 % for the semitransparent one. On the other hand, the measurements performed with the aluminium material in the backside of the CE of device A exhibited only an increase of ≈ 4 %. These results showed that the use of a paint film, despite not optimised for the purpose, is more effective in increasing the photocurrent density of a DSC than the aluminium foil material.

The double-layered TiO_2 film allows a lower increase in the photocurrent density after applying the reflective paint layer since it is composed by a 7 μm -thick film of 20 nm-sized TiO_2 particles and further coated by a 5 μm -thick second layer composed of 400 nm-sized light-scattering anatase TiO_2 particles. This scattering layer acts, in fact, also as a reflective layer, diminishing the non-absorbed light that will reach the CE. Thus, in this case the effect of the reflective paint layer was not as effective as in the semitransparent photoanode.

4.3.3 Electrochemical impedance spectroscopy

The overall processes occurring in a DSC can be evaluated by electrochemical impedance spectroscopy (EIS). This technique allows the analysis of the charge-

transfer resistances at the platinum counter electrode and at the TiO_2 /dye/electrolyte interface, as well as the Nernstian diffusion within the electrolyte. All these processes occur with different time constants and so can be discretized in impedance analysis. In the present work, the impedance measurements were performed in the dark and under 0.2 sun irradiation conditions. The EIS results presented in Figure 4.4 were obtained under dark conditions near the open-circuit voltage for device A. In the dark there is neither voltage nor current generation. The Fermi level energy of electrons in the conduction band equilibrates with the redox energy of the electrolyte. Actually, the Nyquist diagrams for device A, with and without reflective paint film, are almost identical, meaning that the cell's charge transfer and diffusion processes remain unchanged. These experiments thus demonstrate that the application of the reflective paint layer does not cause any modification of the internal elements, as expected. The same behaviour was observed for device B under dark conditions.

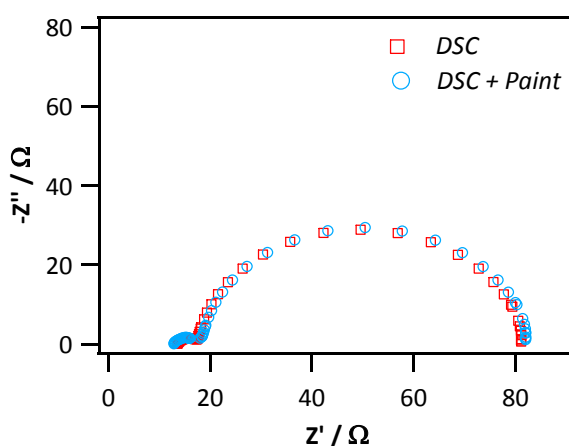


Figure 4.4 - Nyquist diagrams obtained in the dark and under -0.75 V bias for device A. (□) - device with no reflective material; (○) - device with CE backside coated with the reflective paint layer.

Electrochemical impedance spectroscopy data is commonly analysed by means of equivalent electrical circuit models, which may consist of resistors, capacitors, inductors and more complex elements, assembled in series or in parallel. By fitting

the experimental data to specific arrangements of electrical elements, relevant information concerning the reaction kinetics, ohmic conduction processes and mass transfer phenomena occurring in DSCs can be known. A transmission line model¹⁶ based on the diffusion-recombination theory has been developed in order to describe the kinetic processes occurring in the photoelectrode, where the whole mesoscopic TiO_2 film is considered as an interconnected network.¹⁶ In an EIS measurement, electrons are injected from the TCO substrate into the TiO_2 film, which in its turn is charged by electron percolation through the individual particles of the film. This charge transfer process is characterised by a resistance R_w . Then, some of the injected electrons recombine with the oxidised species in the electrolyte, while the remaining electrons are recaptured by the TCO current collector. The recombination process at the TiO_2 /electrolyte interface is characterised by a charge transfer resistance, R_k , and a capacitance, C_μ . Since the impedance experiments were conducted at a very high potential (near the open-circuit condition) the TiO_2 becomes more conductive and the transport resistance becomes negligible.¹⁷ The capacitance C_μ , which reflects the change of electron density, dominates over the double layer capacitance at the TCO/electrolyte interface and the impedance spectrum assumes the typical shape of a DSC Nyquist plot as shown in Figure 4.6 and Figure 4.7. The transmission line model thus reduces to a single parallel arrangement of R_k and C_μ . R_s is the series resistance, which considers the sheet resistance of the TCO glass and the contact resistance of the cell. The diffusion of triiodide ions within the electrolyte solution is described by the Nernst diffusion impedance, Z_d . Finally, the regeneration of triiodide ions at the counter electrode is characterised by R_{CE} and C_{CE} , the charge transfer resistance and the double layer capacitance, respectively. The correspondent equivalent electrical analogue at open-circuit conditions is presented in Figure 4.5. The fittings of the experimental data under illumination (Figure 4.6 and Figure 4.7) were accomplished with the ZView software. For better fittings, all capacitor elements were replaced by constant phase elements (CPE), non-ideal capacitances associated with a non-uniform distribution of current in the heterogeneous TiO_2 film.¹⁸ The fitting parameters are presented in Table 4.2, as well as the electron lifetime τ_n ($\tau_n = R_k C_\mu$).

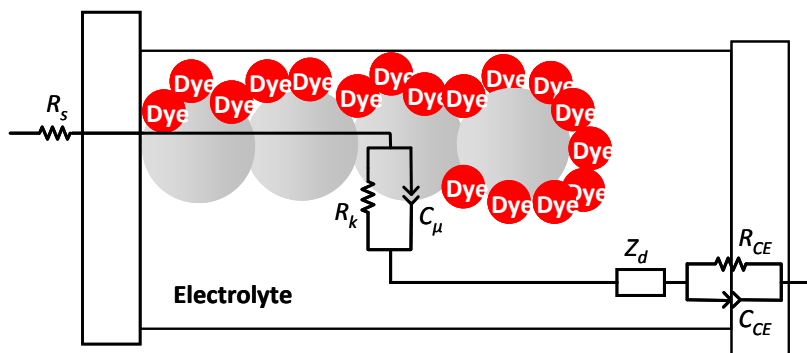
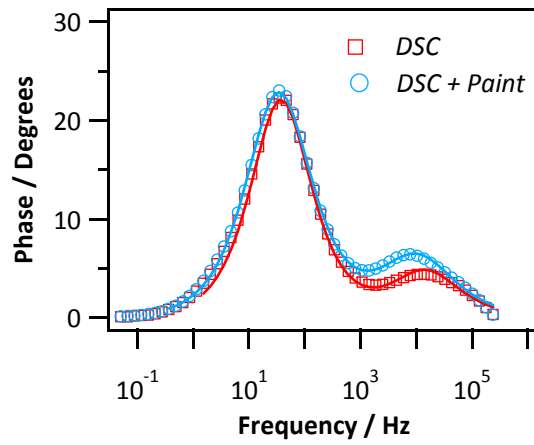
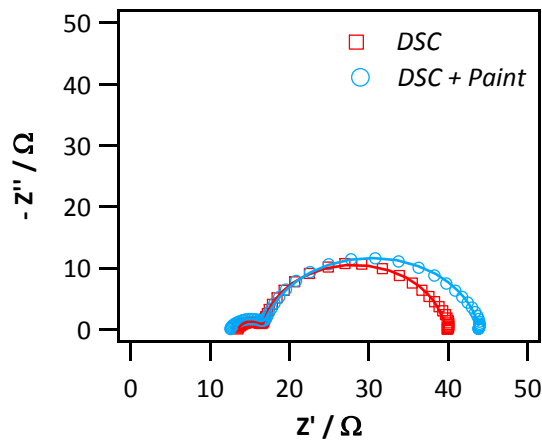


Figure 4.5 - Electrical analogue used to fit EIS data of DSC devices near the open-circuit voltage.

Analysing Figure 4.6 and Figure 4.7 and the correspondent fitted parameters in Table 4.2, it is noticed that the major differences arise in the intermediate semicircle of the Nyquist plot, which corresponds to the middle-frequency peak (1 Hz - 10^3 Hz) in the Bode diagram. This peak reflects the properties of photoinjected electrons within the TiO_2 film, while the peak at higher frequencies (left hand-side arc in Figure 4.6b) is attributed to electron transfer at the counter electrode (10^3 Hz - 10^5 Hz). Finally, the diffusion of the redox species within electrolyte is characterised by the lower frequency range peak (0.1 Hz - 1 Hz).¹⁹ Devices with the CE coated with a reflective paint layer exhibit the highest electron recombination resistance with the electrolyte species, which is related to an increased number of absorbed photons. Moreover, this fact is also reflected on an increased electron lifetime, a parameter of the transmission line model calculated based on the recombination resistance value. This analysis is in straight agreement with the results shown by the I - V characteristic curves.

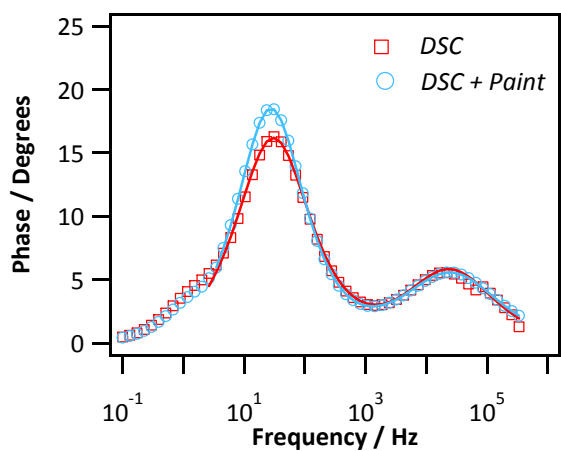


(a)

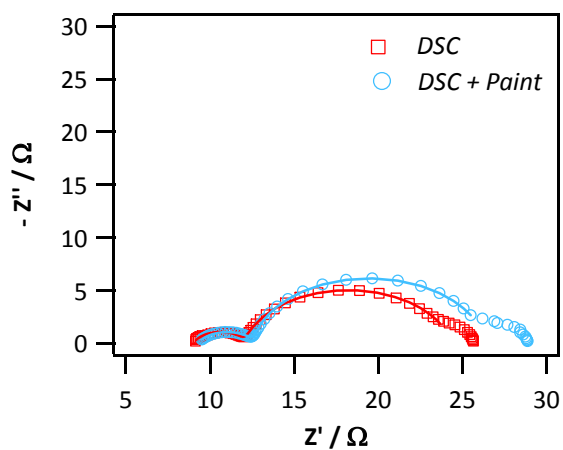


(b)

Figure 4.6 - a) Bode and b) Nyquist diagrams of device A obtained at 0.2 sun irradiation and at -0.75 V bias. Open symbols represent the experimental data; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 4.5.



(a)



(b)

Figure 4.7 - a) Bode and b) Nyquist diagrams of device B obtained at 0.2 sun irradiation and at -0.75 V bias. Open symbols represent the experimental data; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 4.5.

Table 4.2 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 4.5. Measurements performed under illumination and at open-circuit voltage.

	Device	R_s / Ω	R_{CE} / Ω	C_{CE} / F	R_k / Ω	C_μ / F	τ_n / ms
A	<i>DSC</i>	13.6	3.1	2.2×10^{-5} ($n = 0.85$)	22.9	2.9×10^{-4} ($n = 0.95$)	6.6
	<i>DSC + Paint</i>	12.6	4.3	3.8×10^{-5} ($n = 0.80$)	27.0	2.9×10^{-4} ($n = 0.90$)	7.8
B	<i>DSC</i>	9.0	3.1	4.7×10^{-5} ($n = 0.80$)	12.3	6.4×10^{-4} ($n = 0.88$)	7.9
	<i>DSC + Paint</i>	9.3	3.3	6.9×10^{-5} ($n = 0.80$)	13.7	6.3×10^{-4} ($n = 0.93$)	8.6

Devices A and B differ only on the photoanode type and so different electron lifetimes should be expected. Device B, with a double-layered photoanode, presents better conversion efficiencies for the conventional DSC configuration and also with the CE backside coated with the reflective paint film. Consequently, higher values of electron lifetime are achieved for this device, as can be seen in Table 4.2. However, a higher increase in the electron lifetime ($\approx 15\%$) is achieved for device A when its CE is coated with a reflective paint layer, while for device B the increase is only $\approx 8\%$.

4.4 Conclusion

The use of a reflective layer made of a white paint coated onto the outer surface of the counter electrode was proposed. This embodiment was compared with a DSC back wrapped with aluminium foil and a conventional DSC with no reflective material; two systems differing in the TiO_2 film type were used. When back-coated with the white paint, the photovoltaic performance showed an efficiency increase of $\approx 7\%$ for the system with a double-layered TiO_2 film and almost 10% for the semitransparent film. The results also indicate that the paint film coated at the counter electrode allows better efficiencies than the ones obtained with the aluminium foil. Moreover,

the photovoltaic performance characterisation showed that the increased efficiency of the two systems arises due to increase of the photocurrent density, as expected. The other photovoltaic parameters remain almost constant (V_{oc} and FF).

Electrochemical impedance spectroscopy analysis was used to characterise the different devices under study. The correspondent results were in straight agreement with the ones obtained from the I - V characteristics. Analysing the impedance spectra, it was noticed that the major differences appear in the middle-frequency peak in the Bode diagram, reflecting the properties of the photoinjected electrons within the TiO_2 film. The devices with a reflective layer presented higher charge-transfer resistances to the recombination of electrons with the electrolyte redox couple and, consequently, higher electron lifetimes.

The application of a paint film at the backside of a DSC's counter electrode showed to be a very effective way to increase the efficiency of DSC devices, with a negligible increase in their total costs of fabrication.

Acknowledgments

L. Andrade and R. Cruz are grateful to the Portuguese Foundation for Science and Technology (FCT) for their PhD grants (references: SFRH/BD/30464/2006 and SFRH/BDE/33439/2008, respectively) and H. Aguilar Ribeiro is thankful to *Programa Ciência 2007*.

List of abbreviations and symbols

Abbreviations	Definition	Units
AM	Air mass	
C_{CE}	Double-layer capacitance at the platinised TCO	F
CE	Counter electrode	
CPE	Constant phase element	
C_{μ}	Chemical capacitance	F
DSC	Dye-sensitized Solar Cell	
DSC + Al	DSC with an aluminium foil in the backside of the CE	
DSC + Paint	DSC with a reflective paint layer in the backside of the CE	
EIS	Electrochemical impedance spectroscopy	
FF	Fill factor	
FRA	Frequency response analyser	
FTO	Fluorine-doped SnO_2 conducting glass electrode	
I	Current	mA
I_s	Intensity of the incident light	mW cm^{-2}
IPCE	Incident photon-to-current conversion efficiency	%
J_{sc}	Short-circuit photocurrent density	mA cm^{-2}
NIR	Near infrared	
R_{CE}	Charge-transfer resistance at the platinised TCO	Ω
R_k	Recombination resistance	Ω
R_s	Series resistance	Ω
R_w	Electron transport resistance	Ω
SCN	Thiocyanate	
TCO	Transparent conductive oxide	
UV	Ultraviolet	
V	Voltage	V
V_{oc}	Open-circuit photovoltage	V

VIS	Visible	
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

<i>Greek symbols</i>	Definition	Units
η	Global efficiency of a DSC	%
τ_n	Electron lifetime	ms
$\Delta\eta$	Relative increase percentage of the overall conversion efficiency	%

References

- (1) Nazeeruddin, M.; DeAngelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
- (2) Nazeeruddin, M.; Péchy, P.; Grätzel, M. *Chem. Commun.* **1997**, 1705.
- (3) Grätzel, M. *C. R. Chim.* **2006**, *9*, 578.
- (4) Kay, A.; Grätzel, M. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 99.
- (5) Ferber, J.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 265.
- (6) Liu, Y.; Shen, H.; Huang, X.; Deng, Y. *Chin. Sci. Bull.* **2006**, *51*, 369.
- (7) Seo, H.; Son, M.; Hong, J.; Lee, D. Y.; An, T. P.; Kim, H.; Kim, H. J. *Sol. Energy* **2009**, *83*, 2217.
- (8) Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.; Teuscher, J.; Kantelehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 6850.
- (9) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (10) Cao, Y.; Bai, Y.; Yu, Q.; Cheng, Y.; Liu, S.; Shi, D.; Gao, F.; Wang, P. *J. Phys. Chem. C* **2009**, *113*, 6290.
- (11) Shi, D.; Pootrakulchote, N.; Li, R.; Guo, J.; Wang, Y.; Zakeeruddin, S. M.; Grätzel, M.; Wang, P. *J. Phys. Chem. C* **2008**, *112*, 17046.
- (12) Wang, P.; Zakeeruddin, S.; Moser, J.; Nazeeruddin, M.; Sekiguchi, T.; Grätzel, M. *Nat. Mater.* **2003**, *2*, 402.
- (13) Liu, Y.; Shen, H.; Huang, X. R.; Deng, Y. J. *Chin. Sci. Bull.* **2006**, *51*, 369.
- (14) Kohjiro Hara, H. A. In *Handbook of Photovoltaic Science and Engineering*; Antonio Luque, S. H., Ed. 2004, p 663.
- (15) Zhou, C.-h.; Yang, Y.; Zhang, J.; Xu, S.; Wu, S.-j.; Hu, H.; Chen, B.-l.; Tai, Q.-d.; Sun, Z.-h.; Zhao, X.-z. *Electrochim. Acta* **2009**, *54*, 5320.
- (16) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. J. *J. Phys. Chem. B* **2000**, *104*, 2287.

- (17) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.
- (18) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, 2005.
- (19) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.

Chapter 5.

CHARGE-COLLECTION EFFICIENCY IN DYE-SENSITIZED SOLAR CELLS CALCULATED FROM ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Luísa Andrade, Shaik M. Zakeeruddin, Helena Aguilar Ribeiro, Adélio Mendes, Michael Grätzel

(to be submitted, 2010)

Abstract

A new approach based on charge-collection efficiency was used to evaluate the performance of a dye-sensitized solar cell. The charge-collection efficiency is only related to the competition between recombination of photoinjected electrons with the redox electrolyte and electron transport in the mesoporous semiconductor. Electrochemical impedance spectroscopy was used to assess, at specific conditions of bias voltage and illumination, electron transport in the porous semiconductor film and electron recombination in TiO_2 /electrolyte interface. The proposed methodology to calculate the collection efficiency based on impedance spectroscopy experiments was validated by incident photon-to-current conversion efficiency measurements performed with front- and rear-side irradiation. These experiments showed that the main differences in photovoltaic performance of the cell illuminated by both sides are only due to changes in the collection efficiency of the cells, thus enabling the calculation of a global charge-collection efficiency parameter. The corresponding values calculated from impedance and incident photon-to-current conversion efficiency data were compared and an equation to calculate the charge-collection efficiency was proposed. This model, based on the balance of transport and recombination resistances obtained by impedance spectroscopy, was shown to be useful for predicting the performance of different solar cells.

Keywords: Dye-sensitized solar cells, electrochemical impedance spectroscopy, electron transport, electron recombination, collection efficiency, incident photon-to-current conversion efficiency.

5.1 Introduction

Dye-sensitized Solar Cells (DSCs) are a new generation of solar cells technology that emerged in the early 1990s, targeting to achieve moderate efficiency devices at a very low cost.¹ Its initial configuration consists of a porous nanocrystalline TiO₂ layer deposited onto a transparent conducting oxide (TCO) glass substrate. Since TiO₂ is almost insensitive to the visible solar spectrum due to its large band gap, light harvesting is accomplished by a monolayer of dye chemically bonded to the surface of the TiO₂ particles. During the illumination of the cell, the dye absorbs the radiation and, once excited, electrons are injected into the conduction band of TiO₂. The photoinjected electrons then percolate through the semiconductor network, being collected at the TCO. Following electron injection, oxidised dye molecules are regenerated by electron donation from the electrolyte solution containing a redox couple of iodide/triiodide. The triiodide ions formed in the semiconductor's surface during the redox reaction diffuse towards the Pt-catalysed counter electrode, where they are reduced back to iodide by electrons arriving from the external circuit. Presently, state-of-the-art lab-scale DSCs achieve 11.1 % energy conversion at air mass (AM) 1.5 full sunlight intensity.²

Understanding the underlying physical and chemical processes involved in the functioning of DSCs is crucial. Moreover, the development of accurate characterisation tools relating DSCs performance is also required. For a cell under operation, the main performance parameters under standard solar illumination conditions (usually AM 1.5G) are the open-circuit voltage, V_{OC} , the short-circuit photocurrent density, J_{SC} , and the fill factor, FF . The overall conversion efficiency of a dye-sensitized solar cell, η , operating at maximum power point is determined by the product of these three factors, divided by the intensity of the incident light.³ The incident photon-to-current conversion efficiency (IPCE) is a measure of the number of electrons produced in the external circuit as a function of the number of incident photons for a given wavelength. Therefore, IPCE can be expressed as the product of three components:

$$IPCE(\lambda) = \eta_{abs}(\lambda) \eta_{inj}(\lambda) \eta_{col}(\lambda) \quad (5.1)$$

where η_{abs} is the light absorption efficiency of the dye, η_{inj} is the quantum yield of electron injection and η_{col} is the efficiency of collecting the injected electrons at the conducting glass substrate.⁴ High efficient cells can achieve very high IPCE values for a broad range of the visible spectrum, which implies that injection and collection efficiencies are close to 100 %, after considering reflection losses at the glass surface.⁵ However, in many cells the delivered photocurrent is small indicating a significant decrease in the IPCE values. The problem relies on discriminating which of the three parameters (light absorption, charge injection or charge collection efficiency) contributes mostly to that efficiency drop.

Two different main competing processes rule the performance of a DSC (Figure 5.1): electron transport in the mesoporous semiconductor and recombination losses in the semiconductor/electrolyte interface.⁶ The electron percolation across the semiconductor refers to the process by which the injected electrons hop through the colloidal oxide particles and are collected in the back contact (TCO). This transport occurs mainly by diffusion since the macroscopic electric field in the TiO_2 film becomes negligible due to the high ionic strength electrolyte.⁷ Nevertheless, electrons will only be efficiently collected if they are not lost by recombination with triiodide ions in the electrolyte. Thus, the interfacial charge recombination rate has to be much smaller than the electron diffusion through TiO_2 . Several uncertainties surround the recombination kinetics in DSCs and the respective parameters that govern the solar cells behaviour. Some models assume that the rate at which electrons are transferred from the conduction band to the redox electrolyte is first order in free electron concentration.⁸⁻⁹ On the other hand, it has been suggested by other authors the non-ideal behaviour of DSCs, which may arise from the fact that the recombination process is mediated by electronic surface states below the conduction band of the oxide. The two competing processes of transport and recombination can be described on the basis of the diffusion length parameter L_n ($L_n = \sqrt{D_{e^-} \tau_{e^-}}$, where D_{e^-} is the electron diffusion coefficient and τ_{e^-} is the electron lifetime). When $L_n \gg L$, being L

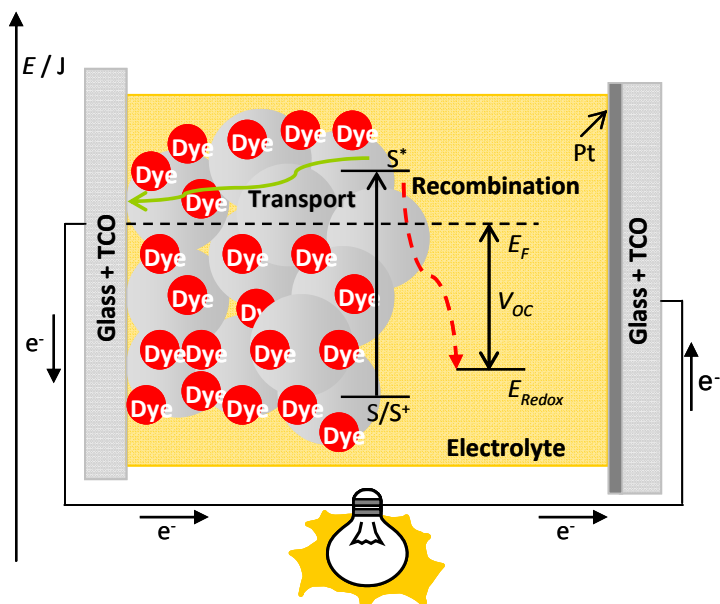


Figure 5.1 - Competing pathways in a working DSC: electron transport through the mesoporous semiconductor (—→) and electron recombination with electrolyte species (---→).

the thickness of the semiconductor layer, most electrons have time to cross the entire length before recombining with the electrolyte, which is an essential requirement for efficient cells. By contrast, in the case of high reactivity, $L_n \ll L$, most electrons recombine at the TiO_2 /electrolyte interface. However, if recombination does not occur predominantly via the conduction band, the electron diffusion length can no longer be defined as previously, giving rise to a non-linear reaction order and a voltage-dependent τ_{e^-} value.¹⁰⁻¹³ As a consequence of this uncertainty, some recent papers discuss the differences in diffusion length measured by small perturbation techniques (e.g. EIS, IMPS/IMVS) and by steady-state measurements.^{9,14} Furthermore, if the recombination rate is not linear the steady-state measurements and the corresponding constitutive equations⁹ can no longer be applied. The present work contributes to this discussion in terms of the definition of a parameter that only considers the balance between these two competing processes and is independent of the electron recombination kinetics. A modified charge-collection efficiency, η_{col} is then proposed in the present work. For that purpose, electrochemical impedance

spectroscopy (EIS) studies and IPCE measurements with back and front illumination of three different cells were carried out. The results of the two techniques are compared and an equation to calculate η_{col} is derived. The proposed definition of the charge-collection efficiency shows a good agreement with the experimental IPCE data.

5.2 Experimental section

5.2.1 Synthesis

Three cells with the dye Z907 were prepared differing only in the electrolyte composition. Z907 dye was synthesised as reported earlier.¹⁵ Cell A: Z959 electrolyte containing 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I_2 , 0.1 M guanidinium thiocyanate and 0.5 M *ter*-butylpyridine in acetonitrile and valeronitrile solvent mixture (85:15 v/v). Cell B: Z946 electrolyte containing 1.0 M 1,3-dimethylimidazolium iodide, 0.15 M I_2 , 0.1 M guanidinium thiocyanate and 0.5 M *N*-butylbenzimidazole in 3-methoxypropionitrile. Cell C: Z380 electrolyte containing 0.5 M *N*-methylbenzimidazole, 0.12 M guanidinium thiocyanate and 0.2 M iodine in a mixture of 1-methyl-3-propylimidazolium iodide and 1-methyl-3-ethylimidazolium thiocyanate (65:35 v/v).

5.2.2 Dye-sensitized solar cell fabrication

Cells were fabricated as described previously.¹⁶ An 8.3 μm -thick transparent film of 20 nm-sized TiO_2 particles was printed on the fluorine-doped SnO_2 conducting glass electrode (FTO). The detailed preparation procedures of transparent TiO_2 nanocrystals and pastes for screen-printing have been reported elsewhere.¹⁷ Films were dyed for 10 minutes in Z907 dye and then rinsed in acetonitrile solution prior to cell construction to remove possible aggregated dye molecules from the TiO_2 surface. The working electrode, described above, was sealed with a 25 μm -thick transparent Surlyn ring (from DuPont) at 130 $^\circ\text{C}$ for 15 s to the counter electrode (FTO glass - 15

Ω/square - coated with a platinum solution chemically deposited at 450 °C for 15 min). The cells were filled with the correspondent electrolyte solutions through a pre-drilled hole done in the counter electrode. The hole was then sealed with a Surlyn disc and a thin glass lamella to avoid leakage of the electrolyte.

5.2.3 Photovoltaic measurements

A 450 W xenon light source (Oriel, USA) was used to give an irradiance of 100 mW cm^{-2} (the equivalent to 1 sun at AM 1.5G) at the surface of solar cells. A Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) was used so as to reduce the mismatch between the simulated and true solar spectra in the region of 350-750 nm. Various incident light intensities were regulated with wavelength neutral wire mesh attenuators. The current-voltage characteristics of the cells under these conditions were obtained by applying an external potential bias to the cells and measuring the generated photocurrent with a Keithley 2400 series digital source meter (Keithley, USA). This process was fully automated using Wavemetrics software. Photovoltaic performance was measured by using a metal mask on top of the cell with an aperture area of 0.159 cm^2 .

5.2.4 IPCE measurements

A data acquisition system similar to that of I - V measurements was used to control the IPCE measurements. Under full computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE defined as $IPCE(\lambda) = 124000(J_{sc} / \lambda \varphi)$, where λ is the wavelength (nm), J_{sc} is short-circuit photocurrent density (mA cm^{-2}) and φ is the incident radiative flux (mW cm^{-2}). The cells were illuminated from both photoelectrode and counter electrode sides. IPCE of the cells was measured by using also a metal mask with an aperture area of 0.159 cm^2 .

5.2.5 Electrochemical Impedance Measurements

Electrochemical impedance spectra of DSCs were performed with an Autolab Frequency Analyser setup consisting of the Autolab PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) and the Frequency Response Analyser (FRA) module. The spectra were obtained at 20 °C, both in the dark and at 20 % full light intensity (white LED light radiation), at various forward bias voltages (from -0.80 V to 0 V) in the frequency range of 0.05 Hz - 1 MHz. The amplitude of the modulation signal was 10 mV. The photoanode was connected to the working electrode. The counter electrode was connected to the auxiliary and the reference electrodes. The EIS spectra were fitted to an appropriate electrical analogue by means of the ZView software (v2.5b, Scribner Associates Inc.).

