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DEVELOPMENT OF CATHODES FOR SODIUM ION BATTERIES

HUGO GOMES CRUZ

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Hugo Gomes Cruz

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Supervisor at FEUP: Prof. Adélio Mendes

Co-supervisor at FEUP: Dr. Rita Figueira

Coordinator at Simoldes Plásticos, Lda: Eng. Jaime Monteiro



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Abstract

Rapid population growth and technological developments have increased the demand for electrical energy. Therefore, it is essential to develop new energy storage systems to facilitate the integration of renewable energies into the electrical grid and strive towards a sustainable future. Sodium ion batteries (SIBs) is a promising energy storage technology to complement the commercially available lithium-ion batteries (LIBs). SIBs are regarded as an interesting drop-in technology due to their similar arrangements and storage mechanism to LIBs. In addition, SIBs have a higher power density, safety, stability, are more environmentally friendly, and less expensive than LIBs; however, due to the intrinsic properties of sodium ions, SIBs currently exhibit lower energy density than LIBs. As a result, in practical applications, SIBs have mostly been recognized as a promising technology for stationary applications. The electrochemical performance and storage capacity of a SIB is heavily influenced by the different components within a battery cell, the most important of which is the active cathode material. From the different families of cathode materials, layered transition metal oxides surge as one of the most attractive due to their high capacity, low cost, simple and scalable synthesis.

The goal of this project was to synthesize, by solid-state reaction, and study seven distinct layered oxide cathode materials derived from $\text{Na}_x\text{NiMnO}_2$ and NaMnO_2 . Electrode preparation and experimental optimization was also conducted by testing different binders, mixing strategies and solvent evaporation rates. Coin cells CR2032 were assembled and electrochemically tested to achieve a working SIB.

An initial parametric study of different synthesis conditions was carried out. It was determined that an additional calcination step can minimize the presence of carbonate compounds. Also, cathodes subjected to the ball mill revealed a lower carbonate content. In addition, it was concluded that the use of water must be avoided. Almost all the materials exhibited the expected crystalline structure with a low impurities content, with only one cathode material showing a mixture of two different phases. The developed optimal electrode preparation procedure includes a mass fraction of 85 % active material, 5 % conductive carbon, and 10 % binder- PVDF. These components were mixed using a magnetic stirrer at 200 rpm, and the solvent (NMP) was evaporated at room temperature. Fresh coin cells were submitted to EIS testing; these tests indicated that a higher mass loading and differences in electrolyte volume may lead to an increase in the ohmic resistance. Finally, a coin cell prepared with commercial $\text{Na}_{0.7}\text{MnO}_{2+x}$ cathode was electrochemically tested and revealed smooth charge discharge curves, and an initial charge and discharge capacity of $73.5 \text{ mAh}\cdot\text{g}^{-1}$ and $24.4 \text{ mAh}\cdot\text{g}^{-1}$, respectively. The capacity decay observed during cycling may be related with SEI formation.

Keywords:

Sodium ion battery, cathode material, layered oxides, O3-structure.

Resumo

O rápido crescimento populacional e os recentes desenvolvimentos tecnológicos têm vindo a aumentar a procura de energia elétrica. Deste modo, o desenvolvimento de novos sistemas de armazenamento de energia é essencial, de modo a facilitar a integração de fontes de energias renováveis na rede elétrica e diminuir o uso de fontes de energia fósseis.

As baterias de íão sódio (do inglês, SIBs) apresentam-se como uma tecnologia de armazenamento de energia capaz de complementar as baterias de lítio (LIBs). As SIBs são consideradas como uma tecnologia capaz de ser produzida nas linhas da manufatura já existentes para as baterias de lítio, uma vez que apresentam uma constituição e princípios de funcionamento muito semelhantes. Além disso, as SIBs apresentam maior densidade de potência, são mais seguras, apresentam menor impacto ambiental e são mais baratas em comparação com as LIBs. No entanto, devido às intrínsecas propriedades dos íões de sódio, as SIBs apresentam, atualmente, uma menor densidade de energia quando comparadas com as LIBs. Assim sendo, em aplicações práticas, as SIBs têm sido reconhecidas como uma tecnologia viável para aplicações em sistemas estacionários. O desempenho eletroquímico e a capacidade de armazenamento de uma bateria de sódio são fortemente influenciados pelos diferentes componentes de uma célula de bateria, sendo o cátodo o mais importante destes componentes. Das diversas famílias de materiais existentes para o cátodo, os óxidos metálicos surgem como os mais atraentes devido à sua alta capacidade, baixo custo e fácil síntese.

O principal objetivo deste projeto consiste em sintetizar, por reação em estado sólido, sete óxidos metálicos, derivados das famílias $\text{Na}_x\text{NiMnO}_2$ e NaMnO_2 , como possíveis cátodos para baterias de sódio. Para além disso, o processo de preparação dos elétrodos e respetiva otimização experimental foi realizada através do teste de diferentes ligantes, estratégias de mistura e taxas de evaporação de solventes. Finalmente, baterias CR2032 (tipo moeda) foram construídas e testadas electroquimicamente, com objetivo de produzir uma bateria de sódio funcional.

Inicialmente, foi realizado um estudo paramétrico de diferentes condições de síntese. Foi observado que uma etapa adicional de calcinação permite minimizar a presença de carbonatos. Além disso, os cátodos preparados no moinho de bolas revelaram um menor teor de carbonatos. Por outro lado, a utilização de água durante o processo de produção do cátodo revelou-se inviável. Quase todos os materiais sintetizados apresentam a estrutura cristalina esperada com um baixo teor de impurezas, verificando-se uma mistura de duas estruturas cristalinas em apenas um material. O procedimento desenvolvido e otimizado para a preparação dos elétrodos inclui uma composição em percentagem, em massa, de 85 % de material ativo, 5 % de carbono condutor e 10 % de ligante (PVDF), uma mistura dos diferentes componentes com rotação magnética a 200 rpm e evaporação do solvente (NMP) à temperatura ambiente.

Células de moeda CR2032 foram submetidas a testes de EIS, a partir dos quais foi possível concluir que uma maior quantidade de material ativo por área de eletrodo, ou diferenças no volume de eletrólito presente podem levar a uma maior resistência ôhmica. Finalmente, uma célula tipo moeda preparada com o cátodo comercial $\text{Na}_{0.7}\text{MnO}_{2+x}$ foi testada electroquimicamente, sendo observadas curvas de carga e descarga com poucos planaltos, e uma capacidade inicial de carga e descarga de $73,5 \text{ mAh}\cdot\text{g}^{-1}$ e $24,4 \text{ mAh}\cdot\text{g}^{-1}$, respetivamente. A diminuição da capacidade da bateria encontra-se diretamente ligada com a formação da SEI.

Palavras-Chave:**Bateria de sódio, cátodo, óxido metálico, estrutura O3.**

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source.

Hugo Gomes Cruz

(Hugo Gomes Cruz)

4 July 2022

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Notation and Glossary

a	Lattice parameter	Å
A	Area of each electrode	cm ²
b	Lattice parameter	Å
c	Lattice parameter	Å
E^0	Standard Electrode Potential	V
m_{coat}	Coating mass in the positive electrode	mg
$Q_{\text{theo,cat}}$	Theoretical capacity of the cathode material	mAh·g ⁻¹
$Q_{\text{theo,cell}}$	Theoretical capacity of the coin cell	mAh
r	Ionic radius	Å
$r_{\text{cat,elec}}$	Ratio of active cathode material in the positive electrode coating	
R_{ct}	Charge transfer resistance	Ω cm ²
R_{p}	Reliability factor	%
R_{WP}	Reliability factor	%
R_{Ω}	Ohmic resistance	Ω cm ²
W	Walburg impedance	Ω

Indexes

x	Stoichiometric amount of sodium in the cathode material
ϵ	Monoclinic distortion

List of Acronyms

2D	Two dimensional
3D	Three dimensional
CDC	Charge-discharge cycles
CEI	Cathode electrolyte interphase
CV	Cyclic voltammetry
EC	Ethylene carbonate
ECL	Ethyl cellulose
EIS	Electrochemical Impedance Spectroscopy
EU	European Union
FTIR	Fourier transform infrared spectroscopy
GHG	Greenhouse gas
LIB	Lithium-ion battery
n	Chemistry number
NMP	N-methyl-2-pyrrolidone
PC	Propylene carbonate
PVDF	Poly(vinylidene) fluorine
RSC	Residual sodium compounds
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SIB	Sodium Ion battery
TM	Transition metal
XRD	X-ray diffraction

1 Introduction

1.1 Energy Storage

Energy consumption has risen exponentially due to population and economic growth. Global electric power consumption *per capita* has increased from 2200 kWh in 2000 to 2900 kWh in 2020, with the latter being 5 % lower than the value recorded in 2019 due to the pandemic situation (Appendix A, Figure A.1) [1,2]. Still, most of the primary energy sources are fossil, namely coal, oil and natural gas (Appendix A, Figure A.2) [3]. For instance, in 2020, the use of fossil fuels accounted for 70 % of the primary energy used in the European Union (EU), 1 % less than in 2019 (Appendix A, Figure A.3) [4]. Aside from being a finite energy source, the use of fossil fuels highly impacts the environment, contributing to global warming.

Even though fossil fuels have been a reliable energy source for more than a century, global efforts are now underway to fully decarbonize the economy. One example of such efforts is the Paris Agreement, proposed by the United Nations in 2015, which established a goal to limit the increase in global average temperature to 1.5 °C above pre-industrial levels [5]. To comply with this agreement, all parties involved must make major pledges to significantly reduce greenhouse gas (GHG) emissions and, therefore, reduce the impact on the environment. Recently, the EU proposed the Fit for 55 package, a collection of legislative initiatives across different sectors aimed at reducing GHG emissions by at least 55 % in 2030 compared with 1990 levels [6]. Renewable energy sources such as solar, wind, geothermal, wave, tidal and others, have seen a gradual growth in their use to control GHG emissions and strive towards a clean future (*cf.* Figure 1.1). In 2020, renewable energies accounted for 22 % of the energy consumed in the European Union [7]. Nonetheless, major transformations in the energy sector are required to fulfill the EU target of renewable energy accounting for, at least, 32 % of the final energy consumption by 2030 [8].

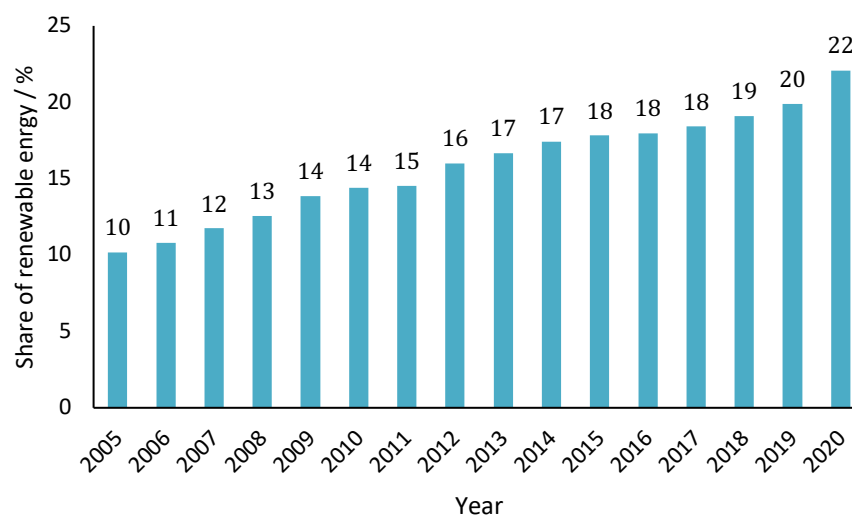


Figure 1.1 - Share of renewable energy in gross final energy consumption [9].

Even though renewable energy sources are inexhaustible on a human scale, do not contribute to the green-house effect, and are mostly available worldwide, they are often intermittent and hence not dispatchable. Therefore, energy storage systems that can store energy during periods of lower energy demand (off-peak hours) and subsequently employing it during periods of over demand are essential. Global energy storage installations are expected to reach a total of 360 GW/1000 GWh by the end of 2030, more than twenty times than the 17 GW/34 GWh recorded at the end of 2020 [10].

1.2 Sodium Ion Batteries

Among the different energy storage technologies (Appendix A, Figure A.4), rechargeable batteries, also known as secondary batteries, have received unparalleled attention. Rechargeable batteries can store chemical energy and efficiently converting it to electricity. This is a promising technology for large-scale energy storage, as well as for portable devices due to their high flexibility, high energy conversion efficiency and simple maintenance [11].

Within the rechargeable batteries, lithium-ion batteries (LIBs) have been widely implemented and have achieved unmatched progress since their first commercialization by Sony in 1991 [11]. Currently, LIBs are widely implemented in portable devices such as smartphones and laptops, household energy storage systems, and in the automotive sector as an alternative to combustion engines due to their high energy and power densities and long cycle life. Additionally, LIBs may also be used in stationary applications to smooth the intermittency of the renewable electricity in the grid [12].

Even though LIBs have the potential to contribute to sustainable energy usage, the sustainability of lithium exploration must be considered. Lithium abundance is limited to only 20 ppm in the earth's crust, as shown in Figure 1.2. This emphasizes the critical importance of a sustainable use of this resource [13].

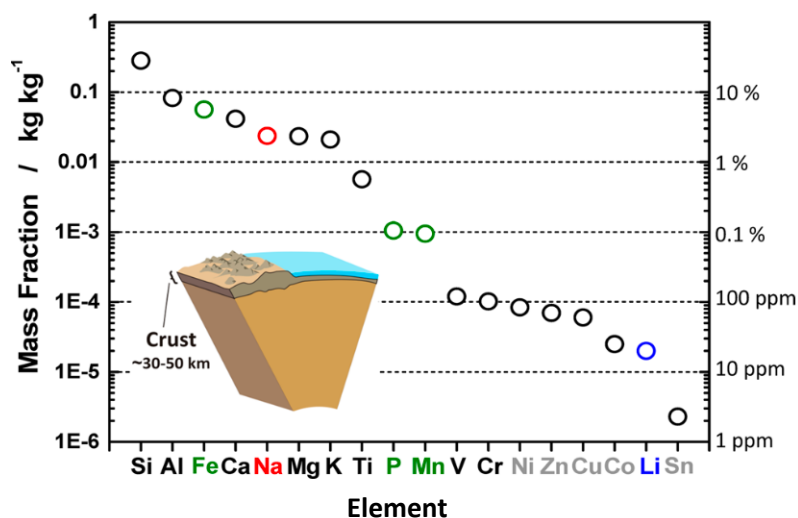


Figure 1.2 - Distribution of several elements in the earth crust [13].

Furthermore, aside from the fact that the reserves of this resource are highly geographically concentrated, mostly limited to South America (Appendix A, Figure A.5) [14], the increased use of LIBs in recent decades has resulted in a rise in demand for raw materials. The rising demand for lithium and, in particular, critical raw materials such as cobalt, has led to an exponential increase in their prices [15]. Therefore, worldwide concerns and tremendous attention have been paid to search for new LIBs replacements, with sodium-ion batteries (SIBs) emerging as an attractive alternative. This can be shown by the notable increase in SIB-related articles reported since 2010 [16]. The 1970s and 1980s saw the development of LIBs and SIBs. However, due to the successful commercialization and technological advances of the LIB technology, subsequent research on SIBs was abandoned until very recently. Rising demand for LIBs because of current technological breakthroughs, as well as unsustainable lithium exploration and ultimate depletion, sparked the search for alternative energy storage technologies. One major breakthrough regarding SIBs was reported in 2000. Stevens and Dahn observed that hard carbon used as an anode material could result in a reversible gravimetric capacity fairly close to the observed on graphite anodes used in LIBs [17]. Currently, most studies focus on the electrochemical performance of new electrode materials, with the aim of developing materials with high capacity, good cyclability and extended cycle life at the lowest possible cost.

1.3 SIB versus LIB technology

Sodium-ion batteries have very similar structures, components, systems, and charge storage mechanisms to LIBs. Thus, the manufacturing protocols and processes for SIBs are projected to be the same as those for LIBs, with no significant investments in new manufacturing lines, making SIBs a very interesting drop-in replacement for LIBs [18]. Additionally, sodium is one of the most abundant elements in the earth's crust and endless sources of sodium can be easily found. Therefore, the price of sodium is substantially lower than lithium: lithium costs roughly 14000 € a tonne to mine and process while sodium costs only 140 € per tonne [19]. Furthermore, instead of using materials such as cobalt and natural graphite, classified as critical raw materials by the European Commission [20], SIBs use more abundant and environmentally friendly resources.

Another key advantage of SIBs over LIBs is their superior safety characteristics. Aluminum foils can be used as current collectors on both electrodes in SIBs. In LIBs case, aluminum and copper are used as current collectors in the cathode and anode, respectively [12,21]. Using aluminum as the current collector in both electrodes allows for the discharge and storage of a SIB at 0 V with no degradation, allowing for easier and safer battery handling and transport [22]. NOVASIS Energies Inc. exhibited SIBs with outstanding safety features by subjecting a pouch cell to a crush test and nail piercing without catching fire, a major hazard associated with LIBs applications [12]. Moreover, the lower cost of aluminum compared to copper, as well as a the lower weight and improved recyclability, make SIBs a more cost-

effective and ecologically friendly alternative to LIBs [11]. Additionally, SIBs reveal a higher power density when compared to LIBs, which allows for a fast charge and discharge process.

Sodium is in the same group of the periodic table as Li and has several chemical and physical properties that are similar to Li, as shown in Table 1.1 [13,23]. Nevertheless, even though SIBs are substantially less expensive than LIBs, SIBs have a lower energy density when compared to LIBs. This results from the fact that sodium atoms are larger (higher ionic radius, r) and heavier than lithium atoms, as well as having a lower standard electrode potential (E^0) [23]. Therefore, for the same energy storage capacity, a SIB will have a substantially higher weight and volume in comparison to a LIB [14].

Table 1.1 - Comparison of lithium and sodium as charge carriers.

Charge Carrier	Li	Na
Ionic Radius / Å	0.76	1.02
E^0 (vs SHE) / V	3.04	2.71
Atomic Mass / g mol⁻¹	6.94	22.99
Gravimetric capacity / mAh g⁻¹	3829	1165
Melting point / °C	180.5	97.7
Coordination preference	Octahedral and tetrahedral	Octahedral and prismatic

1.4 Presentation of the company

Simoldes Plásticos is an international manufacturer of plastic components for the automotive industry (Tier 1), with companies such as Stellantis, Volkswagen, Renault and Toyota Groups among its customers. Simoldes Plásticos is the leading company of Simoldes Group plastics division, which is a renowned Portuguese business group of international success, composed of 2 divisions: the mold division, dedicated to the production of molds for thermoplastic injection and plastics division, dedicated to the production of plastic injection parts. With unique engineering and product development capabilities in terms of thermoplastic injection molding and feasibility analysis, Simoldes also has extensive knowledge of the needs and expectations of markets and customers. Simoldes Plásticos has a department called "Research and Innovation", which integrates 12 people. Over the years, Simoldes Plásticos has actively participated in several R&D projects, revealing a strong competitive positioning and a concern to monitor, or even anticipate, the needs of demand and present differentiating solutions to its customers. According to its new strategic vision, Simoldes Plásticos has been developing knowledge in the area of energy storage, both for mobility and stationary applications, area in which this work is inserted.

1.5 Contribution of the author to the work

In recent years, the search for novel and sustainable solution to integrate renewable energies into the electrical grid has been gaining a lot of attention and interest. Many researchers have devoted their efforts on developing new energy storage systems, more energy efficient technologies, and new materials that can enhance the safety of these technologies, all while making a cost-effective process with potential large-scale application to achieve a fully decarbonized economy.

In this work, the author synthesized seven different active cathode materials derived from $\text{Na}_x\text{NiMnO}_2$ and NaMnO_2 , already reported in the literature, for sodium-ion batteries. The author performed FTIR analysis on the synthesized materials, and the physical characterization of the synthesized cathode materials by XRD and SEM was performed and assessed by the author with the assistance of the Universidade de Trás-os-Montes e Alto Douro. The author also accomplished the electrode fabrication and the associated optimization process. Finally, the author assembled the coin cells, conducted electrochemical tests, and characterized the electrochemical performance of such coin cells.

1.6 Organization of the dissertation

Energy storage systems have become essential with the development of the modern world. However, due to the unsustainable exploration of lithium, a potential replacement for LIBs is an area of great research. The goal of this project was to acquired knowledge regarding the synthesis and characterization of cathode materials and assembly of a working sodium-ion battery. This master thesis is divided into 6 chapters.

Chapter 1 addresses the present issues surrounding the integration of renewable energies into the grid and compares the major technological differences between sodium and lithium-ion batteries.

Chapter 2 examines the fundamentals principles of operation of a sodium-ion battery, including information on the different components of a sodium ion cell and respective properties, as well as prospective applications for this technology. This significance and impact of the cathode material on the electrochemical performance of a sodium-ion battery are also discussed in this chapter.

Chapter 3 describes the entire experimental procedure of the laboratory work performed, including material synthesis, electrode and electrolyte preparation, and coin cell assembly.

Chapter 4 covers and discusses the main results obtained from different synthesis procedures, physical characterization of the synthesized materials, optimization of the electrode preparation process, and electrochemical performance on the coin cells assembled.

Chapter 5 describes the main conclusions taken from the work performed during this project.

Chapter 6 highlights the main objectives accomplished from this project.

2 Context and State of the Art

2.1 Working principles of a sodium-ion battery

SIBs have very similar components, arrangements, and charge storage mechanism as LIBs. However, the charge carries instead of being lithium ions (Li^+) are sodium ions (Na^+). Conventional SIBs have five main components: a positive electrode, a negative electrode, a liquid electrolyte, current collectors, and a separator [13]. Figure 2.1 shows a schematic representation of a SIB.

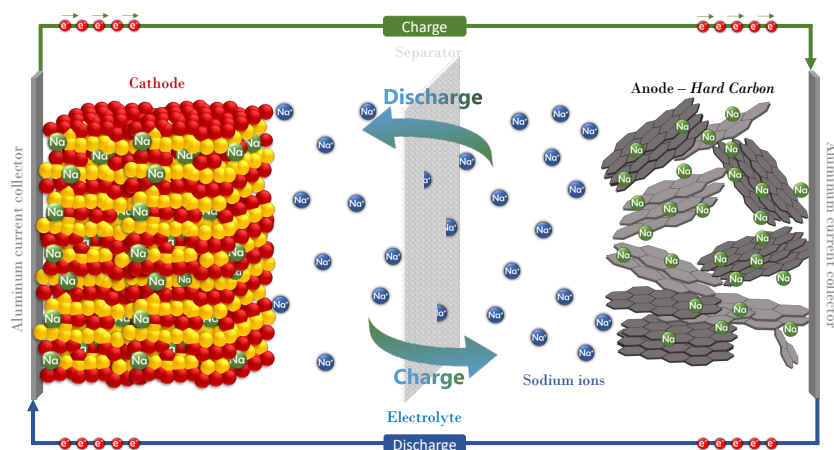


Figure 2.1 - Sketch of a sodium-ion battery.

The negative and positive electrode of a SIB are both intercalation compounds, where sodium ions are reversible incorporated during charge and discharge, respectively. During the charge state of a battery, the positive electrode undergoes oxidation - anode, releasing electrons to the negative electrode - cathode. On the other hand, during the discharge, electrons travel in the opposite direction, from the negative to the positive electrode. In this second situation, the positive electrode is the cathode since it receives electrons and is reduced. As commonly accepted, and used throughout this project, the terms cathode and anode refer to the positive and negative electrodes during discharge, respectively.

When the battery is assembled, the ionic charges are located in the positive electrode and the battery is completely discharged. When connected to an external power source, however, Na^+ ions and electrons are transported to the negative electrode by the electrolyte through the separator and the external circuit, respectively [24]. On the other hand, when the battery is being discharged, the process is reversed: Na^+ ions and electrons will flow from the negative electrode to the positive electrode in the same way as during the charge process.

An external circuit connects the cathode and anode and allows the transport of electrons during charge and discharge. To achieve this connection, the cathode and anode are coated onto an aluminum foil substrate, the current collectors, with this foil also serving as a physical support [21].

The electrolyte works as an ionic conductive medium, allowing the movement of Na^+ ions from the cathode to the anode and vice-versa. Furthermore, to protect the battery from short-circuiting, the separator keeps the cathode and anode separated [24].

However, it is worth noting that the most used electrolytes have a narrow thermodynamical stability window and start to decompose at potentials above (positive electrode) or below (negative electrode) their electrochemical stability limits. Therefore, in the initial cycle of the battery, as the voltage increases during the charging process, the electrolyte decomposes as a result of the chemical reaction between the sodium in the electrodes and the electrolyte salt/solvent, and an interfacial layer is formed at the interface between the electrodes and the electrolyte, known as SEI (solid-electrolyte interphase) at the anode and CEI (cathode-electrolyte interface) at the cathode [25]. As a result, the sodium that reacts with the electrolyte becomes unavailable in succeeding cycles, reducing the battery's capacity [26].

The stable interfacial layer, once formed, prevents further electrolyte decomposition, and consequently, prevents additional capacity loss. However, without a stable SEI, the passivation reaction continues, resulting in a drop in battery capacity (due to the continuous consumption of Na^+ ions), as well as an increase in impedance, both of which reduce the battery's electrochemical performance. Therefore, the formation of these interfacial layers is crucial for the functionality of the cell, as they must be electronically insulating, highly conductive for Na^+ ions, and insoluble and inert in the electrochemical environment of the cell [25].

Various parameters such as specific capacity, energy density, power density, cycle life, C-rates, and coulombic efficiency are used to evaluate the electrochemical performance of the batteries. These parameters are discussed in greater detail in Appendix B.

2.2 Components and Materials of SIBs

A sodium-ion battery consists of a combination of two or more cells connected in a series/parallel mode to satisfy the specific requirements of a given application. The core components of a sodium-ion battery are the electrodes, the electrolyte, the separator and the current collectors [27]. The mass fraction of each component within a SIB is depicted in Figure C.1, Appendix C.

2.2.1 Electrodes

The electrodes are the most important components of an electrochemical cell. As previously stated, the positive electrode is generally referred as cathode and the negative electrode known as the anode. Both electrodes are comprised of an active material (which defines the capacity and potential of the cell), a conductive additive (typically carbon black or other conduction carbon), and a binder coated onto thin aluminum substrate. The binder acts as an adhesive that keeps the active material and the conductive additive settled on the aluminum substrate [27].

Cathode material

The cathode material determines the overall performance of a SIB, particularly the capacity and the potential of the cell. Therefore, it is critical to develop cathode materials with exceptional electrochemical properties. Since the synthesis and optimization of the cathode material is the topic of this project, the cathode materials will be examined in greater detail from section 2.4 onwards.

Anode material

The search for a suitable anode material for SIBs is more challenging than the search for a cathode material, since only a few materials have been identified as useful anodes [27]. For instance, graphite, a commonly used material for the negative electrode in LIBs, cannot be employed as an insertion host of sodium ions due to the formation of an unstable SEI [13]. Metal oxides, metal alloys and carbonaceous materials have been reported as potential active anode materials, with hard carbon (also known as graphitic carbon) considered as the prime choice due to its lower working potentials, high capacity, and high reversibility and cycling stability [28].

2.2.2 Electrolyte

The electrolyte, for any electrochemical energy storage device, is substantially less explored when compared to other active materials such as the electrodes. The reasoning for this is that the qualities of the electrode materials define more eye-catching properties, such as energy density [29]. However, the electrolyte significance should not be overlooked since it is responsible for factors such as life-length, reversible capacity, rate capability, and safety of the cell.

The electrolyte works as an ionic conductive medium, allowing the movement of Na^+ ions from the cathode to the anode and vice-versa. Therefore, the electrolyte must have high ionic conductivity to allow an efficient transport between electrodes. In addition, the electrolyte must be electronically insulating to prevent short-circuiting and self-discharge, have a large electrochemical window to avoid decomposition during the process, and must be chemically inert with all battery components [30]. In most situations, the electrolyte is a mixture of aprotic polar solvents with dissolved Na salts (typically NaPF_6 or NaClO_4), with additional additives that can be added to improve the compatibility between the electrolyte and the electrodes [29,31]. Apart from liquid electrolytes, solid-state electrolytes have also been developed to improve safety and to simplify the cell design [32].

2.2.3 Separator

The separator is a porous membrane that prevents the battery from short-circuiting during the crimping of the cell, and so, ensures the safety of the cell, allowing Na^+ ion to flow freely while preventing electronic flow [27]. Even though it is the least critical component regarding battery performance, the separator should be chemically inert, have high porosity, high wettability and low cost [30].

2.2.4 Current collectors

Despite the fact that current collectors are considered as non-active materials, current collectors can have a substantial impact on the performance of SIBs [21]. For instance, reducing the thickness of the current collectors can reduce their mass fraction, and thus, increase the energy density of the cell. Nevertheless, reducing its thickness will sacrifice electrical conductivity by increasing the resistance. As a result, when designing these current collectors, the point of thickness that maximizes energy density without endangering cell performance must be identified [21].

2.2.5 Cell geometry

The geometry of a battery cell can take several shapes such as coin, pouch, cylindrical or prismatic cells, as shown in Figure 2.2 [27]. The decision of which cell type to build and test depends on the technology readiness level of a given sodium-ion battery specification.

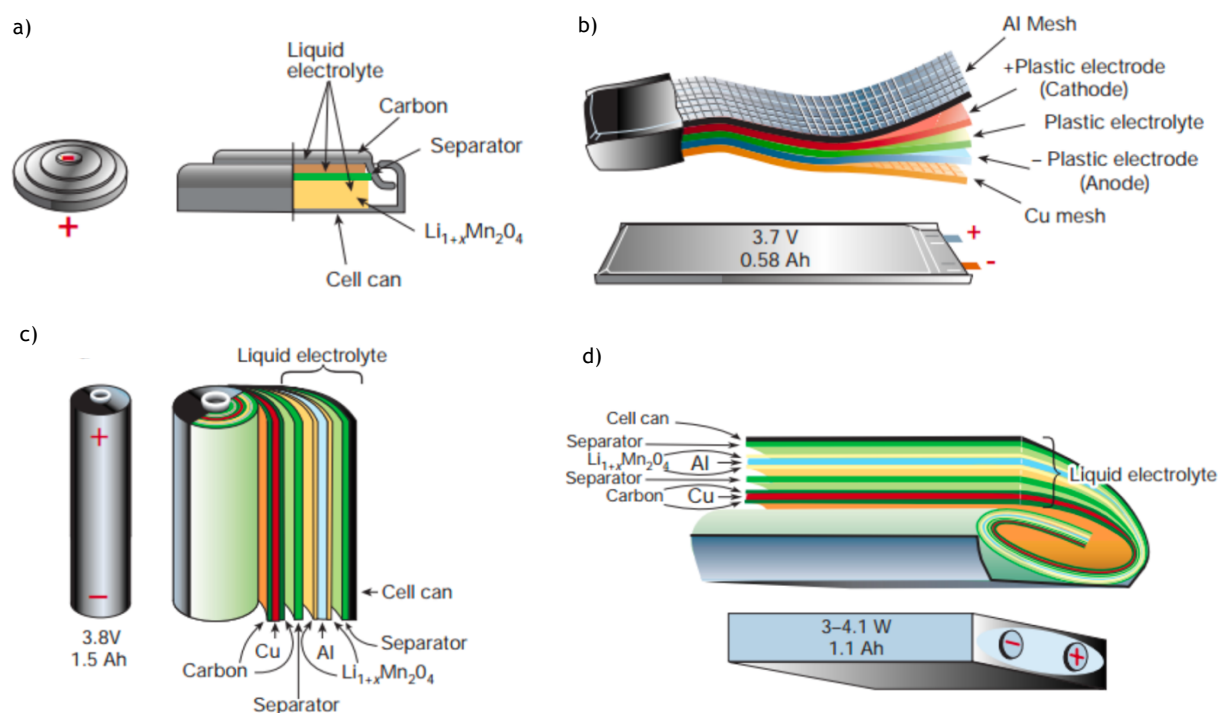


Figure 2.2 - Different types of cell geometry a) coin, b) pouch, c) cylindrical, d) prismatic [33].

Coin and pouch cells are frequently used for basic electrochemical tests of potential active materials. Coin cells are relevant to perform basic electrochemical tests as they allow to use a small amount of active material, lowering costs; however, the high performance of coin cells is hardly replicated on a larger scale. In contrast, despite using more material and having a more complex assembly, the results achieved by a pouch cell are more representative of the cell's actual performance. Cylindrical and prismatic cells are used industrially since they hold more active material and, so, have higher specific capacities; however, these features exclude them from being used for testing when the active material is not yet well specified.

2.3 Potential applications of SIBs

Currently, different SIBs configurations, in different stages of development, with different cathodes, anodes and electrolytes are already available. Therefore, the selection of the most suitable battery for a given application should be made based on an evaluation of different aspects such as cost, energy density, reliability, and safety. At an industrial level, it is worth noting that in the production and development of SIBs, the companies Faradion Limited, Tiamat, HiNa Battery, and Natron Energy stand out (Appendix C, Table C.1) [34].

To explore the applicability of currently available SIBs, it is necessary to compare them with some of the most commonly used LIBs. Figure 2.3 depicts the Ragone plot in which the energy density of SIBs is compared with the energy density of LIBs used in various applications.

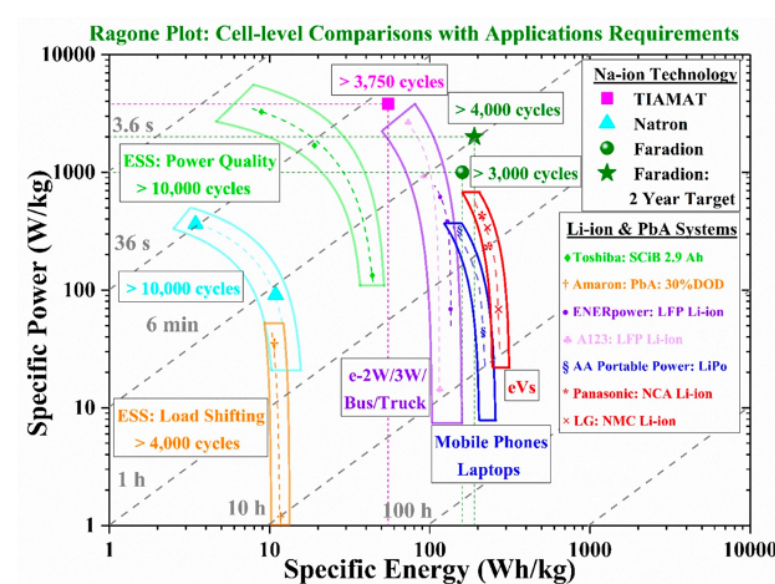


Figure 2.3 - Comparison of SIBs with the energy requirements of various applications [18].

The analysis of Figure 2.3 reveals that, as previously stated, SIBs currently have lower energy density than LIBs, and thus, are not yet suited for applications that demand this feature, such as portable electronic devices and battery vehicles [34].

An example of a SIB application identified by Natron Energy is one where SIBs are primarily used to power data centers and where they also function as a backup system for off-grid sites [35]. In addition, Figure 2.3 also illustrates that Faradion Limited's technology has, or at least currently reports, the highest energy density. The reported technology was introduced in 2013 in electric bicycles and scooters with a high degree of success [36]. In 2018, Faradion Limited was able to produce a pouch cell with a capacity of 12 Ah and $140 \text{ Wh}\cdot\text{kg}^{-1}$, with this value increasing to 32 Ah and $160 \text{ Wh}\cdot\text{kg}^{-1}$ in 2020 [36].

Nonetheless, it is expected that the energy density of LIBs will always be higher than SIBs [12]. Therefore, the use of SIBs in applications requiring high energy density, such as long-range battery vehicles

and electronic devices, is not the most appropriate choice. However, in stationary applications (e.g., in the electrical grid), where size and weight are not such limiting factors as power density, high durability, safety, and battery cost, SIBs are a promising and complementary technology to LIBs [14]. Faradion is currently developing batteries to replace conventional lead acid batteries, with applications ranging from low-speed battery vehicles to stationary energy storage systems. Due to their fast response and safety assurance, SIBs are a strong contender to replace other traditional systems and may have applications in short-range battery vehicles such as scooters, buses, and cars [36,37].

In addition to isolated applications of SIBs, considering the level of development of this technology, its integration in hybrid systems has begun to be explored, with the first reference to a hybrid sodium-lithium battery appearing in 2006 [38]. Hybrid batteries, in addition to higher performance and compatibility with different materials for electrode development, also allow to combine the high energy density of LIBs with the power density, safety, availability, and low price of sodium [39].

Due to these advantages, hybrid batteries have been attracting a lot of interest, both in terms of scientific and industrial development. CATL, one of the world's largest battery manufactures, has already announced that it intends to use, in battery cars, a battery pack consisting of sodium and lithium cells in a single system, with the primary goal of enhancing the most attractive properties of each individual system, while also increasing the lifetime of the LIBs included in that pack. In the medium to long term, this type of system will undoubtedly lead to a reduction in the cost of the raw materials involved in the development of LIBs, hence creating a market niche for SIBs [40].

2.4 Cathode material

The cathode material is one of the critical components for the actual performance of SIBs, since the energy density, cycle life and operating potential of the battery are intimately related to the properties of the selected material [41]. Moreover, this component accounts for over 30 % of the total manufacturing cost of a sodium battery [42]. As a result, the cathode material must be carefully selected, with an ideal cathode material having a high redox potential, large storage capacity of Na^+ ions, high structural, chemical, and thermal stability, a large Na^+ diffusion coefficient, high electronic conductivity, and being easily accessible, environmentally friendly, and cost effective [41,43]. A wide variety of compounds have been investigated as cathode materials for SIBs, with three major families emerging: layered transition metal oxides, polyanionic compounds (such as phosphates and fluorophosphates), and prussian blue analogues (PBAs).

Layered transition metal oxides (Na_xTMO_2 , TM= transition metal) have been studied as promising cathode materials due to their high theoretical capacity and scalable manufacturing; however, these materials suffer from structural instability. Polyanionic compounds ($\text{Na}_x\text{TM}_y(\text{XO}_4)_n$), despite their low

electrical conductivity, have also been extensively researched, and when compared to layered oxides, revealed enhanced structural stability, improved safety and higher operating potential [44]. Prussian blue compounds with the general formula $\text{Na}_x\text{TM}[\text{TM}'(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$ are highly porous positive electrode materials with high ionic conductivity and great structural stability. Nevertheless, prussian blue analogues display a complicated synthesis procedure and environmental problems [45]. Figure 2.4 compares the specific capacity and working potential of selected compounds from each of the cathode materials families previously mentioned.

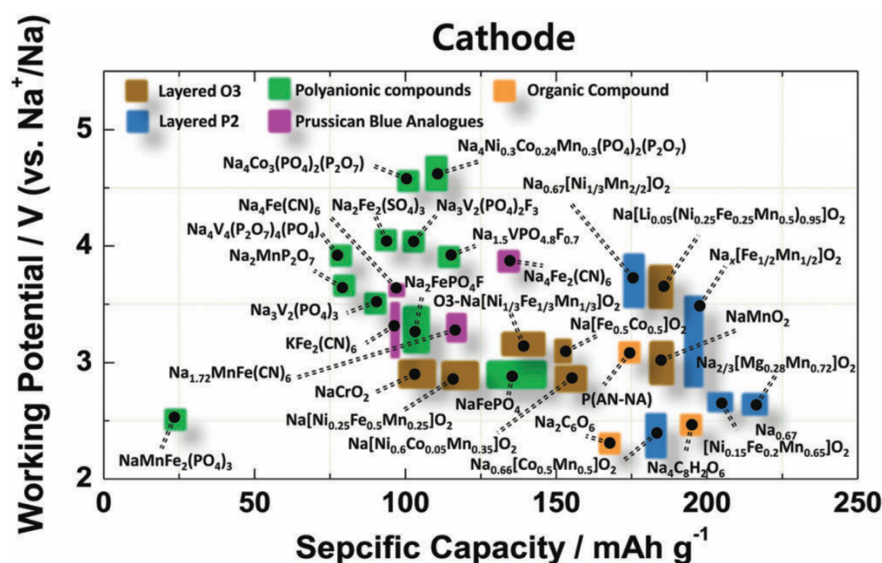


Figure 2.4 - Research progress in cathodes for sodium-ion batteries [11].

Since this project aims to study materials for later industrial manufacture of SIBs, layered metal oxides were selected as cathode materials and were further investigated in section 2.5. These materials have a low cost and simple structure and synthesis, as well as low environmental implications and high operating potential, which favors their industrial application.

2.5 Layered transition metal oxides materials

Layered transition metal oxides, denoted as Na_xTMO_2 (TM= 3d transition metal, $x \leq 1.0$), are one of the most studied cathode materials, not only because their lithium analogues have been extensively studied in recent decades, but also due to their high theoretical capacity, facile and scalable synthesis [46]. Additionally, during the intercalation and deintercalation processes, the material's unique architecture provides a large surface area and short ion diffusion channels, with minimal volume change, both of which are beneficial for cycling stability [47].

Layered transition metal oxides can be categorized into two main groups, either O3-type or P2-type structures, according to the classification first proposed by Delmas and his co-workers in 1980 [48]. In the layered structure of these materials, oxygen atoms form a cubic closed-packed sub-lattice as a basic

matrix, to which transition metal atoms can coordinate with six oxygen atoms to form octahedron structures, which are generally denoted by TMO_6 [49]. These TMO_6 octahedrons are connected to each other by edge sharing, forming TMO_2 layers with the sodium ions being sandwiched between them, and thus, the structure of these materials is comprised by alternating Na and TMO_2 layers along the c -axis direction, as represented in Figure 2.5.

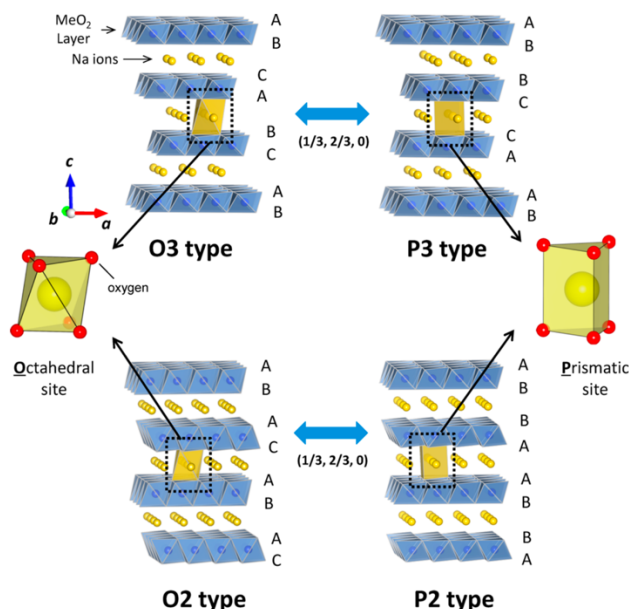


Figure 2.5 - Types of structures of a Na_xTMO_2 material [13].

In contrast to their lithium counterparts, in which only two transition metals could be employed (LiTMO_2 , TM= Co and Ni), sodium layered compounds showed reversible sodium intercalation in a wide variety of transition metals (TM= Ti, Al, Mn, Mg, Fe, Ni, Cu, Al, Cr, Co and V) [43,49].

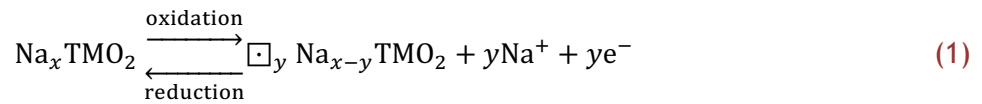
The letter in each type of structure represents the coordination environment of the alkali ions between the TMO_2 layers, with "O" and "P" indicating octahedral and trigonal prismatic coordination environments for Na^+ ions, respectively. On the other hand, the number, "2" or "3", identifies the number of transition metal layers with distinct forms of oxygen stacking in each repeating unit cell, with O3 being composed by three different layers AB-CA-BC, while in P2 the stacking sequence is AB-BA [16,46]. Moreover, when the crystal lattice incorporates in-plane distortion, a prime symbol (') is added to the abbreviation, and thus, O'3 and P'2 represent monoclinic distortion of the O3 and P2 phases respectively [11,50].

Regarding the structure of the layered oxide cathode materials, O3-type oxides ($0.7 < x < 0.1$) frequently have the highest specific energies due to their higher Na content, which, in return, leads to higher battery capacity. Nonetheless, even though P2 phase demonstrates lower capacity than O3 phase, P2 is considered to be more structurally stable, which results in a better cycling stability and rate performance when compared to O3 [36].

In P2-type structure ($0.3 < x < 0.7$), Na^+ ions have an open migration path directly towards the adjacent prismatic site, whereas in O3-type materials, Na^+ migrates from the initial octahedral site to a interstitial tetrahedral site and then to a face shared adjacent octahedral site, which requires more energy than P2-type materials [49]. Therefore, Na^+ ions possess higher mobility in P2-type structures than O3-type structures, which explains the superior rate performance and cycling stability of the P2-type materials.

It should be noted that due to the intercalation and deintercalation processes, phases transitions occur when the sodium ions are extracted and subsequently reinserted on the cathode host material during charge and discharge of the battery. Although the term “phase transition” is most used to refer to a change in physical state, it will be used in this work and throughout the project to refer to changes in the crystalline structure of the cathode material generated by the insertion and extraction of Na^+ ions.

Sodium extraction from a layered transition metal oxide (Na_xTMO_2) as a positive electrode for a SIB is described by eq (1), where $x = 1$ and $\square$ indicates the structural vacancy created, with the charged state of the battery being represented on the right-hand side of the equation [24].



Sodium ions in O3-type structures are initially stable in octahedral edge-share sites with TMO_6 octahedron structures. However, when sodium ions are partially extracted, Na^+ becomes energetically stable at prismatic sites, which are formed by gliding of the TMO_2 layers without breaking the TM-O bonds. As a result, oxygen packing shifts from AB-CA-BC to AB-BC-CA, resulting in a phase transition from O3 to a P3-phase represented in Figure 2.5 [13]. By contrast, P2 phase usually evolves into a O2-type structure by TMO_2 gliding to form octahedral sites after partial sodium extraction. As the TMO_2 layers shift, the oxygen packing will change from AB-BA to AB-AC, resulting in the O2 phase, which is also depicted in Figure 2.5 [49]. It should be noted that the phase transition from O2 or P2 to O3 or P3 is impossible since it requires breaking the TM-O bonds, which needs a high temperature environment [13].

When exploring various candidate positive electrode materials for sodium-ion batteries, it is imperative to understand their fundamental thermodynamic behavior. Structural stability and ordering phenomena have large impacts on different aspects related to the battery performance such as voltage profiles, diffusion rates and degradation mechanisms [51]. Therefore, it is essential to have a thorough understanding of the events that occur during the charge and discharge of the battery in order to avoid or mitigate the impacts of unfavorable phase transitions. The potential curve can be used to get information regarding the complexity of phase transitions that occur during the cycling of the battery, with this relationship explained in Appendix D.

2.5.1 Single transition metal oxide systems

Over the years, different layered transition metal oxides have been investigated, with single metal oxides systems being one of the first and promising systems studied due to their high theoretical reversible capacity as well as excellent electrochemical performance in LIBs [49].

Sodium iron oxide - NaFeO₂

NaFeO₂ as an electrode material for SIBs was first reported by Okada and co-workers, which marked a turning point in sodium battery technology. NaFeO₂ can be easily synthesized by solid-state reaction, represents a cost-effective material due to the abundance of iron (Fe), besides being harmless and environmentally friendly [13]. Furthermore, the high operating potential of NaFeO₂ is an essential benefit that supports its employment as a positive electrode [46].

Okada *et al.* first reported O3-NaFeO₂ as an electrochemical active Na intercalation host, while its lithium analog, layered LiFeO₂, is known to be electrochemical inactive [13]. Based on the reversible redox reaction of Fe³⁺/Fe⁴⁺, O3-NaFeO₂ exhibits, with small polarization, a maximum reversible capacity of 80 mAh·g⁻¹ with a flat discharge profile at 3.4 V, which equates to approximately 1/3 of sodium ions being reversibly extracted and re-inserted from/into the crystal lattice of Na_{1-x}FeO₂ [52,53].

Nonetheless, as illustrated in Figure 2.6, the reversibility of sodium extraction/insertion within the electrode material is significantly influenced by the cut-off conditions [53]. Despite the fact that the charging capacity, which corresponds to the number of sodium ions extracted upon charge, increases as a function of the cut-off potential, the reversible capacity does not. The reversibility appears to gradually deteriorate as the cut-off potential raises above 3.5 V, owing to the significant rise in polarization on the electrochemical cycles following charge to 4.0 V. With a cut-off potential at or above 4.5 V, essentially no capacity is delivered upon discharge [11,53].

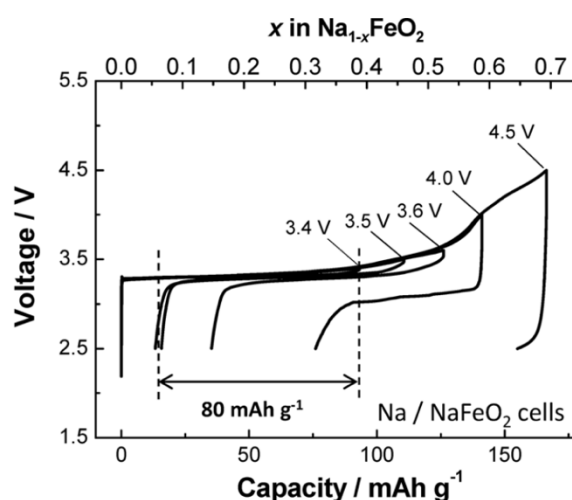


Figure 2.6 - Initial charge/discharge curves of Na/NaFeO₂ cell [53].

The irreversible capacity of Na_xFeO_2 as a cathode can be explained by the irreversible structural transitions that occurs during the charge of the battery. As Na^+ ions are extracted from the crystal structure, vacant tetrahedral sites are created in the Na layer, contacting with the FeO_6 octahedra. Due to the fact that trivalent iron ions are energetically stable at tetrahedral sites, Fe^{3+} can easily migrate into adjacent and vacant tetrahedral sites created in the Na layer, which will disturb the Na diffusion within the electrode material and, thus, degrade its electrochemical properties [53]. Figure 2.7 depicts the mechanism of iron migration during sodium extraction.

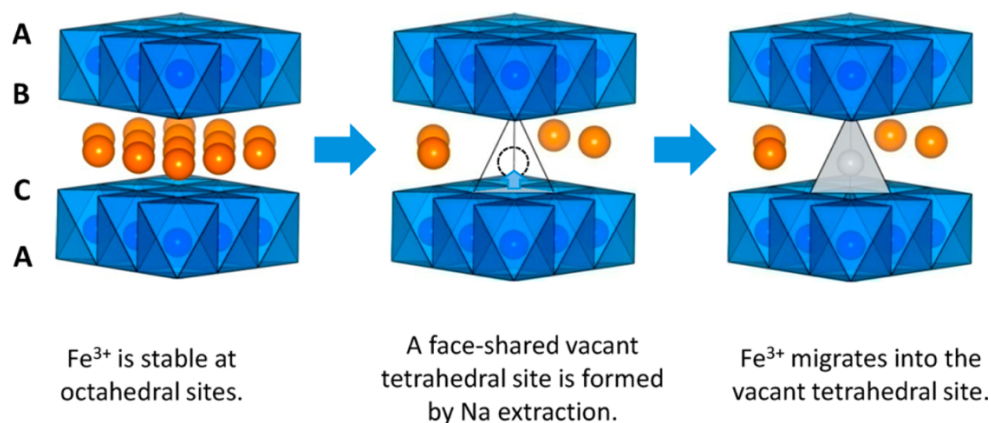


Figure 2.7 - Iron migration during sodium extraction [54].

Furthermore, another drawback related to NaFeO_2 is the Na^+ substitution by H^+ when the electrode contacts with water, and the aging of the electrode material when in contact with ambient air. When exposed to moisture, NaFeO_2 quickly changes to FeOOH and NaOH , resulting in a capacity loss and irreversible structural changes [13], and Na_2CO_3 and NaHCO_3 may accumulate on the material's surface as a result of CO_2 uptake when in contact with ambient air [46].

Sodium manganese oxide - NaMnO_2

Na_xMnO_2 is another prospective sodium layered cathode material that has received great attention due to its high specific capacity and low cost [11]. The structure of Na_xMnO_2 varies from a 3D tunnel structure at $0 \leq x \leq 0.44$ to 2D layered structure at $0.44 \leq x \leq 1.0$, with Parant and colleagues characterizing the different phases in 1971 [55]. In addition, stoichiometric composition of NaMnO_2 crystallizes into two polymorphs according to the synthesis temperature [55].

Delmas and Hagenmuller were the first to study the electrochemical reversibility of Na extraction and insertion from/into O'3-type NaMnO_2 , revealing a restricted reversibility range ($x < 0.2$ in $\text{Na}_{1-x}\text{MnO}_2$) [56]. However, monoclinic NaMnO_2 was again revisited in 2011 by Ceder and co-workers and reported that 0.8 mol of Na could be intercalated reversibly ($x \leq 0.8$), a different behavior from that reported by Hagenmuller and Delmas, corresponding to discharge capacity of $197 \text{ mAh}\cdot\text{g}^{-1}$ in a potential range of 2 - 3.8 V at a rate of C/30 [57].

The capacity retention of O'3-type NaMnO_2 was approximately 70 % for 10 cycles, with the voltage profile of NaMnO_2 at C/30, depicted in Figure 2.8, illustrating a series of plateaus indicating complex phase transitions. Furthermore, the electrode performance of $\text{P2-Na}_{0.6}\text{MnO}_2$ has also been studied and was reported to deliver a reversible capacity of $140 \text{ mAh}\cdot\text{g}^{-1}$ in a range of 2 - 3.8 V. However, the capacity of the electrode decreases on subsequent cycles due to the structure gradually collapsing [58].

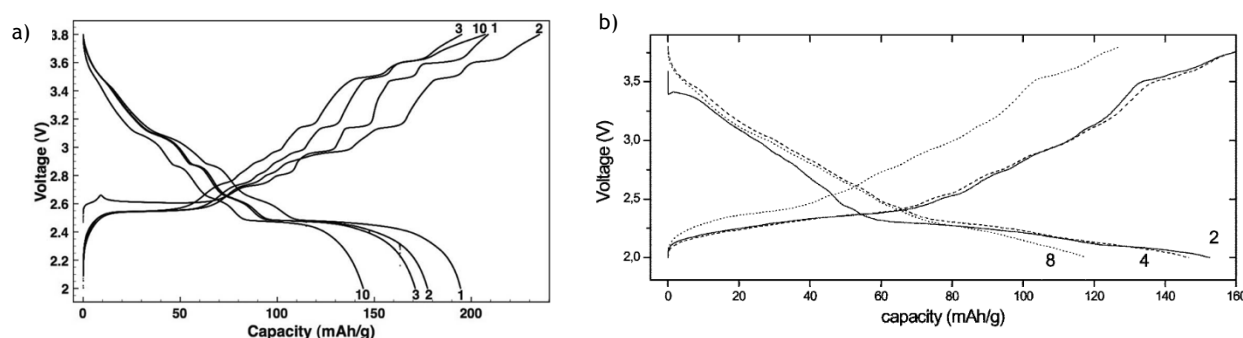


Figure 2.8 - Charge and discharge curves of a) O'3- NaMnO_2 b) $\text{P2-Na}_{0.6}\text{MnO}_2$ [57,58].