5.3 Results and discussion

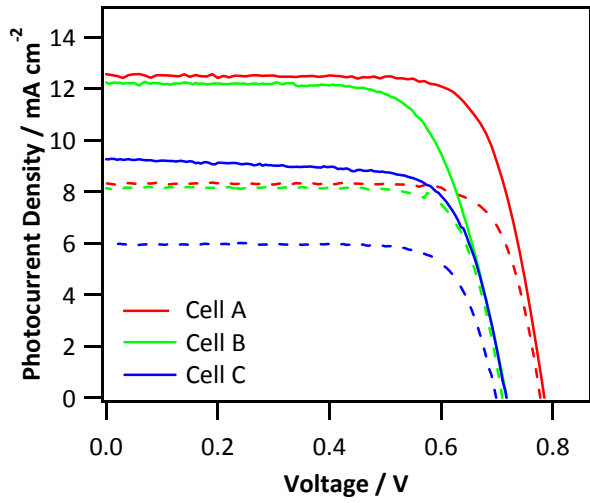
5.3.1 Photovoltaic performance

In the present work three DSC devices were considered, differing only in the electrolyte composition. The redox electrolyte in a DSC is responsible for the regeneration of the dye, which becomes oxidised by electron injection to the TiO_2 conduction band, and conducts the positive charges (holes) to the counter electrode, where the redox-couple itself is regenerated. The regeneration reaction is mainly dependent on the iodide concentration, electrolyte viscosity and dye structure.¹⁸ Moreover, different photovoltage values can be achieved by using different electrolytes, since the photovoltage of a system corresponds to the difference between the redox potential of the electrolyte and the TiO_2 Fermi level. An efficient DSC also requires that electron transport within the mesoporous semiconductor has to be faster than charge recombination of injected electrons with the redox couple. As stated above, this is the most predominant loss pathway to be considered in a DSC (dark current), preventing to achieve higher efficiencies. Dark current often occurs at the semiconductor/electrolyte interface where the sensitizer is not adsorbed.¹⁹ Thus,

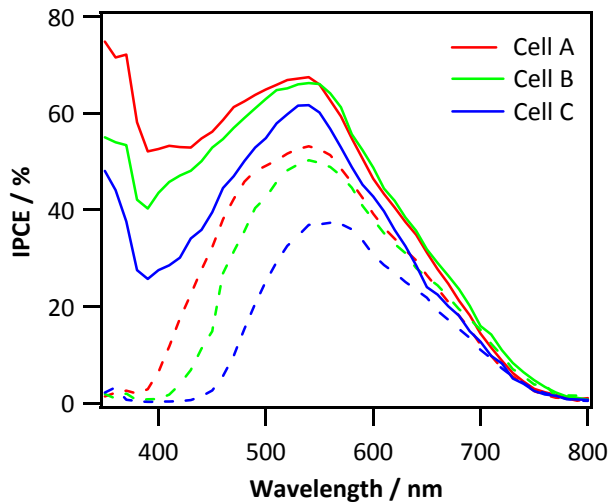
by changing the electrolyte composition in the three systems under study it was expected that the injection and absorption efficiencies remain the same, since the semiconductor/dye system is equal in the three cells. In addition, electrolytes do not absorb in the relevant absorption spectra of DSCs (400-650 nm). This fact can be easily verified by observing Figure 5.2 that shows the photocurrent-voltage characteristics and the IPCE spectra of the three DSCs, illuminated from both the photoelectrode and the counter electrode sides. Indeed, Figure 5.2b) shows that for wavelengths higher than 700-750 nm (spectrum region where redox couples usually absorb) the light absorption by the electrolyte is negligible.

By performing IPCE measurements on the same cell with front- and rear-side irradiation, it is again ensured that the performance differences in the two measurements are only ascribed to variations in the collection efficiency, since all other variables remain constant. Moreover, there are almost no differences in the IPCE spectra for front- and rear-side irradiation for wavelengths higher than 650-700 nm. Thus, information about the global collection efficiency, η_{col} , of the cells can be obtained considering the definition of IPCE by Equation (5.1) and assuming that: i) the differences in the IPCE measurements with illumination through the photoelectrode ($IPCE_{PE}$) and the counter electrode ($IPCE_{CE}$) sides are only due to changes in the collection efficiency parameter; and ii) the global collection efficiency η_{col} equals the value of the collection efficiency through the photoelectrode ($\eta_{col} = \eta_{col}^{PE}$). Moreover, the difference of both IPCE values is proportional to $(1 - \eta_{col}) = (IPCE_{PE} - IPCE_{CE})$ - Table 5.1. This means that when the IPCE values with irradiation from both sides approximate each other, the global collection efficiency of the cell approaches 100 % and the cell becomes very efficient. These calculations were performed for the wavelength corresponding to the maximum incident photon-to-current conversion efficiency.

The overall energy conversion efficiencies with illumination through the photoanode of cells A, B and C are 7.37 % (V_{OC} , 0.785 V; J_{SC} , 12.56 mA cm⁻²; FF, 0.748), 6.13 % (V_{OC} , 0.718 V; J_{SC} , 12.26 mA cm⁻²; FF, 0.696) and 4.75 % (V_{OC} , 0.716 V; J_{SC} , 9.26



(a)



(b)

Figure 5.2 - Experimental photovoltaic characteristics of Cells A, B and C with front- (solid line) and rear-side (dashed line) irradiation. (a) I - V curves at 1 sun illumination (AM 1.5G, 100 mW cm^{-2}) and (b) incident photon-to-current-efficiency spectra (20 % light bias).

mA cm^{-2} ; FF , 0.716), respectively. With illumination through the counter electrode, the overall energy conversion efficiencies of cells A, B and C are 5.15 % (V_{OC} , 0.777 V;

J_{SC} , 8.42 mA cm⁻²; FF, 0.787), 4.42 % (V_{OC} , 0.709 V; J_{SC} , 8.11 mA cm⁻²; FF, 0.768) and 3.16 % (V_{OC} , 0.707 V; J_{SC} , 5.98 mA cm⁻²; FF, 0.748), respectively.

Table 5.1 - Collection efficiency values calculated based on IPCE measurements with front- and rear-side irradiation.

Cell	$IPCE_{PE}$ / %	$IPCE_{CE}$ / %	$(1 - \eta_{col})^{(*)}$ / %	η_{col} / %
A	67.5	53.2	14.3	85.7
B	66.3	50.3	16.0	84.0
C	63.7	33.3	30.4	69.6

$$^{(*)}(1 - \eta_{col}) = IPCE_{PE} - IPCE_{CE}$$

5.3.2 Electrochemical impedance spectroscopy

As stated before, the charge-collection parameter is directly related to the competition between recombination of photoinjected electrons with the redox electrolyte and electron collection in the collecting electrode (TCO). If charge-collection is much faster than charge recombination, then η_{col} value will be high because electrons are collected before they have time to recombine. As the time constants approach each other, the charge collection efficiency decreases.²⁰ The ratio of recombination and collection phenomena can be easily obtained by electrochemical impedance spectroscopy, which also allows understanding how recombination and charge transport are affected by the applied potential. Impedance measurements consist of superimposing a small harmonic voltage perturbation on a constant applied bias potential and monitor the resulting current response of the system at the corresponding frequency of the perturbation. This technique has been widely used to characterise the electrical behaviour of systems in which the overall performance is determined by a number of strongly coupled processes, each proceeding at different time rates. At specific conditions, electron transport in the porous semiconductor film, electron recombination in TiO₂-electrolyte interface,

charge transfer at the counter electrode and diffusion of the redox species in the electrolyte can be well distinguished according to the spectral shapes of the impedance response as a function of frequency.²¹⁻²⁶

Equivalent electrical analogues are usually used to fit the EIS experimental data, allowing the identification and interpretation of some of the characteristic parameters of the system. Figure 5.3 shows the complete equivalent circuit used to describe the phenomena occurring in a DSC. In particular, the electron transport, accumulation and charge recombination in nanocrystalline TiO₂ films are described by an infinite transmission line model, based on the diffusion-recombination theory (shown in the inset of Figure 5.3).²⁷ In an EIS measurement, under forward bias, electrons are injected from the TCO substrate into the TiO₂ film, which in its turn is charged by electron percolation through the individual particles of the film. This charge transfer process is characterised by a resistance R_w . Meanwhile, a fraction of the injected electrons are lost by the reduction of triiodide ions present in the electrolyte. The recombination phenomenon is characterised by a charge transfer resistance, R_k , and a capacitance, C_μ . If L is the thickness of the mesoscopic TiO₂ film, the electron transport resistance is defined as $R_w = r_w L$, while the interfacial charge recombination resistance is $R_k = r_k / L$. The capacitance measured here, generically noted by $C_\mu = c_\mu L$, refers in fact to the sum of the capacitance contribution of the electronic states (C_μ) and the space charge on the semiconductor side (C_{sc}), *i.e.* $C_\mu \parallel C_{sc}$, and by the Helmholtz layer (C_H) and the surface adsorbed ionic species on the electrolyte side (C_{ad}), *i.e.* $C_H \parallel C_{ad}$. Nevertheless, C_{sc} can be neglected in the entire potential range since there is no space charge region for nanocrystalline TiO₂. Furthermore, the double layer capacitance ($C_H \parallel C_{ad}$) is only a small contribution to the total capacitance at high bias potential values.²⁵

In what concerns the other processes occurring in a DSC, the diffusion-like element Z_d in the equivalent analogue shown in Figure 5.3 characterises the Nernst diffusion impedance of I^-/I_3^- ions in the electrolyte. Regeneration of I_3^- at the counter electrode

is characterised by R_{CE} and C_{CE} , which are the charge transfer resistance and double layer capacitance at the platinised TCO, respectively. R_s is the series resistance, including the sheet resistance of the TCO glass and the contact resistance of the cell.²⁸ $C_{FTO/EL}$ stands for the double layer capacitance at exposed FTO/electrolyte interface.

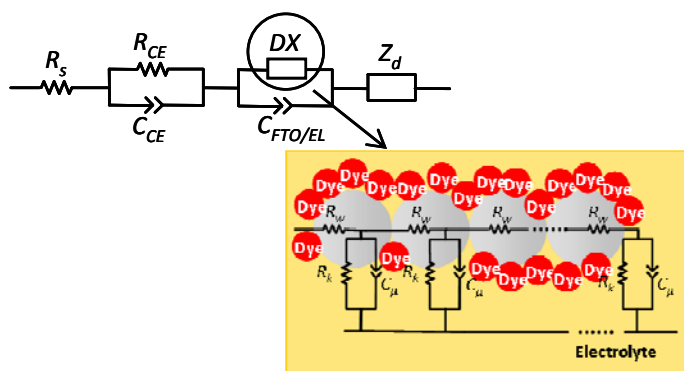


Figure 5.3 - Equivalent circuit used to fit the experimental impedance data in DSCs. The interfacial charge separation across a dye-sensitized heterojunction is represented by a distributed element (DX) shown in the inset.

Impedance experiments can be performed at any bias potential, in the dark or under bias illumination. Of particular interest are experiments performed at open-circuit voltage because at this condition there is no net current flowing and constant triiodide/iodide concentrations can be ensured. Nyquist spectra for cells B and C under illumination and at open-circuit voltage are presented in Figure 5.4(a), where three semicircles can be distinguished. Cell A shows a Nyquist plot similar to cell B. The phenomena involved at these characteristic frequencies, from low to high frequencies (from right to left in Figure 5.4(a)), are: Nernst diffusion within the electrolyte, electron transfer at the TiO₂/electrolyte interface and redox reaction at the platinum counter electrode. In the case of cell B two peaks are overlapped: the low-frequency semicircle is underneath the mid-frequency semicircle. Near the open-

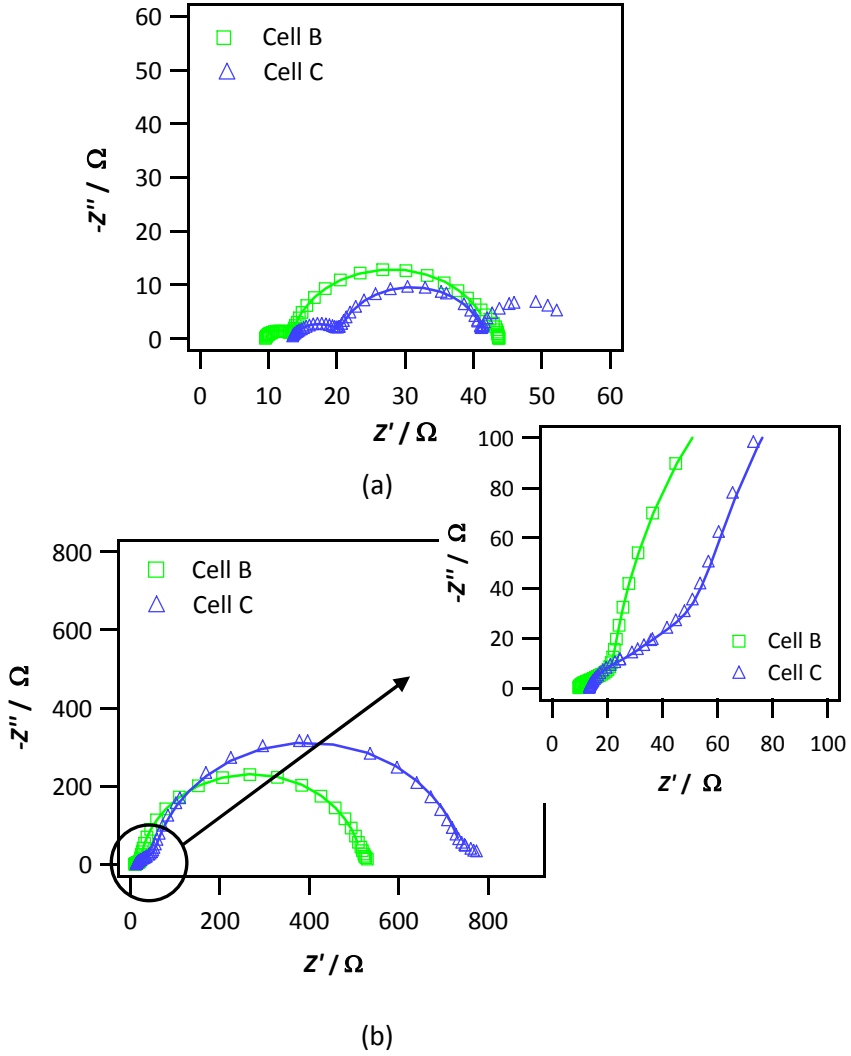


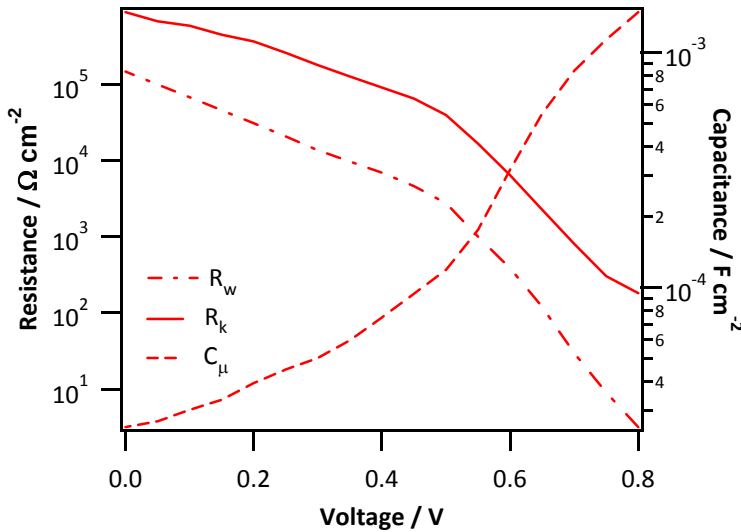
Figure 5.4 - Impedance spectra of cells B and C at different applied potentials: (a) open-circuit potential; (b) maximum power point potential. Symbols correspond to the impedance data obtained experimentally under illumination, while solid lines represent the fittings based on the equivalent electrical circuit shown in Figure 5.3. Inset represents an enlargement of Figure 5.4(b).

circuit voltage, the TiO_2 becomes very conductive and the transport resistance becomes negligible. In this situation, the transmission line model shown in the inset of Figure 5.3 reduces to a parallel arrangement of the recombination resistance R_k and

the total capacitance C_μ . For intermediate potentials - maximum power point voltage - (Figure 5.4(b)), the impedance of the electron kinetics in the porous semiconductor film should now be described by the whole transmission line model. The diffusion component (R_w) is clearly distinguished in the high frequency range, with slope close to 1 (see inset of Figure 5.4(b)), while the low-frequency range of the semiconductor semicircle is the result of the parallel association of C_μ with R_k .

Fitting the transmission line model described above to the experimental EIS data, parameters such as R_k and R_w can be extracted (Figure 5.5). The collection efficiency can then be calculated assuming that the total amount of injected electrons can be described by the electron transport resistance, proportional to the number of electrons that diffuse through the semiconductor and are efficiently collected, and by electron recombination resistance, proportional to the ones that recombine before being collected. Thus, it can be written that:

$$\eta_{col} = \frac{R_k}{R_k + R_w} = \frac{1}{1 + \frac{R_w}{R_k}} \quad (5.2)$$



(a)

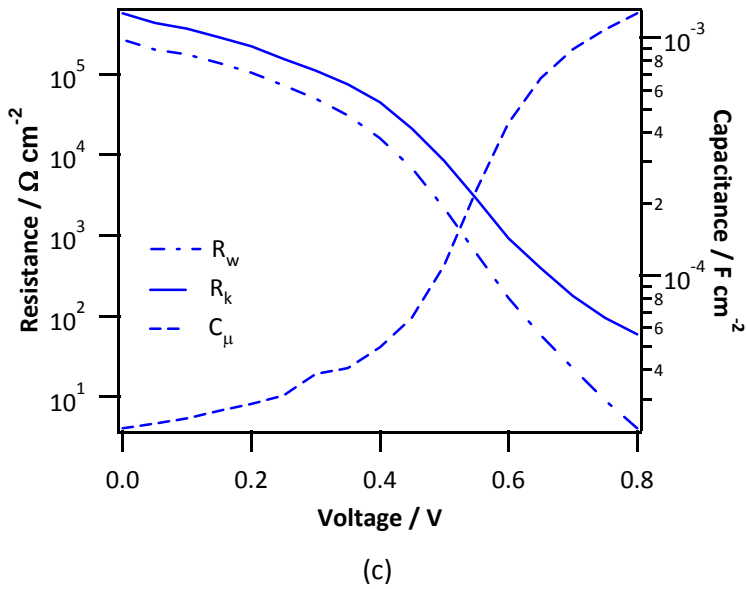
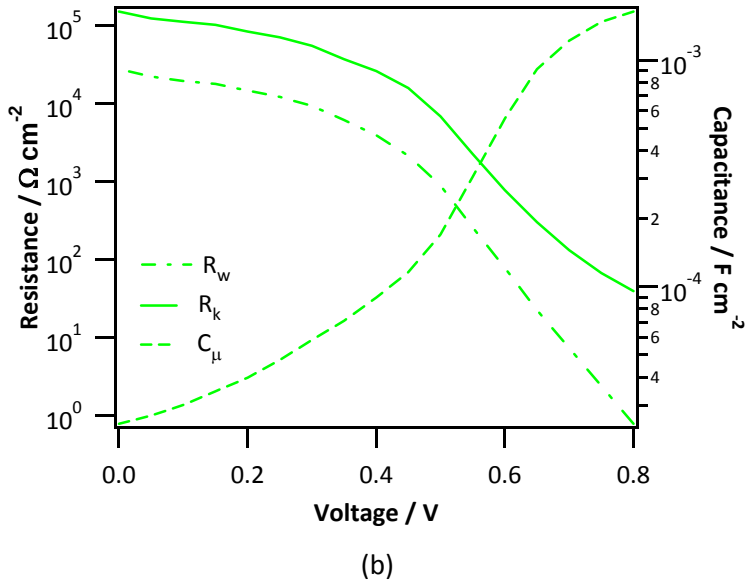


Figure 5.5 - Electron transport resistance R_w , electron recombination resistance R_k and the capacitance C_μ obtained from impedance data, under 20 % illumination, as a function of the bias potential (corrected from the I - R drop due to series resistance) for (a) cell A, (b) cell B and (c) Cell C.

Based on the ratio between the two resistances - Equation (5.2) - one may infer about the effect of applied potential on the charge-collection efficiency η_{col} of the systems (Figure 5.6). Similar approaches can be seen in the literature but in terms of the electron transit time at short-circuit voltage and the electron lifetime at open-circuit conditions.^{20,29-31}

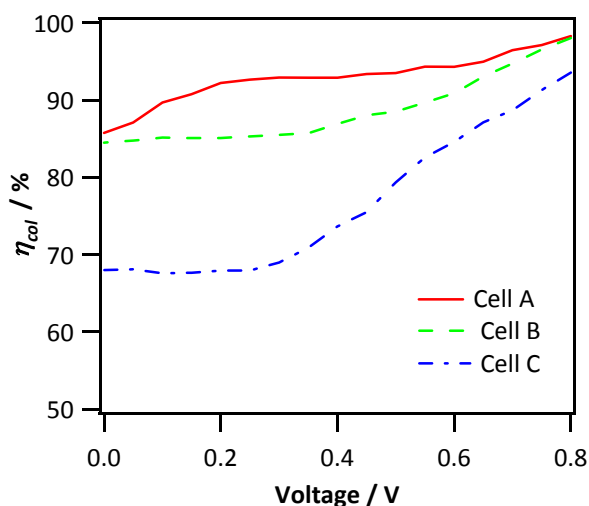


Figure 5.6 - Charge-collection efficiency η_{col} as a function of the bias potential calculated by means of Equation (5.2) for the three devices.

The collection efficiency results shown in Figure 5.6 are in line with the photovoltaic performance of the three cells - Figure 5.2. In fact, device A, the most efficient cell, shows higher values of charge-collection efficiency in the entire voltage range. On the other hand, cell C exhibits the lowest values of η_{col} for all the voltages considered. This behaviour is in straight agreement with its very low efficiency and IPCE values. Moreover, by analysing Figure 5.5, it can be concluded that the performance of the cells is directly related to the ratio of the transport and recombination resistances, *i.e.* the efficiency of the cell will be as higher as the distance between the curves R_k and R_w in Figure 5.5.

5.3.3 Comparison of η_{col} parameter calculated by IPCE and EIS

The main goal of the present work is to assess the validity of Equation (5.2) for estimating the parameter η_{col} . As mentioned previously, IPCE data obtained with front- and rear-side irradiation ensured that the performance differences between cells were only due to variations in the corresponding collection efficiency. Since IPCE measurements were performed under short-circuit conditions, the charge collection efficiency calculated based on IPCE measurements should be compared with the collection efficiency value calculated from impedance data obtained at 0 V as well – Table 5.2.

Table 5.2 - Calculated collection efficiencies based on IPCE^(*) and EIS measurements (at short-circuit conditions) for cells A, B and C. The corresponding efficiency at the maximum power point (MPP) is also presented.

	Cell A	Cell B	Cell C
$\eta_{col}^{IPCE} / \%$	85.7	84.0	69.6
$\eta_{col}^{EIS} / \%$	85.8	84.5	68.7
$\eta_{col}^{MPP} / \%$	94.6	88.5	83.6

^(*) presented on Table 5.1

The results obtained by electrochemical impedance measurements under short-circuit conditions are very close to the ones obtained by the IPCE technique. Therefore, the collection efficiency parameter calculated in terms of the transport and recombination resistances seems to be a suitable parameter to evaluate the performance of a cell. In Table 5.2, the collection efficiency at maximum power point (MPP) is also shown. In fact, for a more realistic evaluation, cells should be characterised under MPP conditions. The main disadvantage pointed out to impedance measurements is that it becomes difficult to measure the transport resistance at high light intensities or near the open-circuit voltage, particularly in the

case of cells with long diffusion lengths. As the transport resistance becomes much smaller than the series R_s and cathode R_{CE} impedances, the fittings become unreliable. However, this is not the case at maximum power point since the transport resistance can be easily identified at this potential (slope close to 1 in Figure 5.4(b)).

The use of η_{col} based on impedance measurements is also a good parameter to evaluate performances for very efficient cells ($> 11\%$), where the collection efficiency should be almost 100 %. Considering cell A in ref. 25 with an efficiency of 11.1 %, the transport and recombination resistances at 0.60 V are approximately 100 Ω and 3000 Ω , respectively. These values correspond to a collection efficiency of almost 97 % (calculated from Equation (5.2)), confirming the high-performance of the cell.

The results obtained for the three cells under study and for a very efficient DSC reported in the literature are in agreement with Equation (5.2). The use of a collection efficiency parameter to characterise the recombination and the transport of the injected electrons proved also to be easy and broadly applicable.

5.4 Conclusion

It has been shown that the charge-collection efficiency can be calculated based on impedance spectroscopy measurements. For that, an equation based on the balance of transport and recombination phenomena was proposed. This approach allows to overcome the problematic concerning the calculation of diffusion length due to the uncertainties that surround the recombination kinetics of injected electrons with the redox electrolyte species. In fact, the collection efficiency only depends on two main competing processes that rule the performance of a DSC: electron transport in the mesoporous semiconductor and recombination losses within electrolyte. If charge-collection is much faster than charge recombination, then η_{col} value will be high since electrons will be collected before they have time to recombine, an essential requirement for efficient cells. To support the proposed model to calculate η_{col} , IPCE measurements were performed with illumination both from the photoelectrode and

the counter electrode sides. IPCE depends on the light absorption efficiency of the dye, η_{abs} , the quantum yield of electron injection, η_{inj} , and the efficiency of collecting the injected electrons at the conducting glass substrate, η_{col} . These IPCE experiments also allowed confirming that light absorption by the electrolyte is negligible in wavelengths higher than 650 nm. Consequently, the changes in the IPCE response, when illuminating the cells from both sides, were only due to changes in the collection efficiency and a global collection efficiency value can be then calculated. The results obtained by both techniques are in straight agreement, thus validating the proposed collection efficiency model based on the transport and recombination resistances. This conclusion was shown to be valid for very high, intermediate and low efficiency DSCs.

Acknowledgments

L. Andrade is grateful to the Portuguese Foundation for Science and Technology (FCT) for her PhD grant (reference: SFRH/BD/30464/2006). H. Aguilar Ribeiro acknowledges the *Programa Ciência 2007*. The authors also acknowledge Thomas Moehl for the interesting discussions about impedance spectroscopy technique.

List of abbreviations and symbols

Abbreviations	Definition	Units
AM	Air mass	
C_{ads}	Capacitance of the adsorbed species on the electrolyte side	F
C_{CE}	Double-layer capacitance at the platinised FTO	F
C_H	Capacitance of Helmholtz layer	F
C_{sc}	Capacitance of the space charge on the semiconductor side	F
$C_{FTO/EL}$	Double-layer capacitance at exposed FTO/electrolyte interface	F
C_μ	Electronic states capacitance	F
CE	Counter electrode	
D_{e^-}	Diffusion coefficient of electrons in the TiO_2 semiconductor	$cm^2 s^{-1}$
DSC	Dye-sensitized solar cell	
DX	Distributed element	
E	Energy	J
E_F	Electron Fermi energy	J
E_{Redox}	Redox energy of the redox electrolyte	J
EIS	Electrochemical impedance spectroscopy	
e^-	Electron	
FF	Fill factor	
FRA	Frequency response analyser	
FTO	Fluorine-doped SnO_2 conducting glass electrode	
I	Current	mA
IMPS	Intensity modulated photocurrent spectroscopy	
IMVS	Intensity modulated photovoltage spectroscopy	
IPCE	Incident photon-to-current conversion efficiency	%

$IPCE_{CE}$	Incident photon-to-current conversion efficiency with illumination through the counter electrode	%
$IPCE_{PE}$	Incident photon-to-current conversion efficiency with illumination through the photoelectrode	%
J_{sc}	Short-circuit photocurrent density	$mA\ cm^{-2}$
L	Thickness of the semiconductor film	μm
L_n	Electron diffusion length	μm
MPP	Maximum power-point	
R	Resistance	Ω
R_{CE}	Charge-transfer resistance at the platinised FTO	Ω
R_k	Recombination resistance	Ω
R_s	Series resistance	Ω
R_w	Electron transport resistance	Ω
TCO	Transparent conductive oxide	
V	Voltage	V
V_{oc}	Open-circuit photovoltage	V
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

Greek symbols	Definition	Units
η	Global efficiency of a DSC	%
η_{abs}	Absorption efficiency	%
η_{col}	Global collection efficiency	%
η_{col}^{CE}	Collection efficiency calculated based on IPCE experiment with illumination through the CE	%
η_{col}^{PE}	Collection efficiency calculated based on IPCE experiment with illumination through the PE	%

η_{inj}	Injection efficiency	%
λ	Wavelength	nm
τ_{e^-}	Electron lifetime	ms
φ	Incident light intensity	mW cm ⁻²

References

- (1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- (2) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jap. J. Appl. Phys., Part 2: Letters* **2006**, *45*, L638.
- (3) Grätzel, M. *J. Photochem. Photobiol. C* **2003**, *4*, 145.
- (4) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.
- (5) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- (6) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.
- (7) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.
- (8) Peter, L. M. *J. Phys. Chem. C* **2007**, *111*, 6601.
- (9) Barnes, P. R. F.; Anderson, A. Y.; Koops, S. E.; Durrant, J. R.; O'Regan, B. C. *J. Phys. Chem. C* **2009**, *113*, 1126.
- (10) Bisquert, J.; Mora-Seró, I. n. *J. Phys. Chem. Lett.* **2009**, *1*, 450.
- (11) Villanueva-Cab, J.; Wang, H.; Oskam, G.; Peter, L. M. *J. Phys. Chem. Lett.* **2010**, *1*, 748.
- (12) Bisquert, J.; Fabregat-Santiago, F.; Mora-Seró, I.; Garcia-Belmonte, G.; Giménez, S. *J. Phys. Chem. C* **2009**, *113*, 17278.
- (13) Salvador, P.; Hidalgo, M. G.; Zaban, A.; Bisquert, J. *J. Phys. Chem. B* **2005**, *109*, 15915.
- (14) Wang, H.; Peter, L. M. *J. Phys. Chem. C* **2009**, *113*, 18125.
- (15) Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.; Teuscher, J.; Kantelehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 6850.
- (16) Ito, S.; Murakami, T.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M.; Grätzel, M. *Thin Solid Films* **2008**, *516*, 4613.
- (17) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (18) Grätzel, M.; Durrant, J. R. In *Nanostructured and photoelectrochemical systems for solar photon conversion*; Imperial College Press: London, 2008.

- (19) Green, A. N. M.; Palomares, E.; Haque, S. A.; Kroon, J. M.; Durrant, J. R. *J. Phys. Chem. B* **2005**, *109*, 12525.
- (20) Schlichthorl, G.; Park, N. G.; Frank, A. J. *J. Phys. Chem. B* **1999**, *103*, 782.
- (21) Wang, Q.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. B* **2005**, *109*, 14945.
- (22) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.
- (23) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (24) Bisquert, J.; Vikhrenko, V. S. *J. Phys. Chem. B* **2004**, *108*, 2313.
- (25) Wang, Q.; Ito, S.; Grätzel, M.; Fabregat-Santiago, F.; Mora-Sero, I.; Bisquert, J.; Bessho, T.; Imai, H. *J. Phys. Chem. B* **2006**, *110*, 25210.
- (26) Adachi, M.; Sakamoto, M.; Jiu, J.; Ogata, Y.; Isoda, S. *J. Phys. Chem. B* **2006**, *110*, 13872.
- (27) Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C. *J. Phys. Chem. B* **2000**, *104*, 2287.
- (28) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 334.
- (29) Lagemaat, J.; Park, N. G.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 2044.
- (30) Wong, D. K.-P.; Ku, C.-H.; Chen, Y.-R.; Chen, G.-R.; Wu, J.-J. *ChemPhysChem* **2009**, *10*, 2698.
- (31) J. Frank, A.; Kopidakis, N.; Lagemaat, J. v. d. *Coord. Chem. Rev.* **2004**, *248*, 1165.

Chapter 6.

PHENOMENOLOGICAL MODELLING OF DYE-SENSITIZED SOLAR CELLS UNDER TRANSIENT CONDITIONS

Luísa Andrade, José Sousa, Helena Aguilar Ribeiro and Adélio Mendes

(*Solar Energy* 2010, accepted for publication)

Abstract

A phenomenological model is proposed for a better understanding of the basic working mechanisms of Dye-sensitized Solar Cells (DSCs). A steady-state approach allows the construction of the I - V characteristics, giving important informations about the main factors that influence DSCs' performance. On the other hand, the transient approach model is an important tool to relate the phenomenological behaviour with certain dynamic techniques, such as Electrochemical Impedance Spectroscopy (EIS). Bearing in mind the uncertainty arising from fitting the experimental Nyquist diagrams to general electrical analogues, this transient model contributes for a deeper understanding of the DSCs and for obtaining the relevant kinetic parameters with higher accuracy. The one-dimensional transient phenomenological model presented here assumes that the injected conduction-band electrons may recombine only with the electrolyte redox species. Due to the small dimension of the titania particles, no significant electrical potential gradient is considered, resulting only in a diffusive electron transport across the semiconductor. For modelling purposes, the mesoscopic porous structure, consisting of TiO_2 nanoparticles covered with light absorbing dye molecules and interpenetrated by the I^-/I_3^- redox mediator (electrolyte), is considered as a homogeneous nanocrystalline structure of thickness L . The continuity and transport governing equations are defined for the mobile species involved: electrons in the TiO_2 conduction band and I^-/I_3^- ions in the electrolyte. The simulated results are in straight agreement with the experimental data.

Keywords: Dye-sensitized Solar Cells; Phenomenological Modelling; I - V characteristic; Electrochemical Impedance Spectroscopy; Transient Conditions.

6.1 Introduction

In the last two decades, several studies focused on theoretical approaches for insightful understanding of the basic working mechanisms of dye-sensitized solar cells (DSCs). Sodergren *et al.*¹ developed a steady-state phenomenological model based on electron diffusion through the porous semiconductor and considered a constant diffusion length. The presented I - V characteristic equation was similar to the expression for a p-n junction solar cell, but the properties of the electrolyte were not taken into account. Later on, Papageorgiou *et al.*² presented a comprehensive analysis on the relevance of mass transport in the steady-state operation of nanocrystalline photoelectrochemical solar cells. This work was intended to provide a better understanding of the role of the electrolyte species and not to predict power characteristics or energy conversion properties. Ferber *et al.*³ suggested an electrical model for DSCs allowing the calculation of the internal properties of the cell as well as the charge carriers' density distributions. Based on this complex electrical model a complete I - V characteristic was simulated and a simplified electric model of a DSC was published in the same year.⁴ The later uses the experimentally obtained external current as an input to the model. In 2001 Ferber *et al.*⁵ extended their previous work³ by developing a two-dimensional steady-state model. In this work the electric fields within the TiO_2 semiconductor and within the redox electrolyte are distinguished. The numerical calculations presented address specifically the spatial distribution of the electric and electrochemical potential in the cell. Other studies concerning several specific phenomena occurring in DSCs have been widely developed, but a global integrated model has never been presented. Peter⁶ and many other authors⁶⁻⁹ contributed to a better understanding of the physical and chemical processes taking place in DSCs. Their works show that kinetic properties can be drawn from the charge transport and recombination phenomena.

The present work aims at contributing for the progressive understanding of the charge transfer mechanisms that govern DSCs' mode of operation. The steady-state I - V characteristic gives the performance parameters of the cell, such as the short-circuit current (I_{sc}), open-circuit potential (V_{oc}) and fill factor (FF). Nevertheless, more

detailed properties cannot be extracted from steady-state measurements and so dynamic techniques should be considered. These techniques allow the interpretation of the kinetics, mainly characterised by diffusion coefficients and lifetime of the different carriers. One of the most powerful characterisation techniques of DSCs involving transient probing is electrochemical impedance spectroscopy (EIS). The experimental Nyquist plot is often fitted to general electrical analogues, providing internal electrical mechanisms working in the solar cell.¹⁰⁻¹¹ However, since the electrical analogues have many parameters there is a great uncertainty in their determination. A phenomenological transient model, such as the one presented in this work, has the potential for a deeper understanding of the relevant phenomena occurring in a DSC, and the ability to be related to the EIS analysis; the phenomenological transient approach combined with the EIS analysis is a powerful tool for obtaining the relevant kinetic parameters with higher accuracy. All the models presented until this moment only considers the steady-state approach in order to obtain the I - V characteristic.

6.2 Development of the DSC model

Figure 6.1 shows a scheme of the modelled DSC. The photoanode consists of a homogeneous nanocrystalline TiO_2 structure, with thickness L and porosity ϵ_p , where a monolayer of a light absorbing dye is adsorbed and interpenetrated by the redox mediator of I^-/I_3^- . This structure is deposited on a conductive substrate (TCO), which defines the interface TCO/ TiO_2 at $x = 0$. This interface is modelled as an ideal ohmic contact. The electrolyte/platinised TCO interface at $x = L$ is described by the Butler-Volmer equation. For simplicity, the contact between the electrolyte and the platinum-free areas at this interface is neglected, since in absence of platinum the charge-transfer resistance is very high.⁵

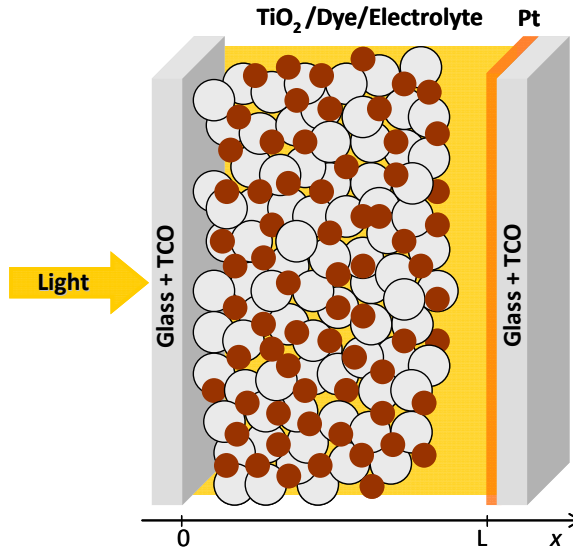


Figure 6.1 - Scheme of the modelled DSC. The TiO_2 nanoparticles that form the mesoscopic film are covered with light-absorbing dye molecules. The free volume between $x = 0$ (TCO/ TiO_2 interface) and $x = L$ (electrolyte/platinum interface) is filled with triiodide/iodide electrolyte. Here, TCO stands for transparent coating oxide, typically a fluorine-doped tin oxide film.

The mobile charges considered in the present model are the electrons in the TiO_2 conduction band, e^- , and the iodide and triiodide ions in the electrolyte. From a chemical point of view, the positively charged holes h^+ should be considered because when an electron is photo-injected, the respective hole is transferred to the counter electrode through the electrolyte. Equation (1.4) in the *Introduction* chapter, corresponding to the reduction of triiodide to iodide in the counter electrode, can be rewritten including the holes in order to guarantee total charge neutrality within the cell: $\text{I}_3^- + 2e^- + 3h^+ \rightleftharpoons 3\text{I}^- + 3h^+$. However, from a mathematical point of view the net number of cations in the previous equation is zero and so they will not be considered.

It is assumed that the cell is irradiated perpendicularly to its photoelectrode. All the electrons are assumed to be injected from the excited dye and not from band gap excitation of the TiO_2 . Moreover, it is considered that each absorbed photon injects one electron into the TiO_2 conduction band.

In Chapter 1 of this thesis – *Introduction* - three electron loss pathways were illustrated in Figure 1.2 - reactions (1.5) to (1.7). In the present model, only the recombination of TiO₂ conduction band electrons with the triiodide species in the electrolyte is taken into account – reaction (1.7). The other two reactions may be neglected since their kinetic rate constants are too small.¹²⁻¹³ Furthermore, it is assumed that the concentration of the I⁻ ions is high enough to assure that the dye regeneration reaction is very fast. First-order kinetics is assumed for the recombination of electrons in the TiO₂ conduction band with the triiodide ions in the electrolyte.^{7,14}

Concerning the charge transport within the semiconductor, it can take place via diffusion and migration. However, due to the small dimension of the titania particles, no significant electrical potential gradient is generated, resulting only in a diffusive charge transport. Additionally, band bending within a TiO₂ nanoparticle is also negligible due to its small size and so is the presence of Helmholtz layers.¹³

Taking into account the previous assumptions, the proposed phenomenological model for DSCs comprises the continuity and transport equations for the mobile species in unsteady-state and isothermal conditions:

$$-\frac{\partial j_i}{\partial x} + G_i(x) - R_i(x) = \frac{\partial n_i}{\partial t}, \quad i = e^-, I_3^- \text{ and } I^- \quad (6.1)$$

The first term on the left-hand side of the equation represents the carrier flux. The second and third terms are the generation and recombination rates of carrier i , respectively. Both reaction kinetics are characterised by a time constant. The term on the right-hand side of the equation corresponds to the i carrier concentration history. The respective equations, initial and boundary conditions for the three mobile charges are presented hereafter.

6.2.1 Electrons

As explained before, a diffusive transport of electrons within the TiO_2 film towards the transparent conductive substrate is considered. Equation (6.2) relates the electron flux, j_{e^-} , at any position x to the gradient of electron concentration across the TiO_2 layer, n_{e^-} , by means of the electron coefficient of diffusion, D_{e^-} - Fick's law:¹⁵

$$j_{e^-} = -D_{e^-} \frac{\partial n_{e^-}}{\partial x} \quad (6.2)$$

The absorption of each photon by a dye molecule is assumed to result in the injection of one electron into the TiO_2 conduction band and the consequent oxidation of the I^- to I_3^- . The electron generation term in Equation (6.1) is given by the Beer-Lambert equation, which relates the absorption of light to the properties of the material through which the light is travelling:

$$G_{e^-} = \eta_{inj} \alpha(\lambda) I_s e^{-\alpha(\lambda)x} \quad (6.3)$$

The wavelength-dependent absorption coefficient of the dye, $\alpha(\lambda)$, is a function of its optical cross-section and the density of active molecules of dye adsorbed in the TiO_2 surface. The proposed model considers a uniform distribution of dye molecules throughout the TiO_2 film. The incident photon flux I_s is corrected for reflection losses of the TCO glass and can be changed according to the incident radiation intensity. η_{inj} is the electron injection efficiency.

The recombination of electrons with triiodide species follows a first-order kinetic:

$$k_{e^-} = \frac{1}{\tau_{e^-}} \quad (6.4)$$

$$R_{e^-} = \frac{n_{e^-}(x, t) - n_{eq}}{\tau_{e^-}} \quad (6.5)$$

The dark equilibrium density n_{eq} , corresponding to the match between the electron's Fermi level in the TiO_2 and the redox potential, is given by:

$$n_{eq} = N_{CB} \exp \left[-\frac{(E_{CB} - E_{Redox})}{k_B T} \right] \quad (6.6)$$

Bringing all these considerations together, the continuity equation becomes:

$$D_{e^-} \frac{\partial^2 n_{e^-}(x,t)}{\partial x^2} + n_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} - \frac{n_{e^-}(x,t) - n_{eq}}{\tau_{e^-}} = \frac{\partial n_{e^-}(x,t)}{\partial t} \quad (6.7)$$

Initial Conditions

Considering that for $t=0$ the cell is under dark equilibrium conditions:

$$t=0 \quad n_{e^-}(x,0) = n_{eq} \quad (6.8)$$

Boundary Conditions

If a defined external potential difference is applied to the cell, a specific electron concentration is established at the contact between the nanoporous semiconductor (TiO_2) and the conducting substrate (TCO) - $x=0$. In addition, if a voltage drop and band bending at this interface (Figure 6.2) is neglected,³ a simple ohmic resistance may be considered to define the electron transfer resistance at the TCO/ TiO_2 interface - Section 6.2.3. According to Equation (6.9), a charge balance at this interface determines that the current density at $x=0^-$, $j_{e^-}^{0^-}$, equals the current density at $x=0^+$, $j_{e^-}^{0^+}$:

$$j_{e^-}^{0^-} = j_{e^-}^{0^+} \quad (6.9)$$

where

$$j_{e^-}^{0^-} = \frac{J_{cell}}{q} \quad (6.10)$$

and

$$j_{e^-}^{0^+} = -D_{e^-} \left. \frac{\partial n_{e^-}}{\partial x} \right|_{x=0^+} \quad (6.11)$$

The current density flowing across $x=0^+$ results from the diffusive electrons that percolated through the semiconductor - equation (6.11) - which, in steady-state conditions, corresponds to the net current density, J_{cell} , generated by the cell under operation.

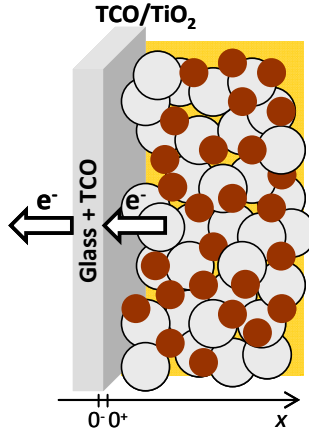


Figure 6.2 - Detail of the TCO/TiO₂ interface ($x=0$), showing the transport of electrons towards the TCO coating and, consequently, to the external circuit. Here, $x=0^+$ refers to the surface close to the semiconductor; $x=0^-$ refers to the external surface of the TCO layer.

At $x=L$ there are no electrons flowing from the electrolyte to the platinised counter electrode. The presence of a layer of electrolyte in contact with the cathode, which thickness is specified by the spacer ring used to seal the cell, ensures that there is no contact between the TiO₂ and the counter electrode. Electrons are thus reflected and diffuse back into the inner layers of the TiO₂ film.¹ The corresponding boundary condition can be written as follows:

$$x=L \quad \frac{\partial n_{e^-}(L,t)}{\partial x} = 0 \quad (6.12)$$

6.2.2 Redox species

The oxidation of iodide ions, as well as the reduction of triiodide, occurs in the electrolyte present in the interstitial space among the TiO₂ nanoparticles. Taking into account the stoichiometry of reactions (1.3) and (1.4), the terms of generation and recombination of triiodide and iodide species must be affected by the corresponding

coefficients, $\frac{1}{2}$ and $-\frac{3}{2}$, respectively:

$$D_{I_3^-} \frac{\partial^2 n_{I_3^-}(x,t)}{\partial x^2} + \frac{1}{2\varepsilon_p} \left[\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} - \frac{n_{e^-}(x,t) - n_{eq}}{\tau_{e^-}} - \frac{\partial n_{e^-}(x,t)}{\partial t} \right] = \frac{\partial n_{I_3^-}(x,t)}{\partial t} \quad (6.13)$$

$$D_{I^-} \frac{\partial^2 n_{I^-}(x,t)}{\partial x^2} - \frac{3}{2\varepsilon_p} \left[\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x} - \frac{n_{e^-}(x,t) - n_{eq}}{\tau_{e^-}} - \frac{\partial n_{e^-}(x,t)}{\partial t} \right] = \frac{\partial n_{I^-}(x,t)}{\partial t} \quad (6.14)$$

In unsteady-state, the accumulated electrons do not participate in the redox reactions and therefore must be discounted from the ions' generation term:

$$\underbrace{\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x}}_{\text{generation}} - \underbrace{\frac{\partial n_{e^-}(x,t)}{\partial t}}_{\text{electron accumulation}}.$$

Initial Conditions

At instant $t = 0$, initial concentrations of the electrolyte species are assumed:

$$t = 0 \quad n_{I_3^-}(x, 0) = n_{I_3^-}^{init}; \quad n_{I^-}(x, 0) = n_{I^-}^{init} \quad (6.15)$$

Boundary Conditions

At the TCO/TiO₂ interface only the photoinjected electrons are able to flow. The net flux of I⁻ and I₃⁻ is zero:

$$x = 0 \quad \frac{\partial n_{I_3^-}(0,t)}{\partial x} = 0; \quad \frac{\partial n_{I^-}(0,t)}{\partial x} = 0 \quad (6.16)$$

The total amount of redox species contained in the TiO₂ nanopores remains constant during the DSC operation. This may be described as:²

$$x = L \quad \int_0^L n_{I_3^-}(x) dx = n_{I_3^-}^{init} L; \quad \int_0^L n_{I^-}(x) dx = n_{I^-}^{init} L \quad (6.17)$$

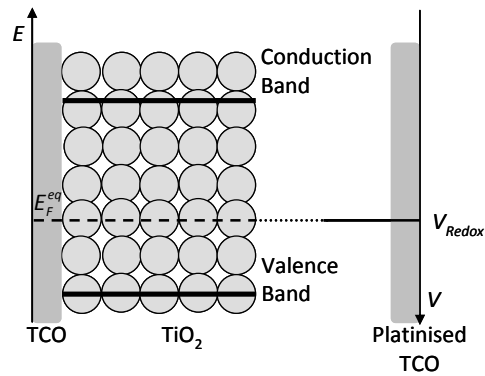
6.2.3 Electrolyte - Platinised contact: Butler-Volmer Equation

For the three charged species, e^- , I^- and I_3^- , the initial and boundary conditions, Equations (6.8), (6.9), (6.12) and (6.15)-(6.17), necessary to integrate the three non-linear differential equations, Equations (6.7), (6.13) and (6.14), were discussed. However, additional information is required at $x=0$. In fact, the net current density J_{cell} at this interface must be known. Assuming that there are no resistances in the external circuit load, J_{cell} equals the current density that is returned to the cell via the counter electrode. Here, electrons take part in the iodide/triiodide redox reaction catalysed by the platinum layer coated onto the TCO. Consequently, the electrolyte/platinised TCO interface can be treated as an electrochemical half-cell.³ A Butler-Volmer approach is therefore considered to describe the electrochemical kinetics:

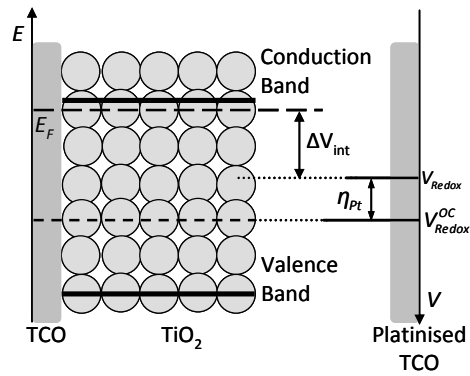
$$J_{cell} = J_0 \left[\frac{n_{I_3^-}(L)}{n_{I_3^-}^{oc}(L)} e^{\frac{\theta q \eta_{pt}}{k_B T}} - \frac{n_{I^-}(L)}{n_{I^-}^{oc}(L)} e^{\frac{-(1-\theta) q \eta_{pt}}{k_B T}} \right] \quad (6.18)$$

Equation (6.18) states that the current generated by the electrochemical reaction at $x=L$ increases exponentially with the activation overvoltage η_{pt} . It is important to hold that this overvoltage is the voltage sacrificed or lost to overcome the energy activation barrier.¹⁶ If the current density value is zero, which corresponds to open-circuit conditions, Equation (6.18) reduces to the Nernst equation. In this case, the concentration of triiodide and iodide under open-circuit conditions can be calculated.

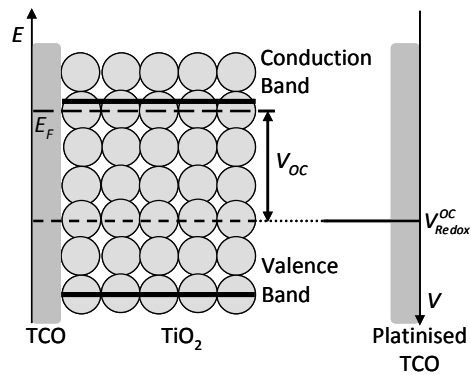
The only value that is unknown at this moment is the overvoltage in the platinum layer η_{pt} . To determine this overvoltage it is important to understand the behaviour of the cell under dark equilibrium, under illumination ($\Delta V_{int} < V_{oc}$) and at open-circuit conditions ($\Delta V_{int} = V_{oc}$).



(a)



(b)



(c)

Figure 6.3 - Schematic energy level diagrams of the TCO/TiO₂ interface and electrolyte/platinised TCO under different operating conditions: (a) under dark equilibrium; (b) under illumination and applied bias lower than V_{OC} ; (c) under illumination at open-circuit conditions.

In the dark equilibrium scenario, the electron Fermi level equals the redox energy of the electrolyte: $E_F^{eq} = E_{\text{Redox}}$. The variation of the applied external load, $\Delta V_{\text{int}} = (E_F - E_{\text{Redox}})/q$, causes a displacement of the Fermi level inside the metal oxide nanostructure from the equilibrium value towards the conduction band level. This potential difference reaches its maximum value at open circuit conditions, when there is no overvoltage in the platinum electrode (no external load): $\Delta V_{\text{int}} = V_{\text{OC}}$.

The internal voltage of a DSC is defined as the difference in electrochemical potentials between the boundaries $x=0$ and $x=L$. Bearing in mind the assumptions of the present model concerning the TCO/TiO₂ interface, the respective electrochemical potential is assumed to be continuous and equals the electron Fermi level at $x=0$. On the other hand, the electrochemical potential of the platinum electrode at $x=L$ equals the electrolyte redox energy. The value of the internal voltage can then be calculated as:

$$\Delta V_{\text{int}} = [E_F(x=0) - E_{\text{Redox}}]/q \quad (6.19)$$

According to the theory of semiconductors, the energy of the Fermi level is related to the spatial electron density:¹⁷

$$E_F(x=0) = E_{\text{CB}} + k_B T \ln \frac{n_{e^-}(x=0)}{N_{\text{CB}}} \quad (6.20)$$

Again observing Figure 6.3b), it can be clearly seen that the redox energy of the electrolyte has two contributions: the redox energy under open-circuit conditions and the platinum overvoltage. Considering this fact and the Nernst's equation to define the $E_{\text{Redox}}^{\text{OC}}$, Equations (6.21) and (6.22) can be written:

$$E_{\text{Redox}} = E_{\text{Redox}}^{\text{OC}} + q\eta_{\text{Pt}} \quad (6.21)$$

$$E_{\text{Redox}}^{\text{OC}} = E_{\text{Redox}}^{\circ} - \frac{k_B T}{2} \ln \frac{n_{\text{I}_3^-}^{\text{OC}}(L)}{[n_{\text{I}^-}^{\text{OC}}(L)]^3} \quad (6.22)$$

Substituting these two equations into Equation (6.19) and solving in order to η_{Pt} :

$$\eta_{\text{Pt}} = \frac{1}{q} (E_{\text{CB}} - E_{\text{Redox}}^{\circ}) + \frac{k_B T}{2q} \ln \frac{n_{\text{I}_3^-}^{\text{OC}}(L)}{[n_{\text{I}^-}^{\text{OC}}(L)]^3} + \frac{k_B T}{q} \ln \frac{n_{e^-}(x=0)}{N_{\text{CB}}} - \Delta V_{\text{int}} \quad (6.23)$$

Equation (6.23) should now be included in the Butler-Volmer equation – Equation (6.18). Analysing equations (6.10) and (6.23) it can be concluded that the flux of electrons at $x=0$, and consequently the electron concentration profiles, are a function of the internal voltage of the cell.

Up to this point, the model does not account for external resistances, which have to be considered for real systems. Ferber *et al.*³ proposed an electrical analogue able to describe additional external series (R_{TCO}) and shunt resistances (R_p). A correlation between the internal and external voltages can be established applying the Kirchhoff's and Ohm's laws:³

$$\Delta V_{int} = (R_{TCO} + R_{ext}) \left(\frac{R_p}{R_{ext} + R_{TCO} + R_p} \right) A \cdot J_{cell} \quad (6.24)$$

$$V_{ext} = R_{ext} \left(\frac{R_p}{R_{ext} + R_{TCO} + R_p} \right) A \cdot J_{cell} \quad (6.25)$$

Substituting Equation (6.24) in Equation (6.23), the external resistance, R_{ext} , determines the applied bias potential.

6.2.4 Dimensionless equations

The model variables were made dimensionless with respect to electron parameters and to the thickness of the cell. Changing for dimensionless variables and introducing suitable dimensionless parameters, equations (6.7), (6.13)-(6.14) and (6.8)-(6.9), (6.12), (6.15)-(6.17) become as follows:

$$D_{e^-}^* \frac{\partial^2 n_{e^-}^*}{\partial x^{*2}} + \left[D\alpha \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) \right] = \frac{\partial n_{e^-}^*}{\partial \vartheta} \quad (6.26)$$

$$\vartheta = 0 \quad n_{e^-}^*(x^*, 0) = n_{eq}^* \quad (6.27)$$

$$x^* = 0 \quad j_{cell}^* = \frac{n_{ref} D_{ref} q}{L} \left(-D_{e^-}^* \frac{\partial n_{e^-}^*}{\partial x^*} \right) \Big|_{x^*=0^+} \quad (6.28)$$

$$x^* = 1 \quad \frac{\partial n_{e^-}^*}{\partial x^*} = 0 \quad (6.29)$$

$$D_{I_3}^* \frac{\partial^2 n_{I_3}^*}{\partial x^{*2}} + \frac{1}{2\varepsilon_p} \left[Da \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) - \frac{\partial n_{e^-}^*}{\partial \vartheta} \right] = \frac{\partial n_{I_3}^*}{\partial \vartheta} \quad (6.30)$$

$$D_{I^-}^* \frac{\partial^2 n_{I^-}^*}{\partial x^{*2}} - \frac{3}{2\varepsilon_p} \left[Da \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) - \frac{\partial n_{e^-}^*}{\partial \vartheta} \right] = \frac{\partial n_{I^-}^*}{\partial \vartheta} \quad (6.31)$$

$$\vartheta = 0 \quad n_{I_3}^*(x^*, 0) = n_{I_3}^{*init}; \quad n_{I^-}^*(x^*, 0) = n_{I^-}^{*init} \quad (6.32)$$

$$x^* = 0 \quad \frac{\partial n_{I_3}^*(0, \vartheta)}{\partial x^*} = 0; \quad \frac{\partial n_{I^-}^*(0, \vartheta)}{\partial x^*} = 0 \quad (6.33)$$

$$x^* = 1 \quad \int_0^1 n_{I_3}^*(x^*) dx^* = n_{I_3}^{*init}; \quad \int_0^1 n_{I^-}^*(x^*) dx^* = n_{I^-}^{*init} \quad (6.34)$$

where $n_i^* = \frac{n_i}{n_{ref}}$, $x^* = \frac{x}{L}$, $D_i^* = \frac{D_i}{D_{ref}}$ ($i = \text{electrons, } I_3, I^-$), $\vartheta = \frac{D_{ref}}{L^2} t$, $J_{cell}^* = \frac{J_{cell}}{J_0}$,

$$Da = \frac{L^2 n_{inj} \alpha I_s}{D_{ref} n_{ref}}, \gamma = \alpha L \text{ and } \Phi = L \sqrt{\frac{k_{e^-}}{D_{ref}}}.$$

6.2.5 Numerical solution strategy

To simulate the operating behaviour of a DSC is necessary to solve Equations (6.26), (6.30) and (6.31) with the respective boundary and initial conditions. In order to apply the boundary condition at $x^* = 0$ for the electrons, Equation (6.24) should be substituted in Equation (6.23); the result should then be inserted into Equation (6.18), to obtain the current density in the external circuit. The partial differential equations were spatially discretized using the finite differences method. The time integration was accomplished by LSODA,¹⁸ a numerical package developed at the Lawrence Livermore National Laboratory. For the calculation of I - V curves, the equations were solved for steady-state conditions (whenever the time derivative was smaller than a pre-defined value).

6.3 Results and discussion

6.3.1 *I-V* characteristic

The simulated *I-V* characteristic was experimentally validated by comparison with data from Wang *et al.*¹¹ The input data used for simulation purposes are compiled in Table 6.1. The triiodide diffusivity was obtained by fitting the experimental EIS spectra under illumination to an appropriate electrical analogue^{15,19} by means of the ZView software (v2.5b, Scribner Associates Inc.). The diffusion of I_3^- in the electrolyte is usually well described by a Nernst diffusion impedance, characterised by a Warburg parameter and a characteristic diffusion time constant.²⁰ The diffusion constants of I_3^- and I^- are of the same order of magnitude.²¹ In fact, I^- does not contribute to the diffusion impedance due to the large excess of this species compared to I_3^- .²² The electrolyte-platinum interface is identified as a low-frequency semicircle in the Nyquist diagram and may be expressed as a charge transfer resistance and a double layer capacitance. Hauch *et al.*²² observed that there is a relation between the exchange current density at this interface and the corresponding charge transfer resistance, allowing the calculation of the former parameter.

Figure 6.4 compares the experimental data with the corresponding simulated *I-V* curve. As it can be realised from this figure, the model agrees quite well with the experimental data: Wang *et al.*¹¹ reported a cell's efficiency of 6.2 % ($j_{sc} = 12.2 \text{ mA cm}^{-2}$; $V_{oc} = 0.74 \text{ V}$; $FF = 0.69$; $V_{MPP} = 0.65 \text{ V}$; $j_{MPP} = 9.5 \text{ mA cm}^{-2}$), in straight agreement with the simulated parameters ($\eta = 6.4 \%$; $j_{sc} = 12.1 \text{ mA cm}^{-2}$; $V_{oc} = 0.74 \text{ V}$; $FF = 0.72$; $V_{MPP} = 0.64 \text{ V}$; $j_{MPP} = 10.1 \text{ mA cm}^{-2}$). The experimental and simulated *I-V* curves were fitted by means of the parameters R_p and η_{inj} . In fact, the fill factor strongly depends on the shunt resistance value (R_p), which cannot be determined theoretically.

Table 6.1 - Simulator input parameters.

Parameter	Value	Observed ¹
$C_{I_3}^{init}$	0.1 M	11
$C_{I^-}^{init}$	1.1 M	11
D_{e^-}	$1.10 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	11
D_{I_3}	$4.91 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	<i>Calc.</i>
D_{I^-}	$4.91 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	<i>Calc.</i>
N_{CB}	$1.0 \times 10^{21} \text{ cm}^{-3}$	14
$E_{CB}-E_{Redox}$	0.93 eV	<i>Fit</i>
τ_{e^-}	23.6 ms	11
A	0.158 cm^2	11
L	10 μm	11
ϵ_p	0.63	11
η_{inj}	0.90	<i>Fit</i>
$\alpha(\lambda)$	1000 cm^{-1}	23
I_s	$1.50 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$	11
β	0.78	3
J_0	68.1 mA cm^{-2}	<i>Calc.</i>
R_{TCO}	8.4 Ω	<i>Calc.</i>
R_p	2.8 k Ω	<i>Fit</i>
T	298 K	-

¹ The parameters calculated by means of a ZView fitting are identified by “*Calc.*”; the model values fitted to the experimental *I-V* curve are identified by “*Fit*” and values extracted from the literature are indexed to the corresponding reference.

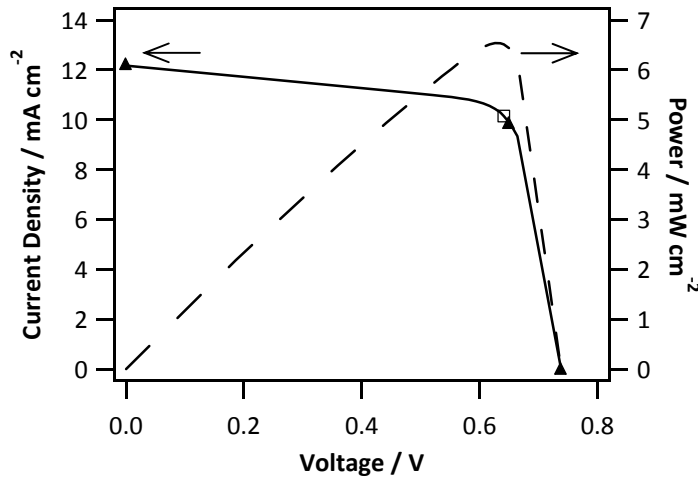


Figure 6.4 - Experimental and simulated I - V characteristics for the system described in Table 6.1, under 1 sun illumination. (▲) Experimental performance parameters taken from Ref. 11; (◻) Simulated maximum power point. Solid and dashed lines correspond to the simulated I - V curve and power output, respectively.