Despite the economic advantages of Na and Mn, this electrode exhibits rapid capacity deterioration, as shown in Figure 2.8, which is mostly related to the strong Jahn-Teller effect of Mn^{3+} , and/or structure instability in the presence of moisture [46,59]. High spin Mn^{3+} is considered unstable and can readily disproportionate and transform to Mn^{2+} and Mn^{4+} ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) during the Na^+ insertion and extraction. Then, the easily dissolved Mn^{2+} can migrate to the electrolyte towards the anode, destroying the solid-electrolyte interphase (SEI). As a result, the reversible capacity of the battery will degrade with the subsequent cycles [49]. Moreover, carbon dioxide (CO_2) can also be easily inserted into the Na active sites, which hinders the battery capacity [59].

Sodium nickel oxide - NaNiO_2

NaNiO_2 is another potential cathode material for sodium batteries, with Ni-based oxides particularly appealing due to the high potential of $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ [46]. Moreover, in contrast to its lithium analog, LiNiO_2 , a stoichiometric NaNiO_2 can be easily prepared, which encourages the use of this electrode material [49]. Additionally, due to the fact that Ni^{2+} ions can be present in the lithium layers of lithium oxides, the electrode performance suffers significantly, whereas NaNiO_2 exhibits good electrode performance since the Ni^{2+} cannot be found within the sodium layers due to the larger size gap [13].

NaNiO_2 is stable as two polymorphs, one with an O3 layered structure with monoclinic structure distortion at low temperatures and the other with a rhombohedral structure at high temperatures [60]. The Ni-O layer in the O3 phase is formed by edge-sharing NiO_6 octahedra, each of which is elongated due to the Jahn-Teller distortion of the Ni^{3+} ion, being this low temperature form of NaNiO_2 isostructural to NaMnO_2 [57,60].

Nickel based sodium layered oxides have been heavily studied as a positive electrode material, with Delmas and co-workers conducting early studies on monoclinic NaNiO_2 and reported that an approximately $50 \text{ mAh}\cdot\text{g}^{-1}$ of capacity was deintercalated from NaNiO_2 , based on the $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox reaction in the potential range of 1.7 - 3.5 V, which corresponded to 0.2 mol of Na^+ being deintercalated, with the potential profile illustrating multiple phase transitions [11].

In contrast, recently, Vassilaras *et al.* revisited the performance of monoclinic NaNiO_2 as host material and observed a reversible capacity of $123 \text{ mAh}\cdot\text{g}^{-1}$ within a potential range of 1.25 - 3.75 V, and a reversible capacity of $147 \text{ mAh}\cdot\text{g}^{-1}$ with a range of 2.0 - 4.5 V (both at a C/10 rate) which corresponds to around 0.52 and 0.63 mol of Na being intercalated back reversibly respectively [60], which is in accordance with the result obtained by Caballero *et al.* [58]. Figure 2.9 exhibits the voltage profile of NaNiO_2 within the potential ranges referred previously obtained by Vassilaras.

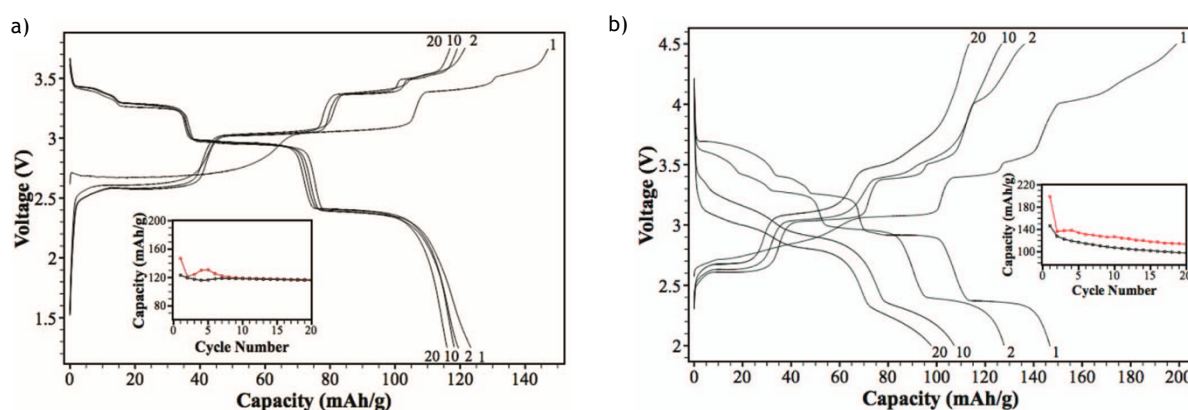


Figure 2.9 - Voltage profile of NaNiO_2 at a) 1.25-3.75 V b) 2.0-4.5 V [60].

Despite the good electrode performance, several potential plateaus are observed on the potential curves, which indicates complicated phase transitions during charge and discharge of the battery. Nevertheless, the similarities in plateaus suggest that the charge and discharge processes go through the same phase transitions [60]. Furthermore, the prospect of high-Ni content cathode materials for SIBs is challenging due to their poor chemical stability against air [46]. These cathodes typically exhibit a significant performance losses during the handling and storage processes in an ambient environment, which are believed to originate from the formation of electrochemically inactive NaOH or Na_2CO_3 [61].

Other single transition metal oxides such as NaCoO_2 , NaCrO_2 and NaVO_2 have also been studied as potential positive electrode materials for sodium batteries [11,47]. However, these positive electrode materials will not be addressed in this project. Table 2.1 makes a comparison between the different single layered oxides materials referred previously.

Table 2.1 - Comparison of NaTMO₂ single metal oxides [46].

Single metal oxides	Advantages	Disadvantages	Practical capacity / mAh g ⁻¹	Cycling Stability
NaFeO ₂	Inexpensive and high voltage	Fe ³⁺ migration	80 (12 mA g ⁻¹ , 2.5 - 3.4 V)	75 % after 30 cycles
NaMnO ₂	Inexpensive and large specific capacity	Jahn-Teller effect of Mn ³⁺	197 (C/30, 2.0 - 3.8 V)	70 % after 10 cycles (C/10)
NaNiO ₂	High Voltage	Complicated structure evolution	123 (0.1C, 1.25 - 3.75 V)	95 % after 20 cycles (C/10)
NaCoO ₂	Good ionic diffusivity	Expensive and complicated structure evolution	40 (70 μA cm ⁻² , 2.0 - 3.5 V)	90% after 20 cycles
NaCrO ₂	Reversible phase transition	Poisonous Cr	120 (25 mA g ⁻¹ , 2.0 - 3.6 V)	90 % after 10 cycles
NaVO ₂	-	Poisonous V	120 (C/20, 1.2 - 2.4 V)	≈ 100 % after 15 cycles

2.5.2 Multiple transition metal oxide systems

Single transition metal layered oxides have been considered as great candidates for the positive electrode material due to their features such as high redox potential, high specific capacity, ease of manufacture and scalability. However, fast capacity decay, irreversible phase transitions and structure instability when in contact with air and water limit their practical application. As a result, various modification strategies have been proposed to help alleviate these issues, including structure design, surface coating, and heteroatom doping [62], with the latter receiving particular attention. The introduction of heteroatoms in the layered structure is employed to take advantage of the synergetic effect observed between different transition metals in order to improve their electrochemical performance, specifically, by reducing multiple phase transitions, increasing the working potential and reversible capacity of the electrode material [46]. In active cathode materials, metal element doping has been demonstrated to be an effective technique to improve the electrochemical performance [62]. Additionally, these multi-cations compounds may be beneficial in terms of cost reduction and environmental benignity [27].

In the context of heteroatom doping in cathode materials, inactive metal ions such as magnesium (Mg²⁺), titanium (Ti⁴⁺) and aluminum (Al³⁺) or active metal ions such as iron (Fe³⁺), nickel (Ni²⁺) and copper (Cu²⁺) have been demonstrated as dopants with effective promotion on performance.

Inactive metal ions are particularly used to improve cycling stability by inhibiting phase transformation, prevent structure degeneration, and suppress the Jahn-Teller effect [62]. However, since these inactive ions do not participate in redox reactions, a reduction of reversible capacity is expected. Magnesium ion, a commonly used dopant, mitigates the irreversible phase transition P2-O2 in layered $\text{Na}_{2/3}\text{Mn}_{2/3}\text{Ni}_{1/3}\text{O}_2$, that leads to a fast capacity decay [63]. The presence of Mg^{2+} immobile ions in the TMO_2 layers allows more Na^+ ions to reside in the prismatic sites, stabilizing the overall charge balance [63]. Aluminum ions has also been proved to improve the cycling stability of $\text{O3-NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [64]. Al doping not only increases interlayer spacing and Na-O length, resulting in a higher sodium diffusion, but also increases TM-O and O-O bonding energies, which results in a robust layered structure [64,65]. Wang *et al.* has also demonstrated that substitution of Ti for Mn enlarges interlayer spacing and restrains multiple phase transformation at high voltage that is observed in $\text{O3-NaFe}_{1/2}\text{Mn}_{1/2}\text{O}_2$. As a result, Ti doping broadens the solid solution zone with P3 phase, resulting in a higher cycling retention and rate performance [66].

Active metal ions such as iron (Fe^{3+}), nickel (Ni^{2+}) and copper (Cu^{2+}), on the other hand, are mainly applied to increase the specific capacity and improve Na^+ ion diffusion [62]. To increase the capacity of an active material, the number of electrons transferred in the electrode for a given mass must be increased. It is not the charge of the intercalated ions, but the charge change in the oxidation state of the active ions in the electrode that is the key to improve the capacity [16]. From these three active metal ions, $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples exhibit the largest potential in SIBs [67]. Furthermore, these active metal ions can also slightly improve structural stability [62]. Figure 2.10 illustrates an electrochemical summary of various layered oxides cathode materials, comparing voltages, capacity, and energy density. As it can be seen, multiple metal transition metal oxide reveals higher performance when compared to single metal oxides. A more detailed analysis of several multiple layered oxides can be found in the Appendix E.

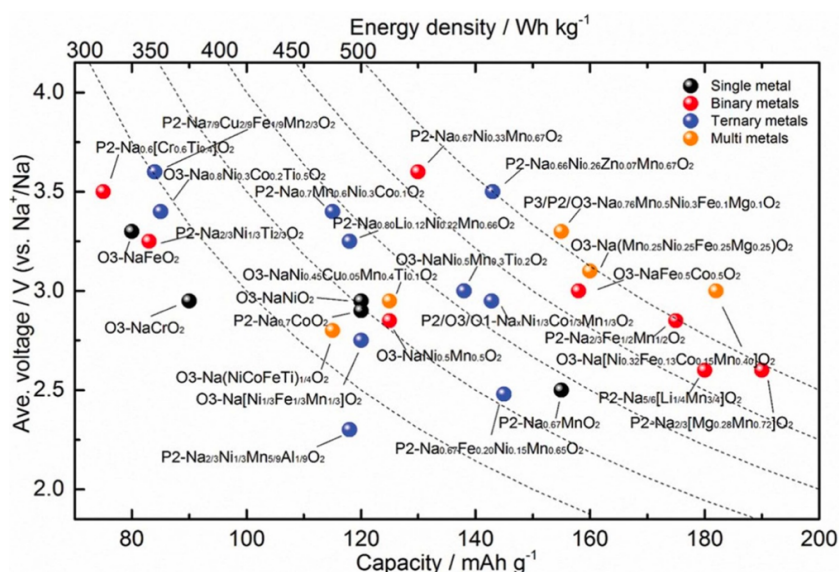


Figure 2.10 - Electrochemical summary of various layered oxide cathode materials [41].

3 Materials and Methods

3.1 Overview

The general procedure followed in this work is illustrated in Figure 3.1. Seven distinct cathode materials derived from $\text{Na}_x\text{NiMnO}_2$ and NaMnO_2 , already reported in the literature [59,64,68–70], were initially obtained through chemical solid-state reaction. The obtained materials were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The electrochemical performance of the obtained cathode materials was also assessed. Coin cells were assembled and electrochemically tested via galvanostatic charge/discharge cycles (CDC), and electrochemical impedance spectroscopy (EIS).

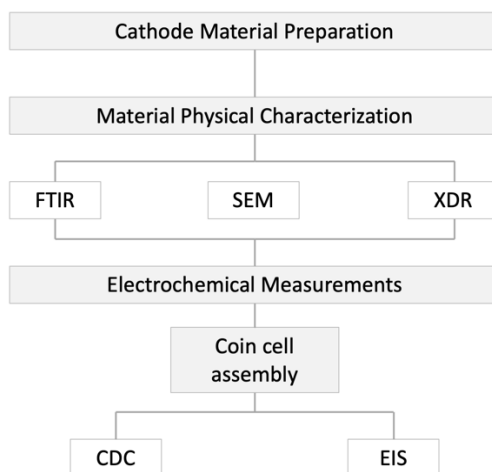


Figure 3.1 - General procedure of this thesis work.

3.2 Material preparation

In this project, seven different layered transition metal oxides, listed on Table 3.1, derived from $\text{Na}_x\text{NiMnO}_2$ and NaMnO_2 materials were synthesized as prospective cathode materials.

Table 3.1 - Cathode materials synthesized and respective chemistry designation.

Chemistry number	Cathode material	Literature Reference
1	$\text{O3-NaNi}_{0.1}\text{MnTi}_{0.1}\text{O}_2$	[59]
2	$\text{O3-NaNi}_{0.5}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$	[69]
3	$\text{O3-NaNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$	[68]
4	$\text{O3-NaNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{0.3}\text{Ti}_{0.2}\text{O}_2$	[69]
5	$\text{O3-NaNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$	[70]
6	$\text{O3-NaNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{(1/3-x)}\text{Al}_x\text{O}_2$ ($x=0.01$)	[64]
7	$\text{O3-NaNi}_{0.25}\text{Mn}_{0.25}\text{Fe}_{0.25}\text{Al}_{0.25}\text{O}_2$	[64]

These active cathode materials were produced by solid-state reaction, with a general scheme of the essential steps required illustrated in Figure 3.2, and the whole comprehensive procedure for each cathode material described in Appendix F. Solid-state reaction involves chemical decomposition reactions, in which a mixture of solid reactants is heated to produce a new solid composition and gases. Nevertheless, it should be noted that other preparation methods such as co-precipitation and thermal polymerization can be used. However, these different production methods have different impacts on the structure of the resulting material. Therefore, to minimize the variability associated with this step, and because the purpose of this work was not to investigate the effect of different preparation processes, all materials were synthesized via simple solid-state reaction method. The chemistry number shown in Table 3.1 are used to facilitate the identification of the different active materials without using their complete chemical composition.



Figure 3.2 - Guidelines to cathode synthesis by solid-state reaction.

Initially, stoichiometric amounts of raw materials required to synthesize the active materials were calculated and measured considering a 90 % yield. However, owing to the sodium volatility in high temperatures, an excess of sodium carbonate (Na_2CO_3) was considered in all synthesis. Table F.1 in Appendix F lists the chemicals and materials used in the synthesis of all active materials. It should be noted that since most chemicals, as well as the resulting active material are obtained in powder form, the specific safety precautions must be accomplished. The homogenization and milling process begins after the precursors have been measured. This process is essential not only to ensure that the active material particles are of similar size, but also to ensure that the different elements (Na, Ni, Mn, etc.), are evenly distributed throughout the bulk of the material. An agate mortar and a PM 100 Retsch Planetary ball miller, both illustrated in Figure 3.3, were used during this operation to grind the precursor materials.

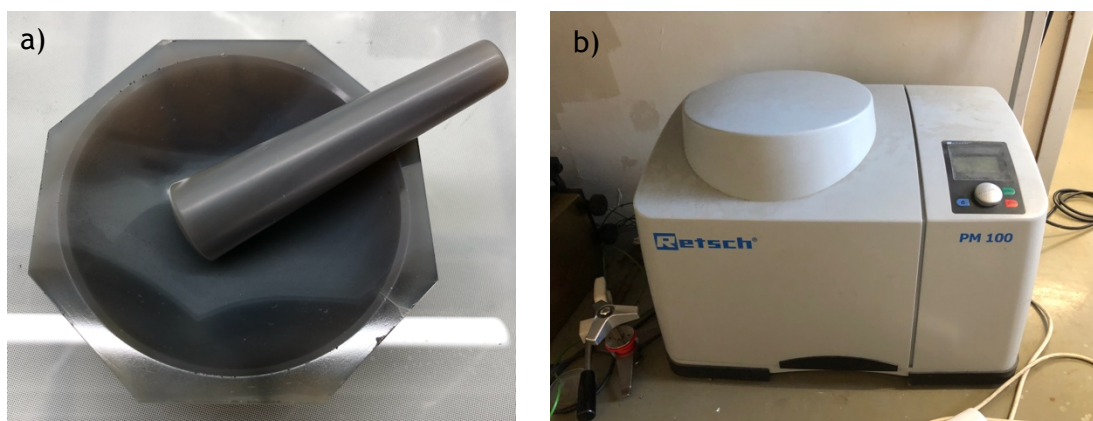


Figure 3.3 - Grinding equipment a) mortar and pestle b) Retsch ball mill PM100.

However, it was observed that the samples handled in the ball mill were completely cemented to the balls and wall of the mill cup. For that reason, to remove the material from the mill cup, the sample was dissolved in deionized water. Thereafter, the samples were vacuum filtered and dried in order to remove the powder from the filter. Besides that, in some synthesis (cathodes 2 and 4), 4 mL of deionized water was added to the ball mill before grinding the materials, and it was observed that, while the filtration process was still required, the powder was easier to remove from the mill cup. Nevertheless, and as discussed later in section 4.1, using water during the milling process promotes sodium leaching, resulting in a sodium-free material. As a result, the resulting powder should be scraped from the mill cup and the use of water must be avoided in all synthesis steps.

Following the homogenization process, the samples were placed in a crucible, for the subsequent calcination procedure, which was used to remove impurities and volatile compounds such as carbonates. A Termolab tubular furnace, shown in Figure 3.4, was used to carry out the calcination process, with the atmosphere within the oven set to a nitrogen atmosphere at a rate of $100 \text{ mL} \cdot \text{min}^{-1}$. Three separate steps could be defined throughout the calcination process: a heating ramp till the desired temperature, a constant temperature step for the desired period, and a colling ramp. Due to equipment restrictions and to ensure that the materials crystallized as well as possible, heating and colling ramps were limited to 1 or $2 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$. Moreover, two distinct types of crucibles, a taller and a lower version, shown in Figure 3.4, were used during this procedure. However, and as discussed in section 4.1, only the lower crucibles should be used. After the calcination process, the active materials were stored at room temperature before being stored in the glovebox.

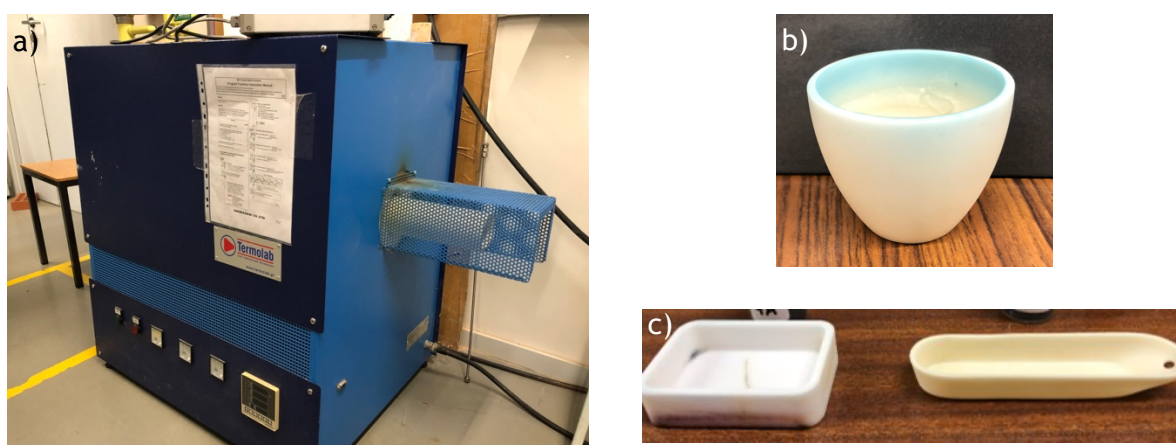


Figure 3.4 - Calcination equipment a) Termolab tubular furnace b) taller crucible c) lower crucibles.

3.3 Electrode Fabrication and Coin Cell assembly

3.3.1 Electrode fabrication

Electrodes were prepared by mixing the active material with conductive carbon black, specifically TIMCAL Super C45, and poly(vinylidene fluoride) (PVDF) as the binder in the mass ratio of 85:5:10 for the

cathode electrode and 85:5:10 for the anode electrode. For the anode, hard carbon provided by Kuraray was used as active material, specifically, the KURANODE™ type 2 (5 μm).

Initially, PVDF was mixed with N-methyl-2-pyrrolidone (NMP) as a solvent to produce a mixture with 4.5 % (m/m) PVDF. The mixture was placed in a glass jar and stirred at 200 rpm for 2 hours until a paste with a consistency similar to liquid glue is obtained, as illustrated in Figure 3.5. Following that, the active materials and super C45 were added to the mixture and stirred for another hour to produce a slurry with the desired consistency, as shown in Figure 3.5. It should be noted that the consistency is an important aspect to be considered when preparing electrodes. A high viscosity slurry will make producing uniform coatings more difficult and may cause material to clump together, resulting in an uneven reaction distribution in the electrode surface. On the other hand, a low slurry viscosity can cause runniness and polling [71]. Therefore, during the blending of the active material and conductive carbon into the PVDF and NMP mixture, additional NMP, if necessary, can be added to achieve and control the consistency of the slurry. However, due to equipment limitation, the viscosity of the resulting slurry was just controlled through visual observation.

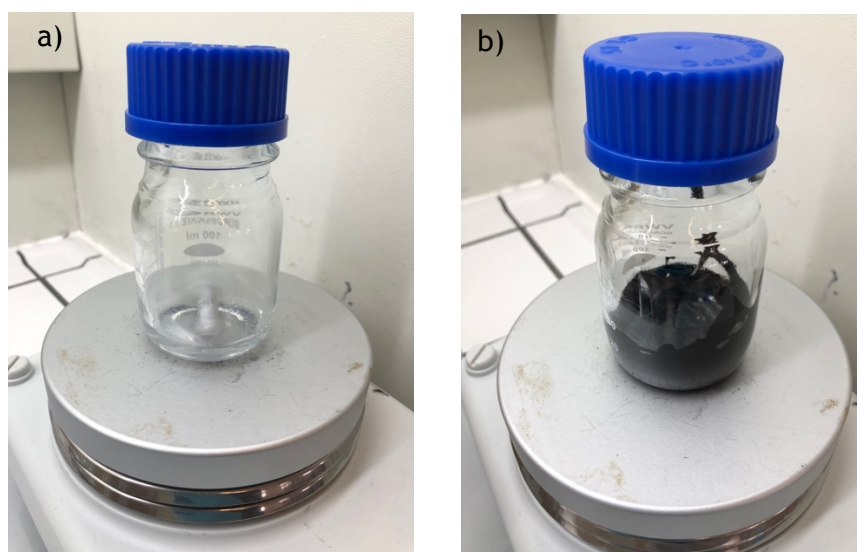


Figure 3.5 - a) Mixture of PVDF and NMP b) slurry produced.

The obtained slurry was then casted on an aluminum foil from Nanografi, 15 μm thickness and purity of 99.3 %, by using a doctor-blade (Figure 3.6). In a first step, 99.97 % ethanol is used to clean the surface where the aluminum foil will be placed. Before the ethanol evaporates, the aluminum foil is placed on the surface to ensure that the foil adheres to the surface. Once placed, ethanol is again used to clean the surface of the aluminum foil and to remove any air pockets that may exist beneath the aluminum foil. Thereafter, the slurry is applied to the aluminum foil and coated by a doctor-blade (*cf.* Figure 3.6). The wet coating thickness is controlled by the doctor-blade, which is adjusted to 150 μm for the cathode and 150 μm for the anode. Due to its impact on cell performance, it is crucial that the thickness of the coating is regulated during electrode fabrication. A thicker electrode will contain more active material, and thus,

more capacity. However, due to the longer diffusion path for the Na^+ ions, the power density and rate performance will be poorer. Finally, the prepared slurry was dried at room temperature for 24 hours to ensure that all solvent (NMP) had evaporated (Figure 3.6).

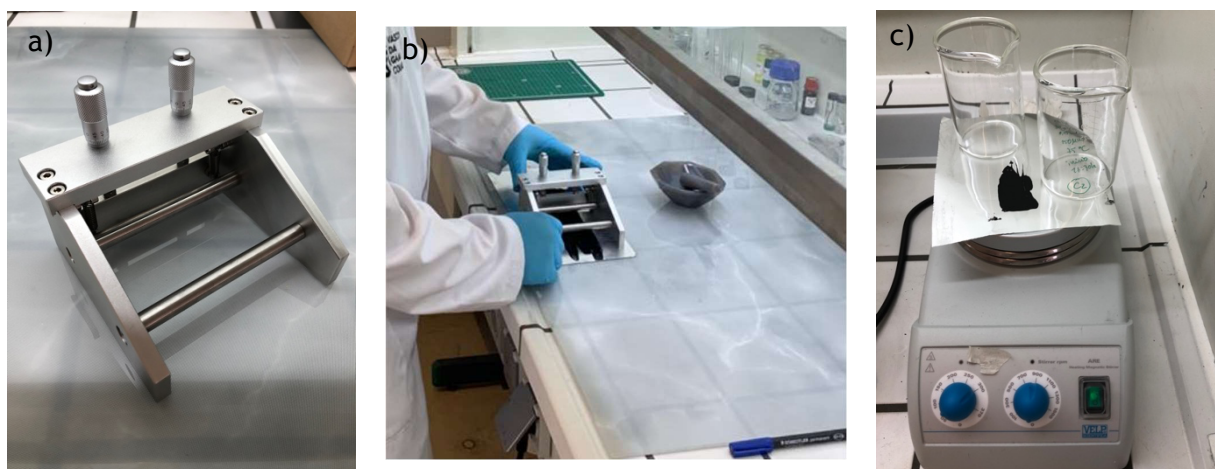


Figure 3.6 - a) Doctor-blade; b) Aluminum foil being coated with the slurry; c) slurry drying.

3.3.2 Coin cell assembly

The as-synthesized electrodes were cut into small disks with a diameter of 14 mm. Each electrode was weighted before entering the nitrogen filled UNILab Pro glovebox (Figure 3.7) with water and oxygen level lower than 0.1 ppm. In addition, several 14 mm disks of aluminum foil were cut out and weighted, and the average aluminum mass per disk was calculated.