The main uncertainty that surrounds the simulated results is related to the kinetics of recombination in a DSC. In fact, it has been suggested by other authors the non-ideal behaviour of DSCs, which may arise from the fact that the recombination process is mediated by electronic surface states below the conduction band of the oxide.²⁴ This way, if the recombination does not occur predominantly via the conduction band, the electron diffusion length cannot be anymore defined as $L_n = \sqrt{D_e \tau_e}$, giving rise to a non-linear reaction order and hence a voltage-dependent τ_e value. Even though, for the non-linear case, the electron lifetime dependency with voltage is needed to be known. The origin of the non-linearity recombination mechanisms is still very speculative as a consequence of the need to make simplifying assumptions. Therefore, the linear behaviour was considered here based on the fact that the discrepancies between linear and non-linear recombination should be more acute when the diffusion length is very high. Another important assumption made in the present work is related to the electrolyte free volume between the semiconductor-electrolyte interface and the platinum counter electrode.

In fact, these two interfaces cannot be in contact to avoid short-circuit and so its thickness is assumed to be very small and, consequently, the corresponding resistance negligible.

Figure 6.5 shows the simulated steady-state electron density profiles through the thickness of the TiO_2 film for short-circuit, open-circuit and maximum power point conditions under 1 sun illumination. Since radiation is considered to hit the cell from the anode side (working electrode), most electrons are generated near the front side of the cell due to the exponential absorption law, as shown in equation (6.3). A large electron density gradient is noticed for short-circuit and maximum power point conditions, reaching its maximum at $x^*=0$. Under these conditions, the TiO_2 layers closest to the current collector (TCO) contribute mostly to the electron flux towards the external circuit. This fact is related to the higher concentration gradients and increased diffusion mechanisms, limiting the electron recombination kinetics. By contrast, the electron density at open-circuit conditions is almost constant across the entire TiO_2 film and so no current is delivered to the external circuit.

For a cell delivering current, triiodide is formed in the vicinity of the semiconductor nanoparticles and has to move towards the cathode, while the iodide regenerated in the platinum cathode must diffuse back to the vicinity of the dye molecules through the electrolyte. As a result, the triiodide concentration diminishes with x^* and, since iodide flows in the opposite direction, its concentration increases in the proximity of the front contact ($x^*=0$) - Figure 6.6. The concentration profiles under short-circuit and maximum power point are very similar, whereas in open-circuit conditions they remain almost constant.

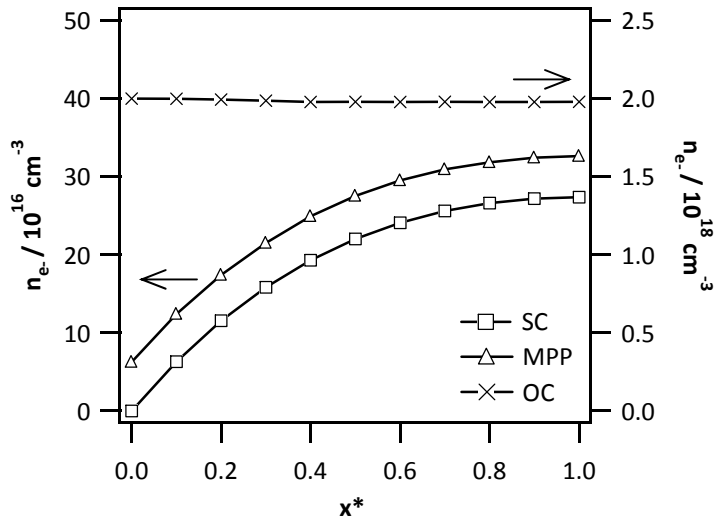


Figure 6.5 - Simulated electron density profiles for the system characterised by parameters given in Table 6.1 under 1 sun illumination at short-circuit (SC), open-circuit (OC) and maximum power point (MPP) conditions.

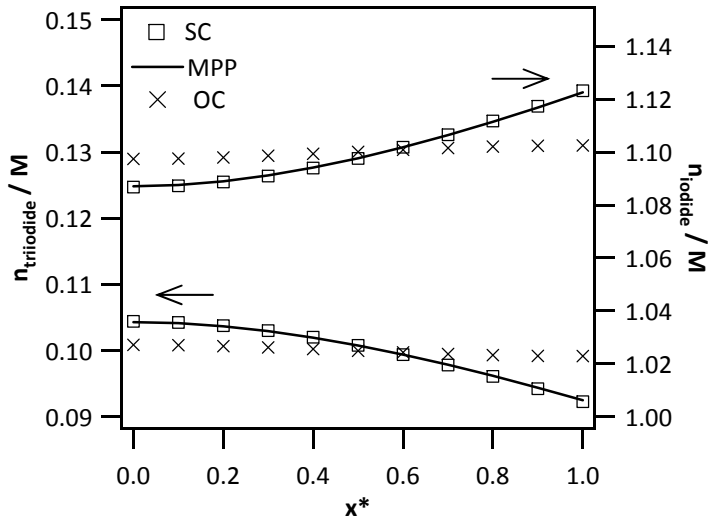


Figure 6.6 - Simulated triiodide and iodide concentration profiles for the system characterised by parameters given in Table 6.1 under 1 sun illumination at short-circuit (SC), open-circuit (OC) and maximum power point (MPP) conditions.

Figure 6.7 shows the evolution of the transient electron density profiles at short-circuit conditions before reaching the steady-state condition. The electron density profiles during the first micrometres of the TiO_2 film is characterised by a steady increase, becoming a flat profile towards $x^*=1$. For higher values of ϑ , the electron density profile tends to the steady-state condition (shown in Figure 6.5).

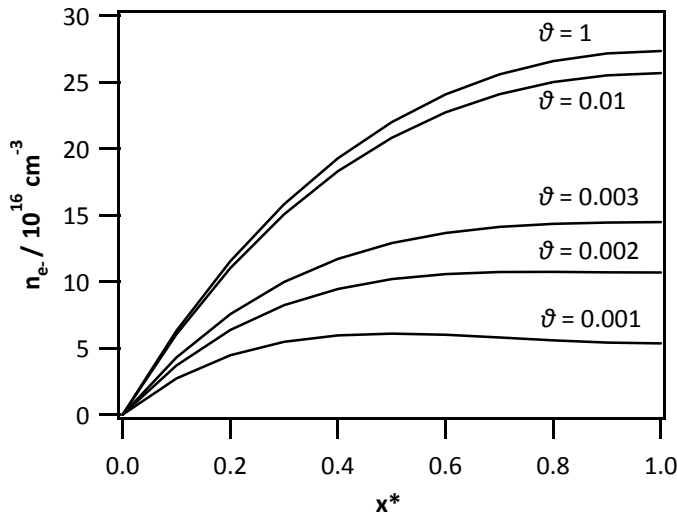


Figure 6.7 - Transient electron density profiles simulated for the system characterised by parameters given in Table 6.1 under 1 sun illumination and at short-circuit conditions. ϑ is the dimensionless time variable; $\vartheta = 1$ corresponds to the steady-state stage.

Transient concentrations of electrolyte species evolve from initial concentration (see Table 6.1) to steady-state values - Figure 6.8. It can be seen that triiodide evolves towards a higher concentration at $x^*=0$ and smaller at $x^*=1$, where the total number of triiodide ions should be kept constant, following the charge transport driving force. Triiodide is mainly formed in the region where a higher number of electrons are efficiently injected into the TiO_2 nanoparticles, where simultaneously iodide is consumed by reducing the oxidised dye molecules. A symmetric concentration profile is formed for the iodide.

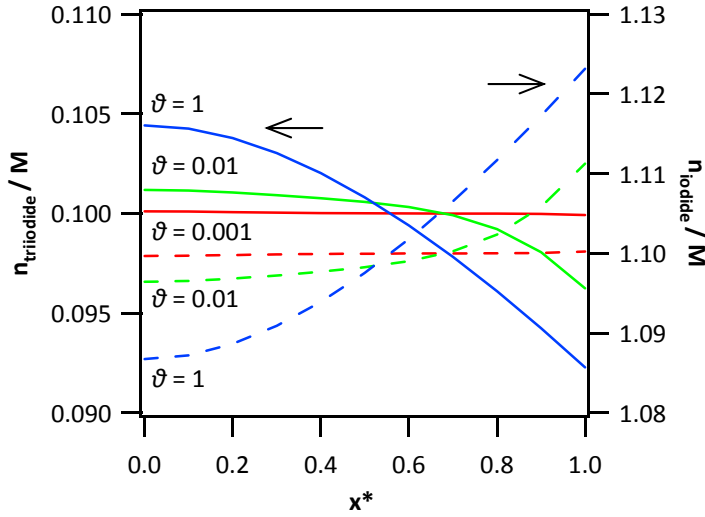
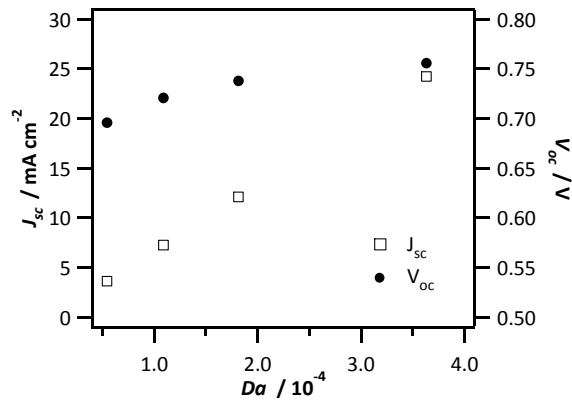


Figure 6.8 - Transient triiodide (solid line) and iodide (dashed line) concentration profiles simulated for the system characterised by parameters given in Table 6.1 under 1 sun illumination and at short-circuit conditions. ϑ is the dimensionless time variable; $\vartheta=1$ corresponds to the steady-state operation. (red - $\vartheta=0.001$; blue - $\vartheta=0.01$; green - $\vartheta=1$)

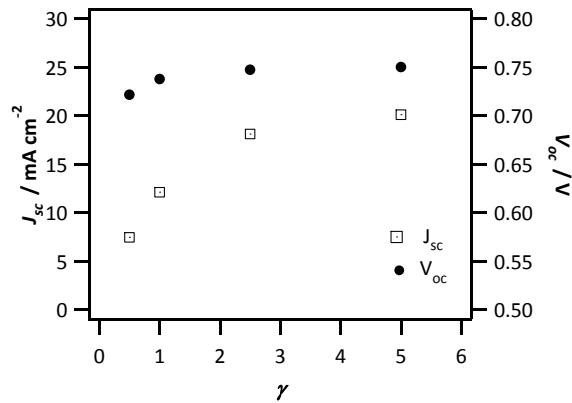
The solution of equations (6.26), (6.30) and (6.31) with the respective boundary conditions is described in terms of three dimensionless parameters: $Da = \frac{L^2 \eta_{inj} \alpha I_0}{D_{ref} n_{ref}}$,

$\gamma = \alpha L$ and $\Phi = L \sqrt{\frac{k_{e^-}}{D_{ref}}}$. The variation of these dimensionless numbers will result in

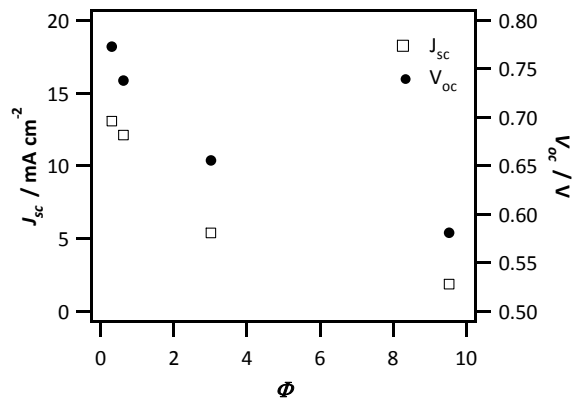
different DSCs' performances. Thus, a systematic study on the effect of these numbers is made. From Figure 6.9 it can be seen that both J_{sc} and V_{oc} increase with Da and γ , and decrease with Φ . For the three situations a more significant influence in J_{sc} is noticed. The dimensionless number Da is the ratio between characteristic reaction and transport kinetic parameters (equivalent to a Damköhler number),²¹ between injected electrons and their diffusion in the photoelectrode. As more electrons are injected into the TiO_2 conduction band, the electron density is increased and, if no extra recombination processes occur, a more significant current density will



(a)



(b)



(c)

Figure 6.9 - Influence of the dimensionless numbers (a) Da , (b) γ and (c) Φ on the DSCs' photovoltaic performance.

flow towards the TCO. A nearly linear relation between J_{SC} and Da is observed and, to higher values of Da , V_{OC} values tend to stabilise at a maximum value (near to the maximum theoretical value of V_{OC}) - Figure 6.9a). Parameter γ is related to the absorption coefficient α of the dye. In fact, increasing α for the same film thickness results in a higher amount of electrons generated close to $x^*=0$. As the TiO_2 nanoparticles located near the TCO/ TiO_2 interface contribute mostly to the electrons flowing into the external circuit, it is easily understood that a higher J_{SC} will be found for higher γ values, which is in straight agreement with Figure 6.9b). However, it can be observed that both J_{SC} and V_{OC} tend to a steady value for γ above a threshold value. Making the analogy with mass transfer phenomena, a recombination Thiele modulus can be defined as a means of expressing the ratio of recombination reaction to diffusion rates.²¹ Here, the reaction rate is related to the electron back transfer to triiodide species, the main kinetic process that limits the photocurrent and photovoltage in DSCs – dark current. Higher Φ means higher back reaction and so lower electron lifetimes and lower photocurrents - Figure 6.9c). In what concerns the voltage at open-circuit conditions, increasing Da and γ and decreasing Φ results in an increase of the V_{OC} parameter. This fact is due to the higher electron concentration in the TiO_2 at $x^*=0$, meaning a higher Fermi level and thus a higher voltage - see equations (6.19) and (6.20).

6.3.2 EIS spectra

Electrochemical Impedance Spectroscopy (EIS) is a technique widely used for characterising the electrical behaviour of systems in which the overall performance is determined by a number of strongly coupled processes, each proceeding at a different rate. The most common and standard procedure in impedance measurements consists of applying a small sinusoidal voltage perturbation and monitoring the resulting current response of the system at the corresponding frequency. The single-frequency voltage perturbation is usually done at open-circuit conditions with magnitude V_0 of the modulation signal:

$$V(t) = V_{oc} + V_0 \cos(\omega t) \quad (6.35)$$

The current response has the same period as the voltage perturbation but will be phase shifted by φ :

$$I(t) = I_0 \cos(\omega t - \varphi) \quad (6.36)$$

V_0 and I_0 are the amplitudes of the voltage and current signals, respectively, and ω is the radial frequency in radians per second.

Similar to resistance, impedance is a measure of the ability of a system to impede the flow of electrical current. Thus, impedance is the ratio of a time-dependent voltage and a time-dependent current as defined by Equations (6.35) and (6.36). Applying complex notation, the impedance response of a system can be expressed in terms of real ($Z' = Z_0 \cos \varphi$) and imaginary components ($Z'' = Z_0 \sin \varphi$).²⁵ With this information the Nyquist diagram can be plotted.

The transient model described in this paper allows obtaining the theoretical Nyquist diagram for the given system. For that purpose, the external load should be expressed in terms of voltage, instead of external resistances, calculated at each instant t by means of Equation (6.35). The cyclic steady-state is reached when the process starts exhibiting periodically identical dependent-variable values. In this work, the cyclic steady-state condition was defined by a current response change less than 0.01 % obtained for a large number of consecutive cycles. Figure 6.10 compares the experimental EIS spectra¹¹ with the simulation results. As expected, three semicircles were obtained for the system under study. These correspond to the typical interfaces of a DSC: counter electrode, photoelectrode and electrolyte (from left to right in Figure 6.10). The model accurately represents the behaviour of the system under study.

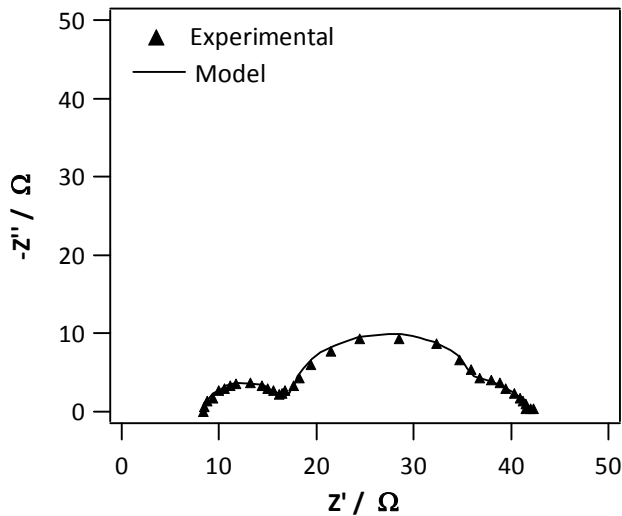


Figure 6.10 - Experimental and simulated Nyquist diagrams for the system described in reference 11. The single-frequency voltage perturbation was done at open-circuit conditions (0.638 V) with modulation signal magnitude of 10 mV. The input parameters used in the simulation are presented in Table 6.1.

The relevance of such phenomenological approach is mainly related to the uncertainty arising from fitting the experimental Nyquist diagrams to general electrical analogues. In fact, several analogues can fit the same Nyquist diagram, resulting in different process parameters. Consequently, various interpretations of the system's behaviour may be obtained. As the transient phenomenological model is developed based on physical parameters, it gives a more accurate description of the phenomena involved in DSCs. It is therefore a very important tool to predict the performance of DSCs, to identify bottlenecks in their performance, to improve the understanding of the underlying phenomena and for optimisation purposes.

6.4 Conclusion

Understanding the underlying mechanisms connected with DSCs' operation usually implies the application of transient probing. This way, a transient phenomenological model was developed in order to compare the experimental EIS results with the

theoretical data. Moreover, several operating parameters of DSCs cannot be predicted theoretically or experimentally. This can be overcome by fitting the experimental I - V characteristic and Nyquist diagram to the phenomenological model under steady and unsteady-state, respectively. In the present study, the experimental data showed very good agreement with the simulation results.

Steady-state electron density profiles were obtained, suggesting that most electrons are generated near the front side of the cell under short-circuit and maximum power point conditions. In this part of the cell, higher concentration gradients were observed, enhancing electron diffusion rate, which in its turn limits electron recombination kinetics. The transient profiles are characterised by a steady increase, levelling out in the vicinity of the counter electrode.

The electrolyte species profiles under steady-state showed a decreasing triiodide concentration towards the counter electrode. Since iodide flows in the opposite direction, its concentration increases in the vicinity of the front contact ($x^*=0$). The concentration profiles under short-circuit and maximum power point conditions are close each other, whereas in open-circuit conditions the profiles are flat. As expected, the triiodide evolves towards a higher concentration at $x^*=0$ and smaller at $x^*=1$, following the iodide a symmetric behaviour.

The continuity and transport equations are described in terms of three dimensionless parameters (Da , γ and Φ), which characterise the DSCs' performance. From the systematic study on the effect of these parameters, one may conclude that both J_{SC} and V_{OC} increase with Da and γ and decrease with Φ .

Acknowledgments

L. Andrade is grateful to the Portuguese Foundation for Science and Technology (FCT) for her PhD grant (reference: SFRH/BD/30464/2006). H. Aguilar Ribeiro acknowledges the *Programa Ciência 2007*. The authors also acknowledge FEUP and LEPAE for the computational facilities and João Ranita for helping with Linux compilation.

List of abbreviations and symbols

Abbreviations	Definition	Units
A	Cell area	cm^2
C_i	Concentration of specie i	M
CB	Conduction band	
CE	Counter electrode	
Da	Dimensionless number (equivalent to Damköhler number)	
D_i	Diffusion coefficient of species i	$\text{cm}^2 \text{s}^{-1}$
D_{ref}	Reference diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$
DSCs	Dye-sensitized solar cells	
E	Energy	J
E_{CB}	Conduction Band energy	J
E_F	Fermi energy	J
E_F^{eq}	Dark equilibrium Fermi energy	J
E_{Redox}	Redox energy	J
E_{Redox}°	Standard redox energy	J
E_{Redox}^{OC}	Open-circuit redox energy	J
e^-	Electrons	
EIS	Electrochemical impedance spectroscopy	
FF	Fill factor	
G_i	Generation rate of species i	$\text{cm}^{-3} \text{s}^{-1}$
h	Planck constant ($h = 6.62606896(33) \times 10^{-34} \text{ J s}$)	J s
h^+	Holes	
$init$	Initial	
I	Electric current	mA
$I(t)$	Current response	mA
I_s	Incident photon flux corrected for reflection losses	$\text{cm}^{-2} \text{s}^{-1}$

I_0	Amplitude of the current signal	mA
j_i	Current density of specie i	$\text{s}^{-1} \text{cm}^{-2}$
J_{cell}	Net current density	mA cm^{-2}
J_{sc}	Short-circuit current density	mA cm^{-2}
J_0	Exchange current density at Pt electrode	mA cm^{-2}
k_B	Boltzman constant ($k_B = 1.3806504(24) \times 10^{-23} \text{ J K}^{-1}$)	J K^{-1}
k_{e^-}	Back reaction rate constant	s^{-1}
L	Thickness of the inner cell	μm
L_n	Electron diffusion length	μm
MPP	Maximum power-point	
n_i	Density of species i	cm^{-3}
n_{eq}	Dark equilibrium electron density	cm^{-3}
n_{ref}	Reference carrier density	cm^{-3}
N_{CB}	Effective density of states in the TiO_2 conduction band	cm^{-3}
OC	Open-circuit	
q	Elementary charge ($q = 1.60217646 \times 10^{-19} \text{ C}$)	C
R_i	Recombination rate of species i	$\text{cm}^{-3} \text{s}^{-1}$
R_p	Shunt-resistance	Ω
R_{TCO}	External series-resistance	Ω
R_{ext}	Load parameter	Ω
SC	Short-circuit	
T	Absolute temperature	K
TCO	Transparent conductive oxide	
t	Time	s
V	Voltage	V
$V(t)$	Voltage perturbation	V
V_0	Amplitude of the voltage signal	V
VB	Valence band	

V_{int}	Internal cell voltage	V
V_{ext}	External cell voltage	V
V_{OC}	Open-circuit photovoltage	V
x	Coordinate	cm
$Z(t)$	Impedance	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω
Z_0	Ratio of the amplitude of the voltage signal and the amplitude of the current signal	Ω
O^+	Point close to the photoanode	
O^-	External point of the current collector	
*	Dimensionless variable	

Greek symbols	Definition	Units
η	Global efficiency of a DSC	%
λ	Wavelength	nm
φ	Phase angle	degree
ω	Radial frequency	rad s^{-1}
$\alpha(\lambda)$	Wavelength-dependent absorption coefficient	cm^{-1}
β	Symmetry coefficient	
γ	Dimensionless number	
δl	Infinitesimal thickness of the interface TCO/TiO ₂	cm
ΔV_{int}	Variation of the applied voltage	V
ε_p	TiO ₂ film porosity	
η_{Pt}	Electrochemical overvoltage at Pt electrode	V
η_{inj}	Electron injection efficiency	
ϑ	Dimensionless time variable	
τ_{e^-}	Electron lifetime	ms

Φ	Dimensionless number (equivalent to Thiele modulus)
--------	---

References

- (1) Soedergren, S.; Hagfeldt, A.; Olsson, J.; Lindquist, S.-E. *J. Phys. Chem.* **1994**, *98*, 5552.
- (2) Papageorgiou, N.; Grätzel, M.; Infelta, P. P. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 405.
- (3) Ferber, J.; Stangl, R.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *53*, 29.
- (4) Stangl, R.; Ferber, J.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 255.
- (5) Ferber, J.; Luther, J. *J. Phys. Chem. B* **2001**, *105*, 4895.
- (6) Peter, L. *J. Electroanal. Chem.* **2007**, *599*, 233.
- (7) Fisher, A. C.; Peter, L. M.; Ponomarev, E. A.; Walker, A. B.; Wijayantha, K. G. U. *J. Phys. Chem. B* **2000**, *104*, 949.
- (8) Huang, S. Y.; Schlichthorl, G.; Nozik, A. J.; Gratzel, M.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 2576.
- (9) Dloczik, L.; Ieperuma, O.; Lauermann, I.; Peter, L. M.; Ponomarev, E. A.; Redmond, G.; Shaw, N. J.; Uhlendorf, I. *J. Phys. Chem. B* **1997**, *101*, 10281.
- (10) Hanmin, T.; Xiaobo, Z.; Shikui, Y.; Xiangyan, W.; Zhipeng, T.; Bin, L.; Ying, W.; Tao, Y.; Zhigang, Z. *Sol. Energy* **2009**, *83*, 715.
- (11) Wang, Q.; Moser, J.-E.; Gratzel, M. *J. Phys. Chem. B* **2005**, *109*, 14945.
- (12) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- (13) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.
- (14) Lobato, K.; Peter, L. M.; Würfel, U. *J. Phys. Chem. B* **2006**, *110*, 16201.
- (15) Bisquert, J. *J. Phys. Chem. B* **2002**, *106*, 325.
- (16) Bard, A. J.; Faulkner, L. R. *ELECTROCHEMICAL METHODS: Fundamentals and Applications*; 2nd Edition; John Wiley & Sons, Inc.: USA, **2001**.
- (17) Würfel, P. *Physics of Solar Cells: From Principles to New Concepts* Weinheim, **2005**.
- (18) Petzold, L. *Siam J. Sci. Stat. Computing* **1983**, *4*, 136.
- (19) Andrade, L.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Ribeiro, H. A.; Mendes A.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 1117.

- (20) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (21) Froment, G. F.; Bischoff, K. B. *Chemical Reactor Analysis and Design*; Second Edition ed.; John Wiley and Sons, **1990**.
- (22) Hauch, A.; Georg, A. *Electrochim. Acta* **2001**, *46*, 3457.
- (23) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808.
- (24) Bisquert, J.; Fabregat-Santiago, F.; Mora-Seró, I.; Garcia-Belmonte, G.; Giménez, S. *J. Phys. Chem. C* **2009**, *113*, 17278.
- (25) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, **2005**.

PART III:

PHOTOELECTROCHEMICAL CELLS FOR WATER SPLITTING

Chapter 7

TRANSIENT PHENOMENOLOGICAL MODELLING OF PHOTOELECTROCHEMICAL CELLS FOR WATER SPLITTING - APPLIED TO UNDOPED HEMATITE ELECTRODES

Luísa Andrade, Tânia Lopes, Helena Aguilar Ribeiro and Adélio Mendes

(International Journal of Hydrogen Energy 2010, submitted)

Abstract

A phenomenological model is proposed for a better understanding of the basic mechanisms of photoelectrochemical (PEC) cells for water splitting. The main assumptions of the one-dimensional transient phenomenological model are: i) bulk recombination of the conduction band electrons with holes in the valence band; ii) mobile charge transport takes place via diffusion, which arises from the concentration profiles, and migration, caused by a macroscopic electric field; iii) negligible effects of microscopic electric fields in the cell and screening effects, as well as negligible Helmholtz and diffuse layers. For modelling purposes, the photoanode was assumed to be a homogeneous nanocrystalline hematite structure, with thickness L , porosity ϵ_p and tortuosity τ . The TCO/semiconductor interface was modelled as an ideal ohmic contact, while the electrolyte/platinised TCO interface was described by a Butler-Volmer approach. An alkaline electrolyte solution was used, allowing the transport of the ionic species from the counter electrode to the photoanode. The continuity and transport governing equations are defined for the mobile species involved: electrons in the conduction band of the semiconductor, holes in the valence band and hydroxyl ions in the electrolyte. Simulated I - V characteristic were computed and the corresponding results compared with the experimental values. The simulated results were in straight agreement with the experimental data.

Keywords: Photoelectrochemistry, modelling, water splitting, hydrogen.

7.1 Introduction

It is known that world demand for energy is forecasted to duplicate by 2050 and it is also widely recognised that the existing energy networks are not adequate to supply this demand in a sustainable way.¹ The increasing public awareness concerning the carbon dioxide emissions and the enhanced depletion of fossil fuels motivate the development of alternative technologies based on non-polluting and clean energy sources.²⁻³ So far, the sun is our primary source of clean and abundant energy, striking 120 PW of radiation onto the surface of earth at any given moment and is the most powerful resource able to cope with the world's energy needs.¹ However, the present technologies that take advantage of solar energy have a limited ability to store energy due to the variability of daily solar radiation and so an effective method to store energy for later dispatch is therefore needed.⁴ A practical way to overcome this problem is using sunlight to split water into hydrogen and oxygen - photoelectrolysis³ - by means of a photoelectrochemical (PEC) cell. The water split phenomenon was first reported by Fujishima and Honda in 1972, but it was only recently that this technology received special attention from researchers as a potential renewable energy source.^{3,5-7}

A photoelectrochemical cell is made of a semiconductor, such as iron oxide (Fe_2O_3) - hematite - and a counter electrode (cathode), both immersed in an aqueous electrolyte solution. When exposed to sunlight, the semiconductor absorbs photons with sufficient energy to inject electrons from the valence band to its conduction band, creating electron-hole pairs. The holes exhibit oxidation potential while the electrons are transferred over the external circuit to the cathode to promote water reduction into hydrogen gas. The energy conversion efficiency of such process is therefore highly determined by the structure and properties of the semiconductor and the electronic junction formed at the semiconductor/electrolyte interface.⁸⁻⁹ Presently, these devices achieve very low conversion efficiencies since most of the semiconductors used for this application have a large energy bandgap. Furthermore, the band edge potentials of many semiconductors are not suitable for oxygen and hydrogen evolution and the water split reaction cannot take place. This is the case of

hematite, whose conduction band edge is positioned at a more positive potential than the reduction potential of water. As a result, an additional bias voltage is required to promote the reduction reaction at the cathode side.³

In the last decade, several studies focusing on promising photoelectrodes were carried out. Doped and undoped semiconductor materials were synthesised and characterised regarding their photoelectrochemical, structural, electrical and optical properties.^{7,10-12} Recent studies report hematite as a promising material with several advantages: it has a suitable bandgap energy around 2.0 eV, is able to use 40 % of the incident solar spectrum, it is chemical and thermally stable in aqueous solutions and also towards photocorrosion, its valence band is appropriate for oxygen evolution and it is abundant and a low-cost material.^{3,7,13} Despite several efforts have been made to develop new more adequate materials for water splitting in photoelectrochemical cells, very few research works focused in the insightful understanding of the working mechanisms of PEC cells. An important work was developed by Gerischer¹⁴⁻¹⁵ on the kinetics and energetics of electron transfer across semiconductor/electrolyte junctions and on the nature of the space-charge layer - the semiconductor layer adjacent to the semiconductor/electrolyte interface. Nozik¹⁶ evaluated the energy level scheme for p-n photoelectrolysis cells in order to demonstrate an enhanced efficiency by simultaneously illuminating the n- and p-type electrodes. Khan and Bockris¹⁷ derived an analytical expression for the resulting photocurrent as a function of the physical properties of an illuminated p-type semiconductor electrode and the neighbouring electrolyte solution. Boudjemaa and co-authors¹¹ studied the transport properties of hematite and its application for hydrogen production. Nevertheless, a global and integrated transient phenomenological model for a better understanding of the phenomena occurring in a PEC cell and how they contribute for its performance has never been presented. Simple models were already developed for other water splitting systems, pointing out some relevant aspects. Choi *et al.*¹⁸ studied a water electrolysis system with a solid polymer electrolyte by means of a simple model based on the Butler-Volmer kinetics. Also based on the Butler-Volmer approach, Nie *et al.*¹⁹ modelled a proton exchange membrane water electrolyser and Marangio *et al.*²⁰

studied a high pressure polymer electrolyte membrane water electrolyser. Ni²¹⁻²³ developed an interesting work based on the mathematical modelling of solid oxide steam electrolyzers for hydrogen production.

In the present work, an integrated transient phenomenological model for PEC cells is presented. This model aims at contributing to a better understanding of the phenomena occurring in a PEC cell and how they contribute for its performance. The simulated *I-V* characteristic curves of the PEC cell allowed the calculation of the cells' performance parameters.

7.2 Development of the PEC cell model

Photoelectrolysis of water is the dissociation of water molecules into hydrogen and oxygen by the direct use of light: the conversion of light into electrical current allows the transformation of a chemical entity - water - into another - hydrogen - known to be a preferential energy vector.²⁴ The principle of operation of a photoelectrochemical cell for water splitting is governed by the kinetics of the charge carriers and reaction mechanisms that take place at the electrodes of the PEC cell. Therefore, the understanding of the electronic processes occurring at the semiconductor nanoparticles level, as well as the dynamics of charge separation/transport and reactive mechanisms in the different interfaces is of great importance. Photons with energy $h\nu$ higher than the semiconductor's bandgap generate electron-hole pairs $(e_{CB}^- + h_{VB}^+)$ in the conduction and valence band, respectively:



In an alkaline media, holes oxidise water to oxygen in the semiconductor surface (photoanode),



while the photoexcited conduction band electrons, transported to the counter electrode (cathode) of the PEC cell, reduce water to form hydrogen gas:



The mechanisms behind oxidation of water by photogenerated holes are not completely understood and depend most probably on the interfacial properties of the semiconductor. On the other hand, the reduction of water into hydrogen is a kinetically simple process compared to the water oxidation reaction.²⁵ In fact, the efficiency of the oxidation process occurring at the semiconductor can be limited by several competing electron loss pathways: bulk recombination via bandgap states or direct electron loss to holes in the valence band; surface recombination; electron loss from the conduction band; photocorrosion of the semiconductor; and dissolution reactions. The last two processes are responsible for the degradation of the electrode and for the consequent stability problems.²⁶

Figure 7.1 shows a scheme of the modelled PEC cell. The photoanode consists of a homogeneous nanocrystalline hematite structure, with thickness L , porosity ε_p and tortuosity τ . The photoanode is deposited onto a transparent conductive substrate (TCO), defining the interface TCO/semiconductor at $x = 0$. This interface is modelled as an ideal ohmic contact. Since the semiconductor considered herein is a hematite film, an alkaline electrolyte solution should be used, such as sodium hydroxide, allowing the transport of the ionic species from the counter electrode, a platinum wire, to the photoanode.²⁷ At $x = b$, the electron transfer phenomenon occurring at the electrolyte/platinised TCO interface is described by the Butler-Volmer equation. The semiconductor/electrolyte interface is defined at $x = L$. The mobile charges considered in the development of the present model are the electrons in the conduction band of the semiconductor, e^- , the holes in the valence band, h^+ , and the hydroxyl ions in the electrolyte.

For simplicity, the model considers a cell design where the photoelectrode faces its counter electrode and the space in between is filled with the electrolyte solution. However, typical current-voltage characterisation of the PEC cells are performed in a cell configuration known as “cappuccino”,²⁸ in which the surface of the platinum counter electrode is far away from the semiconductor/electrolyte interface. Thus, in the present model $b \gg L$. Furthermore, the PEC cell is irradiated perpendicularly to its

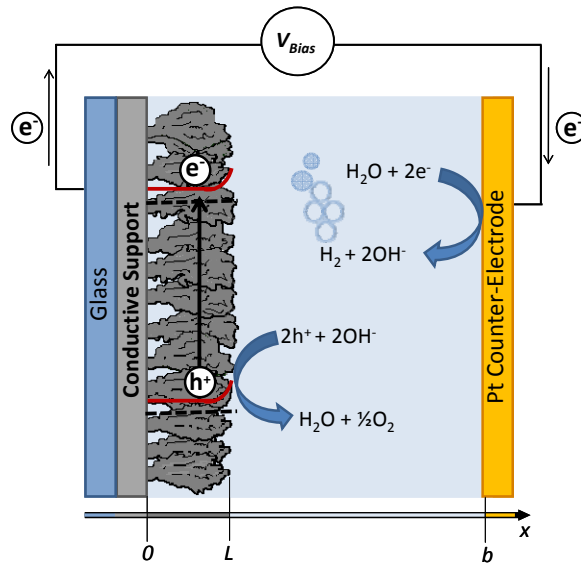


Figure 7.1 - Schematic representation of the modelled PEC cell for photo-assisted water splitting. The TCO/semiconductor interface at $x = 0$ and the electrolyte/platinised TCO at $x = b$ define the limits of the photoanode and the cathode, respectively. The electrolyte solution fills the pores in the photoanode with thickness L and the free volume between $x = L$ and $x = b$. The dimensions of L and b are not in scale since $b \gg L$.

photoelectrode and it is assumed that each absorbed photon injects one electron into the hematite conduction band.

Concerning the electron loss pathways, only the bulk recombination of conduction band electrons with holes in the valence band is taken into account. The space-charge recombination as well as the remaining recombination mechanisms mentioned above are therefore neglected.¹⁷

The mobile charge transport can take place via diffusion, which arises from the concentration profiles, and migration, caused by a macroscopic electric field E . Effects of microscopic electric fields in the cell and screening effects, as well as Helmholtz and diffuse layers are neglected. Thus, charge transport can be described with sufficient accuracy using diffusion constants D_i and mobilities μ_i , connected by the Einstein relation:²⁹

$$D_i = \frac{k_B T}{q} \mu_i, \quad i = e^-, h^+ \text{ and } OH^- \quad (7.4)$$

Taking into account the previous assumptions, the proposed phenomenological model for PEC cells comprises the continuity and transport equations for the mobile species in unsteady-state and isothermal conditions. The continuity equation for the carrier density n_i is:

$$-\frac{\partial j_i}{\partial x} + G_i(x) - R_i(x) = \frac{\partial n_i}{\partial t}, \quad i = e^-, h^+ \text{ and } OH^- \quad (7.5)$$

The first term on the left-hand side of the equation represents the charge carrier flux defined by the respective transport equation. The second and third terms are the generation and relaxation rates of species i , respectively. Both reaction kinetics are characterised by a time constant. The term on the right-hand side of the equation corresponds to carrier i concentration history. The respective continuity equations, initial and boundary conditions for the three mobile charges are presented hereafter.

7.2.1 Electrons

As described above two contributions for the electron flux, j_{e^-} , are considered: a diffusive transport of electrons within the hematite film towards the transparent conductive substrate and a migration transport driven by a macroscopic electric field across the semiconductor layer. Equation (7.6) relates the electron flux at any position x to the gradient of electrons concentration across the semiconductor layer, n_{e^-} , by means of the electron diffusion coefficient, D_{e^-} , the electron mobility, μ_{e^-} , and the macroscopic electric field, E :

$$j_{e^-} = -D_{e^-} \frac{\partial n_{e^-}}{\partial x} - \mu_{e^-} n_{e^-} E \quad (7.6)$$

The generation term for electrons in Equation (7.5) is described by the following absorption equation:²⁹

$$G_{e^-} = \eta_{inj} \alpha(\lambda) I_s e^{-\alpha(\lambda)x} \quad (7.7)$$

It is assumed that each photon, with energy $h\nu \geq E_g$, absorbed by the semiconductor results in the injection of one electron into its conduction band. $\alpha(\lambda)$ is the wavelength-dependent absorption coefficient, which is a property of the material; I_s is the incident photon flux, corrected for reflection losses of the TCO glass; and η_{inj} is the electron injection efficiency.

The electron recombination term is here represented by a generic equation based on an excess electron density regarding its equilibrium value, $\Delta n_{e^-} = n_{e^-}(x, t) - n_{eq}$, and a first-order kinetics, $k_{e^-} = 1/\tau_n$:

$$R_{e^-} = k_{e^-} \Delta n_{e^-} \quad (7.8)$$

where τ_n is the lifetime of carriers before recombine and n_{eq} is the dark equilibrium electron density, corresponding to the match between the electron's Fermi level in the semiconductor and the redox potential of the electrolyte:

$$n_{eq} = N_{CB} \exp\left[-\frac{q(E_{CB} - E_{redox})}{k_B T}\right] \quad (7.9)$$

N_{CB} is the effective density of states of the respective conduction band and can be calculated by the following equation:²⁹

$$N_{CB} = 2 \left(\frac{2\pi m_{e^-}^* k_B T}{h^2} \right) \quad (7.10)$$

The continuity equation, initial and boundary conditions for electrons can now be written taking all these considerations into account:

$$D_{e^-} \frac{\partial^2 n_{e^-}}{\partial x^2} + \mu_{e^-} E \frac{\partial n_{e^-}}{\partial x} + \mu_{e^-} n_{e^-} \frac{dE}{dx} + \eta_{inj} I_0 \alpha e^{-\alpha x} - \frac{(n_{e^-} - n_{eq})}{\tau_n} = \frac{\partial n_{e^-}}{\partial t} \quad (7.11)$$

Initial Conditions

For $t=0$ the cell is considered to be under dark equilibrium conditions:

$$t=0 \quad n_{e^-}(x, 0) = n_{eq} \quad (7.12)$$

Boundary conditions

Considering the TCO/semiconductor interface at $x = 0$ as an ohmic contact with negligible energy band bending, a simple charge balance at this interface can be written in terms of the current densities at $x = 0^-$ and $x = 0^+$, i.e. $j_{e^-}^{0^-}$ and $j_{e^-}^{0^+}$, respectively:

$$x = 0 \quad j_{e^-}^{0^-} = j_{e^-}^{0^+} \quad (7.13)$$

The current density flowing across $x = 0^+$ results from the transport of electrons by diffusion and drift across the semiconductor - Equation (7.15) - which, in steady-state conditions, corresponds also to the net current density, J_{cell} , generated by the cell under operation (see Figure 7.2). This term will be analysed and defined in more detail in Section 7.2.5. Thus,

$$j_{e^-}^{0^-} = \frac{J_{cell}}{q} \quad (7.14)$$

$$j_{e^-}^{0^+} = -D_{e^-} \left. \frac{\partial n_{e^-}}{\partial x} \right|_{x=0^+} - \mu_{e^-} n_{e^-} E \Big|_{x=0^+} \quad (7.15)$$

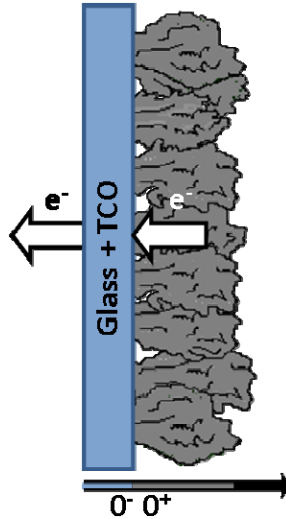


Figure 7.2 - Detail of the TCO/semiconductor interface at $x = 0$; $x = 0^+$ denotes the surface close to the semiconductor and $x = 0^-$ refers to the external surface of the TCO layer.

At $x=L$ there are no electrons flowing from the semiconductor into the electrolyte and across it, so the respective continuity equation for electrons is only integrated between $x=0$ and $x=L$. Between the limits $x=L$ and $x=b$ only the electrolyte redox species are present.

$$x=L \quad \frac{\partial n_{e^-}(L,t)}{\partial x} = 0 \quad (7.16)$$

7.2.2 Holes

When the semiconductor absorbs solar radiation with enough energy to excite an electron from the valence band to the conduction band, an electron-hole pair is generated. Thus, they are generated at the same rate:

$$G_{h^+} = G_{e^-} \quad (7.17)$$

On the other hand, if a radiative recombination phenomenon is considered, a hole in the valence band reacts with an electron from the conduction band and the correspondent energy is dissipated. The recombination of a hole with a conduction band electron occurs at the same rate of the spontaneous transition of an electron from the conduction band to an unoccupied state in the valence band:

$$R_{h^+} = R_{e^-} \quad (7.18)$$

The respective continuity equation for holes is similar to the one defined for electrons:

$$D_{h^+} \frac{\partial^2 n_{h^+}}{\partial x^2} + \mu_{h^+} E \frac{\partial n_{h^+}}{\partial x} + \mu_{h^+} n_{h^+} \frac{dE}{dx} + \eta_{inj} I_0 \alpha e^{-\alpha x} - \frac{\Delta n_{e^-}}{\tau_n} = \frac{\partial n_{h^+}}{\partial t} \quad (7.19)$$

Initial Conditions

The initial concentration of holes equals the dark equilibrium electrons density since electrons and holes are generated at the same rate:

$$t=0 \quad n_{h^+}(x,0) = n_{e^-}(x,0) \quad (7.20)$$

Boundary conditions

There are no holes flowing from the semiconductor to the TCO substrate neither from the semiconductor to the electrolyte:

$$x=0 \quad \frac{\partial n_{h^+}(0,t)}{\partial x} = 0 \quad (7.21)$$

$$x=L \quad \frac{\partial n_{h^+}(L,t)}{\partial x} = 0 \quad (7.22)$$

7.2.3 Hydroxyl ions

Hydroxyl ions are formed in the counter electrode by reduction of water to hydrogen gas. Then OH^- ions diffuse to the semiconductor surface where they react with holes to produce oxygen gas. However, the transport of hydroxyl ions occurs in two different regions of the PEC cell: in the pores of the mesoscopic semiconductor film (with porosity ε_p and tortuosity τ , between $x = 0$ and $x = L$) and within the free volume between $x = L$ and the counter electrode at $x = b$. Generation and recombination of hydroxyl ions occur only in the pores of the semiconductor and not in the bulk electrolyte layer (with thickness $b-L$) where only ionic transport is considered. Thus, two distinct equations should be written for this redox species.

Hydroxyl ions transport in the pores of the semiconductor: $0 \leq x \leq L$

Attempting to the stoichiometry of Equations (7.2) and (7.3), the generation of two hydroxyl ions is always linked with the consumption of two electrons, while the consumption rate of hydroxyl ions equals the generation rate of holes. The charge transport is again by diffusion and drift:

$$D_{\text{OH}^-}^L \frac{\partial^2 n_{\text{OH}^-}^L}{\partial x^2} + \mu_{\text{OH}^-}^L E \frac{\partial n_{\text{OH}^-}^L}{\partial x} + \mu_{\text{OH}^-}^L n_{\text{OH}^-}^L \frac{dE}{dx} - \frac{1}{\varepsilon_p} \left(\eta_{\text{inj}} I_0 \alpha e^{-\alpha x} - \frac{\Delta n_{e^-}}{\tau_{e^-}} - \frac{\partial n_{e^-}}{\partial t} \right) = \frac{\partial n_{\text{OH}^-}^L}{\partial t} \quad (7.23)$$

where

$$D_{OH^-}^L = \frac{\epsilon_p}{\tau} D_{OH^-}^b \text{ and } \mu_{OH^-}^L = \frac{\epsilon_p}{\tau} \mu_{OH^-}^b \quad (7.24)$$

are the effective diffusion and mobility constants defined for the hydroxyl ions. The superscript L is included to clearly show that the region under consideration is between $x = 0$ and $x = L$. The sixth term in Equation (7.23), $\partial n_{e^-} / \partial t$, is included since in unsteady-state the accumulated electrons do not participate in the redox reaction and therefore must be discounted from the generation term:

$$\underbrace{\eta_{inj} \alpha(\lambda) I_0 e^{-\alpha(\lambda)x}}_{\text{generation term}} - \underbrace{\frac{\partial n_{e^-}}{\partial t}}_{\text{electron accumulation}}$$

Hydroxyl ions transport in the bulk electrolyte layer: $L < x \leq b$

Only electrolyte exists in this region and so no ions are generated or lost by recombination with holes. So, the continuity equation is as follows:

$$D_{OH^-}^b \frac{\partial^2 n_{OH^-}^b}{\partial x^2} + \mu_{OH^-}^b E \frac{\partial n_{OH^-}^b}{\partial x} + \mu_{OH^-}^b n_{OH^-}^b \frac{dE}{dx} = \frac{\partial n_{OH^-}^b}{\partial t} \quad (7.25)$$

where the superscript b denotes the region between $x = L$ and $x = b$.

Initial and boundary conditions may now be defined for hydroxyl ions in the total spatial range $0 < x \leq b$.

Initial Conditions

At instant $t = 0$, initial concentration of the electrolyte species is assumed:

$$t = 0 \quad n_{OH^-}^L(x, 0) = n_{OH^-}^b(x, 0) = n_{OH^-}^{init} \quad (7.26)$$

Boundary conditions

At the TCO/semiconductor interface only the photoinjected electrons are able to flow. Thus, the net flux of OH^- is zero:

$$x = 0 \quad \frac{\partial n_{OH^-}^L(0, t)}{\partial x} = 0 \quad (7.27)$$

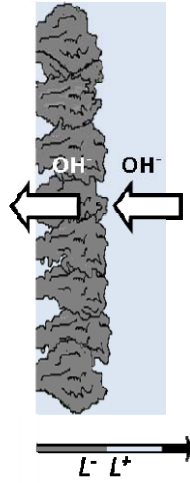


Figure 7.3 - Detail of the semiconductor/electrolyte interface at $x = L$. Here, $x = L^-$ and $x = L^+$ denote the limit of the interface semiconductor/electrolyte at the semiconductor and electrolyte sides, respectively.

For $x = L$, corresponding to the transition between the porous material and the bulk liquid, additional considerations have to be taken into account. At this interface the concentrations of OH^- ions in the liquid electrolyte filling the pores of the semiconductor and in the bulk liquid are identical:

$$n_{\text{OH}^-}^{L^-} = n_{\text{OH}^-}^{L^+} \quad (7.28)$$

Moreover, by evaluating the charge balance at the interface semiconductor/electrolyte - see Figure 7.3 - the hydroxyl ions flux at $x = L^-$ (within the porous semiconductor structure) equals the hydroxyl ions flux at $x = L^+$ (bulk electrolyte):

$$x = L \quad j_{\text{OH}^-}^{L^-} = j_{\text{OH}^-}^{L^+} \quad (7.29)$$

where:

$$j_{\text{OH}^-}^{L^-} = -D_{\text{OH}^-}^L \left. \frac{\partial n_{\text{OH}^-}^L}{\partial x} \right|_{x=L^-} - \mu_{\text{OH}^-}^L n_{\text{OH}^-}^L E \Big|_{x=L^-} \quad (7.30)$$

$$j_{OH^-}^{L^+} = -D_{OH^-}^b \frac{\partial n_{OH^-}^b}{\partial x} \bigg|_{x=L^+} - \mu_{OH^-}^b n_{OH^-}^b E \bigg|_{x=L^+} \quad (7.31)$$

The total amount of redox species contained in the semiconductor nanopores and in the free electrolyte volume remains constant during the PEC cell operation. This may be described as:

$$x = b \quad \int_0^L n_{OH^-}^L(x) dx + \int_L^b n_{OH^-}^b(x) dx = n_{OH^-}^{init} L + n_{OH^-}^{init} (b - L) \quad (7.32)$$

7.2.4 Macroscopic electric field: Poisson equation

In undoped semiconductors the number of charge carriers is determined by the properties of the material itself instead of the amount of impurities. Thus, the number of excited electrons and the number of holes are equal. For this type of semiconductors the macroscopic electric field E is also related to the charge carrier densities by the Poisson's equation:²⁴

$$\frac{d^2 E}{dx^2} = \frac{qn_{int}}{\epsilon\epsilon_0} \exp\left[\frac{qE(x)}{k_B T}\right] \quad (7.33)$$

where n_{int} is the intrinsic carrier concentration given by

$$n_{int} = (N_{CB} N_{VB})^{1/2} \exp\left(-\frac{E_g}{2k_B T}\right) \quad (7.34)$$

and ϵ and ϵ_0 are the static relative permittivity or dielectric constant of the material and the permittivity of free space, respectively. The dielectric constant describes the effective dielectric behaviour of the quasi-homogeneous medium. N_{CB} and N_{VB} are the effective density of states in the conduction band and in the valence band, respectively.

The model assumes that there are no unbalanced electric charges for $x \leq 0$ and $x \geq b$. Thus, the electric field vanishes exactly at these boundaries:³⁰

$$E(x=0) = E(x=b) = 0 \quad (7.35)$$

7.2.5 Electrolyte - Platinum contact: Butler-Volmer equation

The non-linear differential Equations (7.11), (7.19), (7.23) and (7.25) for the three charged species are integrated with the respective initial and boundary conditions. All these conditions were described and defined mathematically, but the boundary condition for electrons at $x = 0$ requires a deeper analysis. In fact, it was mentioned above that the current density flowing across $x = 0^+$ results from the transport of electrons by diffusion and drift through the semiconductor - Equation (7.15) - which, in steady-state conditions, corresponds to the net current density, J_{cell} , generated by the cell under operation. This variable J_{cell} corresponds to the current density that is returned to the cell via the counter electrode and is a consequence of the external potential difference applied to the cell. At the counter electrode, electrons take part in the water reduction reaction catalysed by the platinum wire. Consequently, the electrolyte/platinum interface can be treated as an electrochemical half-cell and a Butler-Volmer kinetics is therefore considered:³¹

$$J_{cell} = J_0 \left[\frac{n_{H_2O}(b)}{n_{H_2O}^{ref}(b)} \exp\left(\frac{\beta n q \eta_{Pt}}{k_B T}\right) - \frac{n_{H_2}(b) n_{OH^-}^2(b)}{n_{H_2}^{ref}(b) (n_{OH^-}^{ref}(b))^2} \exp\left(\frac{-(1-\beta) n q \eta_{Pt}}{k_B T}\right) \right] \quad (7.36)$$

The Butler-Volmer equation defines an exponential relation between the electric current crossing the electrolyte/platinum interface and the activation overpotential, η_{Pt} , in the platinum cathode, where water is reduced to hydrogen gas with the consumption of two electrons ($n = 2$ in Equation (7.36)). The overpotential may be regarded as the extra voltage needed to reduce the energy barrier of the rate determining step to a value such that the electrode reaction proceeds at a desired rate. The concentrations of the species involved in such reaction have to be normalised by a reference concentration: $n_{H_2O}^{ref}$, $n_{H_2}^{ref}$, $n_{OH^-}^{ref}$. For dilute solutions in pure water at a given pressure, water concentration is virtually constant. So, if pure water at approximately atmospheric pressure is taken as the standard state for H_2O , n_{H_2O} and $n_{H_2O}^{ref}$ concentrations in Equation (7.36) are equal. Additionally, the reference concentration for hydroxyl ions is its initial concentration, while the reference

hydrogen concentration is taken as the maximum solubility of hydrogen in water at 1 bar and 25 °C: $8.465 \times 10^{-5} \text{ mol dm}^{-3}$.³²

In what concerns the definition of the total overpotentials in the PEC cell, a thoughtful analysis needs to be made. The operation of a photoelectrochemical cell is analogous to that of a Schottky barrier and therefore the input energy of an absorbed photon is equal to the semiconductor bandgap E_g . Energy losses in the semiconductor result from the movement of electrons and holes from their point of generation to the respective electrolyte/electrode interface, and from the difference between the energy conduction band edge in the bulk and the Fermi level, $\Delta E_F = E_F(x=0) - E_{CB}$. The former phenomenon is responsible for the energy band bending E_B observed at the electrolyte/electrode interface. In the electrolyte, only a fraction of this energy is used to originate free energy per electron for the overall cell reaction ($\Delta G / nF = 1.23$ eV for water decomposition). The remaining energy is lost through overpotentials at the anode and the cathode, η_a and η_{pt} , respectively, and through ohmic losses, η_{ohmic} . The following energy balance can be written:⁹

$$E_{Bias} + E_g - E_B - \Delta E_F = q \left(\frac{\Delta G}{nF} + \eta_a + \eta_{pt} + \eta_{ohmic} \right) \quad (7.37)$$

The term E_{Bias} in the left-hand side of Equation (7.37) is added when an external bias applied to the PEC cell is required.

When a semiconductor is brought into contact with an electrolyte, equilibrium of the electrochemical potentials of the two phases is established by electron transfer across the interface.¹⁴ This produces a positive space charge layer in the semiconductor side, also called depletion layer since the region is depleted of majority charge carriers (electrons). Additionally, a charged layer is also formed in the electrolyte side, adjacent to the interface with the solid electrode – known as Helmholtz layer. However, this is not considered in the present model. Finally, the extent of band bending is given by:⁹

$$E_B = E_F(x=0) - E_{fb} \quad (7.38)$$

where E_F is the Fermi level energy of the semiconductor and E_{fb} is the semiconductor flat band energy, which reflects the energy state at which the semiconductor bands are flat (zero space charge in the semiconductor).

The anodic overpotential is considered as the difference between the valence band edge energy and the oxidation energy of water:³³

$$\eta_a = \frac{1}{q} (E_{VB} - E_{O_2/OH^-}) \quad (7.39)$$

where the oxidation energy of water is directly related to the water reduction energy by the standard free enthalpy for water splitting (1.23 eV):

$$E_{O_2/OH^-} = 1.23 \cdot q - E_{H_2O/H_2} \quad (7.40)$$

In its turn, the electrochemical energy of water reduction to hydrogen at the platinum electrode is given by the Nernst equation:

$$E_{H_2O/H_2} = E_{H_2O/H_2}^\circ - \frac{k_B T}{2} \ln \frac{n_{H_2}(b) n_{OH^-}^2(b)}{n_{St}^3} \quad (7.41)$$

The standard concentration n_{St} is here defined as a reference concentration of 1 mol dm⁻³. Finally, the ohmic losses through the electrode area A may be written in terms of an ohmic resistance, R_{ohmic} :

$$\eta_{ohmic} = J_{cell} A R_{ohmic} \quad (7.42)$$

At this moment all the terms of Equation (7.37) can be evaluated and thus it can be solved in order to the cathode overpotential, η_{Pt} . Then, the resulting equation can be substituted in the Butler-Volmer equation in order to find the net current density J_{cell} at a defined applied external bias E_{Bias} .

The parameter E_{Bias} is of great importance since it determines the possibility of hydrogen evolution takes place or not. In fact, for efficient water cleavage, the conduction band of the n-type semiconductor needs to be positioned at a more negative potential than the reduction potential of water, *i.e.* $E_{CB} > E_{H_2O/H_2}^\circ$, while the valence band needs to be positioned at a more positive potential than the oxidation reaction, *i.e.* $E_{VB} < E_{O_2/OH^-}^\circ$. However, for a hematite porous film, the conduction band

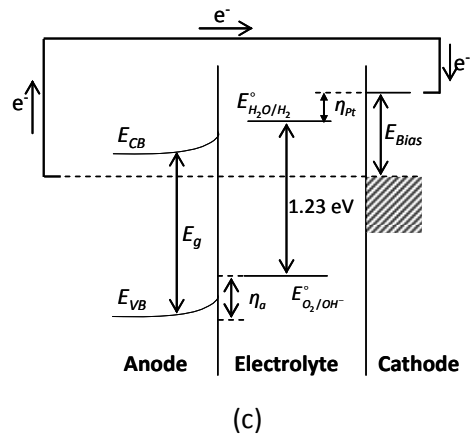
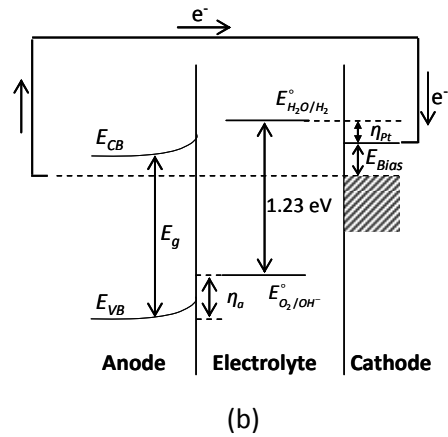
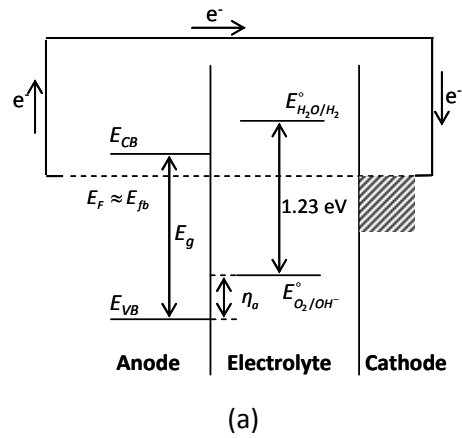


Figure 7.4 - Energy diagram of PEC components with (a) no applied bias E_{Bias} ; (b) applied bias E_{Bias} but not enough for hydrogen evolution and (c) applied bias E_{Bias} enough to produce hydrogen.

potential does not fulfil the required potential position and so an additional bias is needed. Varying the value of the applied bias, three different situations should be considered: i) $E_{Bias} = 0$, meaning that no bias is applied; ii) the applied bias is higher than zero but not sufficiently high to produce hydrogen evolution and iii) the applied bias is high enough to produce hydrogen. The energy diagrams for these three situations are sketched in Figure 7.4 and for each case the energy balance is showed.