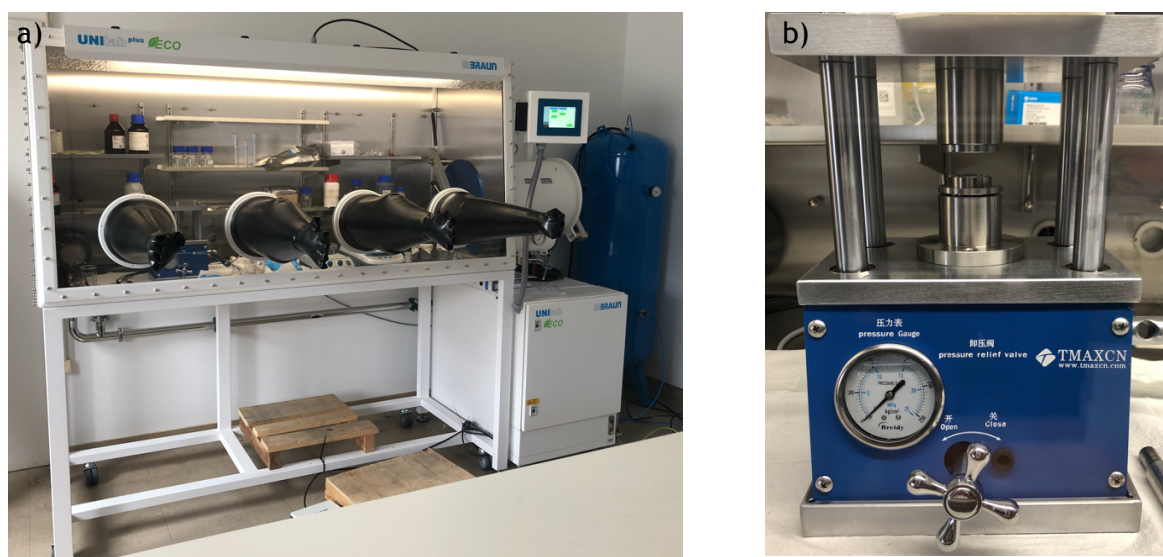


Figure 3.7 - a) Glovebox b) coin cell crimping machine.

Afterwards, these electrodes were used to produce typical CR2032 coin cells. A typical CR2032 coin cell is constituted by a small cap, a spring, a stainless spacer, the negative electrode (anode), a glass fiber separator with several drops of electrolyte, a positive electrode (cathode) and a large cap. However, an extra spacer was placed between the cathode and the positive cap to increase the volume of the coin

cell and make crimping easier. The separators used are 24 mm glass microfiber filter grade GF/F from Whatman®. These separators are then cut into disks with a diameter of 18 mm. Figure 3.8 shows the schematic diagram of the configuration of the CR2032 coin cell. It should be noted that the active material coating in the anode and cathode should be facing the separator. Furthermore, sodium plating may occur in areas where the positive electrode is not covered by the negative electrode, which leads to a reduction of the available capacity of the cell. Therefore, special precaution was taken to ensure that both electrodes were aligned as well as possible in the coin cell.

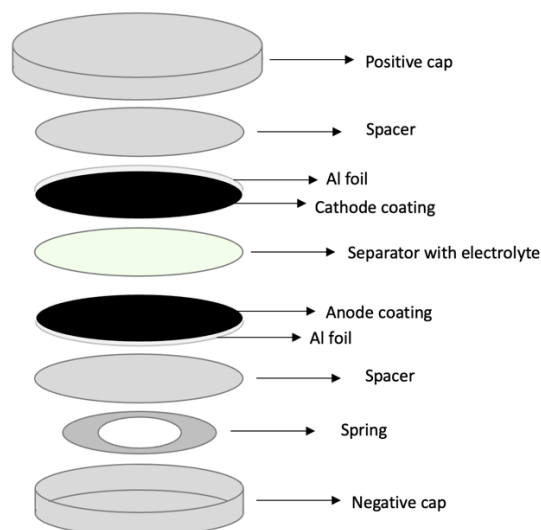


Figure 3.8 - Typical configuration of the CR2032 coin cell.

For the coin cell assembly, an electrolyte solution of 1 M of sodium hexafluorophosphate (NaPF_6) dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (EC:PC, 1:1 m/m) was prepared in the glovebox. Initially, the necessary amount of each polar solvent was measured to produce a 50 mL solution. The solvent mixture was then placed in a hot plate at 50 °C with continuous magnetic rotation at 200 rpm, and NaPF_6 was gradually added. The steady addition of NaPF_6 allows for the observation of salt precipitation. It should be noted that the electrolyte solution must be prepared in the glovebox due to the fact that NaPF_6 produces hydrofluoric acid (HF) when it comes into contact with water.

Once the electrolyte was prepared, the coin cell assembly was performed using tweezers. During assembly, several drops of electrolyte solution were placed in the negative cap and on the side of the electrolyte with direct contact to the surface coating of the cathode material. Once assembled, the coin cells were sealed on a hand operated TMAX manual hydraulic coin cell crimper machine (TMAX-SF120) with a pressure of 50 MPa (*cf.* Figure 3.7). Afterwards, the coin cells were removed from the glovebox and left to rest for at least 12 hours. Thus, the electrolyte can thoroughly soak the working electrodes prior to the electrochemical measurements.

3.4 Physical characterization

Physical characterization of the active cathode materials is critical to execute throughout material synthesis since they allow to examine features essential to the function of the final cell, such as chemical composition, crystalline structure, and interplanar distance. In this work, Fourier Transform Infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) were used to characterize the active materials synthesized. These characterizations techniques are discussed in greater detail in Appendix G.

The infrared spectra were recorded using a VERTEX 70 FTIR spectrometer (BRUKER) in absorbance mode with a high sensitivity DLaTGS detector at room temperature. Samples were measured in ATR mode, with a A225/Q PLATINUM ATR Diamond crystal with single reflection accessory. The spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

The morphology and particle size of the samples was examined using a FEI Quanta 400 scanning electron microscope with tungsten filament and a 4 nm resolution. All the SEM analysis were performed at 30 kV. The chemical composition of the cathode active materials was verified by energy dispersive spectroscopy (EDS) from EDAX.

The crystalline structure of active materials was measured on a PANalytical X'Pert Pro MPD X-ray diffractometer using Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation ($\lambda_1 = 1.540598 \text{ \AA}$ and $\lambda_2 = 1.544426 \text{ \AA}$). A X'Celerator detector and secondary graphite monochromator were used in Bragg-Brentano geometry. The XRD patterns were obtained by measuring the diffraction angle (2θ) from 10 to 85° with a scanning rate of step size and 65 s step^{-1} and a step size of 0.0167°. The diffractograms were qualitatively analyzed with HighScore 4.8® software and Crystallography Open Database. Rietveld refinement was performed with HighScore 4.8® to quantify the amount of each phase and to obtain crystal structure parameters.

3.5 Electrochemical Tests

Electrochemical testing is used to assess the electrochemical performance of the cathode materials and assembled coin-cells. These procedures are essential since they allow to examine electrochemical behaviors and performances such as phase transition, specific capacity, energy density, cycle life, columbic efficiencies, and rate capacities. In this work, galvanostatic charge/discharge cycles, and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical performance of the active cathode material and of the coin-cells assembled. These characterizations techniques are discussed in detail in Appendix G. A Zahner power potentiostat was used to carry out the electrochemical tests.

4 Results and Discussion

4.1 Material characterization

This subchapter summarizes the key results addressing the physical and chemical characterization of the synthesized cathode materials, including chemical composition, crystal structure, lattice parameters, and morphology.

4.1.1 FTIR analyses

In the initial step of the project, two different synthesis procedures were carried out to compare the effects of the manufacturing process on the final product. In a first synthesis, the cathode materials were obtained according to the 1st synthesis steps described, for each cathode, in Appendix F. This first synthesis process was used as a basis of comparison for the following synthesis. A recalcination step was performed to the products of the 1st synthesis, to evaluate the viability of an extra heat treatment step for carbonate removal. In a second synthesis, the cathodes were prepared and subjected to a ball milling process for 20 hours and scraped from the ball mill afterwards (methodology described in Appendix F). This final synthesis was performed to evaluate the impact of the milling process and the use of water in the cathode preparation. From this point on, the materials derived from the 1st synthesis are represented by n.1, in which n indicates the chemistry number of the cathode materials (Table 3.1), while the materials synthesized using the 2nd synthesis procedures are known as n.2.

Due to the limited resources available at the time of performing this preliminary analysis, only the materials 1, 2, 3, and 4 were synthesized. The FTIR analyses were carried out for the cathode materials mentioned previously, to provide insights regarding chemical reactions and composition of the active materials. The results obtained are illustrated in Figure 4.1.

Since the produced cathode materials lack any functional group in their structure, there should be no peaks in the infrared spectra. However, a close analysis of the spectra depicted in Figure 4.1 reveals:

- a peak at 3000 to 2840 cm^{-1} associated with a C-H alkane stretching band in materials 2.1, 3.1, and 4.1, but not in material 1.1;
- a peak at 2350 cm^{-1} attributed to the stretching vibration of O=C=O [72]. This peak, observed in all materials, is directly related to the carbon dioxide (CO_2) detection. However, it was experimentally observed that, this particular peak, could be the result of a faulty baseline correction and, thus, identifying CO_2 present in the ambient atmosphere. As a result, this peak was not considered in this preliminary material analysis;
- a peak around 1400 cm^{-1} related to a CO_3^{2-} stretching band [64], and another one around 870 cm^{-1} related to a C-O bending vibration of the CO_3^{2-} group [72] in most materials.

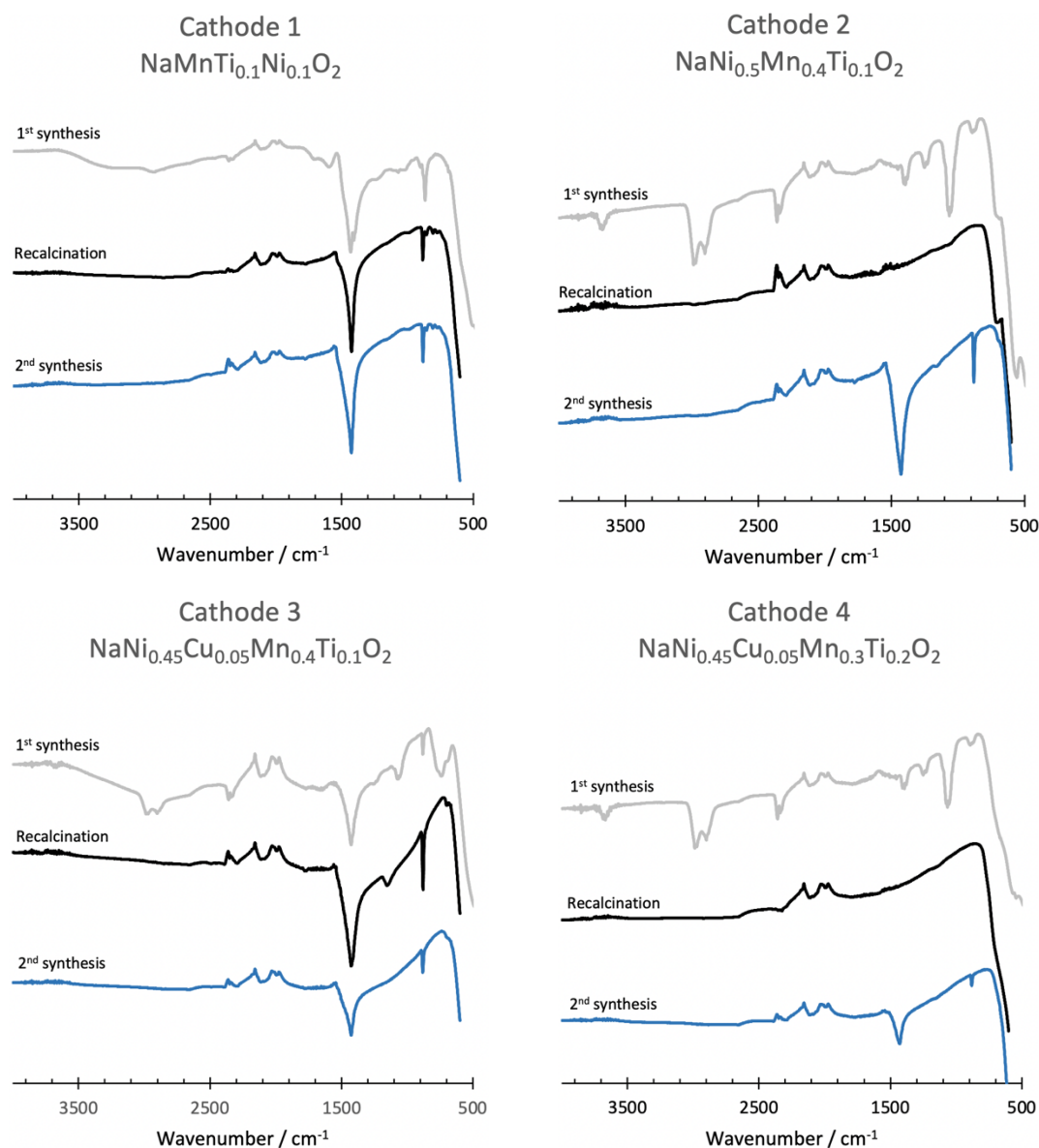
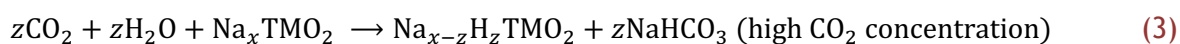
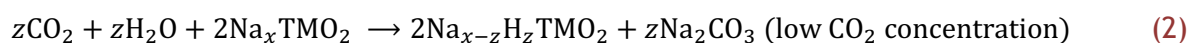


Figure 4.1 - Infrared spectra of the synthesized cathodes (1st synthesis, Recalcination of products from 1st synthesis, and 2nd synthesis).

The presence of the CO_3^{2-} group in the synthesized materials, suggests that residual sodium compounds (RSC) such as Na_2CO_3 and NaHCO_3 , are present in all cathode samples. These RSC could result from direct contact of the sample powders with air, moisture or water [73,74]. When in contact with ambient atmosphere, Na^+ ions are extracted spontaneously from the bulk of the material and replaced by H^+ ($\text{Na}^+\text{-H}^+$ exchange mechanism). The extracted Na^+ ions move to the surface of the material and react with H_2O and CO_2 present in ambient atmosphere, according to eq (2) and (3) [73], to form the previously mentioned RSC.



Based on the findings of the 1st synthesis, an additional calcination (recalcination) was performed to the previously described cathodes (1.1, 2.1, 3.1, and 4.1). From the results shown in Figure 4.1, the most notable differences were seen in cathodes 2.1 and 4.1, in which all peaks disappeared. The stretching C-H alkane bond also disappeared in material 3.1. On the other hand, the RSC peaks at 1400 cm⁻¹ and 870 cm⁻¹ in materials 1.1 and 3.1 are still visible. These results show that an extra heat treatment step can be added to minimize the carbonate content in the cathode powders. However, carbonate content is not fully eliminated. The remaining presence of RSC could be attributed to the active material's reaction with ambient air after being removed from this extra calcination step and before being stored in the glovebox.

From the results obtained in the 2nd synthesis procedure, illustrated in Figure 4.1, material 1.2 and 3.2 show a straighter spectrum in the region 3600 cm⁻¹ to 2500 cm⁻¹. In addition, materials 2.2, 3.2 and 4.2 do not exhibit the stretching C-H band, however, the characteristic peak at 1400 cm⁻¹ can still be observed in all samples. These results are related with the preparation process of the cathodes. In material 1.2 and 3.2, the straighter spectra in 3600-2500 cm⁻¹, expected in these materials [64], results from the use of the ball mill instead of the agate mortar used in the 1st synthesis. Since during the ball milling process, the samples are contained in the mill cup, these are more protected from ambient air. In addition, the heat formed from the rotation may reduce the humidity present in the mill cup, which hinders the reaction between the sample powders and air, and thus, reduces the amount of residual sodium compounds formed. Moreover, the disappearance of the peak at 3000-2840 cm⁻¹ is connected to the use of a flat crucible in the 2nd synthesis. It is believed that the taller crucible used in the 1st synthesis may hinder the calcination process by an insufficient contact between the gas's atmosphere of the oven and the sample, due to the establishment of a stagnation zone between the sample and the top of the crucible.

For the cathodes 2.1 and 4.1, deionized water was used to remove the powder from the mill cup. Since the 2nd synthesis (cathodes 2.2 and 4.2) does not show the peak at 3000-2840 cm⁻¹ when compared to the 1st synthesis, it can be concluded that using water in the milling process should be avoided. Based on these results, the 2nd synthesis procedure proved to be a more efficient cathode preparation method.

4.1.2 XRD and Rietveld refinement

Even though FTIR analyses can provide insights regarding chemical composition of the cathode material, infrared spectroscopy alone is insufficient for a thorough characterization of the material under study. Therefore, following the preliminary FTIR analyses, the cathode materials 5.2, 6.2 and 7.2 were synthesized, and the crystal structure of all as-prepared n.2 materials was studied through XRD, with the patterns of each cathode material shown in Figure H.1-H.7, Appendix H. All the experimental Bragg diffraction peaks are sharp and well defined, indicating high crystallinity of the obtained materials after calcination at high temperature [75]. The Rietveld refinement of the synthesized cathode materials was also performed, and the results are listed in Table 4.1.

Table 4.1 - Rietveld refinement results on the XRD patterns of the different cathode materials.

Material	Main Space Group	Lattice Parameters / Å		Crystallite size / nm	Reliability Factors / %	
1.2	P6 ₃ /mm _c	$a = b = 2.898$	$c = 11.17$	50.0	$R_p = 22.3$	$R_{WP} = 31.5$
2.2	$R\text{-}3m$	$a = b = 2.958$	$c = 16.08$	65.8	$R_p = 11.5$	$R_{WP} = 15.9$
3.2	$R\text{-}3m$	$a = b = 2.958$	$c = 16.06$	77.0	$R_p = 9.75$	$R_{WP} = 13.1$
4.2	$R\text{-}3m$	$a = b = 2.974$	$c = 16.09$	71.7	$R_p = 9.26$	$R_{WP} = 12.5$
5.2	$R\text{-}3m$	$a = b = 2.973$	$c = 16.05$	89.5	$R_p = 9.30$	$R_{WP} = 13.0$
6.2	$R\text{-}3m$	$a = b = 2.972$	$c = 16.04$	70.0	$R_p = 9.42$	$R_{WP} = 12.2$
7.2	$R\text{-}3m$	$a = b = 2.970$	$c = 16.00$	66.0	$R_p = 13.5$	$R_{WP} = 18.0$

The XRD patterns of most cathode materials were successfully indexed to an O3-type structure, isostructural with $\alpha\text{-NaFeO}_2$ and with a $R\text{-}3m$ space group, as expected for cathodes with these chemical compositions [69,70]. On the other hand, material 1.2 exhibits a mixture of P2 (90 mass %) and monoclinic O3 (10 %) phases with P6₃/mmc and C2/m space groups, respectively.

Material 1.2, based on its chemical composition, should display an O3-type structure, specifically, an O'3 structure formed by monoclinic distortion of the O3 lattice induced by Jahn-Teller distortion of Mn³⁺ [57]. However, the XRD pattern shows that cathode 1.2 displays mainly a hexagonal P2-type structure. This biphasic coexistence is caused by the nickel and titanium doping into the layered structure, instead of the traditional co-substitution method [59]. According to the results obtained by Lee *et al.*, adding Ni and Ti leads to the formation of a P2-type structure [76], since Ni and Ti share the transition metal sites with Mn and, thus, the Na/TM (TM= Mn, Ni, and Ti) ratio is lower than 1. From these results, it is also expected that cathode 1.2 demonstrates topotactic intergrowth at an atomic scale [76]. An illustrative example of intergrowth stacking of the P2 and O3 lattice is shown in Figure H.8, Appendix H.

The lattice parameters for the observed O'3 phase in material 1.2 are $a = 5.642$ Å, $b = 2.852$ Å, and $c = 5.786$ Å, which are very similar to the lattice parameters of O'3-NaMnO₂ [57]. The lattice parameters for the P2-type structure are listed in Table 4.1.

In addition, according to the results obtained by Guo *et al.*, the synthesized material 1.2 should display a similar mass fraction of the O'3 and P2 phases [59]. However, the sample revealed a much higher P2 mass fraction. This result suggests a lower overall occupancy of the sodium layer sites, with one of the possible mechanisms responsible for this phenomenon the spontaneous reaction of Na⁺ ions with ambient H₂O and CO₂ [76].

Material 2.2 exhibits an increase in the c -axis lattice parameter when compared to the cathode material O3- $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($a=b= 2.962 \text{ \AA}$, $c= 15.91 \text{ \AA}$) [77]. Such increase can be explained by the substitution of larger Ti^{4+} ($r= 0.60 \text{ \AA}$) for smaller Mn^{4+} ($r= 0.53 \text{ \AA}$), confirming the successful incorporation of Ti into the host material, while maintaining the O3 structure [69]. In addition, the XRD patterns reveal that instead of a single O3 phase, the cathode material 2.2 has a small amount of NiO (0.2 %) and hydration (1.0 %) phases. Both phases result from direct contact of the samples with air. When in contact with ambient atmosphere, particularly, in materials with a high Ni content, chemical degradation mechanisms occur in the surface of the material, and form NiO that can accumulate on the particle surface [61,73].

The hydration phase, detected by the two new peaks around 12° and 25° in the XRD pattern, corresponds to a layered structure formed from the intercalation of H_2O molecules [59]. The presence of water in the sodium layers will lead to a broader interlayer spacing due to the higher ionic radius of H_2O ($r= 1.34 \text{ \AA}$) compared to Na^+ ($r= 1.02 \text{ \AA}$), hence contributing to an increase in the c -axis parameter [61]. An illustrative example of water molecule intercalation can be found in Figure H.9, Appendix H.

Figure 4.2 shows the graphical representation of the lattice parameters a and c for the cathodes 2.2, 3.2, and 4.2.

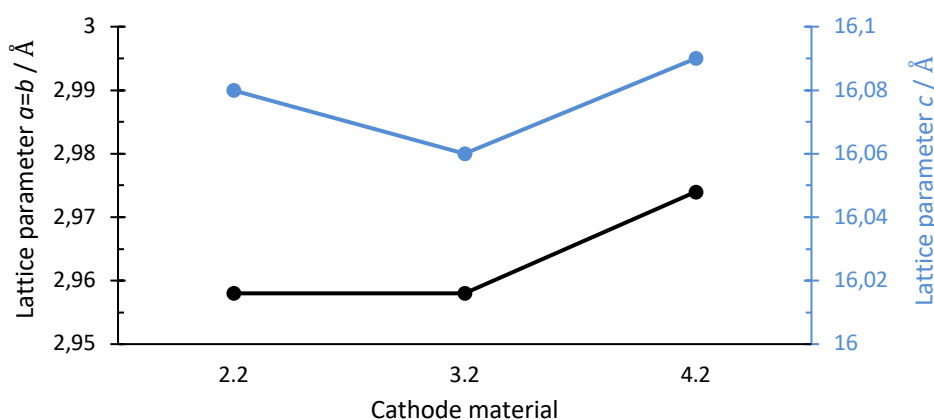


Figure 4.2 - Lattice parameters a , b , and c after Rietveld refinements for cathodes 2.2, 3.2, and 4.2.

The lattice parameters of cathode 3.2 should be higher than for cathode 2.2 since cathode 3.2 has the partial substitution of smaller Ni^{2+} ions ($r= 0.69 \text{ \AA}$) by larger Cu^{2+} ions ($r= 0.73 \text{ \AA}$) [69]. However, due to the intercalation of water molecules in material 2.2, that was not observed. Furthermore, the lattice parameters increase from material 3.2 to 4.2 due to the higher Ti content, which is in agreement with the results of Wang *et al.* [69]. The values obtained in this work for the lattice parameters of the cathodes 3.2 and 4.2 are shown in Table 4.1, and are in agreement with the values found in the literature [68,69]. Cathode 3.2 and 4.2 displays an almost single O3 phase, with a mass percentage of 1.9 % and 0.5 % of NiO impurity, respectively, demonstrating a good air stability.

Materials 5.2, 6.2 and 7.2 show an increase in aluminum content, and the lattice parameters decrease from material 5.2 to 6.2, as seen in Figure 4.3, due to the substitution of smaller Al^{3+} ($r=0.53 \text{ \AA}$) for Fe^{3+} ($r=0.63 \text{ \AA}$), confirming the successful incorporation of Al into the host material [64]. These values are in agreement with the values found in the literature [64].

The accentuated decrease of the lattice parameters in material 7.2 results from a high Al content and lower Ni, Fe and Mn content. In addition, cathodes 5.2 and 6.2 show an almost single O3 phase with a mass percentage of NiO of 2.0 % and 1,3 %, respectively. On the other hand, instead of the typical NiO phase, material 7.2, exhibited a mass percentage of 9.5 % of Al_2O_3 , specifically, a sapphire corundum phase.

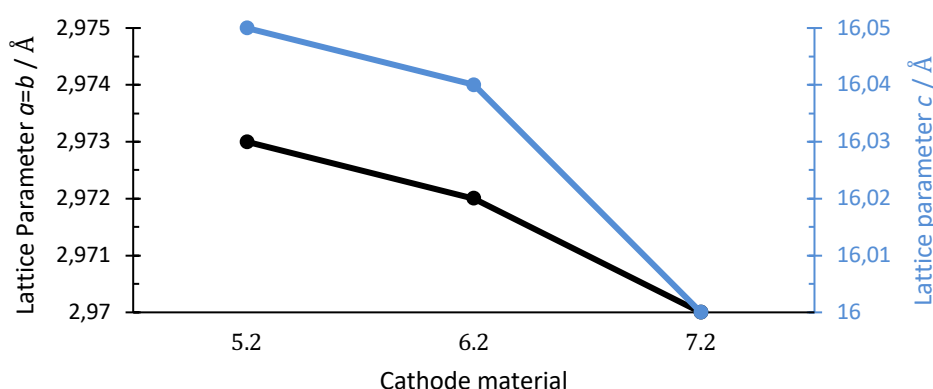


Figure 4.3 - Lattice parameters a , b , and c after Rietveld refinements for cathodes 5.2, 6.2, and 7.2.

Furthermore, the XRD patterns for the materials 1.1, 2.1, 3.1, and 4.1 were also analyzed and compared with the patterns obtained for their respective n.2 samples (Figure 4.4). The most notable differences were detected in the samples 2.1 and 4.1, in which the peak at 16° , indicative of the insertion of Na^+ ions, is not present [59]. These results are related with the preparation process of the cathode; deionized water was used to remove the powder of cathode 2.1 and 4.1 from the mill cup. Metal sodium is highly reactive with water, forming sodium hydroxide and hydrogen, leading to a sodium-free material.

Thus, using water to remove the powder from the mill cup should not be included in the cathode synthesis procedure, and, as a result, the cathode powder should be scrapped from the ball mill. The yields obtained from scrapping the powder from the ball mill for all n.2 cathode materials are listed in Table 4.2, and the values used to calculate these yields are listed in Table F.4, Appendix F. An average yield value of 89 % was obtained, which is an acceptable value for the cathode production at a laboratory scale, but not for an industrial process. Moreover, scrapping the powder from the ball mill is not a practical method at industrial level either, with a solvent-based removal method more appealing for larger scale production.

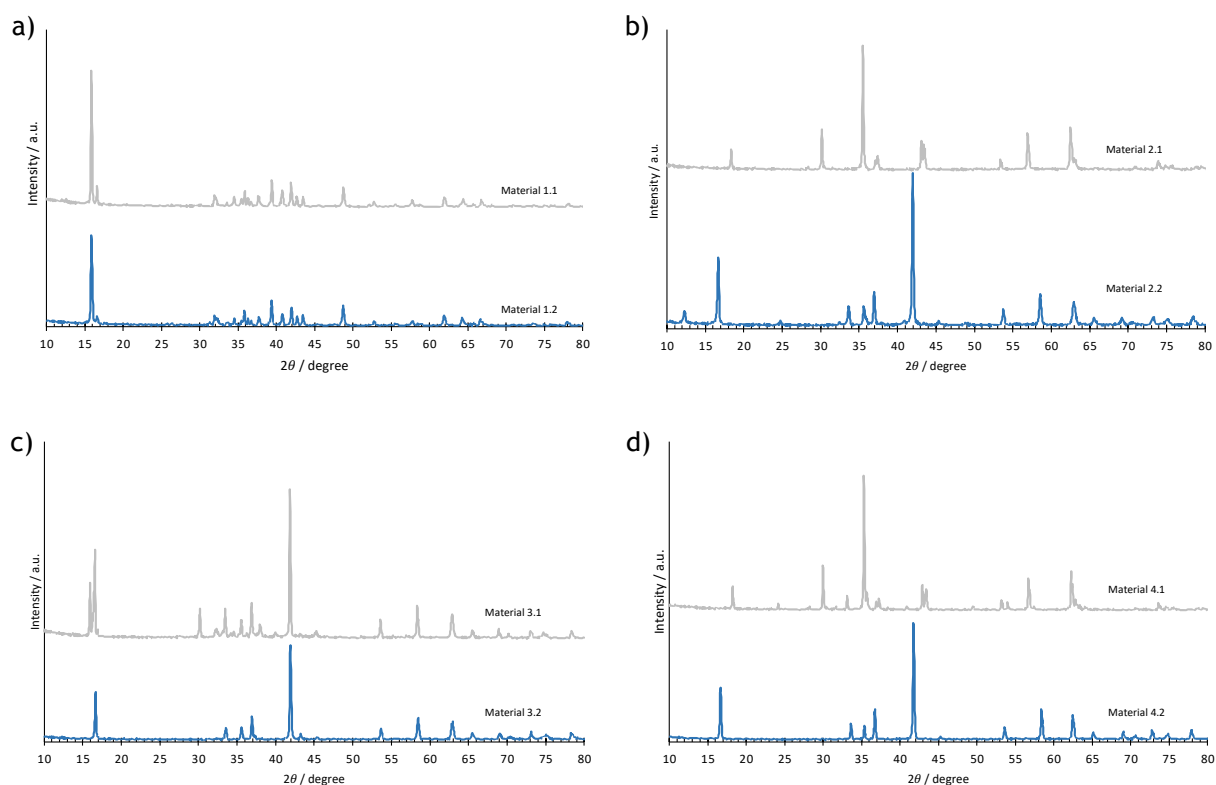


Figure 4.4 - XRD pattern for the materials a) 1.1 and 1.2, b) 2.1 and 2.2, c) 3.1 and 3.2, d) 4.1 and 4.2.

Table 4.2 - Yield obtained from scrapping the cathode materials from the mill cup.

Material	1.2	2.2	3.2	4.2	5.2	6.2	7.2
Yield / %	88.2	87.8	87.8	87.9	88.3	90.8	89.8

4.1.3 SEM and morphology analyses

The surface morphology of the as-prepared n.2 cathode materials was assessed through scanning electron microscopy (SEM). The SEM images obtained are illustrated in Figure 4.5, and show that all the samples are constituted by micron to submicron primary particles, which agglomerate to form larger secondary particles. In addition, all samples show pores between particles, which is beneficial to Na^+ ion diffusions and wettability of the active cathode material. Additional SEM images of the n.2 cathode materials in different amplifications can be found in Figure H.10, Appendix H.

In the material 1.2, well-shaped primary particles form secondary particles composed of layered sheets, which is in agreement with the results obtained by Guo *et al.* [59]. The materials 2.2 and 4.2 show a predominance of well-shaped, polygonal microflakes with smooth facets. When compared to the other samples, the latter were recalcined and, thus, had a longer total calcination period. As a result, a greater crystallization of the materials and smoother facets may be observed [78].

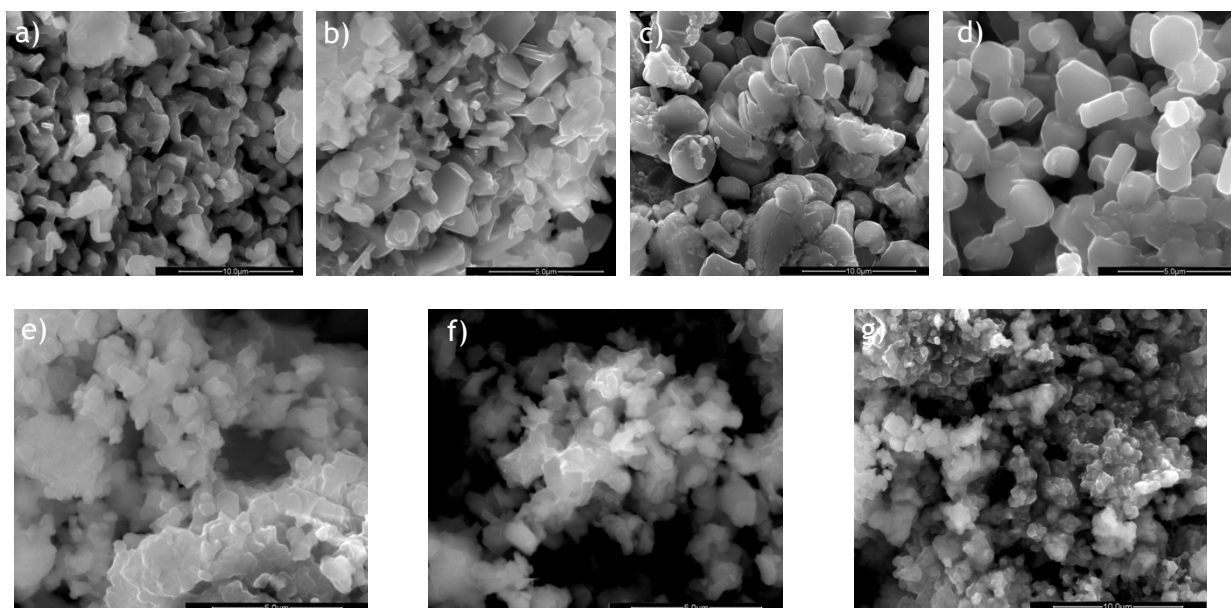


Figure 4.5 - SEM images of the cathode material a) 1.2, b) 2.2, c) 3.2, d) 4.2, e) 5.2, f) 6.2, g) 7.2.

In the material 3.2, nanosized crystals can be observed on the surface of the main particles. These crystals correspond to the NiO rock salt phase detected on the XRD pattern for this material. The formation of NiO particles on the top of the primary particles has also been found in the literature [73]. In the material 5.2, layered sheet structures very similar to those observed in material 1.2 can also be detected. Material 6.2 exhibits sheet-like particles, which is in line with the results obtained by Wang *et al.* [70]. Finally, in material 7.2, polygonal microflakes primary particles and a considerable degree of agglomeration can be observed.

In addition to the SEM analyses, a qualitative EDS analysis for the samples 1.1, 2.1, 3.1 4.1, and their n.2 counterparts was performed, and the results are reported in Appendix H.3. The findings obtained from this qualitative analysis confirms the results obtained from the FTIR and XRD analyses.

Based on the findings, it is determined that the solid-state method was a viable way for producing cathodes for SIBs. Furthermore, these cathodes can be considered appropriate for being used in sodium-ion batteries, since they showed the expected crystalline structure and low mass fraction of impurities.

4.2 Cathode deposition

The as-synthesized cathode materials were then used to produce the electrodes. The electrode fabrication is a complex process with multiple steps, all of which impact the microstructure and the ultimate performance of the battery [79]. The electrode manufacturing process determines the final battery performance as it influences parameters such as porosity, pore size, tortuosity, and, consequently, the transport of Na^+ ions in the electrode [80]. An experimental optimization of the electrode manufacturing process was performed to produce suitable electrodes for coin cell testing.

In this work, the electrode manufacturing procedure was divided into two main phases: slurry preparation and coating of the slurry onto the current collector. Additionally, film testing was performed to evaluate the quality of the coatings.

4.2.1 Slurry preparation and coating

For the electrode preparation, two different binders, ethyl cellulose (ECL) and PVDF, were tested. Even though ethyl cellulose is not a commonly used binder for electrode preparation, this polymeric matrix is soluble in alcoholic solvents rather than the toxic solvents commonly employed for PVDF [80]. Moreover, ethyl cellulose has been demonstrated as a binder material in the pharmaceutical industry for tablet production [81]. In the initial step of the slurry preparation, a mixture of ECL with the solvent terpineol and a PVDF mixture with the solvent N-methyl-2-pyrrolidone (NMP) were prepared. Then, the cathode active material and conductive carbon black were added to each mixture.

During the electrode preparation, three different experimental tests were carried out to compare the influence of different conditions for preparing and drying the slurry. In the first test, the impact of the ratio of binder and solvent, in the initial mixture, on the viscosity of the coating was assessed. The optimum ratio of active material, conductive carbon, and binder, on the slurry was also assessed. In a second test, two solutions containing the binder and the solvent (ECL:Terpineol and PVDF:NMP) were subjected to two different mixing strategies: 1) manual mixing in the agate mortar and 2) mixing with magnetic rotation at 200 rpm. Finally, two different approaches to dry the slurry (at room temperature and placing the electrode on a hot plate at 75 °C), were tested to assess its impact on the final coating. In all these tests, a wet coating thickness of 150 μm was set by the doctor-blade. This coating thickness was selected based on the values reported in the literature [82].

The viscosity of the slurry is a critical property affecting the electrode performance [71]. The viscosity of the resulting slurry was controlled solely through visual analysis since no equipment was available to perform such measurements. In the electrodes prepared with ECL, it was found that a mass percentage lower than 10 % ECL in the initial mixture with terpineol resulted in a very liquid slurry, which is not ideal for slurry coating since it may cause runniness and pooling [71]. The resultant coatings were very similar to the ones showed in Figure 4.6 b and c. Based on these results, an experimental optimization was undertaken, and it was found that an initial solution comprising a mass percentage of ECL close to 50 % was appropriate since it leads to slurry with the desired consistency. Following that, the active material and conductive carbon were added to produce a slurry comprising 90 % cathode powder, 5 % carbon black, and 5 % binder (90:5:5). However, after drying at room temperature, it was observed that the coating peeled, indicating a weak binding of the cathode to the current collector. The ratio 80:10:10 was found to produce more uniform coatings without peeling (Figure 4.6.d) and, thus, was considered as the optimum ratio for ECL-based electrodes.

Likewise, the amount of PVDF used revealed to be a critical point in the electrode fabrication. It was observed that a mass percentage of 10 % PVDF in the initial mixture with NMP lead to a very viscous and granular slurry, which was impossible to spread uniformly with the doctor-blade (*cf.* Figure 4.6.a) [71]. According to the literature, this result may be due to the high viscosity of the PVDF/NMP solution, since a higher viscosity leads to a less uniform mixing of the active material and PVDF/NMP solution, and it will be harder for the binder to spread over the active material upon addition [82]. On the other hand, a low mass percentage of PVDF in the PVDF/NMP mixture, such as 3 %, will result in a slurry with very low viscosity. In this scenario, due to the high amount of solvent, the solid particles are very dispersed in the mixture and thus, after coating and drying, the electrode exhibits numerous cracks (Figure 4.6.b). Moreover, as seen in Figure 4.6.c, a slurry with a very low viscosity may also lead to a nonuniform distribution of the particles in the final coating. Based on these findings, an empirical optimization process was carried out, until an optimal slurry consistency with 4.5 % of PVDF/NMP initial solution was achieved. Following that, the ratio 85:5:10 on the final slurry was found to produce the most uniform coatings and without any peeling for the PVDF binder.

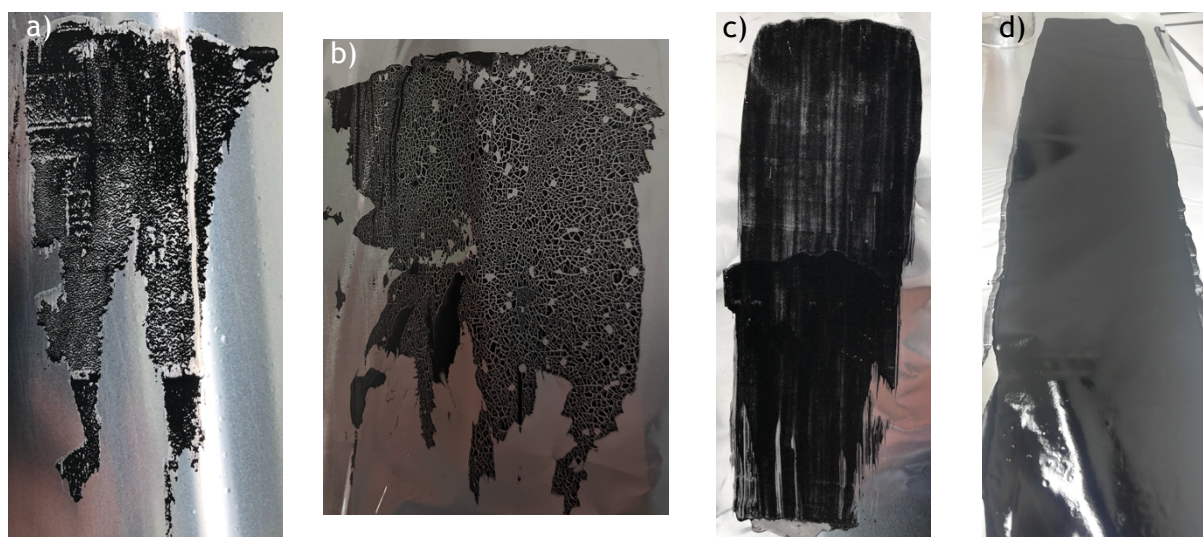


Figure 4.6 - Examples of coating using a slurry with a a) high viscosity, b,c) low viscosity and d) optimized viscosity (uniform coating) with mass ratios of active material, conduction carbon and binder of 80:10:10 and 85:5:10 for ECL and PVDF-based electrodes, respectively.

In a second test, the mixing strategy of the slurry was evaluated. This is a vital step regarding electrode production that contributes to 7 % of the total manufacturing cost [80]. The main objective of this step is to break up agglomerates and achieve a uniform particle distribution [79,80]. Two different mixing strategies were tested: a low-speed manual mixing and a high speed (200 rpm) mixing by magnetic rotation. For the electrodes prepared with ECL, no significant differences were observed, with both strategies producing a uniform coating. However, the same cannot be said for the electrodes prepared with PVDF. In the manual mixture, it was observed that, after drying, the coating was completely peeled

off from the aluminum foil. On the other hand, the coating prepared with magnetic rotation did not peel off from the current collector (*cf.* Figure H.12, Appendix H). Based on these findings, it was concluded that a high-speed mixing strategy is necessary to breakdown the PVDF molecules and activate their binding properties.

In the final test, different slurry drying strategies were considered, by performing a room temperature drying and a higher temperature (75 °C) drying. This is one of the most important steps in electrode preparation since the drying temperature influences the polymer chain mobility and final distribution of the binder on the electrode [83]. For the electrodes prepared with ECL, no significant differences were observed, with both evaporation rates leading to uniform coatings. On the other hand, the evaporation procedure demonstrated a strong impact on the PVDF-based electrodes (*cf.* Figure H.13, Appendix H). Drying the slurry at room temperature resulted in a homogeneous coating layer, while heating the slurry in a hot plate resulted in large fissures in the cathode coating. Therefore, low temperatures (e.g, room temperature) should be used to dry the slurry.

4.2.2 Film testing

After coating and drying the slurry on the aluminum foil, the different electrodes were subjected to several solubility and mechanical tests. Solubility tests are essential to determine the compatibility of the electrode with the selected electrolyte solution. On the other hand, the mechanical tests are used to assess the binding quality between cathode particles and between cathode particles and the aluminum foil. In the solubility test, both electrodes prepared with ECL:Terpineol and PVDF:NMP were submerged in EC:PC electrolyte solution, as shown in Figure 4.7. It was observed that the electrodes prepared with ECL (left flask) fully peeled off from the aluminum foil, whereas the electrodes prepared with PVDF (right flask) did not. Based on these results, it was concluded that ethyl cellulose is soluble in the carbonate electrolyte and, thus, would not reveal a good electrochemical performance since it is expected a very high charge-transfer resistance. After the solubility tests, the PVDF-based electrodes were subjected to several mechanical tests, such as scratch, bending, and exfoliation, showing no degradation.

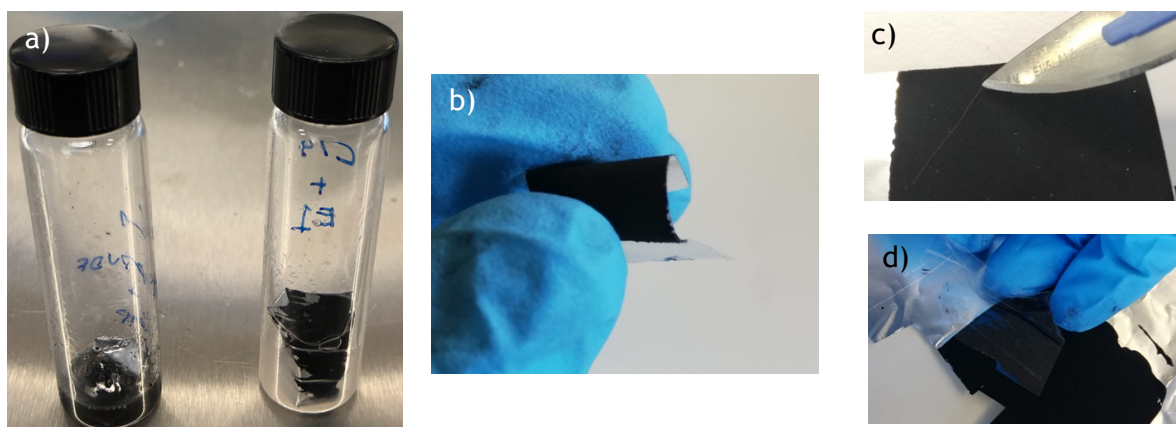


Figure 4.7 - a) Solubility tests b) bend testing, c) scratch testing, d) exfoliation test.

4.3 Coin cell testing

This subchapter summarizes the key results addressing the electrochemical performance of the coin cells assembled as described in section 3.3. In these electrochemical tests, two different cathodes were used: the as-synthesized cathode 2.2 and commercial $\text{Na}_{0.7}\text{MnO}_{2+x}$. Additionally, the two different binders, ECL and PVDF, were also tested. The coin cells assembled with commercial $\text{Na}_{0.7}\text{MnO}_{2+x}$ cathode material (NEI Corporation) were used as a basis of comparison for future tests.

4.3.1 Electrochemical impedance spectroscopy

In a first step, two different types of coin cells were assembled: 1) with cathode 2.2 and ECL as binder and 2) with $\text{Na}_{0.7}\text{MnO}_{2+x}$ and PVDF as binder. All coin cells used KURANODE™ as the anode active material. The fresh coin cells were then subjected to electrochemical impedance spectroscopy (EIS) to determine the different resistances in the cell and to confirm the results discussed in the previous section. The cathode material and binder used, the mass of the coating, as well as the mass loading of each positive electrode, and the theoretical capacity of each coin cell are listed in Table 4.3.

Table 4.3 - Cathode material, binder, coating mass, mass loading and theoretical capacity of each assembled coin cell.

Coin cell	Cathode material	Binder	Positive electrode mass / mg	Coating mass / mg	Mass loading / $\text{mg}\cdot\text{cm}^{-2}$	Capacity / mAh
CC1	2.2	ECL	18.5	11.9	7.74	2.30
CC2	2.2	ECL	20.1	14.1	9.17	2.72
CC3	$\text{Na}_{0.7}\text{MnO}_{2+x}$	PVDF	16.3	9.72	6.31	1.78
CC4	$\text{Na}_{0.7}\text{MnO}_{2+x}$	PVDF	17.4	10.8	7.03	1.98

The mass of the cathode coating on the positive electrode was calculated by subtracting the average mass of aluminum in a single electrode from the mass of the positive electrode. The mass of aluminum in a single electrode was computed as the average mass of six aluminum disks with a diameter of 14 mm, yielding a value of (6.6 ± 0.1) mg. The mass loading of each positive electrode was calculated by dividing the mass of the cathode coating by the area of each electrode ($A = 1.54 \text{ cm}^2$). Finally, the theoretical capacity of each coin cell was computed based on eq (4). $Q_{\text{theo,cell}}$ is the theoretical capacity of the coin cell, m_{coat} the mass of the coating on the positive electrode, $r_{\text{cat,elec}}$ the ratio of active cathode material in each electrode (80 % for the ECL and 85 % for the PVDF-based electrodes, respectively) and $Q_{\text{theo,cat}}$ the theoretical capacity of each cathode material (listed on Table H.1, Appendix H). The theoretical capacity of each cathode material was computed based on the equations shown in Appendix B.

$$Q_{\text{theo,cell}} = m_{\text{coat}} r_{\text{cat,elec}} Q_{\text{theo,cat}} \quad (4)$$

EIS measurements were performed on the fresh coin cells with a frequency range between 10 mHz and 1 MHz, with an electric current perturbation of 1 μ A and an amplitude of 10 mV. The Nyquist plots, obtained from the EIS tests, of the coin cells assembled are shown in Figure 4.8.

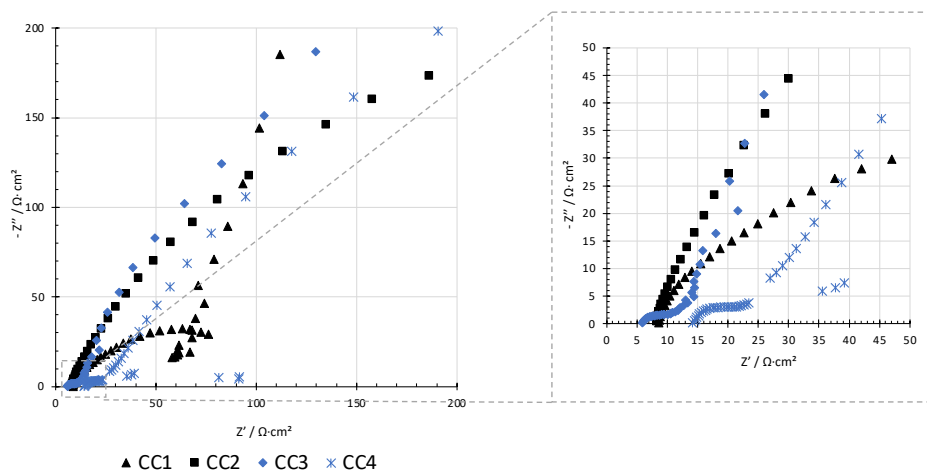


Figure 4.8 - Nyquist plots for the fresh coin cells CC1, CC2, CC3 and CC4.

A Nyquist plot for a lithium or sodium-ion battery is typically composed by two semicircles in the medium frequency region and a linear response in the low frequency region [84,85]. The mid frequency semicircles are associated with charge-transfer resistances from the electrode surface to the electrolyte and from the electrode surface into the bulk of the material (R_{ct}) [85]. The linear response at low frequency is associated with diffusion of the Na^+ ions within the active material (W) [84]. In addition, the interception of the Nyquist plot with the real impedance axis corresponds to the sum of internal ohmic resistances (R_Ω) of the cell, which include ionic conductivity of the electrolyte, and the electronic conductivity of the cathode, anode and current collectors [84].

The R_Ω for the CC1 and CC2 are 8.2 $\Omega\cdot\text{cm}^2$ and 8.6 $\Omega\cdot\text{cm}^2$, respectively, whereas the value of R_Ω for CC3 and CC4 are 5.9 $\Omega\cdot\text{cm}^2$ and 14.2 $\Omega\cdot\text{cm}^2$, respectively (Figure 4.8). As can be seen, the CC2 and CC4 cells have higher ohmic resistance despite having the same active and binder materials as the CC1 and CC3 cells, respectively. This increase in ohmic resistance may be related to increased mass loading. Since there was no active control of the coating thickness after drying, a higher mass loading can lead to a thicker dry coating, leading to a higher ohmic resistance [86,87]. On the other hand, this problem may also be associated with the electrolyte volume. There was no active control of the volume of electrolyte and, during the crimping of the coin cell, electrolyte overflow was observed. A lower amount of electrolyte within the electrode will lower the contact surface area between the electrode and electrolyte, which may result in an increased ohmic resistance.

Additionally, Figure 4.8 shows that coin cells CC1 and CC2, assembled with ECL-based electrodes, show no semicircle in the mid frequency region, while the coin cells with PVDF-based electrodes (CC3 and

CC4) display one semicircle in the same region. Since these EIS measurements were performed before the formation of the SEI layer (before cycling), the semicircle in CC3 and CC4 may be related to the cathode internal resistances. On the other hand, the absence of the semicircle in CC1 and CC2 indicates that no electrochemical reactions are occurring in the coin cell. This result might be due to the incompatibility between the coatings and the electrolyte solution. As shown in section 4.2, the ECL-based electrodes separate from the aluminum foil when in contact with the electrolyte. Thus, coin cells CC1 and CC2 were not further tested. Based on all these results, it was concluded that the coin cell CC3 showed the most promising electrochemical performance due to the lower ohmic and charge transfer resistances. Thus, further performance tests were carried out on this cell.

4.3.2 Charge-discharge cycles

Following the EIS measurements, the coin cell CC3 was subjected to galvanostatic charge-discharge cycles (CDC). This is an essential electrochemical test since it enables the characterization of the cycle life of the coin cell. In this work, fifty galvanostatic charge-discharge cycles were carried out at a constant current rate of 1 mA, and cut-off potentials of 4 V and 0 V were used for charge and discharge steps, respectively. The charge-discharge profiles for the 1st, 2nd, 5th, 10th, 25th, and 50th cycle, as well as the coulombic efficiency and specific capacity of the coin cell CC3 are illustrated in Figure 4.9. The specific capacity of the cell was computed based on the mass of positive electrode coating.

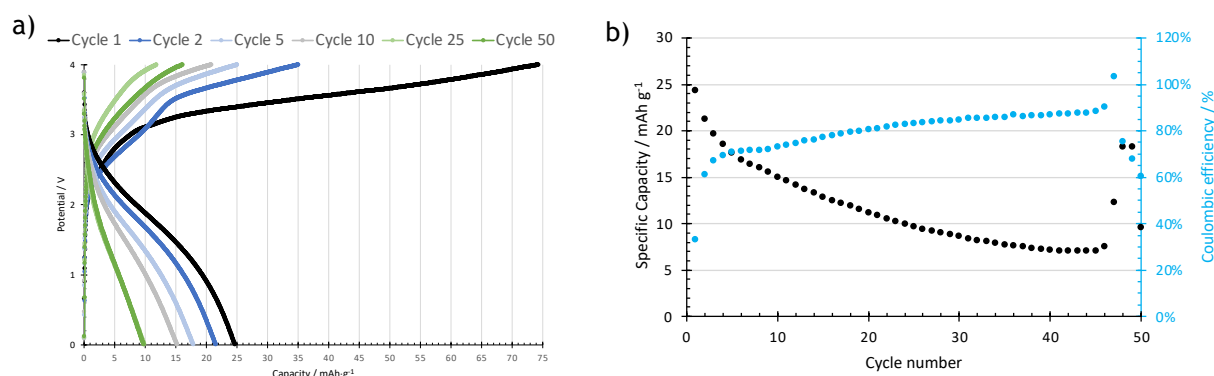


Figure 4.9 - a) charge discharge profiles b) cycling performance at 0-4 V.

From the results shown in Figure 4.9, CC3 exhibited smooth CDC profiles, indicating almost no phase transitions during the cycling process [51]. These smooth charge-discharge curves are consistent with the results published for very similar cathode materials [88]. In the first cycle, the charge capacity of 73.5 mAh·g⁻¹ was considerably higher than the discharge capacity of 24.4 mAh·g⁻¹, which is a small delivery capacity when compared to the values reported in the literature [88]. A low coulombic efficiency of 33 % is, thus, observed in the first cycle. The SEI formation could explain the limited discharge capacity in the first cycle. Sodium ions that form the SEI layer become unavailable in succeeding cycles, leading to a high capacity fade on the first cycle [25]. This results are in agreement with the results reported in the literature [70].