At high intensity illumination the semiconductor potential is driven towards its flat band potential and in the case of zero bias - Figure 7.4(a) - the band bending is negligible - $E_B \approx 0$ since $E_{fb} \approx E_F$. When no bias is applied, Equation (7.37) reduces to:

$$\eta_{Pt} = \frac{1}{q} \left[E_g - (E_{fb} - E_{CB}) \right] - \frac{\Delta G}{nF} - \eta_a - \eta_{ohmic} \quad (7.43)$$

Since there is no bias, the system is not able to produce hydrogen gas and so the water reduction potential equals the standard potential of -0.828 V in alkaline environment and at 25 °C:

$$\eta_a = \frac{1}{q} E_{VB} - \left(1.23 - \frac{1}{q} E_{H_2O/H_2}^\circ \right) \quad (7.44)$$

Equation (7.44) can also be used for the case when an anodic bias is applied but it is not sufficient to produce hydrogen - Figure 7.4(b). In this case the band bending cannot be neglected:

$$\eta_{Pt} = \frac{1}{q} \left[E_{Bias} + E_g - (E_F - E_{fb}) - (E_F - E_{CB}) \right] - \frac{\Delta G}{nF} - \left[\frac{1}{q} E_{VB} - \left(1.23 - \frac{1}{q} E_{H_2O/H_2}^\circ \right) \right] - \eta_{ohmic} \quad (7.45)$$

For the generic case represented in Figure 7.4(c), the overpotential of cathode is given by:

$$\eta_{Pt} = \frac{1}{q} \left[E_{Bias} + E_g - (E_F - E_{fb}) - (E_F - E_{CB}) \right] - \frac{\Delta G}{nF} - \left[\frac{1}{q} E_{VB} - \left(1.23 - \frac{1}{q} E_{H_2O/H_2}^\circ + \frac{k_B T}{2q} \ln(n_{H_2} n_{OH^-}^2) \right) \right] - (J_{cell} AR_{ohmic}) \quad (7.46)$$

For the cases illustrated in Figure 7.4(a) and Figure 7.4(b), since there is no hydrogen gas evolution, the second term of the Butler-Volmer equation - Equation

(7.36) - is zero, becoming $J_{cell} = J_0 \exp\left(\frac{2\beta q}{k_B T} \eta_{Pt}\right)$. The Butler-Volmer equation assumes

its original form given in Equation (7.36) only for the case represented in Figure 7.4(c).

7.2.6 Dimensionless equations

The model variables were made dimensionless with respect to electron parameters and to the thickness of the semiconductor L . Changing for dimensionless variables and introducing suitable dimensionless parameters, the continuity equations for the three charge carrier species and the respective initial and boundary conditions become:

$$D_{e^-}^* \frac{\partial^2 n_{e^-}^*}{\partial x^{*2}} + \mu_{e^-}^* \zeta \left(E^* \frac{\partial n_{e^-}^*}{\partial x^*} + n_{e^-}^* \frac{dE^*}{dx^*} \right) + Da \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) = \frac{\partial n_{e^-}^*}{\partial \vartheta} \quad (7.47)$$

$$\vartheta = 0 \quad n_{e^-}^*(x^*, 0) = n_{eq}^* \quad (7.48)$$

$$x^* = 0 \quad J_{cell}^* = \frac{n_{ref} D_{ref} q}{J_0 L} \left(-D_{e^-}^* \frac{\partial n_{e^-}^*}{\partial x^*} \right) \Big|_{x^*=0^+} - \frac{\mu_{ref} n_{ref} E_{ref} q}{J_0} \left(\mu_{e^-}^* n_{e^-}^* E^* \right) \Big|_{x^*=0^+} \quad (7.49)$$

$$x^* = 1 \quad \frac{\partial n_{e^-}^*}{\partial x^*} = 0 \quad (7.50)$$

$$D_{h^+}^* \frac{\partial^2 n_{h^+}^*}{\partial x^{*2}} + \mu_{h^+}^* \zeta \left(E^* \frac{\partial n_{h^+}^*}{\partial x^*} + n_{h^+}^* \frac{dE^*}{dx^*} \right) + Da \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) - \frac{\partial n_{e^-}^*}{\partial \vartheta} = \frac{\partial n_{h^+}^*}{\partial \vartheta} \quad (7.51)$$

$$\vartheta = 0 \quad n_{h^+}^*(x^*, 0) = n_{eq}^* \quad (7.52)$$

$$x^* = 0 \quad \frac{\partial n_{h^+}^*}{\partial x^*} = 0 \quad (7.53)$$

$$x^* = 1 \quad \frac{\partial n_{h^+}^*}{\partial x^*} = 0 \quad (7.54)$$

$$D_{OH^-}^{L*} \frac{\partial^2 n_{OH^-}^{L*}}{\partial x^{*2}} + \mu_{OH^-}^{L*} \zeta \left(E^* \frac{\partial n_{OH^-}^{L*}}{\partial x^*} + n_{OH^-}^{L*} \frac{dE^*}{dx^*} \right) - \frac{1}{\epsilon_p} \left[Da \cdot e^{-\gamma x^*} - \Phi^2 (n_{e^-}^* - n_{eq}^*) - \frac{\partial n_{e^-}^*}{\partial \vartheta} \right] = \frac{\partial n_{OH^-}^{L*}}{\partial \vartheta} \quad (7.55)$$

$$D_{OH^-}^{b*} \frac{\partial^2 n_{OH^-}^{b*}}{\partial x^{*2}} + \mu_{OH^-}^{b*} \zeta \left(E^* \frac{\partial n_{OH^-}^{b*}}{\partial x^*} + n_{OH^-}^{b*} \frac{dE^*}{dx^*} \right) = \frac{\partial n_{OH^-}^{b*}}{\partial \vartheta} \quad (7.56)$$

$$\vartheta = 0 \quad n_{OH^-}^{L*}(x^*, 0) = n_{OH^-}^{b*}(x^*, 0) = n_{OH^-}^{*init} \quad (7.57)$$

$$x^* = 1 \quad j_{OH^-}^{*1-} = j_{OH^-}^{*1+} \text{ and } n_{OH^-}^{*1-} = n_{OH^-}^{*1+} \quad (7.58)$$

$$x^* = b/L \quad \int_0^1 n_{OH^-}^{*L}(x^*) dx^* + \int_1^{b/L} n_{OH^-}^{*b}(x^*) dx^* = n_{OH^-}^{*init} + n_{OH^-}^{*init}(b/L - 1) \quad (7.59)$$

$$\text{where } n_i^* = \frac{n_i}{n_{ref}}, x^* = \frac{x}{L}, D_i^* = \frac{D_i}{D_{ref}}, \mu_i^* = \frac{\mu_i}{\mu_{ref}} \quad (i = e^-, h^+, OH^-), \quad E^* = \frac{E}{E_{ref}}, \quad \vartheta = \frac{t}{\tau_{ref}},$$

$$\tau_{ref} = \frac{L^2}{D_{ref}}, j_{cell}^* = \frac{j_{cell}}{j_0}, \zeta = \frac{\mu_{ref} E_{ref} L}{D_{ref}}, Da = \frac{L^2 \eta_{inj} \alpha l_s}{D_{ref} n_{ref}}, \gamma = \alpha L \text{ and } \Phi = L \sqrt{\frac{k_{e^-}}{D_{ref}}}.$$

7.2.7 Numerical solution strategy

To simulate a PEC cell it is necessary to solve Equations (7.47), (7.51), (7.55) and (7.56) with the respective boundary and initial conditions. In order to apply the boundary condition at $x^* = 0$ for the electrons, for a given value of E_{Bias} , Equations (7.43), (7.45) or (7.46) should be substituted in Equation (7.36) to obtain the current density in the external circuit. The partial differential equations were spatially discretized using the finite differences method. The time integration was accomplished using LSODA,³⁴ a numerical package developed at the Lawrence Livermore National Laboratory. To compute the I - V characteristic curves, the equations were solved for steady-state conditions (whenever the time derivative was smaller than a pre-defined value).

7.3 Results and discussion

7.3.1 I - V characteristic of an undoped hematite electrode based-PEC cell

The proposed model was used to compute the I - V characteristic curves of a mesoporous undoped hematite photoanode studied by Cesar *et al.*³⁵ and compared

with the corresponding experimental results obtained by these authors. The hematite sample was prepared by atmospheric pressure chemical vapour deposition (APCVD) and the deposition time was 1 minute.³⁵ The experimental current density evolution vs. potential (reported to the normal hydrogen electrode, NHE) was measured using a 1 M NaOH electrolyte solution (pH 13.6), at 50 mV s^{-1} , under 1 sun simulated back-illumination (AM 1.5 G, 100 mW cm^{-2}). The experimental data extracted from the work by Cesar *et al.*³⁵ were used for simulation purposes and are compiled in Table 7.1, together with other model parameters obtained in the literature. The experimental and simulated I - V curves were fitted adjusting parameters R_{ohmic} and η_{inj} .

Figure 7.5 compares the experimental data with the corresponding simulated I - V curve. As it can be realised from this figure, the model agrees quite well with the experimental data, especially for voltages lower than 1.6 V. For higher values of voltage the electrocatalytic oxygen evolution starts by the reaction of holes with the OH^- ions in the electrolyte. This phenomenon explains the accentuated current density increase noticed in both characteristic curves for voltages higher than 1.6-1.7 V.

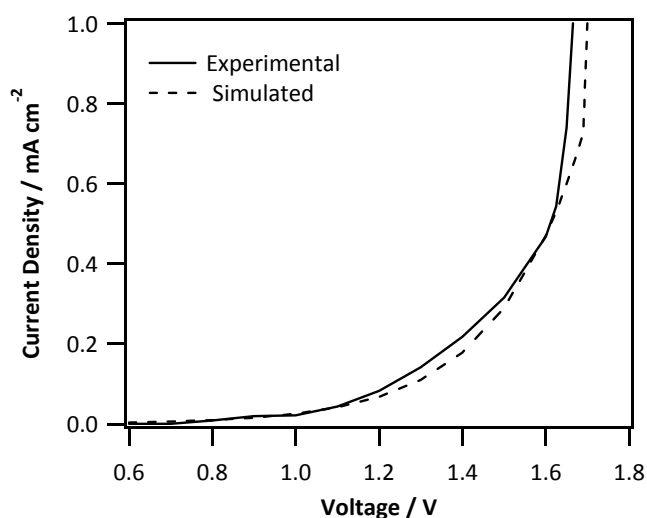


Figure 7.5 - Experimental (solid line) and simulated (dashed line) I - V characteristic for the system described in Table 7.1 ($\eta_{inj} = 0.93$), under 1 sun back-illumination. The experimental curve was taken from Ref. 35, Figure 6, dashed curve labelled “1’bc no si”.

Table 7.1 - Simulator input and fitting parameters.

Parameter	Value	Observed ¹
$C_{OH^-}^{init}$	1 M	35
D_{e^-}	$4.07 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	29
D_{h^+}	$1.25 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$	29
$D_{OH^-}^b$	$5.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	36
A	0.5 cm^2	28
L	63 nm	35
b	~1 cm	35
ϵ_p	0.63	35
τ	1.0	35
N_{CB}	$1.0 \times 10^{19} \text{ cm}^{-3}$	29
τ_n	0.22 ns	35
η_{inj}	0.93	<i>Fit</i>
$\alpha(550 \text{ nm})$	$8.5 \times 10^4 \text{ cm}^{-1}$	35
I_s	$1.50 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$	35
θ	0.50	36
J_0	$1.0 \times 10^{-4} \text{ mA cm}^{-2}$	36
E_{CB} / q	-0.5 V	3
E_{VB} / q	1.7 V	3
E_{fb} / q	-0.43 V	25
$E_{H_2O/H_2}^\circ / q$	-0.828 V	3
$E_{O_2/OH^-}^\circ / q$	0.402 V	3
$\Delta G / nF$	1.23 V	3
R_{ohmic}	50 Ω	<i>Fit</i>
T	298 K	28
pH	13.6	35

¹ The values extracted from the literature are indexed to the corresponding reference and the model values fitted to the experimental I - V curve are identified by “*Fit*”.

Considering a “cappuccino” like PEC cell, described elsewhere,³⁷ the illumination of the photoanode can be made through the front-side (via the electrolyte/hematite interface) or through the back-side (via the substrate/hematite interface). Front- and back-side illumination experiments may be used to distinguish between electron and hole transport limitations, as discussed by Cesar *et al.*³⁵ However, this conclusion can only be taken if the film thickness is larger than the reciprocal value of the absorption coefficient. For undoped samples of hematite, back-side illumination (Figure 7.5) always gives a higher photocurrent than front-side illumination (Figure 7.6). This indicates that the rate-limiting step in undoped Fe_2O_3 samples is the electron transport, in contrast to Si-doped hematite photoanodes where hole transport is found to be rate limiting.³⁸⁻³⁹ The front-side illumination experiment was also simulated in the present work, where Equation (7.7) was replaced by the corresponding one for front-side irradiation:

$$G_{e^-} = \eta_{inj} \alpha(\lambda) I_s e^{-\alpha(\lambda)(L-x)} \quad (7.60)$$

L is the hematite layer thickness. The fitted injection efficiency obtained was 90 %.

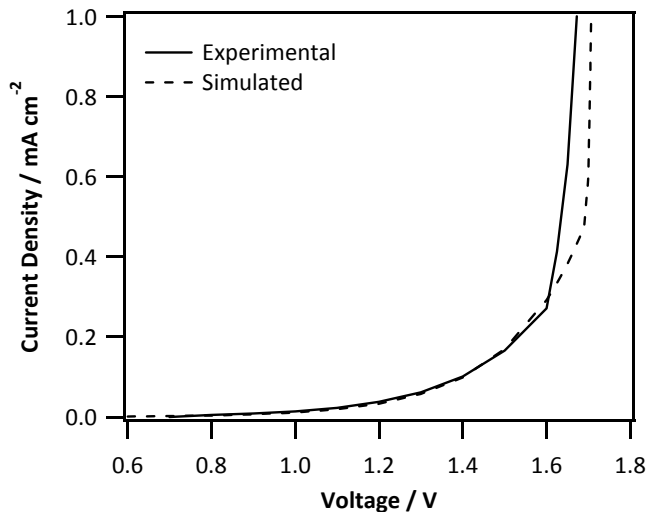


Figure 7.6 - Experimental (solid line) and simulated (dashed line) I - V characteristics for a PEC cell characterised by parameters given in Table 7.1 ($\eta_{inj} = 0.90$), under 1 sun front-side illumination. The experimental curve was taken from Ref. 35, Figure 6, solid curve labelled as “1’ no Si”.

Figure 7.7 shows the simulated steady-state electron density profiles across the 63 nm-thick of the hematite film at 1.23 V and under 1 sun back-side illumination. Since the experiment was performed with back-side illumination (see scheme in Figure 7.1), most electrons were generated near the glass substrate due to the exponential absorption behaviour - Equation (7.7). Thus, the maximum electron density gradient is observed for axial position $x = 0$. Under these conditions, the hematite layers closest to the current collector (TCO) contribute mostly to the electron flux towards the external circuit. This fact is related to high concentration gradients and then diffusion transport, limiting the electron recombination kinetics.

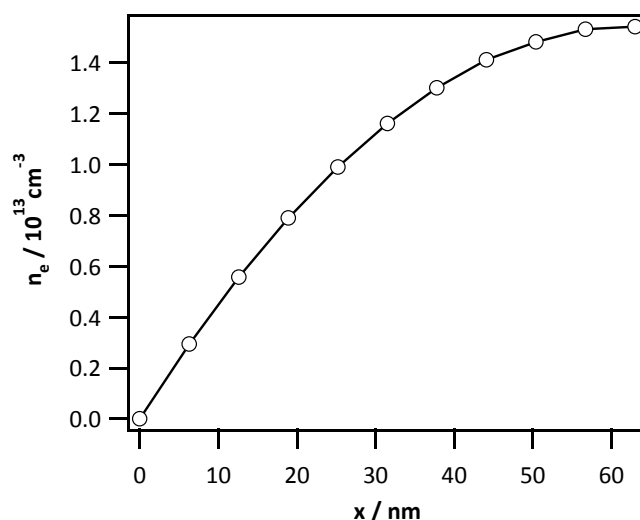


Figure 7.7 - Simulated electron density profiles for the system characterised by parameters given in Table 7.1 under 1 sun back-side illumination at 1.23 V.

Figure 7.8 shows the evolution of the transient electron density profiles of the undoped hematite film at 1.23 V and under 1 sun back-side illumination before reaching the steady-state condition. The electron density profiles during the first micrometres of the hematite film is characterised by a steady increase, becoming a flat profile towards $x = L$. For higher values of ϑ , the electron density profile tends to the steady-state condition (shown in Figure 7.7).

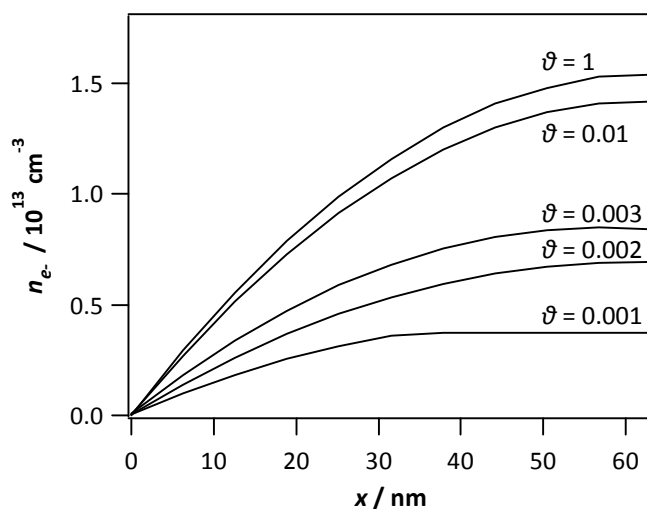


Figure 7.8 - Transient electron density profiles for the system characterized by parameters given in Table 7.1 under 1 sun back-illumination at 1.23 V. Density profiles are presented as a function of dimensionless time ϑ (0.001 -1).

7.3.2 Effect of the electrolyte layer thickness

As mentioned above, the photoelectrochemical characterisation was performed in a PEC cell configuration known as “cappuccino”.³⁵ The illumination of the photoanode is done through an uncoated fused silica window pressed against an o-ring by a metallic window part. A conductive uncoated area of the photoanode sample is clipped onto a titanium contact. This clip can rotate to facilitate front- and back-side illumination. The counter electrode, usually a platinum wire is placed at a distance of ≈ 10 mm from the photoanode. The space between the two electrodes is filled with the electrolyte solution. Consequently, the hydroxyl ions formed at the counter electrode have to diffuse a pathway of around 10 mm until reaching the photoanode, where water oxidation occurs. This distance is $b-L$ in Figure 7.1 (L is almost negligible when compared with b and so from now on $b-L$ will be considered approximately equal to b). Thus, by changing the thickness of the free electrolyte, the resistance that ions OH^- ions have to face crossing the electrolyte layer is also different. In fact, diminishing the value of b , potential losses in the electrolyte are lower and the photocurrent

density increases. From Figure 7.9 it can be noticed that the increase in the photocurrent density is more pronounced when the electrolyte thickness decreases from 10 mm to 5 mm than from 5 mm to 1 mm. This may indicate that the reduction of the electrolyte thickness to values lower than 1 mm is not that worthy for the photocurrent density response.

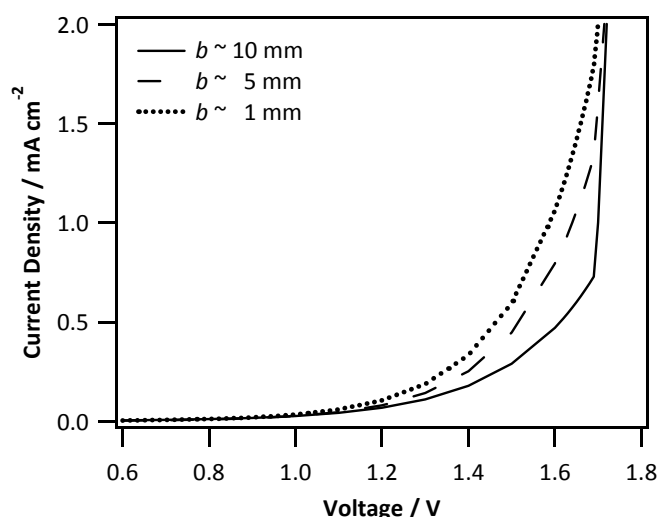


Figure 7.9 - Effect of the electrolyte layer thickness in the photocurrent density produced by the PEC cell system under study. The solid curve ($b \approx 10$ mm) is the base case presented in Table 7.1 and in Figure 7.5.

7.3.3 Effect of the hole diffusion length

The low values of photocurrent observed for the system under study are due to a low water oxidation rate by surface trapped holes⁴⁰ and a short hole diffusion length L_n in hematite photoelectrodes ($L_n = \sqrt{D_{h^+} \tau_n}$, being D_{h^+} and τ_n the diffusion coefficient and lifetime of the holes, respectively). In this present case $L_n = 3$ nm, which implies that most holes are created in the semiconductor bulk and will recombine with electrons before having reached the surface.³⁷ Increasing the hole diffusion length allows a significant increase in the photocurrent density - Figure 7.10 - and, consequently, in the hydrogen production by the PEC cell. However, undoped hematite shows a hole

diffusion length of only 2-4 nm since the photon penetration depth at visible wavelengths in hematite ($\alpha^{-1} = 118$ nm at $\lambda = 550$ nm) causes the majority of photogenerated carriers to be produced at a distance of *ca.* 100 nm from the semiconductor liquid junction;⁴¹ the recombination time constants of the photogenerated carriers are on the order of 10 ps;⁴² and the minority charge carrier has a poor mobility (maximum of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁴³ Thus, it is almost impossible to achieve the photocurrent values shown in Figure 7.10 for diffusion lengths higher than 10 nm, which explains the need of doping hematite. In fact, the performance of these photoanodes is significantly improved by doping with silicon.⁵

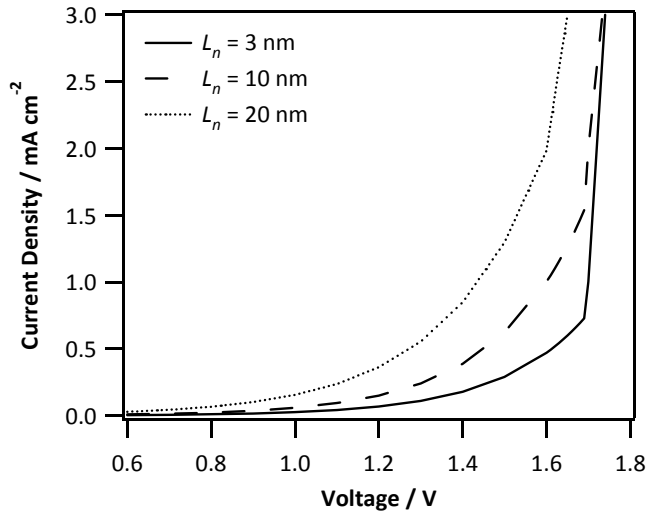


Figure 7.10 - Effect of the diffusion length value in the photocurrent density produced by the PEC cell system under study. The solid curve for $L_n = 3$ is the base case presented in Table 7.1 and in Figure 7.5.

7.3.4 Effect of the Butler-Volmer kinetics

The potential of the electrodes strongly affects the kinetics of reactions occurring on their surface. As explained before, this current-potential dependence is described by the Butler-Volmer equation. In electrochemical reactions activation losses take place, which are caused by the slowness of the reactions taking place on the surface of the electrodes. Once an electrochemical reaction is initiated, the concentration of the species taking part in the reaction at the electrode/electrolyte interface will normally be different than those in the bulk of the solution. Thus, concentration profiles arise due to effects of simple diffusion and/or effects of migration in the electric field at or near the electrode. A point to holdback at this stage is that the transport to or from the electrode surface of the species involved in the electrochemical process may not be sufficiently fast to maintain the same concentration at the electrode surface as in the bulk. If transport processes are rapid compared to charge transfer, then bulk concentration and electrode surface concentration are similar. On the other hand, when there is a considerable current flowing, the electrode surface concentration is lower than the bulk concentration and thus the potential must be increased in order to maintain the desired current density.⁴⁴ This increased potential is in fact called overpotential, here labelled as η_{Pt} . By increasing the current density, more voltage is needed to be sacrificed in order to maintain those values of current. The platinum overpotential also increases with the applied voltage – Figure 7.11. The present model allows to predict the platinum overpotential occurring at each specific case and how it evolves through the current-voltage characteristic.

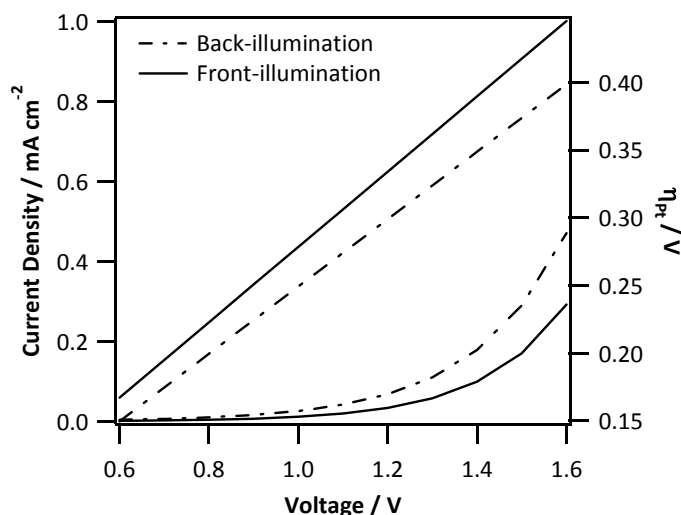


Figure 7.11 - Relation between the characteristic curves with the correspondent platinum overpotentials at the counter electrode for back- (dashed line) and front-side illumination (solid line).

The transfer coefficient β that appears in the Butler-Volmer equation depends on the symmetry of the activation barrier and, for that reason, is also known as symmetry parameter. Its value expresses how the change in the electrical potential across the reaction interface changes the sizes of the forward *versus* reverse activation barrier. For $\beta = 0.5$ the anodic and cathodic branches of the total current will be symmetrical. However, for β value near unity the cathodic branch rises much more steeply than the anodic branch, whereas for β near zero the inverse is found. The transfer coefficient depends on the reaction involved and on the electrode materials.⁴⁵ Nevertheless, for the system under analysis the variation of β , which can be obtained *e.g.* by using different materials, have a little impact on the performance of the PEC cell - Figure 7.12.

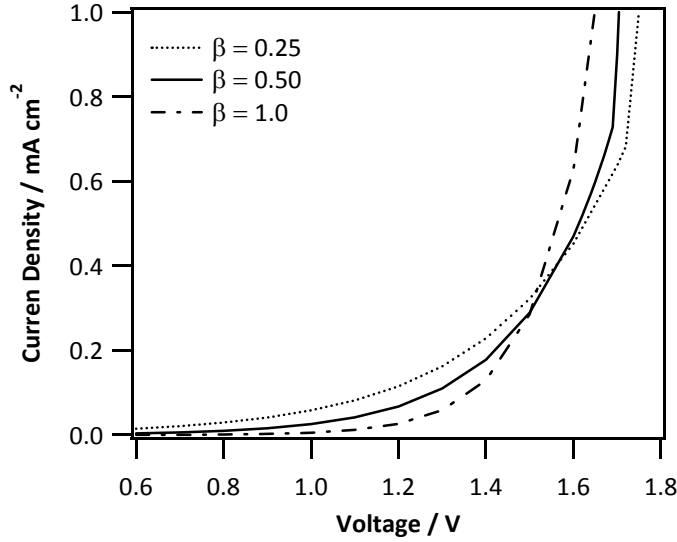


Figure 7.12 - Effect of the transfer coefficient in the photocurrent density produced by the PEC cell system under study. The solid curve for $\beta = 0.5$ is the base case presented in Table 7.1 and in Figure 7.5.

As overpotentials become larger than about 50-100 mV, the second term of Equation (7.36) becomes negligible, meaning that the forward-reaction direction dominates. Hence, simple exponential relationships between current density and overpotential are obtained, *i.e.* the overpotential can be considered as logarithmically dependent on the current density. The Butler-Volmer equation simplifies to:

$$J_{cell} = J_0 \exp\left(\frac{\beta n q}{k_B T} \eta_{Pt}\right) \quad (7.61)$$

Equation (7.61) is known as the Tafel equation and plotting $\ln(J_{cell})$ versus η_{Pt} one obtains a straight line. Therefore, the approximation to the Tafel equation is valid. The slope of a Tafel plot is related to the transfer coefficient β accordingly to: slope = $\beta n q / (k_B T)$ - Figure 7.13.³¹

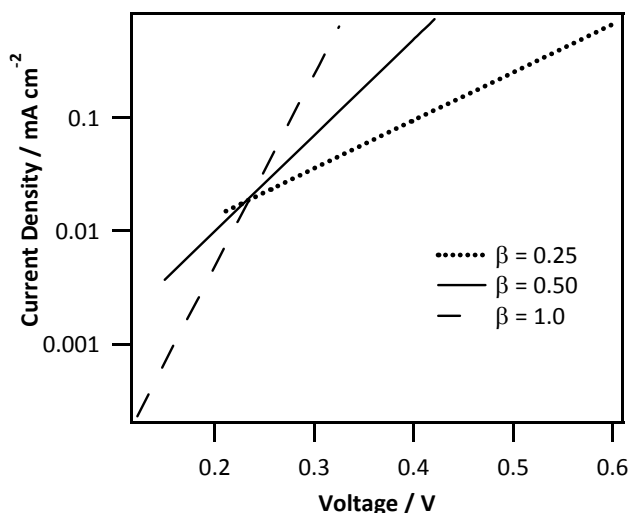


Figure 7.13 - Logarithmic representation of the current density *versus* overpotential for the platinum counter-electrode and for high values of η_{Pt} - Tafel plots.

7.4 Conclusion

A transient phenomenological model of a PEC cell using an undoped hematite photoanode was developed. The model results were critically compared with an experimental I - V characteristic and a very good agreement was observed.

This model allowed the study of the underlying mechanisms of the PEC cell. Steady-state electron density profiles for back-illumination were obtained, suggesting that most electrons are generated near the current collector. In this part of the cell, higher concentration gradients were observed and then enhanced electron diffusion rates, which in its turn limits electron recombination kinetics. Front- and back-side illumination experiments (via the electrolyte/hematite and via the substrate/hematite interfaces, respectively) were simulated in order to distinguish between electron and hole transport limitations. For undoped samples of hematite, back-side illumination showed higher photocurrent than front-side illumination.

The influence of several operation conditions was simulated and namely thickness of free electrolyte, hole diffusion length and Butler-Volmer kinetics. By decreasing the thickness of the free electrolyte, the ionic mass transfer in that region is lower and

the photocurrent density increases. The increase of hole diffusion length allows a significant increase in the photocurrent density and, consequently, in the hydrogen production by the PEC cell. Even though the simulation results showed considerable photocurrent densities for $L_n > 10$ nm, using undoped hematite samples it is almost impossible to achieve hole diffusion lengths in that range due to structural limitations. This fact explains the need of doping hematite photoanodes. Finally, the reduction of water at the platinum counter electrode was described based on the Butler-Volmer equation. The present model allows obtaining the platinum overpotential as a function of the observed current density. The effect of the transfer coefficient was assessed using the simulator. The results showed, for the system under analysis, that this variation causes little effect in the performance of the PEC cell.

Acknowledgments

This research has been funded by the European Commission (Project NanoPEC, contract number 227179) and the Portuguese Foundation for Science and Technology (Project PTDC/EQU-EQU/107990/2008). L. Andrade and T. Lopes are grateful to the Portuguese Foundation for Science and Technology (FCT) for their PhD grants (references: SFRH/BD/30464/2006 and SFRH/BD/62201/2009, respectively). H. Aguilar Ribeiro acknowledges the *Programa Ciência 2007*.

List of abbreviations and symbols

Abbreviations	Definition	Units
A	Cell area	cm^2
AM	Air mass	
b	Cell thickness	cm
C_i	Concentration of species i	mol dm^{-3}
CB	Conduction band	
CE	Counter electrode	
D_i^b	Diffusion coefficient of species i in the electrolyte bulk	$\text{cm}^2 \text{s}^{-1}$
D_i^L	Diffusion coefficient of species i in the electrolyte in the pores	$\text{cm}^2 \text{s}^{-1}$
D_{ref}	Reference diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$
E	Macroscopic electric field	V cm^{-1}
E_{Bias}	External bias energy	J
E_B	Band bending energy	J
E_{CB}	Conduction band energy	J
E_{fb}	Flat band energy	J
E_g	Semiconductor bandgap	J
E_F	Fermi level energy of the semiconductor	J
E_{H_2O/H_2}	Water reduction energy	J
E_{O_2/OH^-}	Water oxidation energy	J
E_{Redox}	Redox energy	J
E_{VB}	Valence band energy	J
F	Faraday constant ($F = 9.6485339 \times 10^4 \text{ C mol}^{-1}$)	C mol^{-1}
FF	Fill factor	
G_i	Generation rate of species i	$\text{cm}^{-3} \text{s}^{-1}$

h	Planck constant ($h = 6.6260693(11) \times 10^{-34}$ J s)	J s
$init$	Initial conditions	
I_s	Incident photon flux corrected for reflection losses	$\text{cm}^{-2} \text{s}^{-1}$
j_i	Current density of species i	$\text{cm}^{-3} \text{s}^{-1}$
j_i^L	Current density of species i in the electrolyte in the pores	$\text{cm}^{-3} \text{s}^{-1}$
J_{cell}	Net current density	mA cm^{-2}
J_0	Exchange current density at Pt electrode	mA cm^{-2}
k_B	Boltzman constant ($k_B = 1.3806504(24) \times 10^{-23}$ J K ⁻¹)	J K ⁻¹
k_{e^-}	Back reaction rate constant	s^{-1}
L	Thickness of the semiconductor	nm
$m_{e^-}^*$	Effective electron mass	kg
n	Number of electrons transferred in the reaction	
n_{eq}	Dark equilibrium electron density	cm^{-3}
n_i	Density of species i	cm^{-3}
n_i^b	Density of species i in the electrolyte bulk	cm^{-3}
n_i^L	Density of species i in the electrolyte in the pores	cm^{-3}
n_{int}	intrinsic carrier concentration	cm^{-3}
n_{ref}	Reference particle density	cm^{-3}
N_{CB}	Effective density of states in the conduction band	cm^{-3}
N_{VB}	Effective density of states in the valence band	cm^{-3}
PEC	Photoelectrochemical	
q	Elementary charge ($q = 1.60217646 \times 10^{-19}$ C)	C
ref	Reference	
R_i	Recombination rate of species i	$\text{cm}^{-3} \text{s}^{-1}$
R_{Ohmic}	Ohmic resistance	Ω
T	Absolute temperature	K

TCO	Transparent conductive oxide	
t	Time	s
x	Coordinate	cm
VB	Valence band	
O^+	Point close to the photoanode	
O^-	External point of the current collector	
*	Dimensionless variable	

<i>Greek symbols</i>	Definition	Units
α	Wavelength-dependent absorption coefficient	cm^{-1}
β	Transfer coefficient	
ϵ	Dielectric constant	
ϵ_p	Semiconductor film porosity	
ϵ_0	Permittivity of free space ($\epsilon_0 = 8.85419 \times 10^{-12} \text{ F m}^{-1}$)	F m^{-1}
η_a	Overpotential at the anode	V
η_{inj}	Electron injection efficiency	
η_{ohmic}	Ohmic overpotential	V
η_{Pt}	Overpotential at Pt electrode (cathode)	V
λ	Wavelength	nm
μ_i	Mobility of species i	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ_i^b	Mobility of species i in the electrolyte bulk	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ_i^L	Mobility of species i in the electrolyte in the pores	$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
ν	Frequency	s^{-1}
τ	Tortuosity	
τ_n	Carrier lifetime	ns
ΔE_F	Variation of the Fermi level energy	J
ΔG	Free energy for the overall cell reaction	J

ϑ	Dimensionless time variable
-------------	-----------------------------

References

- (1) Nathan, S. L. *Basic Research Needs for Solar Energy Utilization*, Renée M. Nault, 2005.
- (2) Grätzel, M. *Nature* **2001**, 414, 338.
- (3) Krol, R. V. d.; Liang, Y.; Schoonman, J. J. *Mater. Chem.* **2008**, 18, 2311.
- (4) Trieb, F. *Concentrating Solar Power for the Mediterranean Region*, German Aerospace Center (DLR), **2005**.
- (5) Cesar, I.; Kay, A.; Gonzalez Martinez, J. A.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, 128, 4582.
- (6) Archer, M. D.; Nozik, A. J. *Nanostructured and photoelectrochemical systems for solar photon conversion*; Imperial College Press ; World Scientific Pub. Co.: London; Singapore; Hackensack, NJ, **2008**.
- (7) Aroutiounian, V. M.; Arakelyan, V. M.; Shahnazaryan, G. E.; Hovhannisyan, H. R.; Wang, H.; Turner, J. A. *Sol. Energy* **2007**, 81, 1369.
- (8) Aroutiounian, V. M.; Arakelyan, V. M.; Shahnazaryan, G. E.; Stepanyan, G. M.; Turner, J. A.; Khaselev, O. *Int. J. Hydrogen Energy* **2002**, 27, 33.
- (9) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, 29, 189.
- (10) Aroutiounian, V. M.; Arakelyan, V. M.; Shahnazaryan, G. E.; Stepanyan, G. M.; Turner, J. A.; Kocha, S. S. *Electrochim. Acta* **2000**, 45, 1999.
- (11) Boudjemaa, A.; Boumaza, S.; Trari, M.; Bouarab, R.; Bouguelia, A. *Int. J. Hydrogen Energy* **2009**, 34, 4268.
- (12) Glasscock, J. A.; Barnes, P. R. F.; Plumb, I. C.; Savvides, N. J. *Phys. Chem. C* **2007**, 111, 16477.
- (13) Sivula, K.; Formal, F. L.; Grätzel, M. *Chem. Materials* **2009**, 21, 2862.
- (14) Gerischer, H. J. *Electroanal. Chem.* **1975**, 58, 263.
- (15) Gerischer, H. J. *Electroanal. Chem.* **1977**, 82, 133.
- (16) Nozik, A. J. *Appl. Phys. Lett.* **1976**, 29, 150.
- (17) Khan, S. U. M.; Bockris, J. O. M. *J. Phys. Chem.* **1984**, 88, 2504.
- (18) Choi, P.; Bessarabov, D. G.; Datta, R. *Solid State Ionics* **2004**, 175, 535.
- (19) Nie, J.; Chen, Y.; Boehm, R. F.; Katukota, S. J. *Heat Transfer* **2008**, 130, 042409.

- (20) Marangio, F.; Santarelli, M.; Cali, M. *Int. J. Hydrogen Energy* **2009**, *34*, 1143.
- (21) Ni, M., PhD Thesis, University of Hong Kong, **2007**.
- (22) Ni, M.; Leung, M. K. H.; Leung, D. Y. C. *Int. J. Hydrogen Energy* **2008**, *33*, 2337.
- (23) Ni, M.; Leung, M. K. H.; Leung, D. Y. C. *Int. J. Hydrogen Energy* **2008**, *33*, 4040.
- (24) Grimes, C. A.; Varghese, O. K.; Ranjan, S. *Light, Water, Hydrogen: The Solar Generation of Hydrogen by Water Photoelectrolysis*; Springer: New York, **2008**.
- (25) Lindgren, T.; Vayssieres, L.; Wang, H.; Lindquist, S.-E. In *Chemical Physics of Nanostructured Semiconductors*; Kokorin, A. I., Bahnemann, D. W., Eds.; VSP - An imprint of BRILL: Boston, **2003**, p 83.
- (26) Archer, M. D.; Nozik, A. J. *Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion*; Imperial College Press: London, **2008**.
- (27) Cesar, I.; Kay, A.; Gonzalez Martinez, J. A.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4582.
- (28) Cesar, I., PhD Thesis, EPFL, **2007**.
- (29) Würfel, P. *Physics of Solar Cells: From Principles to New Concepts* Weinheim, **2005**.
- (30) Ferber, J.; Stangl, R.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *53*, 29.
- (31) Bard, A. J.; Faulkner, L. R. *ELECTROCHEMICAL METHODS: Fundamentals and Applications*; 2nd Edition; John Wiley & Sons, Inc.: USA, **2001**.
- (32) Baranenko, V. I.; Kirov, V. S. *At. Energy* **1989**, *66*, 30.
- (33) Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. *Int. J. Hydrogen Energy* **2002**, *27*, 991.
- (34) Petzold, L. *Siam J. Sci. Stat. Computing* **1983**, *4*, 136.
- (35) Cesar, I.; Sivula, K.; Kay, A.; Zboril, R.; Grätzel, M. *J. Phys. Chem. C* **2009**, *113*, 772.
- (36) O'Hayre, R.; Cha, S.-W.; Colella, W.; Prinz, F. B. *Fuel Cells Fundamentals*; John Wiley & Sons, Inc.: New York, **2006**.
- (37) Kay, A.; Cesar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 15714.
- (38) Bjoerksten, U.; Moser, J.; Grätzel, M. *Chem. Mater.* **1994**, *6*, 858.

- (39) Liang, Y.; Enache, C. S.; Krol, R. v. d. *Int. J. Photoenergy*, vol. 2008, Article ID 739864, 7 pages, **2008**. doi:10.1155/2008/739864.
- (40) Dare-Edwards, M. P.; Goodenough, J. B.; Hamnett, A.; Trevellick, P. R. *J. Chem. Soc., Faraday Trans. 1F* **1983**, 79.
- (41) Itoh, K.; Bockris, J. O. M. *J. Electrochem. Soc.* **1984**, 131, 1266.
- (42) Cherepy, N. J.; Liston, D. B.; Lovejoy, J. A.; Deng, H.; Zhang, J. Z. *J. Phys. Chem. B* **1998**, 102, 770.
- (43) Bosman, A. J.; van Daal, H. J. *Adv. Phys.* **1970**, 19, 1
- (44) Hamann, C. H.; Hamnett, A.; Vielstich, W. *Electrochemistry*; 2nd Edition ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2007**.
- (45) Larminie, J.; Dicks, A. *Fuel Cells Systems explained*; 2nd Edition ed.; John Wiley & Sons Ltd: England, **2003**.

Chapter 8

IMPEDANCE CHARACTERIZATION OF DYE-SENSITIZED SOLAR CELLS IN A TANDEM ARRANGEMENT FOR HYDROGEN PRODUCTION BY WATER SPLITTING

Luísa Andrade, Rui Cruz, Helena Aguilar Ribeiro and Adélio Mendes

(International Journal of Hydrogen Energy 2010, 35, 8876-8883)

Abstract

The present work reports the photoelectrochemical characterisation of a dye-sensitized solar cell (DSC) to assist water split in a photoelectrochemical (PEC) cell. Performance parameters were extracted from standard current-voltage characteristic (I - V) and the charge transfer phenomena occurring at different interfaces of the DSC were evaluated by electrochemical impedance spectroscopy (EIS). The DSC comprised the N719 dye and a robust electrolyte (1-propyl-3-methylimidazolium iodide in guanidinium thiocyanate additive). At 1 sun illumination the DSC yielded a short-circuit photocurrent density of 14.9 mA cm^{-2} , an open-circuit voltage of 0.797 V, a fill factor of 0.712 and an overall efficiency of 8.5 %. Different PEC systems based on silicon-doped and undoped hematite photoelectrodes were considered. The required additional anodic bias necessary for actual water cleavage was supplied by two DSCs in series operating just under open-circuit voltage (1.56 V), allowing a conversion efficiency of about 1.12 % for the silicon-doped hematite deposited by APCVD, 0.51 % for the silicon-doped prepared by USP and 0.12 % for the undoped hematite sample.

Keywords: Dye-sensitized Solar Cells; Photoelectrochemical cells; Hydrogen production; Electrochemical Impedance Spectroscopy.

8.1 Introduction

The actual dependence on fossil fuels and its most likely shortage in the next decades brings increasing concerns to the scientific, political and civil society. Thus, the development of clean alternatives to produce energy is of utmost importance in order to diminish the greenhouse effect, caused by fossil fuels combustion, and also because this will ensure sustained economic growth. For these reasons, research on renewable energy technologies has strongly increased, namely in photovoltaics (PV). Apart from being one of the most efficient technologies converting solar energy into electricity, photovoltaics require low maintenance while ensuring a stable and long-term energy production. In particular, Dye-sensitized Solar Cells (DSCs) appear to have significant potential as a low-cost process, resulting in a low-cost electricity production from solar radiation.¹

The general principle for conversion of sunlight into electricity by DSCs assumes that the process of light absorption and charge separation are differentiated, opposing to solid state silicon PV cells. Since large bandgap semiconductors, such those typically used in DSCs, are insensitive to the visible solar spectrum, light harvesting is accomplished by a monolayer of sensitizer (S), chemically bonded to the surface of the semiconductor. The sensitizer absorbs the incident radiation and, once excited (S^*), electrons are injected into the conduction band of the mesoporous oxide semiconductor. The photoinjected electrons then percolate through the semiconductor network towards the transparent conducting oxide (TCO) coating of the photoanode and into the external circuit, producing electrical work. Electrons are then returned to the cell by the counter electrode (CE) side, where they take part in an iodide/triiodide redox reaction catalysed by a platinum layer coated onto the TCO of the CE. The redox electrolyte allows the reduction of triiodide to iodide ions which diffuse back to the semiconductor's surface. Here the regeneration of the oxidised sensitizer takes place, while simultaneously the iodide is oxidised back to triiodide. This cycle allows light conversion into electricity without any permanent chemical transformation.²⁻³

Bearing in mind the fact that a solar cell generates electricity only during daytime, a

new challenge emerges: for large-scale use, energy storage solutions are required. A practical way to overcome this problem is using sunlight to split water into hydrogen and oxygen - photoelectrolysis⁴ - by means of a photoelectrochemical (PEC) cell. This process is extremely attractive for several reasons. Firstly, this type of solar energy conversion alleviates the energy storage problem since hydrogen can be stored much more easily than electricity or even heat. Secondly, hydrogen produced from solar radiation is valuable as a potential fuel and energy carrier since it is non-polluting, renewable, inexhaustible and very flexible with respect to further conversion to other forms of energy, such as hydrocarbons.⁵⁻⁶

A photoelectrochemical cell combines visible light harvesting by a nanocrystalline semiconductor (SC) thin film together with electrolysis of water. Photons with energy $h\nu$ higher than the semiconductor's bandgap generate electron-hole pairs ($e_{CB}^- + h_{VB}^+$) in the conduction and valence bands, respectively:⁷



At the semiconductor's surface, holes react with OH^- ions oxidising water to oxygen:



The photoexcited conduction band electrons transferred to the counter electrode of the PEC cell by the external circuit reduce water to form hydrogen gas:



However, these devices achieve very low conversion efficiencies since most of the semiconductors used for this application have a large energy bandgap. Furthermore, the band edge potentials of many semiconductors are not suitable for oxygen and hydrogen evolution. In fact, for efficient water cleavage, the conduction band of the n-type semiconductor needs to be positioned at a more negative potential than the reduction potential of water, *i.e.* $E_{CB} > E_{H_2O/H_2}^\circ$, while the valence band needs to be positioned at a more positive potential than the oxidation reaction, *i.e.* $E_{VB} < E_{O_2/OH^-}^\circ$.

Even though strong efforts have been made in order to develop appropriate semiconductors,⁸⁻¹² no material was found that can simultaneously and efficiently oxidise and reduce water without any external assistance. Alternatively, two devices

with semiconductors of different bandgaps can be coupled in a cell arrangement known as “tandem cell”. This is the most attractive configuration for water photocleavage found to date.

Tandem cells are based on two photosystems connected in series (Figure 8.1): a PEC cell, generating electron-hole pairs by bandgap excitation of the semiconductor due to absorption of the blue part of the solar spectrum (holes then migrate to the semiconductor’s surface where they react with water to produce oxygen and electrons are injected in the conduction band of the semiconductor); and a DSC (able to absorb in the visible and near-infrared light spectrum) that collects the photoexcited electrons of the PEC cell and feed them back through the PEC cell’s counter electrode. By passing through the DSC, the electrochemical potential of the electrons is increased allowing reduction of water to hydrogen at the counter electrode of the PEC cell.¹³ In the proposed embodiment, the two photosystems are not physically connected, *i.e.* they are two independent devices, meaning that the DSC acts only as a supplier of the mandatory additional anodic bias required by the PEC cell to produce hydrogen. This implies that the energy contained in a photon is not shared by both photosystems. Consequently, the DSC can be used to simultaneously provide additional bias to several different PEC cells as well as to generate electricity for other possible applications.

In the present work, we report the photoelectrochemical characterisation of a DSC/PEC tandem cell to assist hydrogen evolution. Performance parameters are extracted from standard current-voltage characteristic (*I-V*) and electrochemical impedance spectroscopy (EIS). EIS has been widely used for the characterisation of several electrochemical systems and, in particular, to analyse internal resistances in DSCs.¹⁴⁻¹⁵ In fact, the theoretical modelling and interpretation of impedance spectroscopy allows not only the understanding of transport and reaction processes occurring in porous electrodes but also the description of anomalous transport effects. The electron transport and charge recombination in nanocrystalline TiO₂ films have been widely studied by Bisquert and co-workers,¹⁴ who suggested an electrical

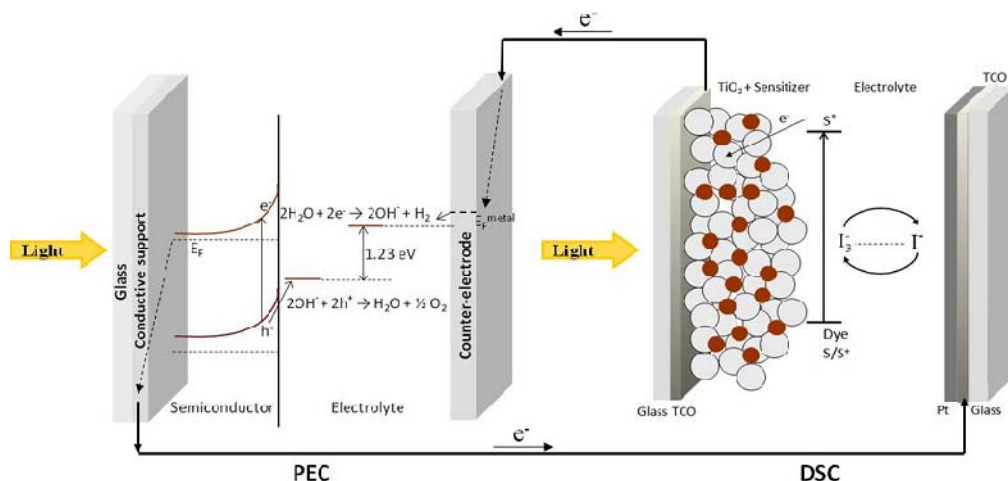


Figure 8.1 - Scheme of a standard DSC/PEC tandem cell configuration.

analogue based on a transmission line model to describe the kinetic processes of DSCs. Following a similar approach, the main internal constrictions that limit the performance of DSCs under study and ultimately the global efficiency of the tandem cell are identified. Invaluable information can therefore be obtained targeting the development of more efficient tandem cells.

8.2 Experimental section

8.2.1 Synthesis

All chemicals used herein were of purest quality. 3-methoxypropionitrile (MPN) was obtained from Fluka and distilled before use. 1-Propyl-3-methylimidazolium iodide (PMII) ionic liquid was prepared according to literature methods and the purity was confirmed by ^1H -NMR (nuclear magnetic resonance) spectra.¹⁶ Guanidinium thiocyanate (GuNCS) was purchased from Fluka. 1-Butyl-1H-benzimidazole (NBB) and N719 dye were synthesised as reported earlier.¹⁷⁻¹⁸ The electrolyte contains PMII (1.0 M), iodine (0.15 M), GuNCS (0.1 M) and NBB (0.5 M) in 3-methoxypropionitrile.

8.2.2 TiO₂ electrode preparation

A screen-printed double-layered film of interconnected TiO₂ particles was used as photoanode. A 7 µm-thick film of 20 nm-sized TiO₂ particles was first printed on the fluorine-doped SnO₂ conducting glass electrode (FTO) and further coated by a 5 µm-thick second layer of 400 nm-sized light-scattering anatase particles. A detailed procedure for the synthesis of screen-printable TiO₂ pastes has been reported elsewhere.¹⁹

8.2.3 DSC and PEC cell fabrication

The working and counter electrodes of the DSC were sealed with a 25 µm-thick transparent Surlyn ring (from DuPont) at 130 °C for 15 s. The counter electrode was prepared by chemical deposition of a platinum solution onto a similar conducting substrate used for the TiO₂ electrode (FTO glass, 15 Ω per square). An annealing step was performed at 450 °C for 15 min to activate the platinum catalyst. After sealing, the cells were filled with an electrolyte solution through a pre-drilled hole done in the counter electrode side. Finally, the hole was sealed with a melted Surlyn disc covered by a thin glass lamella to avoid electrolyte leakage.

As for the PEC cell a configuration known as “Cappuccino” was chosen²⁰⁻²¹ (see Figure 8.2). The “Cappuccino” cell (0.5 cm² active area) was made of polyetheretherketone (Erta Peek) and comprised a 20 mm-diameter uncoated fused silica window (Robson Scientific, England) pressed against an o-ring by a metallic window part. The cell was filled with an electrolyte solution consisting of 1.0 M NaOH (25 °C, pH = 13.3)^{11,22} in which the photoanode was immersed. The photoanode consisted of a *ca.* 2 mm-thick conducting glass (FTO glass, 7-15 Ω per square) coated with undoped hematite (prepared at ENI-Novara by spray pyrolysis as described elsewhere).^{9,23} For characterisation purposes, a standard three-electrode configuration was chosen: Ag/AgCl/sat electrode (Metrohm, Switzerland) as reference electrode; 0.3 mm-diameter 99.9 % pure platinum wire (Alfa Aesar, Germany) as counter electrode and the mentioned photoanode as working electrode. The

hydrogen gas produced at the cathode side was monitored by means of a mass flow meter (MilliGascounter Ritter, Germany).

8.2.4 *I*-*V* measurements

A 150 W xenon light source (Oriel class A solar simulator, Newport USA) was used to illuminate the surface of the DSC/PEC cell at 1 sun (100 mW cm^{-2} , air mass AM 1.5G). Light intensity was calibrated using a single crystal Si photodiode (Model 91150, Newport, USA). A broadband reflector mirror (Model 10D20ER.2, Newport, USA) with an enhanced aluminium coating (Newport, USA) was used to redirect the vertical Xe light beam and to focus it into the active area of the PEC cell. For proper alignment of the beam, the tandem cell was coupled to a steel damped rod mounted onto a precision rail assembled on a scientific grade breadboard (Newport, USA). The current-voltage characteristic of the DSC/PEC tandem cell (Figure 8.1) was obtained by applying an external potential bias to the DSC system and measuring the generated photocurrent by the PEC cell with a digital current meter (Model 2400-series, Keithley, USA). Unless otherwise stated, voltage will be presented in volts referred to the reversible hydrogen electrode (V vs. RHE).

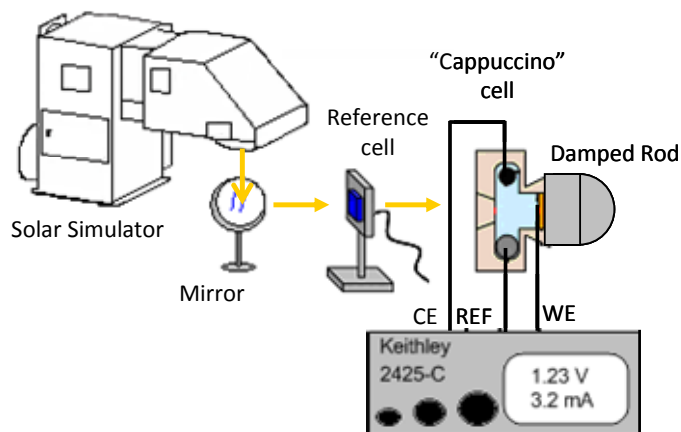


Figure 8.2 - Scheme of the test bench for PEC cell's characterisation.

8.2.5 Electrochemical impedance spectroscopy of DSCs

EIS experiments were carried out with a computer-controlled potentiostat (EG&G M273) equipped with a frequency response analyser (EG&G M1025). The frequency range was 0.005 Hz - 100 kHz and the magnitude of the modulation signal was 10 mV. All the measurements were performed at room temperature in the dark at 0.75 V. The EIS spectra were fitted to an appropriate electrical analogue by means of the ZView software (Scribner Associates Inc.).

8.3 Results and discussion

In the present work a standard DSC was fabricated using the efficient and stable N719 dye in association with a robust electrolyte. The performance of the cell was evaluated by means of its *I*-*V* characteristic curve and electrochemical impedance spectroscopy.

Polypyridyl complexes of ruthenium have been widely used as sensitizers due to their advantageous spectral properties, photostability in the final device and high conversion efficiency.²⁴⁻²⁸ An example of high-performance ruthenium polypyridine complexes in terms of photon-to-current conversion yield and long term stability is the *cis*-di(thiocyanato) bis (4,4'- dicarboxylic acid-2,2'-bipyridine) ruthenium(II) dye, commonly known as the N3 dye.²⁹ In particular, this dye shows a broad range of visible light absorption, with absorption maxima at 518 nm and 380 nm, and long-lived electronic excited states (60 ns lifetime) with energies almost matching those of the TiO₂ conduction band. Moreover, the presence of terminal acidic carboxylic groups allows stable anchoring of the sensitizer to the semiconductor's surface, enabling high electronic coupling between the dye and the semiconductor, a requisite for efficient charge injection with unit quantum yield.³⁰ Since the development of the N3 dye in 1993, its tetrabutylammonium salt N719 has been widely used as the standard red dye because of its unmatched performance.³⁰ This sensitizer is derived from the N3 dye by substituting two protons with two TBA (tetrabutylammonium) cations.

Despite the intrinsic stability of DSC's components, industrial implementation of the technology is still limited by issues related to the sealing process. In fact, stability problems often arise due to the degradation of the sealing material, which allows the standard volatile organic electrolytes to escape from the cell. Thus, alternatives to volatile organic solvents have attracted researchers' attention, namely, room-temperature ionic liquids, which are non-volatile, chemical and thermally stable and have, negligible vapour pressure and low flammability.³¹ Imidazolium iodide-based ionic liquids end up acting simultaneously as an iodide source and as a solvent. However, these ionic liquids have relatively high viscosity, which clearly limits mass transport within the electrolyte. To minimise this effect in the overall performance of the cell and ultimately enhance its photocurrent or photovoltage, several additives are often used. In this work, guanidinium thiocyanate was added to an ionic liquid electrolyte composed by 1-propyl-3-methylimidazolium iodide (PMII) to enhance the self-assembly of the dye molecules in the TiO₂ semiconductor.³² Guanidinium cations are co-adsorbed with the dye molecules, reducing the lateral Coulombic repulsion of the sensitizer. This facilitates the self-assembly of the dye molecules that form a compact monolayer,³¹ which increases substantially the open-circuit voltage of the solar cell by reducing the dark current.³

8.3.1 DSC characterisation

Figure 8.3 shows the photocurrent-voltage characteristic of the system described above at 1 sun light-intensity. The corresponding photovoltaic parameters (short-circuit current density, J_{sc} ; open-circuit voltage, V_{oc} , and fill factor, FF) of the cell are then obtained: $J_{sc} = 14.9 \text{ mA cm}^{-2}$; $V_{oc} = 0.797 \text{ V}$; $FF = 0.712$. The overall efficiency, $\eta = 8.46 \%$, is given by equation (8.4) where I_s is the intensity of the incident light ($I_s = 100 \text{ mW cm}^{-2}$):

$$\eta = \frac{V_{oc} J_{sc}}{I_s} FF \quad (8.4)$$

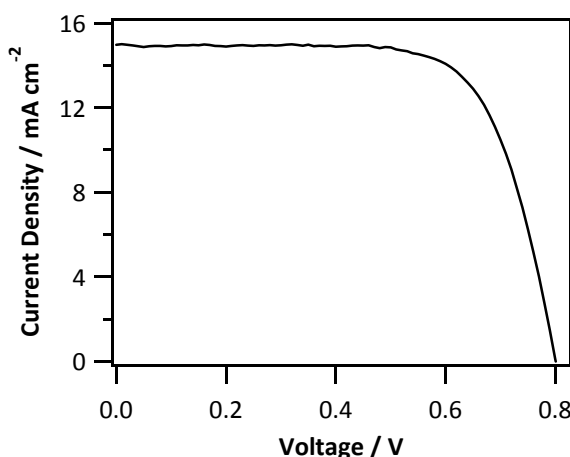


Figure 8.3 - I - V characteristic for the system N719/PMII electrolyte measured at AM 1.5G (100 mW cm^{-2}) global sunlight illumination.

The overall processes occurring in a DSC can also be evaluated by means of electrochemical impedance spectroscopy. This technique allows the analysis of charge transfer and transport processes with different time constants in DSCs components: TiO_2 nanocrystalline film coated on a transparent conducting oxide, redox electrolyte and platinum counter electrode. A typical Nyquist plot shows three semicircles, although in some cases two of them may overlap. In particular the low-frequency peak often vanishes underneath the middle-frequency peak. The low-frequency peak (in the mHz range) corresponds to the Nernstian diffusion of ionic species in the electrolyte, while the middle-frequency peak (in the 10 - 100 Hz range) reflects the transport properties of the photoinjected electrons within the TiO_2 film. The high-frequency peak (in the kHz range) corresponds to the charge-transfer at the platinum counter electrode.³² The most common and standard procedure in impedance measurements consists of applying a small sinusoidal voltage perturbation and monitoring the resulting current response of the system at the corresponding frequency. An EIS measurement can be performed under any bias illumination and at any working condition of the solar cell. Nevertheless, the single-frequency voltage perturbation is usually done in the dark and near the open-circuit conditions, yielding important values of parameters of the cell. Figure 8.4 shows the Bode and Nyquist

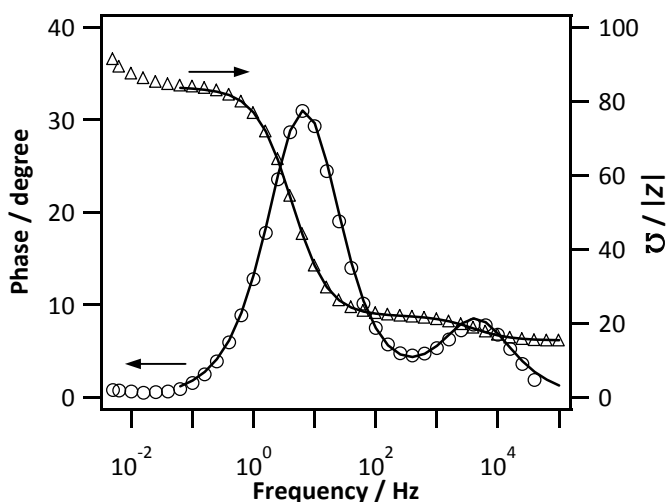
diagrams of the DSC system under study. Here, two semicircles in the Nyquist diagram and two peaks in the Bode plot can be distinguished. The smaller semicircle, corresponding to the higher frequencies, is due to the charge transfer process occurring in the platinum counter electrode, while the second semicircle, representing the complex transport/recombination kinetics occurring in the photoelectrode, is overlapped with the Nernstian diffusion within the electrolyte.