5 Conclusions

Energy storage systems have been continuously developed in recent decades, not only as a result of technological breakthroughs, but also to stabilize the electrical grid when supplied by renewable energy sources. Therefore, significant efforts have been directed into the development of new, sustainable, safe, and low-cost technologies, with rechargeable sodium-ion batteries emerging as a potential and complementary technology to the lithium batteries.

This project, in collaboration with Simoldes Plástico Lda., a major national player on the field of car manufacturing value chain, aimed to onset the research on sodium-ion batteries in Portugal. In this work, seven different layered transition metal oxides, previously reported in the literature, were synthesized and analyzed as potential cathodes materials. Additionally, the electrode preparation and coin cell assembly procedures were assessed and optimized, to produce low-cost, high-power density, and stable sodium batteries for a future industrialization.

Initially, all cathode materials were prepared by solid state-reaction, and FTIR measurements were used to perform a parametric study of different synthesis conditions. It was shown that, due to contact with ambient atmosphere and moisture, all prepared materials showed the presence of sodium-based contaminants such as Na_2CO_3 and NaHCO_3 . An additional calcination step was proven to minimize the carbonate content in the cathode powder but does not eliminate it. Furthermore, the materials prepared in the ball mill, as they were more protected from the ambient atmosphere, and due to the increase in temperature during the grinding process, showed smaller contaminants concentration. Finally, the use of water during this ball milling process was proven to increase the concentration of residual sodium compounds.

The synthesized materials were physically characterized by XRD and SEM. Most of the materials exhibited the expected O3-type structure, isostructural with $\alpha\text{-NaFeO}_2$, and with a $R\text{-}3m$ space group. Material 1.2, however, showed a mixture of P2 and O3 structures, resulting from the addition of nickel and titanium. The successful integration of titanium and copper in materials 2.2, 3.2 and 4.2, and the successful integration of aluminum in materials 5.2, 6.2 and 7.2 was also demonstrated by XRD analysis. The XRD pattern of most materials also revealed a low quantity of NiO impurity, which is commonly seen in high Ni content materials. Furthermore, materials 2.2 showed the presence of a hydration phase, resultant from the contact with ambient atmosphere, which is responsible for the higher *c*-axis parameter in material 2.2 compared to the material 3.2. On the other hand, material 7.2 revealed the presence of a Al_2O_3 phase, specifically, a sapphire corundum phase.

Finally, a XRD comparison of the materials produced with and without water in the milling processes was performed, showing that the use of water results in sodium-free materials due to sodium leaching. The morphology of the materials was also examined by SEM, with all the samples being made by micron to submicron primary particles that agglomerate to form larger secondary particles.

Following the synthesis of all cathode materials, the electrode preparation procedure was studied and experimentally optimized by testing different binders, mixing strategies and solvent evaporation rates. For the ethyl cellulose binder (ECL), it was discovered that a mass fraction of 50 % ECL in the initial mixture with terpineol, and a final slurry ratio of 80 % active material, 10 % carbon black and 10 % binder resulted in uniform coatings. For the PVDF binder, a mass fraction higher than 10 % PVDF in the initial mixture with NMP results in a very viscous liquid, making binder penetration into the active material difficult. An optimum mass fraction of 4.5 % PVDF in the initial mixture in NMP was found, and a slurry ratio of 85 % active material, 5 % carbon black and 10 % binder was discovered to produce uniform coatings. Regarding the mixing strategy, while no significant effects were observed for the ECL binder, the same cannot be said for the PVDF electrodes. On the PVDF electrodes, manual mixing leads to coatings that peel off from the aluminum foil, whereas a mixing strategy with magnetic rotation at 200 rpm resulted in uniform coatings. The rate of solvent evaporation was investigated, with no significant effects observed for the ECL binder for either room temperature or 75 °C. On the other hand, for the PVDF electrode, in contrast to solvent evaporation at 75 °C, room temperature solvent evaporation resulted in crack free coatings. Finally, solubility tests were performed and demonstrated that in ECL-prepared electrodes, the coating peeled off from the aluminum foil, indicating solubility of ECL in the EC:PC electrolyte. The PVDF-prepared electrodes did not exhibit this phenomenon. Scratching, bending, and exfoliation tests were performed on PVDF electrodes, and a promising mechanical stability was observed.

Coin cell testing was completed at the final stage. EIS measurements on fresh coin cells showed that a higher mass loading and different electrolyte volumes may result in larger ohmic resistances. Moreover, coin cells built with ECL-prepared electrodes did not exhibit electrochemical reaction, which could be attributed to the incompatibility between the electrode and the electrolyte. The coin cell CC3 with commercial $\text{Na}_{0.7}\text{MnO}_{2+x}$ cathode and PVDF binder was subjected to fifty charge-discharge cycles, and smooth CDC curves were observed, indicating no phase transitions. The initial charge and discharge capacities were $73.5 \text{ mAh}\cdot\text{g}^{-1}$ and $24.4 \text{ mAh}\cdot\text{g}^{-1}$, respectively. The capacity decrease in the first and following cycles may be linked to the SEI formation.

Therefore, the projected goal of building a working sodium-ion battery was achieved. Based on the achieved results, new cells are now being assembled and tested for assessing the storage and stability performance.

6 Assessment of the work done

6.1 Objectives Achieved

In this work, an overview of the SIB technology, as well as an understanding of the different mechanisms and components was gathered. In addition, an overview regarding the impact of the cathode material on the electrochemical performance of a battery cell was performed.

The synthesis of seven layered oxide cathode materials by solid-state reaction was achieved successfully. The physical characterization of the mentioned materials showed encouraging results. Furthermore, a procedure for cathode deposition and electrode production was successfully developed and optimized. Finally, sodium ion coin cells with commercial cathode were assembled and electrochemically tested. However, no coin cells with the synthesized cathode material were electrochemically tested.

6.2 Other Work Carried Out

Aside from this thesis, three reports were prepared in connection with the development of the project carried out at VG CoLAB. Additionally, a three-electrode cell configuration with an aqueous electrolyte of 1M Na₂SO₄ in ultrapure water, was tried to test the synthesized cathode materials. However, this arrangement was not suitable for electrochemical tests since it was observed that the aluminum foil reacted in the electrolyte solution, and it was possible to detect hydrogen and oxygen evolution reactions due to the low electrochemical window of the aqueous electrolytes.

6.3 Limitations and future work

Due to the limited time available for the completion of this work, only coin cells using the commercial cathode as a positive electrode were successfully assembled and tested. However, after the delivery of this work, is expected that coin cells with the different cathode materials synthesized will be assembled and their electrochemical behavior will be tested.

6.4 Final Assessment

Throughout the course of this work, I was able to get a lot of insights regarding my professional expectations and ambitions. This experience has also provided me with a wealth of knowledge about professional life, learning and working methodologies, and team cooperation. Additionally, this project gave me the opportunity to develop a strong interest in the field of energy storage and renewable energy technologies.

7 Bibliographic References

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Appendix A - Energy consumption and Storage

A.1 Energy consumption

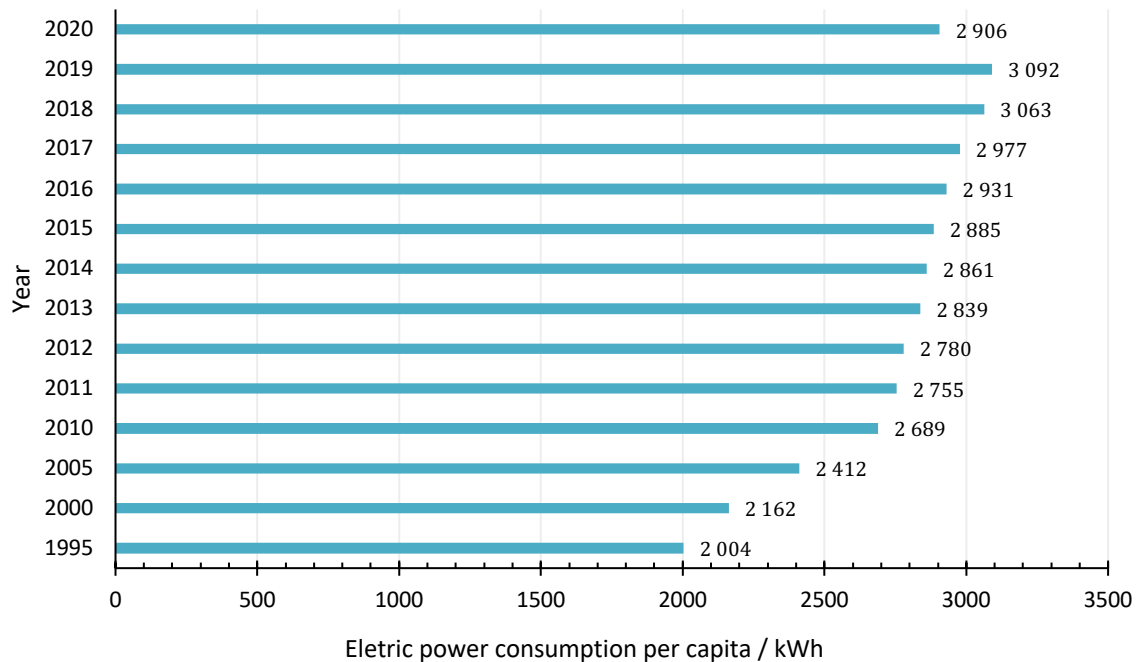


Figure A.1 - Worldwide electric power consumption per capita [1,2].

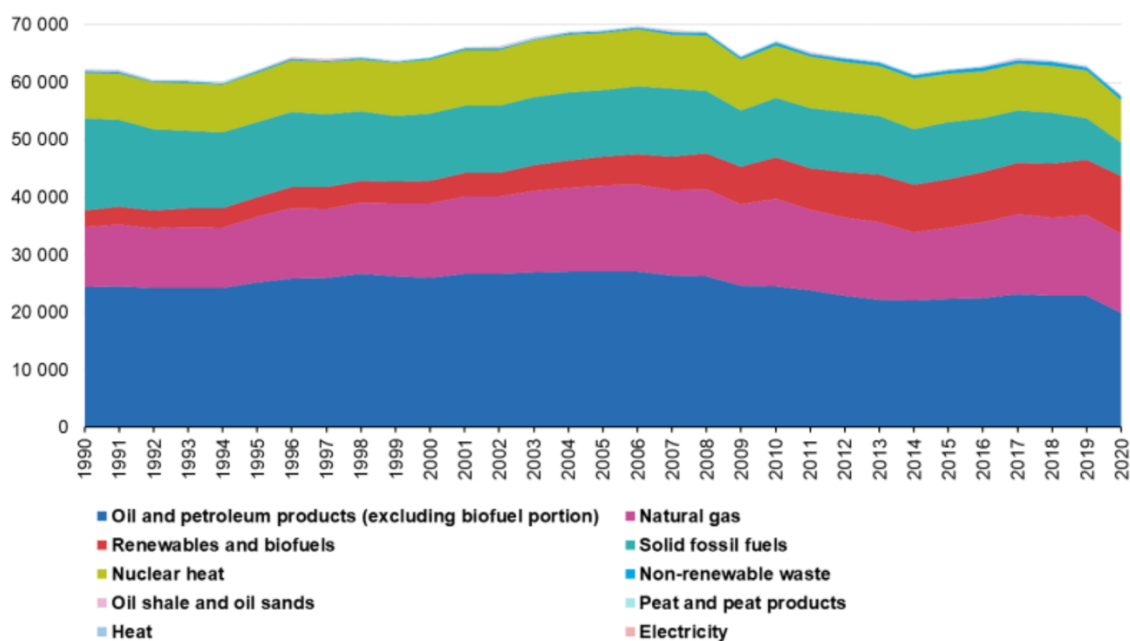


Figure A.2 - Gross available energy by fuel in the European Union [3].

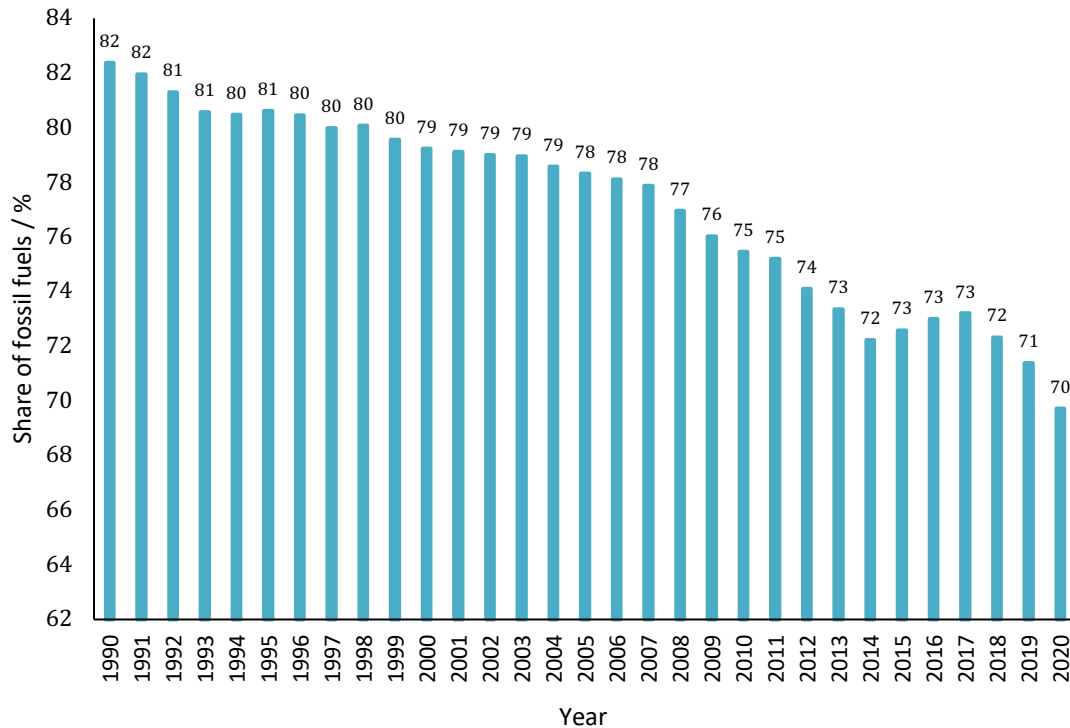


Figure A.3 - Share of fossil fuels in gross available energy in the EU [4].

A.2 Energy Storage

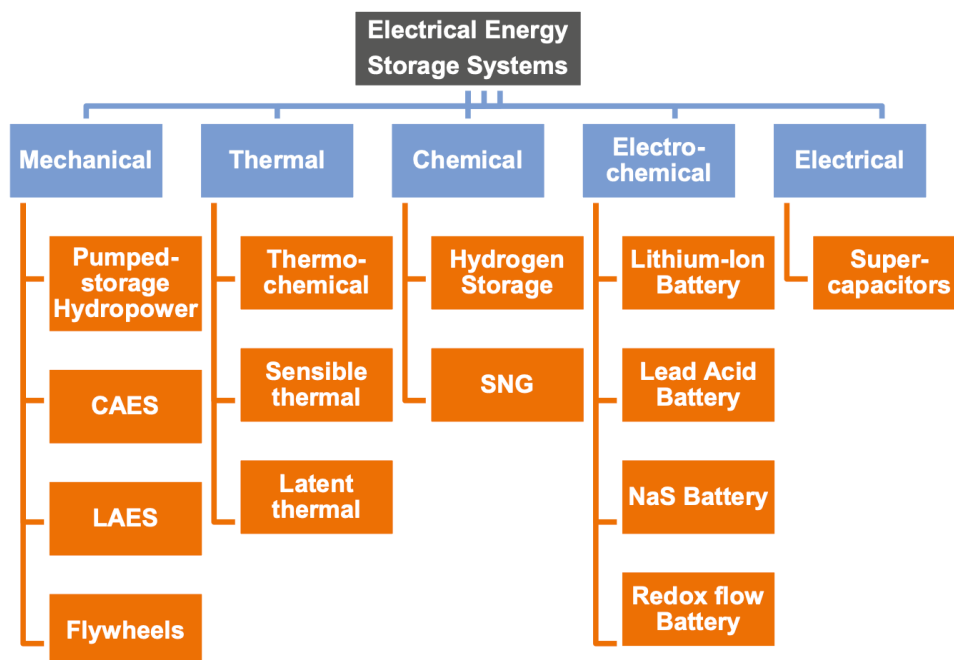


Figure A.4 - Classification of electrical energy storage systems [89].

A.3 Lithium reserves

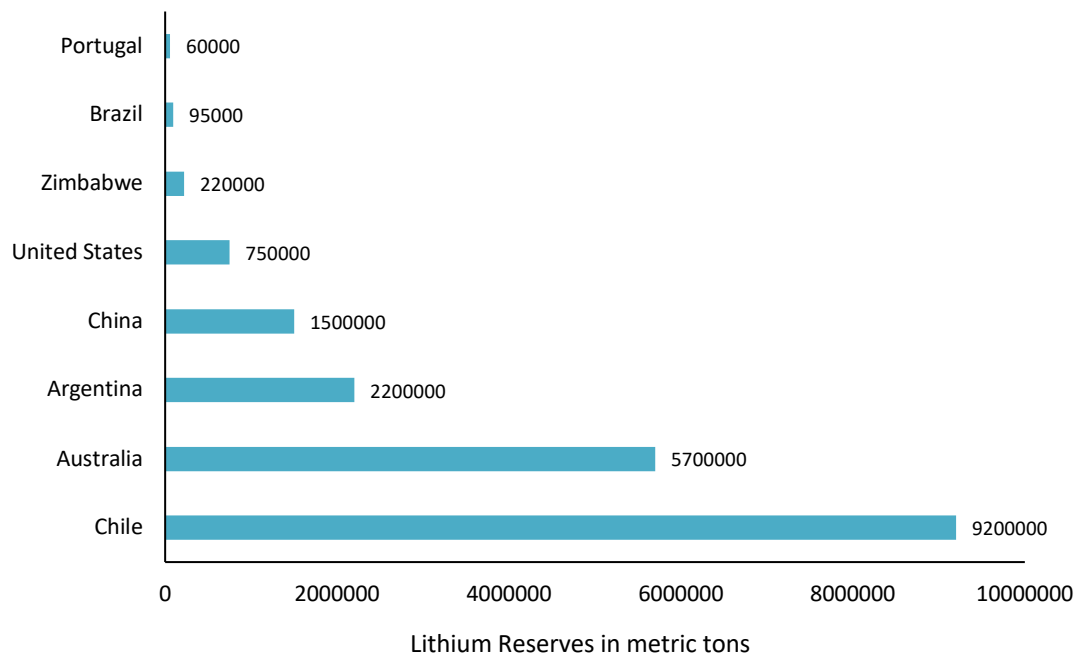


Figure A.5 - Countries with the largest lithium reserves worldwide as of 2021 [14].

Appendix B - Battery technical specifications

This section discusses several parameters that are used to evaluate the quality of the electrode material and the electrochemical performance of battery systems, including specific capacity, energy density, power density, C-rates, and coulombic efficiency.

B.1 Specific and volumetric capacity

The nominal capacity of an active electrode material is one of its most essential characteristics. It is the maximum stored charge that can be injected or extracted during battery cycling. The theoretical capacity ($Q_{\text{theo,cat}}$) in milliamp-hour per mass ($\text{mAh}\cdot\text{g}^{-1}$) of active material is computed according to eq (B.1).

$$Q_{\text{theo,cat}} = \frac{n F}{3,6 \text{ MW}} \quad (\text{B.1})$$

where n is the number of moles of electrons participating in the electrochemical reaction per formula unit of reactant, F is the Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$), MW is the molar weight of the active material ($\text{g}\cdot\text{mol}^{-1}$) and $3,6$ is the conversion factor between coulombs (C) and milliamp-hour (mAh). The volumetric capacity ($\text{mAh}\cdot\text{cm}^{-3}$) can be obtained by multiplying the specific capacity by the material density ($\text{g}\cdot\text{cm}^{-3}$).

B.2 Specific energy and energy density

The total energy discharged from a battery (E) in watt-hour (Wh) is calculated by taking the integral of its voltage with respect to its capacity, as indicated in eq (B.2).

$$E = \int V(C) dC = \int V(t) I dt \quad (\text{B.2})$$

The voltage of the battery depends on the cathode and anode, whereas its capacity is related to the range of Na^+ ions that can be reversibly incorporated into the host material. The specific energy is the nominal battery energy per unit mass ($\text{Wh}\cdot\text{kg}^{-1}$) while energy density is the nominal battery energy per unit volume ($\text{Wh}\cdot\text{L}^{-1}$). This metric is directly proportional to the amount of active material within the battery system. The energy stored in the battery during charge-discharge cycles can be computed using the same equation.

B.3 Specific Power and Power density

Energy and power density are easily confused but differ in one important way: energy density measures how much energy a battery holds, while power density measures how fast it can be provided.

Specific power is the maximum accessible power per unit mass (W kg^{-1}), while power density is the maximum accessible power per unit volume (W L^{-1}).

This metric is also directly proportional to the amount of active material within the battery system. For instance, a thicker coating of the cathode active material will result in longer diffusion path for the Na^+ ions, and thus, a lower power density.

B.4 C-rates

The battery C rating is the measurement of current in which a battery is being charge/discharged. The C-rate can be calculated by eq (B.3), where I represents the current applied during charge/discharge, and Q stands for the theoretical capacity of the battery.

$$C = \frac{I}{Q} \quad (\text{B.3})$$

A charge/discharge at nC rate means a full charge/discharge in $1/n$ hours. A battery's capacity is often rated and labeled at the 1 C rate (1C current), implying that a fully charged battery should be discharged in 1 hour. The C rating is a crucial characteristic to understand since the available stored energy within a battery is affected by the charge and discharge current speeds.

B.5 Coulombic efficiency

Coulombic efficiency (CE), also known as faradaic/current efficiency, defines the ratio of the total charge that exits in the battery during discharge to the total charge that enters the battery during the charging process [27], and is extrapolated by eq (B.4).

$$CE = \frac{\int_0^t i_d dt}{\int_0^{-t} i_c dt} \times 100\% \quad (\text{B.4})$$

where i_d is the discharge current and i_c is the charge current. Coulombic efficiency is an important parameter to monitor the lifetime of a battery cell. If the cell is free of undesired side reactions, the coulombic efficiency should be equal to 1; however, the presence of secondary reactions causes efficiency losses and a coulombic efficiency lower than the unit. As a result, the greater the difference of the CE from the unit, the shorter the lifetime of the battery cell.

B.6 Cycle life

Battery cycle life is always defined as the number of full charge/discharge cycles that a battery can go through before its capacity drops to 80% of its initial value. Several factors such as current (C-rate), atmospheric conditions (temperature, humidity, etc.), and compatibility of the electrode and electrolyte will affect the cycle life of a battery.

Appendix C - SIB technology

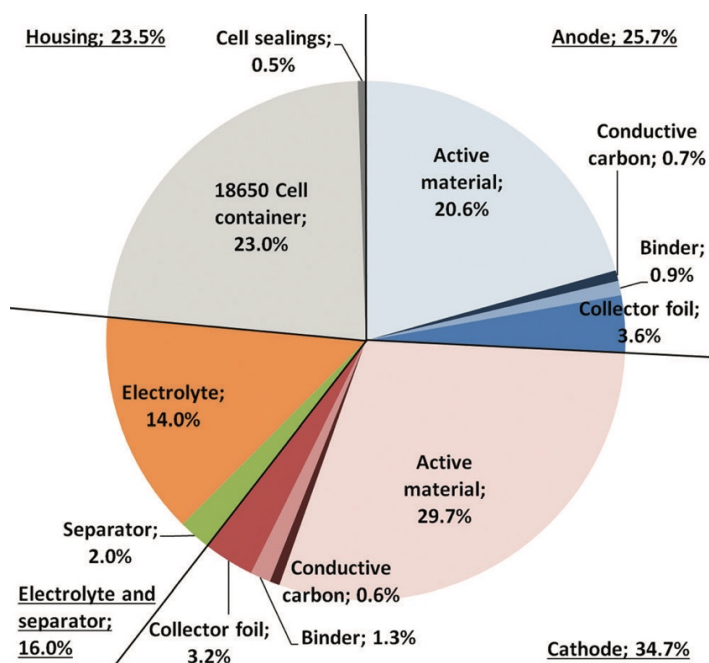


Figure C.1 - Weight breakdown of main battery components [90].

Table C.1 - Comparison between SIB cell chemistry from the most relevant companies in the area.

	Faradion Limited	Tiamat	HiNa	Natron energy
Cathode	Layered Oxides ($\text{Na}_x\text{Ni}_{1-x-y-z}\text{Mg}_x\text{Mn}_y\text{Ti}_z\text{O}_2$)	Polyanionic ($\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$)	Layered Oxide ($\text{Na}_{0.9}\text{Cu}_{0.22}\text{Fe}_{0.3}\text{Mn}_{0.48}\text{O}_2$)	Prussian Blue
Anode	Hard Carbon	Hard Carbon	Soft Carbon	Prussian Blue
Electrolyte	Non-Aqueous Liquid	Non-Aqueous Liquid	NA	Aqueous Liquid
Energy density / Wh kg⁻¹	155 (1 cell of 10 Ah)	90-120	145	≈12.3
Cell type	A5 Pouch cell (Prototype)	Cells 18650 (cylindrical)	NA	Pouch cell
Commercial Product	No	No	No	Yes

Appendix D - Phase transitions

Frist-principles statistical mechanical and thermodynamical studies have been successful at elucidating not only the transport mechanisms of sodium ions within the cathode material, but also the phase transition that occur as Na content varies [91]. The potential curves provide direct access to the chemical potential of Na within the cathode and, as a result, information regarding phase transformations since any changes in the crystal structure of the electrode material will affect its Gibbs free energy and Na-chemical potential, and thus, the voltage profile [92]. Figure D.1 depicts the Gibbs free energy and volatge curve of a general lithium electrode.

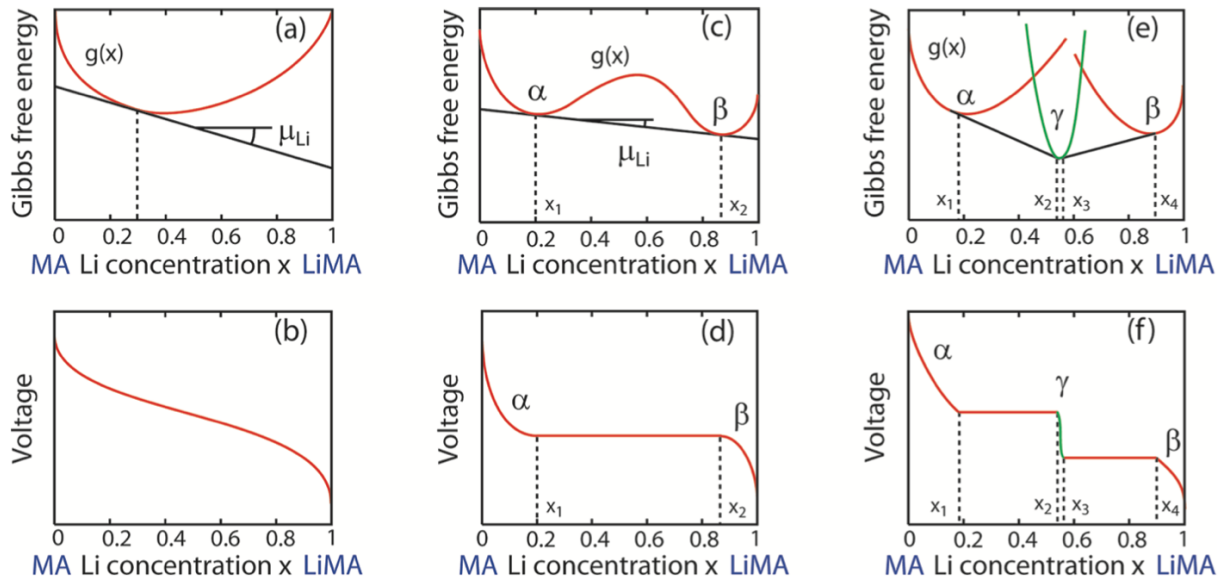


Figure D.1 - Gibbs free energy and voltage curves for a general lithium electrode [91].

Although the graphs shown in Figure D.1 are relative to a lithium electrode, the reasoning behind the voltage curve analysis can be extended to SIBs. The battery potential is given by the difference in chemical potential of the intercalating sodium ions between the cathode and the anode, according to eq (D.1), where $\mu_{Na}^{cat}(y)$ is the chemical potential of Na in the cathode at composition y , μ_{Na}^{ano} is the chemical potential at the anode, and e is the elementary charge [51].

$$V(y) = -\frac{\mu_{Na}^{cat}(y) - \mu_{Na}^{ano}}{e} \quad (D.1)$$

However, when the voltage curve of a cathode material is measured with respect to a reference electrode, in this case the anode, for which the chemical potential of sodium remains constant ($\mu_{Na}^{ano} = \text{constant}$), then the voltage profile is linearly related to minus the Na chemical potential within the cathode. Furthermore, according to eq (D.2), the chemical potential of Na in an intercalation compound is equal to the derivative of the Gibbs free energy versus composition [51,92].

$$\mu_{Na}^{cat} = \frac{dG}{dx} \quad (D.2)$$

As a result, a clear relationship between a measure voltage curve and the Gibbs free energy can be established, and thus, any phase transformation that occurs on the cathode material throughout the charge and discharge of the battery, due to the variation in Na concentration, will leave unambiguous traces in the voltages profile, as seen in Figure D.1. Through this connection, the interpretation of the voltage profiles becomes clear, where plateaus corresponds to two-phase regions (where the chemical potential is constant), smooth sloping are exhibited in Na concentrations where the electrode host material forms solid/single solutions, and steps correspond to ordered phases at fixed composition [51].

Therefore, voltages profiles give significant information about the phase transition in cathode materials during sodium ion extraction and insertion, allowing for an assessment of the electrode electrochemical performance, as complex phase transitions with multiple plateaus degrade the cycle performance of the cathode material.

Appendix E - Multiple Layered oxide Materials

Single transition metal layered oxides have been considered as great candidates for the positive electrode material due to their features such as high redox potential, ease of manufacture and scalability. However, fast capacity decay, irreversible phase transitions and structure instability when in contact with water, air and moisture limit their practical application. As a result, the introduction of heteroatoms to replace transition metal atoms is employed to take advantage of the synergetic effect observed between different metals in order to improve their electrochemical performance, specifically by reducing multiple phase transitions, increasing the working voltage and reversible capacity of the electrode material [46]. This improved mechanism is conceivable since NaTMO_2 provide the same layered structure for a wide spectrum of transition metals, allowing for systematic control of the electronic state [93].

For instance, despite the Jahn-Teller effect, Na_xMnO_2 performance is quite promising due to the previously mentioned high reversible capacity. However, the operating voltage with $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple is less than 3 V vs Na/Na^+ , whereas the working voltage of O3-NaFeO_2 is substantially higher, despite the shorter reversible range associated with irreversible iron migration [13].

Therefore, it is feasible to conclude that Fe/Mn based layered oxides, $\text{Na}_x[\text{Fe}_y\text{Mn}_{1-y}]$, may be appealing systems since they combine iron's natural abundance and high operation voltages with the large capacity of manganese layered oxides. Furthermore, the detrimental effect of the irreversible iron migration can be mitigated by their partially substitution for manganese ion, extending the reversible range that this cathode material can support, and Fe can inhibit the phase transition that occurs in NaMnO_2 materials during successive desodiation processes [13,46].

Among the different $\text{Na}_x[\text{Fe}_y\text{Mn}_{1-y}]$ systems, $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ can be prepared by solid state reaction, and both demonstrated higher reversible ranges when compared to NaFeO_2 [94]. However, despite being synthesized with the same procedure, the two materials crystallize into different layered structures, with $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ having an O3-type structure and $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ having a P2-type, with the galvanostatic charge/discharge curves of both materials shown in Figure E.1.

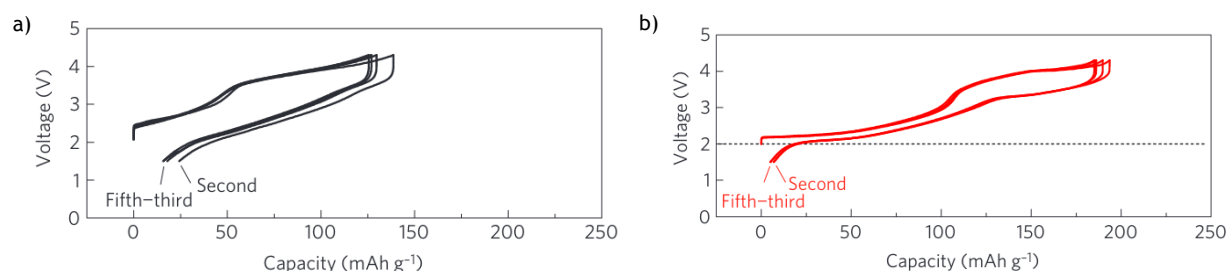


Figure E.1 - Charge/discharge curves for a) $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ b) $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ [94].

As illustrated in Figure E.1, P2-type phase outperforms the O3 phase in terms of electrode performance. Based on the redox couples $\text{Fe}^{3+}/\text{Fe}^{4+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$, O3- $\text{Na}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ has a reversible capacity of 100-110 mAh g^{-1} , whereas P2- $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, similar to O'3-type NaMnO_2 described by Ceder *et al.*, delivers 190 mAh g^{-1} , both within a voltage range of 1.5-4.2 V at a C/20 rate [57,94]. Large polarization (≈ 1 V) between charge and discharge is observed on the O3-type structure [94].

During the charge process, P2- $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ preserves its P2 phase until 3.8 V, since sodium ions are uniformly extracted from all layers; however, beyond 3.8 V, sodium ions are selectively extracted from one out of two layers, resulting in the phase transformation from P2 to OP4. OP4 is an intermediate phase composed by NaO_2 layers that alternate, along the *c*-axis, between octahedral and prismatic coordination sites [94].

When compared to the traditional P2 to O2 phase transition, the formation of the intermediate OP4 phase reduces the damage by gliding of layers, making P2-OP4 phase transition highly reversible and hence strongly related with long-term cycling stability [46,94,95]. However, in addition to possessing a sodium-deficient structure, P2- $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ may be oxidized when exposed to moisture, resulting in the formation of P2- $\text{Na}_{1/2}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and NaOH [46].

$\text{Na}_x[\text{Fe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, a cathode material with a O3-type structure also known as NFNM, is another layered oxide that has received a lot of attention. Kim *et al.*, investigated coin cell configurations with $\text{Na}_x[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ as cathode and pre-sodiated hard carbon as an anode ($\text{Na}_y\text{C}/\text{Na}_{1-y}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ systems) and reported smooth voltages profiles, indicating reversible intercalation reactions in the positive electrode material [96]. Moreover, despite the irreversible capacity loss caused by SEI formation in the first cycle, a reversible capacity of 100 mAh g^{-1} was maintained over 150 cycles at a rate of C/2 and a voltage range of 1.5-4.0 V, with the structure also remaining intact after 123 cycles [70,96].

Nonetheless, the above-mentioned materials are manufactured and studied on a gram scale, with the ability to produce positive electrode materials on a large scale vital for promoting the commercialization and industrialization of SIBs. Wang *et al.* large-scale synthesis of $\text{Na}[\text{Fe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ using co-precipitation combined with solid-state reaction, a methodology already implemented in LIBs [70]. The synthesized material was tested in a half cell format with Na foil as an anode and revealed a reversible capacity of 123 mAh g^{-1} at room temperature at current density of 130 mA g^{-1} . Following the electrochemical test of the material, Wang and colleagues produced a 1 Ah soft pack sodium battery that demonstrated outstanding structure stability over long term cycling, with a capacity retention of 73 % after 500 cycles [70].

Although the material indicated above are promising cathodes for SIBs, there are some drawbacks that must be addressed, most notably composition degradation due to moisture and air sensitivity.

Na_xTMO_2 interacts with moisture and CO_2 , forming electrical insulation species, which leads to a loss of electrochemical performance [64]. Trace substitution of Fe by inactive elements such as magnesium (Mg) [97] and aluminum (Al) has been demonstrated to be an effective strategy to improve the structural stability of layered oxides against ambient air [64].

Li *et al.* applied an Al doping strategy to SIBs in order to improve the air stability of $\text{O3-Na}_x[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, in which the Fe atoms are partially substituted by aluminum to produce $\text{Na}_x[\text{Ni}_{1/3}\text{Fe}_{(1/3-x)}\text{Mn}_{1/3}\text{Al}_x]\text{O}_2$ (known as NFNMA) as a potential cathode material [64]. The effect of Al doping in lithium materials has already been studied and it has been confirmed that it suppresses the irreversible reaction with air due to the strong covalent Al-O bond [98].

In comparison to NFNM, since Fe, an active material, is substituted by Al, the reversible capacity of NFNMA is expected to decrease with the amount of Al due to its inactive trait. However, despite the reduced reversible capacity, Al doping greatly enhances interfacial stability by suppressing the chemical interaction between the layered oxide and ambient air [64].

To highlight the beneficial effects of Al doping, Li and colleagues revealed that when both NFNMA and NFNM are exposed to ambient air for 30 days, the electrochemical performance of NFNMA is significantly higher than that of NFNM. As depicted in Figure E.2, $\text{NFNMA}_{0.01}$ ($x=0.01$) delivered a reversible capacity of 130 mAh g^{-1} at 0.2 C , much higher than the 58 mAh g^{-1} of the 30-day air exposed NFNM. Furthermore, cycling stability has also improved since Al-doped NFNMA retained 86 % of its capacity after 50 cycles, whereas undoped NFNM only delivered a capacity retention of 71 % [64].

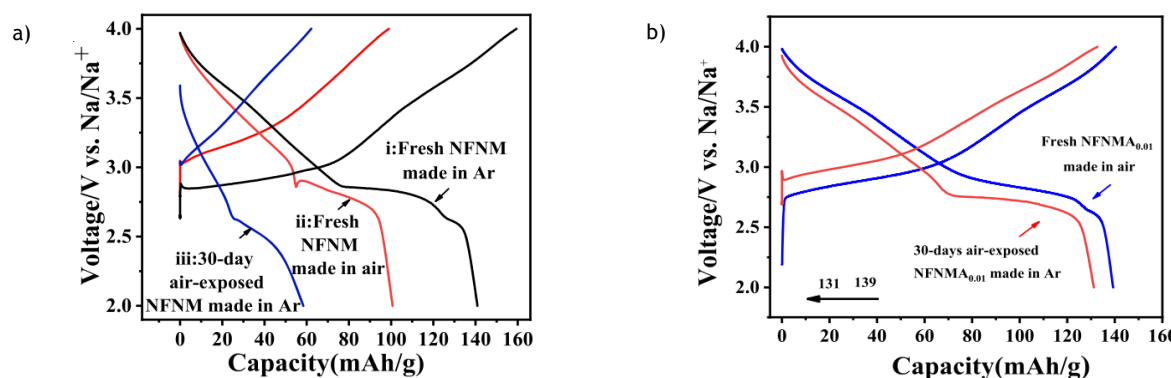


Figure E.2 - Electrochemical performance of a) NFNM b) NFNMA [64].

Aside from Fe/Mn based cathode materials for SIBs, the most extensively studied cathode materials are Ni/Mn binary based layered oxides containing Ni^{2+} and Mn^{4+} . The high operation voltage of the redox reaction $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$, highly symmetric and stable crystal structure, and high reversible capacity of these materials support their use as positive electrodes [46].

For instance, $\text{P2-Na}_{2/3}[\text{N}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, initially reported in 2001, has a reversible capacity of 160 mAh g^{-1} , very similar to the theoretical capacity (173 mAh g^{-1}), and an average operation voltage

greater than 3.5 V due to the redox couple $\text{Ni}^{2+}/\text{Ni}^{4+}$ [99]. Additionally, $\text{P2-Na}_{2/3}[\text{N}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ is stable when exposed to moisture since water molecules cannot insert into the structure, [63].

Nevertheless, the fundamental disadvantage of this Ni/Mn based material its poor cycle life and capacity loss, which has been attributed to the detrimental P2-O2 phase transformation [63,99]. To increase electrochemical performance, chemical elements substitution has been established as an effective technique to mitigate the well-known P2-O2 transformation. For instance, various studies have found Ti^{4+} substitution for Mn to be beneficial in terms of rate capability and cycle stability, notably in reducing the number of phase transitions and therefore allowing better cyclability across a wider voltage range [69,100].

Guo *et al.* have used Ti-enrichment-induced surface reconstruction to develop $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ (known as NMTN) as a viable cathode material for SIBs. After the $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ samples were synthesized by solid state reaction, elemental analysis revealed that, in contrast to Na, Mn and Ni, Ti thinly disperses in the bulk and instead is significantly concentrated within 2 nm of the surface. As a result, titanium oxide is thought to make up the majority of the outer shell, which has a spinel-like structure [59]. Moreover, the cathode material exhibits a spinel-layered heterostructure, with a structural model of spinel to O'3 to P2 structures validated from the surface to the center of the particle.

The effect of the titanium overlayer was evaluated by Guo and co-workers by exposing NaMnO_2 and $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ to humid air for three days before analyzing them using X-ray diffraction (XRD). In contrast to NaMnO_2 , $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ samples did not exhibit structural changes associated with water intercalation, demonstrating the protective effect of titanium oxide interface. The obstruction characteristics of the spinel-like structure may explain the water intercalation resistance [59]. In addition, Guo's surface engineering of $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ not only inhibits Mn dissolution and deposition in the anode, but also enables a higher conductivity [59].

As a result of the beneficial effect of the titanium interface, the electrochemical performance of $\text{NaMnTi}_{0.1}\text{Ni}_{0.1}$ is significantly greater than that of NaMnO_2 . As shown in Figure E.3, at a rate of 0.5 C, NMTN retained 85 % of its capacity after 50 cycles, compared to the 36 % observed for NaMnO_2 , and showed excellent reversibility. Furthermore, NMTN revealed to be suitable for practical applications, with a capacity retention of 81 % over 500 cycles at 5C, and a capacity of 186 mAh g^{-1} at 0.1 C which, based on an average voltage of 3.1 V, equates to an energy density of 576 Wh kg^{-1} , competitive with state-of-art LIB cathodes [59].

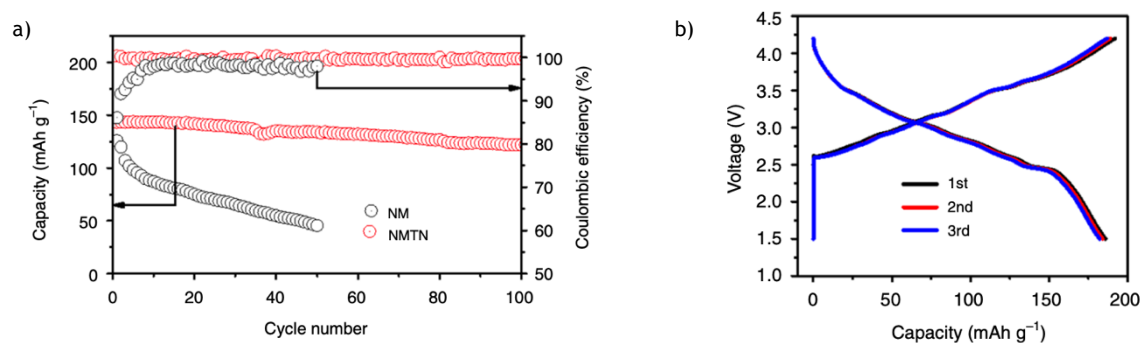


Figure E.3 - Electrochemical tests of NaMnTi_{0.1}Ni_{0.1} a) Cycling performance b) Voltage profile.

Other investigations, besides the well-engineered titanium interface presented by Guo *et al.*, have been conducted to improve the air and moisture stability of the layered transition metal oxides, specifically to improve the stability of Na[Ni_{1/2}Mn_{1/2}]O₂ (known as NaNM). Recently, a combined structure modulation has been proposed to overcome this issue by increasing the valence state of transition metals and simultaneously decreasing reducing Na layers' spacing [46,68].

Yao *et al.*, using density functional theory (DFT), have proved that structure modulation can be achieved by co-substitution of one kind of heteroatom with comparable electronegativity and another one with substantially different Fermi level [68]. Based on these discoveries, Yao *et al.* have synthesized O3-Na[Ni_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}]O₂ (also known as NaNCMT) by solid state reaction via Cu/Ti co-substitution of Na[Ni_{1/2}Mn_{1/2}]O₂ [68].

Due to the difference in Fermi level, partial substitution of Mn⁴⁺ by Ti⁴⁺ results in an expansion of TM layers and a contraction of Na layer spacing, which is associated to a drop in TM-O interaction and an increase in Na-O binding energy [101]. In addition, Ti substitution raises the valence state of Ni, which is also increase by the addition of Cu into the system [68].

To assess the structural integrity of NaNCMT, aging studies such as air and water exposure were performed and compared to NaNM. In contrast to NaNM, which undergoes significant structural changes when exposed to air and water, NaNCMT revealed to be 20 times more stable in the same air-exposure period, with no spontaneous phase transformation in both tests, demonstrating that Cu/Ti co-substitution provides strong morphological stability [68].

The favorable effect of the Cu/Ti co-substitution is also demonstrated in electrochemical data, as illustrated in Figure E.4, where it is obvious that aged NaNCMT present significantly higher capacity retention when compared to aged NaNM. Moreover, NaNCMT displayed smooth charge/discharge profiles with an initial discharge capacity of 124 mAh g⁻¹, while NaNM presented voltage profiles with numerous plateaus reflecting multiple phase transitions. Besides that, NaNCMT exhibited excellent long-term stability with 70 % capacity retention after 500 cycles at 1 C, which is significantly higher than the 8 % obtained by NaNM under the same conditions [68].

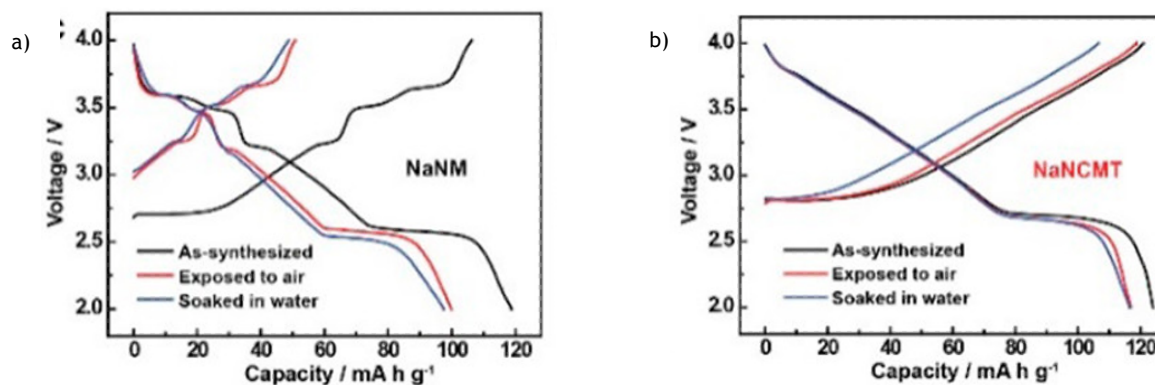


Figure E.4 - First charge/discharge curves of as-synthesized and aged a) NaNM b) NaNCMT.

Based on previous studies realized by Yao *et al.* and Li *et al.* [68,102], Wang and colleagues conducted various experiments of $\text{Na}[\text{Ni},\text{Mn},\text{Ti}]\text{O}_2$ systems with and without Cu substitution [69]. Wang *et al.* initially synthesized $\text{NaNi}_{0.5}\text{Mn}_{0.5-z}\text{Ti}_z\text{O}_2$, a Ti^{4+} substituted material, by solid-state reaction and identified an O3-type structure (isostructural with NaFeO_2), which is consistent with the results reported by Wang in 2017 [66,69].

Na-ion full cells electrochemical tests using the above materials and hard carbon as anode revealed that long cycling stability (70 % capacity retention after 50 cycles), high reversible capacity and energy density (190 mAh g^{-1} and 340 Wh kg^{-1} respectively) were obtained for $z = 0.1$ and 0.2 [69]. These findings are consistent with the findings of Yao *et al.*, who discovered that 0.1 mol of Mn substituted by Ti delivered the best results [68]. Wang and co-workers also identified that increasing the amount of Ti^{4+} increases the Ni-O bond ionicity [69].

Based with the results obtained by Ti substitution, Wang *et al.* studied the effect of Cu^{2+} substitution for Ni^{2+} in $\text{NaNi}_{0.5-y}\text{Cu}_y\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$ and $\text{NaNi}_{0.5-y}\text{Cu}_y\text{Mn}_{0.3}\text{Ti}_{0.2}\text{O}_2$ materials. Electrochemical tests in half cell configurations revealed that, when compared to their non-Cu substituted equivalents, both of these materials had a lower first cycle reversible capacity [69]. This decrease in reversible capacity can be explained by the fact that the oxidation of Cu^{2+} only delivers only one electron ($\text{Cu}^{2+}/\text{Cu}^{3+}$), while Ni^{2+} oxidation releases two electron in the redox process ($\text{Ni}^{2+}/\text{Ni}^{4+}$). In addition, increasing the Cu content results in smoother voltages profiles, and thus, fewer phase transitions [69].

Wang and colleagues also tested the electrochemical performance of the Cu substituted materials in full cell arrangement with hard carbon as anode. Despite the lower energy density when compared to the Cu-free materials as previously explained, a significant increase in cycle life was observed in these materials. Particularly, Cu-substituted material delivered an 80 % capacity retention after 100 cycles, while the Cu-free material only delivered a 50 % capacity retention after 100 cycles [69]. Wang *et al.* observed the best performance in the compositions $\text{NaNi}_{0.4}\text{Cu}_{0.1}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$ and $\text{NaNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{0.3}\text{Ti}_{0.2}\text{O}_2$, which, once again, are very similar to the material reported by Yao *et al.* [68]. These materials

outperformed the popular $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode material, used in Tiamat SIBs technology [103] as showed in Figure E.5, which shows the potential of these cathode materials.

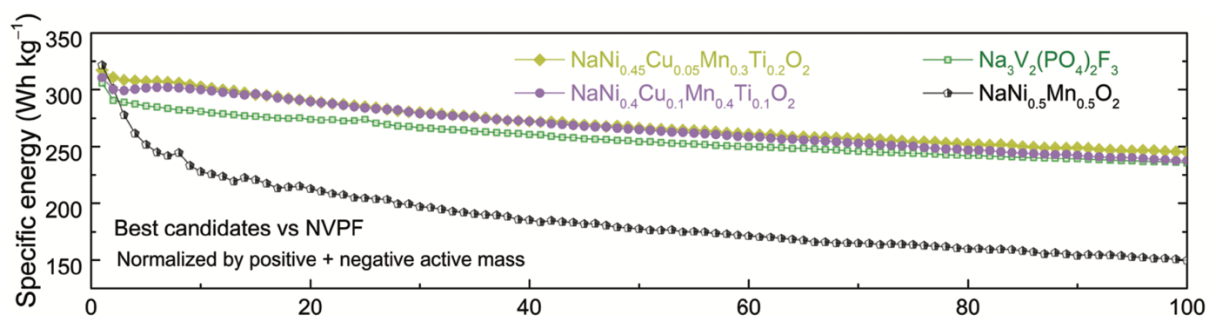


Figure E.5 - Energy density plot of the Ti and Cu co-substituted materials.

Aside from Cu and Ti substitution, magnesium (Mg) has also been extensively studied to increase the structural stability and electrochemical performance of layered oxide materials. Xiao *et al.* have designed a unique stable copper and magnesium co-substituted $\text{P2-Na}_{2/3}\text{Ni}_{1/6}\text{Mn}_{2/3}\text{Cu}_{1/9}\text{Mg}_{1/18}\text{O}_2$ material (denoted as P2-NaNMCM) with a multi-layer oriented stacking nanoflakes structure [95]. The performance of this material was compared to $\text{P2-Na}_{2/3}[\text{N}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (P2-NaNM), being both synthesized by thermal polymerization followed by solid-state reaction at high temperatures.

In addition to having excellent reversible thermostability, P2-NaNMCM exhibits smoother charge/discharge curves when compared to P2-NaNM, as depicted in Figure E.6, indicating fewer phase transitions. Besides that, P2-NaNMCM also demonstrated smaller polarization and improved kinetics properties [95]. The nanoflake structure of this material improves sodium-ion transport due to increased electrode-electrolyte contact area and short diffusion, resulting in improved kinetic characteristics [95].

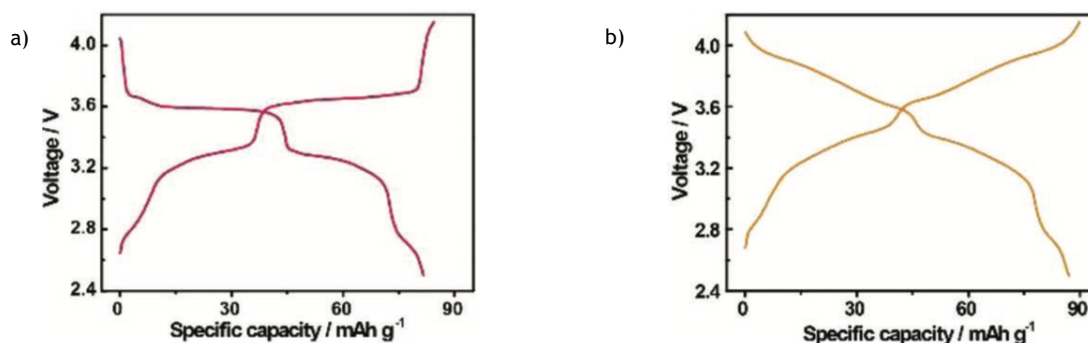


Figure E.6 - Charge/discharge curves at C/2 for a) P2-NaNM b) P2-NaNMCM [95].

Xiao *et al.* further proved the outstanding electrode performance of P2-NaNMCM in half cell and full cell configurations. Na half-cell tests showed that P2-NaNMCM delivered long-term cycling stability (60% capacity retention after 1000 cycles at 5 C), and a specific capacity of 64 mAh g^{-1} with a power density of 11.4 kW kg^{-1} at 30 C [95]. Nevertheless, a full battery performance test is required to identify the possible applicability of the cathode material in real applications [102]. A full cell system comprised

of P2-NaNMCM as the cathode and a pre-sodiated hard carbon anode achieved a capacity of 62.7 mAh g⁻¹ with specific power density of 4.3 kW kg⁻¹ at a rate of 10 C. More crucially, the full cell configuration demonstrated a capacity retention of 89 % after 500 cycles at 5 C and 79 % capacity retention after 1000 cycles, demonstrating the feasibility of this cathode material [95].

The enhanced electrochemical performance of the cathode material can be directly linked to the metal co-substitution. The inactive Mg²⁺ not only retains more Na⁺ in the prismatic sites but also refrains the Jahn-Teller effect which enhances cycling performance [63]. Furthermore, the Cu²⁺/Cu³⁺ redox couple not only participates in the charge compensation mechanism but also contributes to improve the kinetic properties and air stability of the cathode material [102].

Appendix F - Chemicals and Materials used

F.1 Chemicals used

The chemicals used to produce the cathode active materials are listed in Table F.1.