The usefulness of EIS measurements is clear when the experimental data is fitted to representative equivalent electrical analogues. In fact, several equivalent electrical circuit models based on resistors and capacitors have been reported.³³⁻³⁴ In particular, the electron transport, accumulation and charge recombination in the TiO₂ nanoporous photoelectrode have been interpreted based on a well-known transmission line model proposed by Bisquert.¹⁴ This model considers the nanoporous titania structure as an interconnected network and represents it by a quite complex arrangement of resistive and capacitive elements. Under forward bias, electrons are injected from the TCO substrate into the TiO₂ film, which is then charged by electron percolation through its individual particles with a resistance R_w . Some of the injected electrons recombine with the oxidised species in the electrolyte and the remaining ones are recaptured by the TCO current collector during the opposite phase of the sinusoidal voltage modulation. The recombination phenomenon is characterised by a charge transfer resistance, R_k , and a capacitance, C_{μ} , that reflects the change of electron density upon a small variation of the chemical potential. This is the base of the diffusion-recombination theory, which defines an impedance function as:³⁵

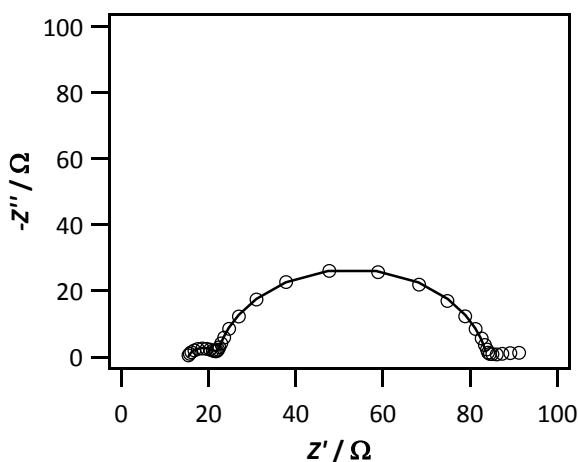
$$Z = \left(\frac{R_w R_k}{1 + j\omega / \omega_k} \right)^{1/2} \coth \left[\left(\frac{\omega_k}{\omega_d} \right)^{1/2} \left(1 + \frac{j\omega}{\omega_k} \right)^{1/2} \right] \quad (8.5)$$

where ω_d is the characteristic frequency of diffusion; ω_k is the characteristic frequency of recombination; ω is the angular frequency of the sinusoidal perturbation and j is the imaginary number.

At very high potentials (near or at open-circuit conditions) the electron Fermi level of the TiO₂ semiconductor approaches the conduction band edge, making it sufficiently conductive so that the electron transport resistance becomes negligible.



(a)



(b)

Figure 8.4 - a) Bode and magnitude diagrams; b) Nyquist diagram. Open symbols represent experimental data obtained in the dark under 0.75 V bias; solid lines are obtained by fitting the experimental data to the electrical analogue shown in Figure 8.5.

Under such conditions, the transmission line model reduces to a parallel assembly of the recombination resistance and the chemical capacitance as shown in Figure 8.5.³⁵ In the same electrical analogue, the diffusion of triiodide ions within the electrolyte solution is described by the Nernst diffusion impedance Z_d . Regeneration of triiodide

at the counter electrode is characterised by R_{CE} and C_{CE} - the charge transfer resistance and the double layer capacitance at the platinised TCO, respectively. R_s is the series resistance, including the sheet resistance of the TCO coated glass and the contacts resistance of the cell.³⁶

The fitting of the experimental Nyquist diagram in Figure 8.4 to the electrical analogue shown in Figure 8.5 was accomplished with the ZView software. Good agreement between the measured and the fitted data was achieved in this case by replacing all the capacitor elements by constant phase elements (CPE). The CPE elements are non-ideal capacitances associated with a non-uniform distribution of current in the heterogeneous TiO_2 film. Additionally, they are characterised by an empirical parameter n , a constant value less than 1 with no real physical meaning. For $n = 1$, the CPE returns to a capacitor.³⁷ Table 8.1 summarises the fitting results obtained with data presented in Figure 8.4.

For the system under study, the charge-transfer resistance associated to recombination of electrons at the TiO_2 /electrolyte interface is much higher than the electron transport resistance in the semiconductor ($R_k \gg R_w$). This means that the electron lifetime τ_n ($\tau_n = R_k C_\mu$) is much higher than the transit time, τ_{tr} , and the respective diffusion length is larger than the thickness of the cell, $L_n \gg L$ ($L_n = L\sqrt{R_k/R_w}$), an essential requirement for efficient cells.

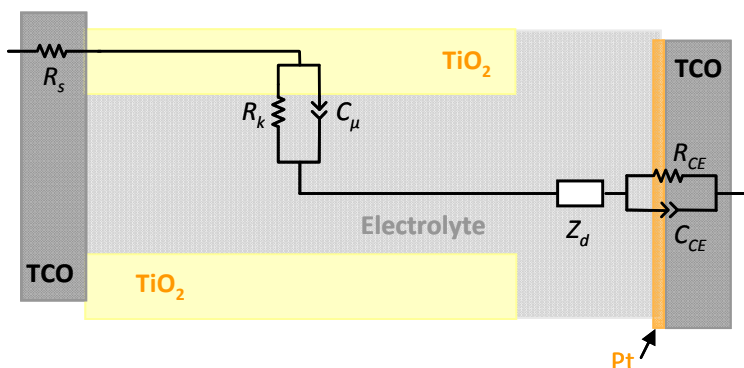


Figure 8.5 - Electrical analogue used to fit EIS experimental data, with a simplified transmission line model.²⁹

Table 8.1 - Parameters determined by fitting the EIS experimental data to the equivalent circuit shown in Figure 8.5.

R_s / Ω	R_{CE} / Ω	C_{CE} / F	R_k / Ω	C_μ / F	τ_n / ms
15.4	6.6	2.6×10^{-5} ($n = 0.87$)	61.9	1.1×10^{-3} ($n = 0.90$)	135

8.3.2 DSC application: tandem cell for water photocleavage

To study the viability of using a DSC as a supplier of the additional anodic bias required for the production of hydrogen by water splitting, it was first necessary to consider the photocurrent-voltage characteristic of the PEC system – Figure 8.6. For that purpose, we address some important considerations regarding the semiconductor of the PEC cell, in particular hematite. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has an indirect bandgap of 2.0 eV, which allows it to absorb photons from the blue and ultraviolet regions of the solar emission (2.2 eV and 2.6 eV, respectively) and makes it a suitable semiconductor to serve as oxygen-evolving anode. $\alpha\text{-Fe}_2\text{O}_3$ is inexpensive, stable under operation resisting both dark and photocorrosion, nontoxic and abundant. However, despite significant research efforts made over recent decades, the photocurrents obtained from $\alpha\text{-Fe}_2\text{O}_3$ thin film anodes under AM 1.5 sunlight conditions have remained quite low.⁹ The poor photoelectrochemical performance of

α -Fe₂O₃ has been attributed to the short charge carrier diffusion lengths and to the slow kinetics of water oxidation by the valence band holes.³⁸ Several methods can be used to produce hematite films (undoped or doped), but in the present work only two different methods are considered: ultrasonic spray pyrolysis (USP) and atmospheric pressure chemical vapour deposition (APCVD). In fact, undoped α -Fe₂O₃ acts as an insulator when used as a semiconductor material in a PEC electrode, with typical current densities in the range of 10 $\mu\text{A cm}^{-2}$.^{11,39-40} Our recent work²¹ reports an undoped hematite film prepared by USP with a photocurrent density of 88.2 $\mu\text{A cm}^{-2}$ at the potential of the reversible hydrogen electrode (1.23 V) - Figure 8.6. As observed, pure hematite is an inefficient photoelectrode and so it has been widely reported that dopants significantly increase the light-to-hydrogen conversion efficiency. Cesar *et al.*⁸ reported the influence of using tetraethoxysilane (TEOS) as silicon dopant of hematite electrodes to increase the water photo-oxidation efficiency. These authors prepared a 145 nm-thick film by USP based on thermal decomposition of iron(III)-acetylacetonate that allowed a photocurrent density of 0.95 mA cm^{-2} at 1.23 V. Moreover, Kay *et al.*⁸ proposed a thin film of silicon-doped hematite with cobalt treatment deposited by APCVD, which led to an unprecedented efficiency, mainly attributed to the dendritic nanostructure of the doped semiconductor. In fact, this kind of structure not only minimises the distance that the photogenerated holes have to diffuse to reach the hematite/electrolyte interface, but also allows efficient light absorption.^{11,41-43} The respective *I*-*V* curve measured under simulated sunlight of 100 mW cm^{-2} (AM 1.5) shows negligible dark current up to about 1.8 V and at 1.23 V, the photocurrent density is 2.3 mA cm^{-2} . As a consequence, the efficiency of the PEC embodied with a DSC strongly depends on the type of hematite that is being used.

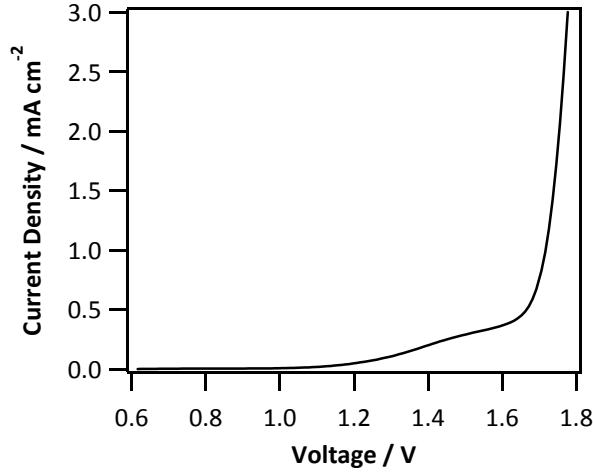


Figure 8.6 - I - V characteristic for the PEC + DSC tandem cell measured at AM 1.5 (100 mW cm^{-2}) global sunlight illumination.

The total conversion efficiency of light and electrical energy to chemical energy (hydrogen) of the photoelectrochemical cell, η_{PEC}^{total} , is given by the following expression (assuming no current losses in the outer circuit):

$$\eta_{PEC}^{total} = \frac{P_{out}}{P_{in}} = \frac{J_p V_{Redox}}{I_s} \quad (8.6)$$

where the total power output is given by $J_p V_{Redox}$. Here, J_p is the photocurrent density (mA cm^{-2}), I_s is the intensity of the incident light (mW cm^{-2}) and V_{Redox} is the thermodynamic standard reversible potential required for water splitting (V). Based on the Gibbs free energy for water splitting at 25°C (237 kJ mol^{-1}), V_{Redox} is considered to be 1.23 V . However, the water splitting reaction does not occur at the ideal potential V_{Redox} . Due to overpotentials and thermodynamic losses, the PEC cell's actual water splitting reaction potential is $\approx 1.9 \text{ V}$.^{4,44} So, because an additional applied potential is necessary for actual water cleavage, the effective conversion efficiency of solar light to chemical energy, η_{PEC}^{pract} , under illumination can be written as follows:

$$\eta_{PEC}^{pract} = \frac{P_{out}}{P_{in}} = \frac{J_p (V_{WSR} - V_{bias})}{I_s} \quad (8.7)$$

where the total power output is given by $J_p(V_{WSR} - V_{bias})$. Here, V_{bias} is the applied potential (V), J_p is the photocurrent density at the applied potential (mA cm^{-2}) and V_{WSR} is the actual water splitting reaction potential. For the tandem cell system under study, the DSC presents an open-circuit voltage of 0.797 V which is lower than the potential required for hydrogen production. Therefore, two series connected DSCs, operating just under open-circuit voltage, are used to supply the additional bias potential to the PEC cell: $V_{bias} = 1.56$ V. At this external bias, the photocurrent density of a PEC cell comprising an efficient semiconductor, as reported by Cesar⁸ and Kay¹¹, is $J_p = 1.51 \text{ mA cm}^{-2}$ and $J_p = 3.30 \text{ mA cm}^{-2}$, respectively. On the other hand, at this external bias and using undoped hematite, as reported in our recent work,²¹ the photocurrent density is $J_p = 0.35 \text{ mA cm}^{-2}$. Taking $I_s = 100 \text{ mW cm}^{-2}$ and $V_{WSR} = 1.9$ V, the effective conversion efficiency is found to be 1.12 % for the Si-doped semiconductor synthesised by APCVD (as reported in Ref. 11), 0.51 % for the Si-doped hematite obtained by USP⁸ and 0.12 % for the undoped hematite.²¹ This corresponds to a hydrogen gas production of $1.71 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}$, $7.83 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $1.81 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, respectively. In summary, the proposed tandem cell embodiment can be used to convert light into chemical energy (hydrogen) even though the efficiency of the process is strongly dependent on the semiconductor's deposition method and on semiconductor's doping agents.

8.4 Conclusion

An efficient dye-sensitized solar cell was prepared using the efficient and stable N719 dye in association with a robust ionic liquid-based electrolyte. The device was then characterised by means of its photocurrent-photovoltage performance and by electrochemical impedance spectroscopy. EIS revealed that under the present conditions the charge-transfer resistance associated to recombination of electrons at the $\text{TiO}_2/\text{electrolyte}$ interface was much higher than the electron transport resistance through the semiconductor: $R_k \gg R_w$. Accordingly, the electron lifetime τ_n was much higher than the transit time τ_{tr} , meaning that electrons tend to percolate through the semiconductor rather than react with the ionic species in the electrolyte;

consequently the diffusion length is greater than the thickness of the cell, ($L_n \gg L$), which is an essential requirement for efficient cells. Different PEC systems were considered, with doped and undoped hematite photoelectrodes, targeting the application of DSCs as suppliers of the required additional anodic bias for the production of hydrogen by water splitting. The additional applied potential necessary for actual water cleavage was supplied by two DSCs connected in series operating just under open-circuit voltage, which led to an effective conversion efficiency of about 1.12 % for the silicon-doped hematite prepared by APCVD, 0.51 % for the Si-doped hematite prepared by USP and 0.12 % for the undoped hematite. Although the efficiency of the tandem cell is still very low, the present work emphasises the ability of DSCs in supplying the external bias necessary for water splitting. Further improvements from the PEC side are therefore necessary to enhance the overall efficiency of the integrated system. In particular, the PEC cell photocurrent, which is related to the effective area of the cell, should be optimised compared to the DSC set photocurrent for obtaining higher overall efficiencies.

Acknowledgments

L. Andrade and R. Cruz are grateful to the Portuguese Foundation for Science and Technology (FCT) for their PhD grants (references: SFRH/BD/30464/2006 and SFRH/BDE/33439/2008, respectively) and H. Aguilar Ribeiro is thankful to *Programa Ciência 2007*. The authors want to thank Prof. M. Grätzel, Dr. S. M. Zakeeruddin and Dr. Md. K. Nazeeruddin at EPFL (École Polytechnique Fédérale de Lausanne, Switzerland) for their assistance and for making available all the facilities necessary to the DSCs' fabrication, making part of this investigation possible. Dr. Laura Meda (ENI Donegani Institute, Italy) is also acknowledged for providing the undoped photoanode samples.

List of abbreviations and symbols

Abbreviations	Definition	Units
AM	Air mass	
APCVD	Atmospheric pressure chemical vapour deposition	
CB	Conduction band	
C_{CE}	Double-layer capacitance at the platinised TCO	F
CE	Counter electrode	
CPE	Constant phase element	
C_{μ}	Chemical capacitance	F
DSCs	Dye-sensitized Solar Cells	
e^{-}	Electrons	
E_{CB}	Conduction band energy	J
$E^{\circ}_{H_2O/H_2}$	Standard water reduction energy	J
$E^{\circ}_{O_2/OH^{-}}$	Standard water oxidation energy	J
E_{VB}	Valence band energy	J
EIS	Electrochemical impedance spectroscopy	
FF	Fill factor	
FTO	Fluorine-doped SnO_2 conducting glass electrode	
h	Planck constant ($h = 6.62606896(33) \times 10^{-34}$ J s)	J s
h^{+}	Holes	
I	Current	mA
I_s	Incident light intensity	mW cm ⁻²
j	Imaginary number	
J_p	Photocurrent density	mA cm ⁻²
J_{sc}	Short-circuit photocurrent density	mA cm ⁻²
L	Thickness of the semiconductor film	μm
L_n	Electron diffusion length	μm
MPN	3-Methoxypropionitrile	
n	Empirical constant in constant phase elements	

NBB	1-Butyl-1H-benzimidazole	
NCS	Isothiocyanato group	
NMR	Nuclear magnetic resonance	
P_{in}	Incident power	mW
P_{out}	Power output	mW
PEC	Photoelectrochemical	
PMII	1-Propyl-3-methylimidazolium iodide	
PV	Photovoltaics	
<i>ref</i>	Reference	
R_{CE}	Charge-transfer resistance at the platinised TCO	Ω
R_k	Recombination resistance	Ω
R_s	Ohmic resistance	Ω
R_w	Electron transport resistance	Ω
RHE	Reversible hydrogen electrode	
S	Ground state of the sensitizer	
S^*	Excited state of the sensitizer	
S^+	Oxidised sensitizer	
SC	Semiconductor	
TBA	Tetrabutylammonium	
TCO	Transparent conductive oxide	
TEOS	Tetraethoxysilane	
USP	Ultrasonic spray pyrolysis	
V	Voltage	V
VB	Valence band	
V_{bias}	External applied potential	V
V_{oc}	Open-circuit photovoltage	V
V_{Redox}	Thermodynamic standard reversible potential required for water splitting	V
V_{WSR}	Actual water splitting reaction potential	V
WE	Working electrode	

$Z(t)$	Impedance	Ω
Z_d	Warburg element of the Nernst diffusion of I_3^- in the electrolyte	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

Greek symbols	Definition	Units
η	Global efficiency of a DSC	%
η_{PEC}^{pract}	Effective conversion efficiency of solar light to chemical energy	%
η_{PEC}^{total}	Total conversion efficiency of light to hydrogen of the photoelectrochemical cell	%
ν	Frequency	Hz
τ_n	Electron lifetime	ms
τ_{tr}	Transit time	ms
ω	Radial frequency	rad s^{-1}
ω_d	Characteristic frequency of diffusion	rad s^{-1}
ω_k	Characteristic frequency of recombination	rad s^{-1}

References

- (1) O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737.
- (2) Grätzel, M. *Inorg. Chem.* **2005**, 44, 6841.
- (3) Grätzel, M. *J. Photochem. Photobiol. C* **2003**, 4, 145.
- (4) Krol, R. v. d.; Liang, Y.; Schoonman, J. J. *Mater. Chem.* **2008**, 18, 2311.
- (5) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, 29, 189.
- (6) Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T. *Int. J. Hydrogen Energy* **2005**, 30, 521.
- (7) Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. *Int. J. Hydrogen Energy* **2002**, 27, 991.
- (8) Cesar, I.; Kay, A.; Gonzalez Martinez, J. A.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, 128, 4582.
- (9) Duret, A.; Grätzel, M. *J. Phys. Chem. B* **2005**, 109, 17184.
- (10) Fu, Y. Y.; Wang, R. M.; Xu, J.; Chen, J.; Yan, Y.; Narlikar, A. V.; Zhang, H. *Chem. l Phys. Lett.* **2003**, 379, 373.
- (11) Kay, A.; Cesar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, 128, 15714.
- (12) Licht, S.; Wang, B.; Soga, T.; Umeno, M. *Appl. Phys. Lett.* **1999**, 74, 4055.
- (13) Grätzel, M. *Nature* **2001**, 414, 338.
- (14) Bisquert, J. *J. Phys. Chem. B* **2002**, 106, 325.
- (15) Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, 106, 8774.
- (16) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, 35, 1168.
- (17) Kuang, D.; Klein, C.; Ito, S.; Moser, J. E.; Humphry-Baker, R.; Evans, N.; Duriaux, F.; Grätzel, C.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Mater.* **2007**, 19, 1133.
- (18) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C. H.; Grätzel, M. *Inorg. Chem.* **1999**, 38, 6298.
- (19) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, 128, 4146.

- (20) Grimes, C. A.; Varghese, O. K.; Ranjan, S. *Light, Water, Hydrogen: The Solar Generation of Hydrogen by Water Photoelectrolysis*; Springer: New York, **2008**.
- (21) Lopes, T.; Andrade, L.; Ribeiro, H. A.; Mendes, A. *Int. J. Hydrogen Energy, In Press, Corrected Proof*, doi:10.1016/j.ijhydene.2010.04.001.
- (22) Aroutiounian, V. M.; Arakelyan, V. M.; Shahnazaryan, G. E.; Hovhannisyan, H. R.; Wang, H.; Turner, J. A. *Sol. Energy* **2007**, *81*, 1369.
- (23) Liang, Y.; Cristina, S. E.; van de Krol, R. *Int. J. Photoenergy* **2008**, volume 2008, 7 pages.
- (24) Gonçalves, L. M.; Bermudez, V. d. Z.; Ribeiro, H. A.; Mendes, A. M. *Energy Environ. Sci.* **2008**, *1*, 655.
- (25) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988.
- (26) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216.
- (27) Kohle, O.; Ruile, S.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 4779.
- (28) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.
- (29) Nazeeruddin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- (30) Nazeeruddin, M.; Klein, C.; Liska, P.; Grätzel, M. *Coord. Chem. Rev.* **2005**, *249*, 1460.
- (31) Gorlov, M.; Kloo, L. *Dalton Trans.* **2008**, 2655.
- (32) Kern, R.; Sastrawan, R.; Ferber, J.; Stangl, R.; Luther, J. *Electrochim. Acta* **2002**, *47*, 4213.
- (33) Han, L. Y.; Koide, N.; Chiba, Y.; Mitate, T. *Appl. Phys. Lett.* **2004**, *84*, 2433.
- (34) Wang, M.; Chen, P.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 290.
- (35) Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A. *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.

- (36) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. J. *Phys. Chem. B* **2002**, *106*, 334.
- (37) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory, Experiment and Applications*; Second ed.; John Wiley & Sons: New Jersey, **2005**.
- (38) Kennedy, J. H.; Karl W. Frese, J. J. *Electrochem. Soc.* **1978**, *125*, 709.
- (39) Gardner, R. F. G.; Sweett, F.; Tanner, D. W. *J. Phys. Chem. Solids* **1963**, *24*, 1175.
- (40) Souza, F. L.; Lopes, K. P.; Nascente, P. A. P.; Leite, E. R. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 362.
- (41) Itoh, K.; Bockris, J. O. M. *J. Appl. Phys.* **1984**, *56*, 874.
- (42) Itoh, K.; Bockris, J. O. M. *J. Electrochem. Soc.* **1984**, *131*, 1266.
- (43) Jorand Sartoretti, C.; Ulmann, M.; Alexander, B. D.; Augustynski, J.; Weidenkaff, A. *Chem. Phys. Lett.* **2003**, *376*, 194.
- (44) Khan, S. U. M.; Akikusa, J. J. *Phys. Chem. B* **1999**, *103*, 7184.

PART IV:

FINAL CONCLUSIONS

Chapter 9

GENERAL CONCLUSIONS AND FUTURE WORK SUGGESTIONS

The present work aimed the study of phenomena occurring in dye-sensitized solar cells: electron transport in the mesoporous photoanode; electron recombination in the interface semiconductor/electrolyte; ion transport in the electrolyte; and catalytic redox reaction in the counter electrode. The objective of this study was incorporating this knowledge in a global phenomenological model able for predicting the performance of DSCs at specific conditions. It was also investigated the effect of specific operating parameters on the photovoltaic performance of the cell. Three dimensionless parameters (Da , γ and Φ) were defined to describe and characterise the performance of DSCs. On the other hand, the model was solved for unsteady-state conditions and critically compared with the transient probing technique of electrochemical impedance spectroscopy (EIS). The development of the phenomenological model is of great relevance since several operating parameters of DSCs cannot be predicted theoretically or experimentally. This can be overcome by fitting the experimental I - V characteristics and Nyquist diagrams to the phenomenological model under steady and unsteady-state, respectively. In the present study, the experimental data showed very good agreement with the simulation results. Moreover, steady-state and transient profiles were obtained, originating pertinent information about the concentration species evolution as a function of the cell thickness (x -axis) and as a function of time.

Another important objective of the present work was to characterise DSCs by electrochemical impedance spectroscopy, showing the potentiality of this technique concerning electrochemical characterisation. EIS was used to assess, at specific conditions of bias voltage and illumination, electron transport in the porous semiconductor film and electron recombination at the TiO_2 /electrolyte interface. In fact, this technique in association with electrical analogues interpretation showed consistent conclusions in line with other characterisation tools as photovoltaic performance and photovoltage transient decay evaluation methods. Ultimately, it

was demonstrated that charge-collection efficiency is an adequate parameter to evaluate the performance of a DSC and it can be computed based on impedance spectroscopy measurements. For that, an equation relating the transport and recombination phenomena was proposed bearing in mind that the collection efficiency only depends on these two main competing processes that rule the performance of a DSC. This approach allows to overcome all the problematic concerning the calculation of diffusion length due to the uncertainties that surround the kinetics of injected electrons recombination reaction with redox electrolyte species.

Some stability tests were also performed. For that, the effect of substituting tetrabutylammonium (TBA) counter ions from the standard N719 dye by sodium and potassium ions on the performance and stability of DSCs was evaluated in the presence of two different electrolytes. It is known that the number of protons and the nature of cations of the dye influence the open-circuit potential and the short-circuit current of DSCs. Thus, the synthesised new dye, where two TBA cations were substituted by sodium ions, in combination with a low-volatile electrolyte, gave a photovoltaic power conversion efficiency of 7.6 % at 1 sun AM 1.5 illumination conditions. Moreover, this system revealed a striking stability when submitted to full sunlight soaking at 50 °C, retaining almost 99 % of its initial photovoltaic performance.

An innovative process to improve the efficiency of dye-sensitized solar cells was also proposed. The conventional structure of DSCs was modified by coating the counter electrode backside with a reflective paint layer in order to reflect back to the semiconductor a portion of the light that crosses the photoelectrode. There was no negative effect of this layer in the inner components of the cell. The material of choice was a cheap commercially available water-base white paint. DSCs back-coated with the white paint showed an efficiency increase of ≈ 7 % for the system with a double-layered TiO_2 film and almost 10 % when using a TiO_2 semitransparent film.

Finally, the knowledge acquired with the photoelectrochemical study of DSCs was applied to study photoelectrochemical (PEC) cells for water splitting. It was developed a transient phenomenological model of PEC cells for water splitting using an undoped

hematite photoanode. The influence of several operating conditions was simulated and namely the free electrolyte thickness, hole diffusion length and Butler-Volmer kinetics. It was observed that the decrease of the free electrolyte thickness originates the decrease of the ionic mass transfer in that region and the increase of the photocurrent density. The reduction of water at the platinum counter electrode was described based on the Butler-Volmer equation allowing to obtain the platinum overpotential as a function of the observed current density. Since the present PEC cells need an external bias to assist water photocleavage, two DSCs were coupled to a PEC cell in a tandem arrangement, illustrating a practical use of DSCs devices. The additional applied potential necessary for actual water cleavage was supplied by two DSCs connected in series operating just under open-circuit voltage, leading to an effective conversion efficiency of about 1.12 % for silicon-doped hematite prepared by APCVD. However, the efficiency of the tandem cell was still very low, allowing to conclude that further improvements from the PEC side are necessary to enhance the overall efficiency of the integrated system. In particular, the PEC cell photocurrent, which is related to the effective area of the cell, should be optimised compared to the DSC set photocurrent for obtaining higher overall efficiencies.

It is believed that dye-sensitized solar cells can be the next generation of power source contributing to an effective entrance of solar devices in our daily lives. Moreover, the easy-of-use of electronic portable equipments based on DSCs and the architectural end-use of dye photovoltaic cells can be important aspects pushing forward these cells to be a decisive alternative to conventional devices. Additionally, the low-cost of fabrication and the versatile applications, as flexible or light-weight products, can state their final penetration in the photovoltaic market - see *e.g.* Figure 9.1. However, to turn all these ambitions to a marketable product several efforts are still needed. Developments in the area of sensitizers should include some new dyes absorbing a broader solar spectrum portion leading to higher efficiencies; in this respect, the production costs and sustainability are also relevant. In fact, the advent



Figure 9.1 - Example of an architectural application of DSCs.¹

of nanotechnology has opened a window of opportunity for the development of more efficient and environmental friendly materials at considerably lower costs. For instance, the application of nanotechnology in recent developments of nanostructured semiconductors with enhanced electric conductivity and more accessible pores to the electrolyte has been especially important for solid-state DSCs, which are typically more stable but less efficient. For liquid-based electrolytes, it is of extreme importance the development of new solutions that suppress electron recombination with the redox mediator. Moreover, the replacement of volatile solvents by additives will increase not only the cell efficiency but mainly its stability. This is, in fact, a basic requirement for all solar cell technologies and for DSCs in particular. Despite all the efforts to enhance DSCs' performance, long-term stability is still a major issue that limits market implementation of this technology. As an example, for construction-integrated applications it is expectable that DSCs

¹ from <http://gadgets.boingboing.net/2008/12/07-week/>

performance remains stable for no less than 20 years. State of the art knowledge in long-term stability suggests that efficient encapsulation of the DSCs must be guaranteed to avoid degradation induced by atmospheric factors. Current materials used to encapsulate DSCs do not ensure hermetic sealing of the cell, as they typically degrade at temperatures around 60-80 °C. New sealing materials and methodologies are now being developed in an effort to foster the commercialisation of DSCs. The use of new materials and sealing processes will certainly require optimisation in terms of operating conditions such as the temperature of sealing and cell design (including the size and shape of the active layers). Here, both the empirical and the phenomenological models described in this thesis may play an important role in the identification of the most promising approach to get an optimised DSC.

In what concerns the phenomenological point of view, several uncertainties surround the recombination kinetics in DSCs and the respective parameters that govern the solar cells behaviour. Some models assume that the rate at which electrons are transferred from the conduction band to the redox electrolyte follows a first reaction order in free electron concentration. On the other hand, it has been suggested by other authors the non-ideal behaviour of DSCs, which may arise from the fact that the recombination process is mediated by electronic surface states below the conduction band of the oxide. This non-linearity should be studied to allow a deeper comprehension of the phenomena behind the recombination process. The simulated results should be experimentally validated for different types of DSCs. Besides the study of the diffusive and migration terms, a more complex model should be developed considering also the effect of microscopic electric fields in the cell and screening effects as well as Helmholtz and diffuse layers. Finally, the generation term should include detailed information about the photoexcitation process by considering the different semiconductor's structures and dye's characteristics.