Table F.1 - Chemicals used to synthesize the active cathode materials.

Material	Formula	Purity / %
Sodium carbonate	Na_2CO_3	99.95-100.05
Iron (III) oxide	Fe_2O_3	99.9
Copper (ii) oxide	CuO	99.7
Nickel (II) oxide	NiO	99.0
Manganese (III) oxide	Mn_2O_3	99.0
Titanium (IV) oxide	TiO_2	≥ 99.5
Aluminum oxide	Al_2O_3	≥ 98.0

Furthermore, the cathode materials synthesis need the use of the following materials and equipment: scale, beakers, mortar and pestle, ball mill, pipettes, kitasato, büchner funnel, filters, furnace (calcination), and glovebox.

F.2 Experimental Protocols for cathode synthesis

(1) $\text{O3-NaNi}_{0.1}\text{MnTi}_{0.1}\text{O}_2$ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na_2CO_3 , 99.95-100.05 %), manganese (III) oxide (Mn_2O_3 , 99.0 %) nickel oxide (NiO , 99.0 %), and titanium oxide (TiO_2 , 99.5 %) considering a 90 % yield. An excess of 5 mol % of Na_2CO_3 was added due to the volatility of sodium at high temperatures. The mixture was then grounded in:

- 1st synthesis: in an agate mortar;
- 2nd synthesis: in the ball mill for 20 hours and 200 rpm, with 5 hours cycles and 15 minute stops with reversal of direction rotation. The resultant powder was then scrapped from the ball mill.

The resultant powder, from both syntheses, was heated at a rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and calcinated at $900\text{ }^\circ\text{C}$ for 15 hours under a nitrogen atmosphere. The heat-treated powder was then quenched (suddenly cooled) to room temperature and stored in the glovebox.

(2) O3-NaNi_{0.5}Mn_{0.4}Ti_{0.1}O₂ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), and manganese (III) oxide (Mn₂O₃, 99.0 %), considering a 90% yield. An excess of 5 % mol of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded in:

- 1st synthesis: in the agate mortar followed by ball milling for 1 hour. The resultant powder was removed from the ball mill with deionized water and a vacuum filtration process;
- 2nd synthesis: in the ball mill for 20 hours and 200 rpm, with 5 hours cycles and 15 minute stops with reversal of direction rotation. The resultant powder was then scrapped from the ball mill.

The resulting powder, from both syntheses, was heated at a rate of 2 °C·min⁻¹ and calcinated at 900 °C for 12 hours under a nitrogen atmosphere, before being slowly cooled until 300 °C at a rate of 1 °C·min⁻¹. Once the temperature reached 300 °C, the recalcination process was repeat for another 12 hours under the same conditions. The calcined products were then stored in the glovebox.

(3) O3-NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O₂ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), copper oxide (CuO, 99.7 %), manganese (III) oxide (Mn₂O₃, 99.0 %) and titanium oxide (TiO₂, ≥ 99.5 %), considering a 90% yield. An excess of 5 mol % of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded:

- 1st synthesis: in the agate mortar;
- 2nd synthesis: in the ball mill for 20 hours and 200 rpm, with 5 hours cycles and 15 minute stops with reversal of direction rotation. The resultant powder was then scrapped from the ball mill.

Finally, the resulting powder, from both syntheses, was heated at a rated of 2 °C·min⁻¹ and calcinated at 1000 °C for 12 hours under a nitrogen atmosphere. Thereafter, the resultant powder was cooled at a rate of 2 °C·min⁻¹ until 20 °C. The calcined products were then stored in the glovebox.

(4) O3-NaNi_{0.45}Cu_{0.05}Mn_{0.3}Ti_{0.2}O₂ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), copper oxide (CuO, 99.7 %), manganese (III) oxide (Mn₂O₃, 99.0 %) and titanium oxide (TiO₂, 99.5 %), considering a 90% yield. An excess of 5 mol % of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded in:

- 1st synthesis: in the agate mortar followed by ball milling for 1 hour. The resultant powder was removed from the ball mill with deionized water and a vacuum filtration process;

- 2nd synthesis: in the ball mill for 20 hours and 200 rpm, with 5 hours cycles and 15 minute stops with reversal of direction rotation. The resultant powder was then scrapped from the ball mill.

The resulting powder, from both syntheses, was heated at a rate of 2 °C·min⁻¹ and calcinated at 900 °C for 12 hours under a nitrogen atmosphere, before being slowly cooled until 300 °C at a rate of 1 °C·min⁻¹. Once the temperature reached 300 °C, the recalcination process was repeat for another 12 hours under the same conditions.

(5) O3-NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), manganese (III) oxide (Mn₂O₃, 99.0 %) and iron (III) oxide (Fe₂O₃, 99.9%), and nickel oxide (NiO, 99.0 %). An excess of 5 mol % of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded in the ball mill for 20 hours and 200 rpm with 5 hour cycles and 15 minutes stop. The resultant powder, after being scrapped from the ball mill was heated at a rated of 2 °C·min⁻¹ and calcinated at 850 °C for 12 hours under a nitrogen atmosphere. Thereafter, the resultant powder was cooled at a rate of 2 °C·min⁻¹ until 20 °C. The calcined products were then stored in the glovebox.

(6) O3-NaNi_{1/3}Mn_{1/3}Fe_(1/3-x)Al_xO₂ (x=0.01) cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), manganese (III) oxide (Mn₂O₃, 99.0 %), nickel oxide (NiO, 99.0 %), iron (III) oxide (Fe₂O₃, 99.9 %), and aluminum oxide (Al₂O₃, ≥ 98.0 %). An excess of 5 mol % of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded in the ball mill for 20 hours and 200 rpm with 5 hour cycles and 15 minutes stop. The resulting powder, after being scrapped from the ball mill was heated at a rated of 2 °C·min⁻¹ and calcinated at 850 °C for 12 hours under a nitrogen atmosphere. Thereafter, the resultant powder was cooled at a rate of 2 °C·min⁻¹ until 20 °C. The calcined products were then stored in the glovebox

(7) O3-NaNi_{0.25}Mn_{0.25}Fe_{0.25}Al_{0.25}O₂ cathode material was synthesized through a solid-state reaction from stoichiometric amounts of sodium acetate (Na₂CO₃, 99.95-100.05 %), nickel oxide (NiO, 99.0 %), manganese (III) oxide (Mn₂O₃, 99.0 %), nickel oxide (NiO, 99.0 %), iron (III) oxide (Fe₂O₃, 99.9%), and aluminum oxide (Al₂O₃, ≥ 98.0 %). An excess of 5 mol % of Na₂CO₃ was added due to the volatility of sodium at high temperatures. The mixture was then grounded in the ball mill for 20 hours and 200 rpm with 5 hour cycles and 15 minutes stop. The resulting powder, after being scrapped from the ball mill was heated at a rated of 2 °C min⁻¹ and calcinated at 850 °C for 12 hours under a nitrogen atmosphere. Thereafter, the resultant powder was cooled at a rate of 2 °C min⁻¹ until 20 °C. The calcined products were then stored in the glovebox

F.3 Experimental data

Table F.2 - Raw materials measured for the 1st synthesis of the active materials.

1 st synthesis / g	1.1	2.1	3.1	4.1
Na ₂ CO ₃	1.06616	1.05987	1.12286	1.06601
NiO	0.13794	0.7424	0.6877	0.6644
Mn ₂ O ₃	1.42459	0.6242	0.6209	0.47649
TiO ₂	0.14710	0.16031	0.1599	0.3222
CuO	----	---	0.0863	0.0818
Total mass / g	2.77579	2.57498	2,67336	2.61690

Table F.3 - Raw materials measured for the 2nd synthesis of the active materials.

2 nd synthesis (g)	1.2	2.2	3.2	4.2	5.2	6.2	7.2
Na ₂ CO ₃	2.0506	2.1279	2.22571	2.12738	2.11313	2.18240	2.37911
NiO	0.27494	1.49711	1.33461	1.35008	1.00476	0.9957	0.79686
Mn ₂ O ₃	2.91288	1.23830	1.26067	0.94875	1.04720	1.05365	0.8421
TiO ₂	0.29204	0.32221	0.31774	0.64381	---	---	---
CuO	----	---	0.15930	0.17273	---	---	---
Fe ₂ O ₃	---	---	---	---	1.06147	1.03030	0.85220
Al ₂ O ₃	---	---	---	---	---	0.02041	0.54497
Total mass / g	5.53146	5.17941	5.29803	5.24275	5.22656	5.28246	5.42524

Table F.4 - Mass of cathode material powder removed by scrapping the ball mill in the 2nd synthesis.

Material	1.2	2.2	3.2	4.2	5.2	6.2	7.2
Initial mass / g	5.54146	5.17941	5.29803	5.24275	5.22656	5.28246	5.42524
Mass scrapped /g	4.88757	4.54139	4.65034	5.60970	4.61348	4.79580	4.86128

Appendix G - Characterization Techniques

G.1 Physical characterization

This subsection outlines different techniques for the physical characterization of cathode materials. These characterizations procedures are critical to execute throughout material synthesis and acquisition since they allow to examine features essential for the functionality of the final cell, such as chemical composition, pore size, and interplanar distance.

G.1.1 Fourier Transform Infrared - FTIR

Fourier transform infrared (FTIR) spectroscopy is an analytical characterization technique used to identify the main functional groups of individual molecules in the material under investigation. This is an important absorption spectroscopy technique that identifies some material properties based on the radiation absorbed by the sample under examination when subjected to a beam of light.

Conventional infrared spectrometers, also known as dispersive infrared spectrometers, are the typical equipment used in infrared spectroscopy (IR spectroscopy or vibrational spectroscopy). This instrument generates a beam of infrared light that is incident on the sample under analysis. After passing through the sample, the radiation beam enters a monochromator, which decomposes it into a continuous spectrum of infrared light frequencies, allowing the frequencies absorbed by the sample to be identified by a detector. The frequencies absorbed by the material are intimately tied to its structure since when the frequency of the IR beam coincides with the vibrational frequency of a bond or collection of bonds in the material structure, absorption occurs, and an infrared spectrum is obtained.

However, Fourier transform infrared spectrometer (FTIR) operates on a different principle. In this type of equipment, a complex signal known as an interferogram is produced, which displays a waveform pattern that contains all the frequencies that comprise the infrared spectrum. To obtain a spectrum in the frequency domain, mathematical operations such as Fourier Transforms (FT) can be performed to separate the frequencies absorbed by the sample, resulting in a spectrum identical to Figure G.1.

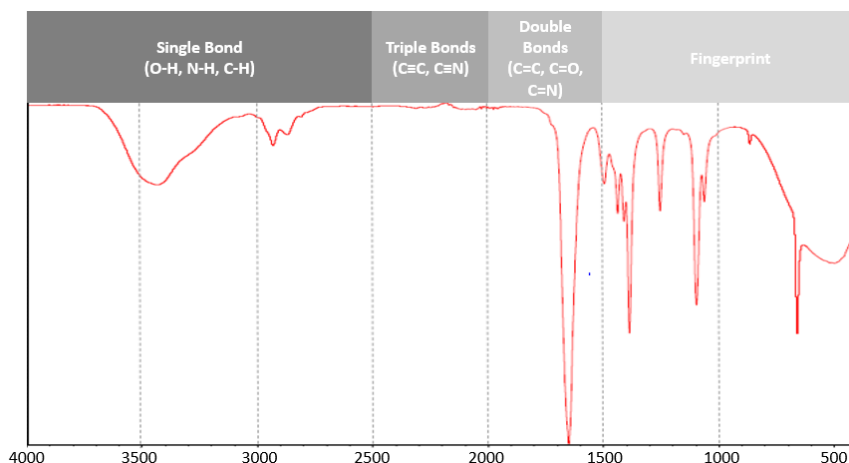


Figure G.1 - Infrared Spectrum [104].

In the image G.1, the x-axis corresponds to the wavenumber of the radiation and the y-axis corresponds to the transmittance, and the vertical and descending peaks observed correspond to the wavelengths of radiation absorbed by the sample. Wavenumbers are expressed in cm^{-1} and can be simply computed by taking the reciprocal of the wavelength. This analysis is performed in the mid-infrared region, with wavenumbers ranging from 400 cm^{-1} to 4000 cm^{-1} . When compared to standard IR techniques, the FTIR characterization technique allows a significantly faster analysis. Furthermore, interferograms are recorded in computer memory to eliminate any interference from air and/or solvents, resulting in greater sensitivity than dispersive infrared spectrometers.

In this work, FTIR analysis will be used to do a preliminary assessment of the presence of carbon in the cathodes following synthesis. However, it should be emphasized that infrared spectroscopy alone is insufficient for a thorough characterization of the material under study, with further characterization techniques required to supplement the FTIR analysis.

G.1.2 Scanning Electron Microscopy - SEM

Scanning electron microscopy (SEM) is a type of electron microscopy and a key technology for material characterization across a wide range of industries. SEM is a versatile tool commonly applied to examine material surfaces. This technology offers several advantages, including the ability to analyze large samples while remaining a non-destructive methodology [105].

Scanning electron microscopy, as opposed to light microscopes that used a light beam, interacts with the sample using an electron beam. Inside a vacuum chamber, a highly focused beam of electrons is generated and impacts the surface of the specimen. The beam then penetrates the surface of a bulk sample and interacts with its atoms, generating a variety of signals that are collected and processed to generate a pixel. Therefore, scanning a larger area will provide an image capable of providing information regarding the topography and even the chemical composition of the sample [105,106]. Figure G.2 represents a schematic setup of an SEM microscope.

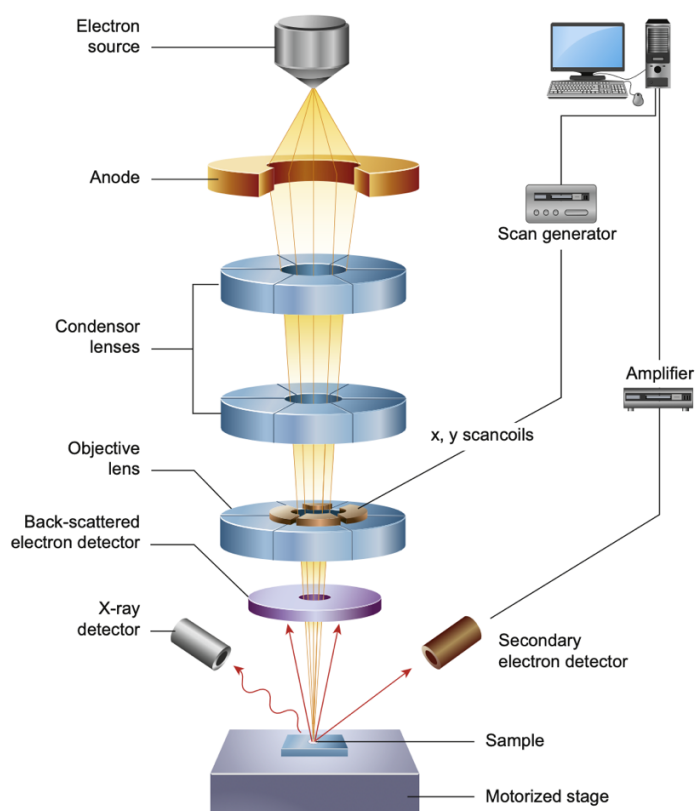


Figure G.2 - Schematic representation of the setup for a SEM analysis [105].

The primary components of an SEM instrument are the electron gun, electromagnetic lenses, a specimen vacuum chamber, and detectors. The electron gun, which is comprised by the electron source and accelerating anode, as depicted at the top of the schematic in Figure G.2, emits the electron beam when heated by an electric current. The electron beam is then guided and intensified to the sample by electromagnetic lenses. When hit by the electron beam, the sample emits electrons (secondary and backscattered electrons) and x-ray photons into the surrounding environment, which are collected by an electron detector that will translate the amount and energy of the collected electrons into pixel intensity [106]. To avoid collisions between the electron beam and other species inside the SEM chamber, the specimen chamber is kept under vacuum. Furthermore, in most circumstances, it is desirable to obtain chemical information from materials examined in the SEM. This specific analysis is accomplished by energy dispersive x-ray spectroscopy (EDS), a qualitative or semi-quantitative technique used to determine chemical compositions [106].

Scanning electron microscopy offers higher resolution and magnification range when compared to light microscopes, since the radiation used in electron microscopy (electron beam) has a shorter wavelength than visible light used in light microscopes. Nevertheless, besides the vacuum environment, due to the SEM operating principle, the sample must be conductive [105]. In this project, the morphologies and size of the cathode materials will be studied using a scanning electron microscopy equipped with an energy dispersive x-ray spectrometer.

G.1.3 X-ray Powder Diffraction - XRD

X-ray diffraction (XRD) is a basic and non-destructive technique used to determine the crystallographic structure of a material. The technology finds numerous applications in various industries, including microelectronics, power generations, aerospace, and many more [107]. This procedure provides information regarding structure, phase purity, crystal orientations and other structural parameters, such as crystallinity, crystal defects and average grain size [107,108].

This technique operates on the principle that the interaction of electromagnetic waves with crystal structures (regular arrays of atoms) produces diffraction effects if the wavelength of the radiation and the periodicity of the crystals are of similar magnitude [109]. In a typical X-ray diffractometer, X-rays are generated in a cathode ray tube, filtered to produce monochromatic radiation, and directed towards the sample. When the monochromatic X-rays strike the crystals, they penetrate and are partially scattered from successive planes within the crystal structure. For a specific interplanar distance (d) there will be a critical angle (θ) at which the X-rays are scattered coherently “in-phase” as they leave the crystal [110], as depicted in Figure G.3.

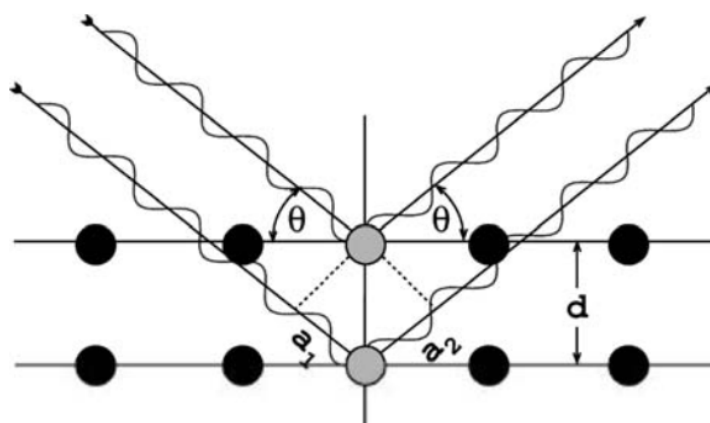


Figure G.3 - Geometric derivation of Bragg's law [109].

The X-rays scattered by each set of lattice planes will be scattered coherently to meet the standard of constructive interference that is determined by Bragg's law, as represented in eq (G.1):

$$2d \sin(\theta) = n\lambda \quad (\text{G.1})$$

Where d represents the distance between atomic planes in a crystal (interplanar distance), λ is the wavelength of the incident radiation, n is an integer and θ denotes the angle of the incident radiation in relation to the considered plane [107]. Based on eq (G.1), the interplanar distance can be calculated with the value of θ (a result obtained from an XRD analysis). Therefore, by combining XRD measurements with Bragg's law it is possible to determine whether the distance between the cathode layers is sufficient to store Na^+ ions.

G.2 Electrochemical Tests

This subsection describes different techniques used to evaluate the electrochemical performance of the cathode materials and assembled coin-cells. These procedures are essential since they allow to examine electrochemical behaviors and performances such as phase transition, specific capacity, energy density, cycle life, columbic efficiencies, and rate capacities. In this work, electrochemical tests were carried out using a Zahner power potentiostat.

G.2.1 Galvanostatic Charge/Discharge

Galvanostatic charge-discharge testing is one of the most common procedures for evaluating rechargeable batteries. The goal of this test is to establish how many times a battery may be used by examining it until it deteriorates following repeated charging and discharging cycles in a certain voltage range. The conventional test method is to charge and discharge repeatedly at constant current densities (constant rates) to evaluate the cycling performance and capacity of the material, with the charge and discharge capacities computed from the applied current and total time. Furthermore, by employing a variety of current densities, this testing technique can be used to estimate the rate capability of the electrode materials.

G.2.2 Cyclic Voltammetry - CV

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique employed to investigate the electrochemical activity of electrode materials, including electron transfer kinetics and the reversibility of a redox reaction [111]. However, despite its versatility and simplicity, when compared to other instrumental procedures such as spectroscopy, this technique is poorly understood.

In CV measurements, the potential of a working electrode is changed linearly with a specified scan rate, and the resulting current output is recorded. The working electrode's potential is controlled in relation to a reference electrode (such as Ag/AgCl), and the controlling potential applied across these two electrodes is regarded as an excitation signal. The excitation signal is a linear potential scan with a triangular waveform as shown in Figure G.4 [112,113]. The potential scan is programmed to start at an initial potential where no reaction occurs and moving to potentials where reduction and oxidation reactions of the electrode material occur. The scan continues at the desired linear scan rate until the switching potential is reached, at which point it reverses direction and returns to the initial potential [113,114]. The output of cyclic voltammetry is a plot of the current flowing at the working electrode during the cyclic potential scan, which is displayed in Figure G.4 as voltammograms.

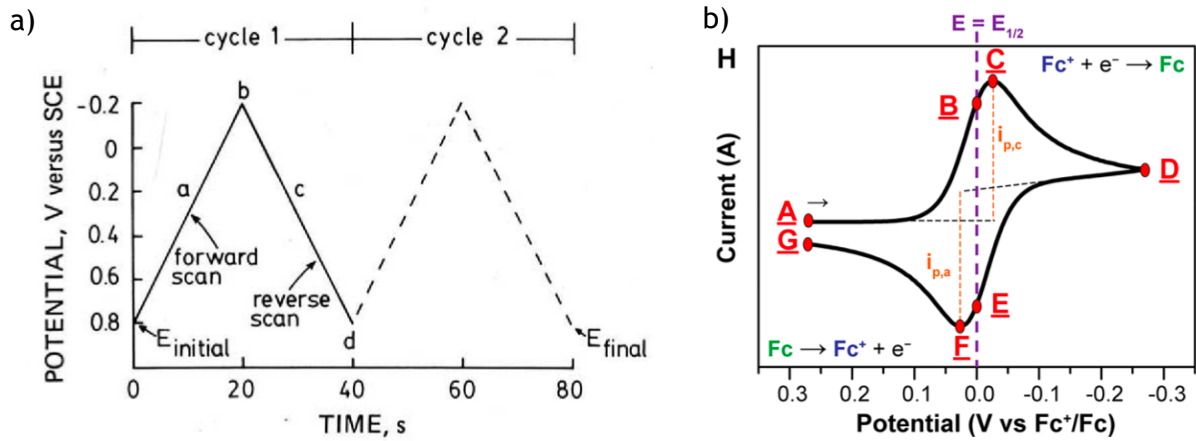


Figure G.4 - Cyclic voltammetry a) Typical Excitation signal b) Voltammogram [111].

The arrow represented in the voltammogram indicates the direction in which the potential was scanned to record the data. The arrow denotes the start and sweep direction of the first segment (forwards scan), which runs from A to D and is also referred to as the cathodic trace. Afterwards, the anodic trace is then obtained by reversing the scan direction, from D to G [111].

The peaks exhibited in the voltammograms are directly related to the equilibrium between the oxidate and reduced species in the electrode, which is defined by the Nernst equation, denoted by equation (G.2). The Nernst equation relates the potential of an electrochemical cell (E) to the formal potential ($E^{0'}$) as well as the concentrations of oxidized ($[Ox]$) and reduced ($[Red]$) species in the electrode at equilibrium [111]. Furthermore, F is Faraday's constant, R is the universal gas constant, n is the number of electrons transferred and T is the temperature. As a result, the Nernst equation provides a powerful way to forecast how the system will react to a change in concentration or a change in the electrode potential.

$$E = E^{0'} + \frac{RT}{nF} \ln \left(\frac{[Ox]}{[Red]} \right) \quad (G.2)$$

Additionally, cyclic voltammetry allows to gather information regarding the diffusion of electroactive species within the electrode material based on equation (G.3), known as the Randles-Sevcik equation. This equation allows to compute the diffusion coefficient (D_o) of the sodium ions in the electrode material based on the peak current (i_p), electrode surface area (A), scan rate (v) and bulk concentration (C^0) of the analyte [111].

$$i_p = 0,446nFAC^0 \left(\frac{nFvD_o}{RT} \right)^{\frac{1}{2}} \quad (G.3)$$

G.2.3 Electrochemical Impedance Spectroscopy - EIS

Electrochemical impedance spectroscopy (EIS) is a powerful and non-invasive technique used to gain valuable insights into the kinetics of electrode materials by monitoring the inner resistances of a

sodium-ion cell. This technique also enables the development of appropriate models within the field of electrochemical cell chemistry to model equivalent electric circuits (EEC), which can provide insight into the material's conductive properties, life cycle predictions among other parameters [115].

This technique investigates the system response to the application of a periodic alternating current (AC) signal. A sinusoidal potential perturbation is applied, and the resultant AC current signal is collected. Small perturbations in EIS are used to guarantee that the response of the system is linear, i.e., the current response to a sinusoidal potential excitation will be a sinusoid at the same frequency but shifted in phase [116,117]. Afterwards, the time-domain response is converted to the frequency domain, and impedance, a complex coefficient between the voltage and current, is computed using equation (G.4) [116,118].

$$Z(\omega) = \frac{V(t)}{i(t)} = Z_0(\cos(\phi) + j \sin(\phi)) \begin{cases} \text{Re}\{Z(\omega)\} = Z_0 \cos(\phi) \rightarrow Z' \\ \text{Im}\{Z(\omega)\} = Z_0 \sin(\phi) \rightarrow Z'' \end{cases} \quad (\text{G.4})$$

Impedance measurements are performed across a wide range of frequencies, resulting in an impedance spectrum, usually represented as a Nyquist plot [118], in which the imaginary part of the impedance is plotted against the real one, as depicted in Figure G.5.

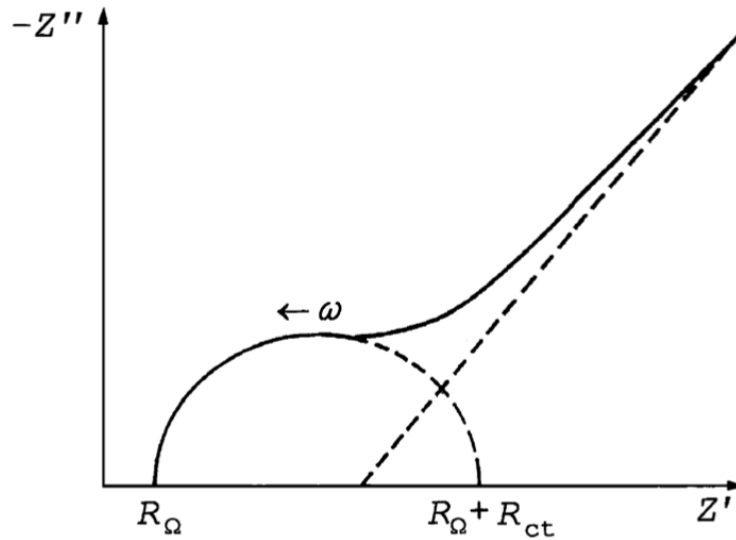


Figure G.5 - Typical Nyquist plot.

A typical impedance spectrum of a cell includes a semicircle at medium frequencies and a low-frequency linear tail. The origin point of the spectrum, represented by R_Ω , corresponds to the ohmic resistance of the cell, whereas the semicircle is attributed to the kinetic processes and reflects the charge transfer resistance. Finally, the linear tail is connected to mass transport resistance and the diffusion of alkali ions until the bulk of the electrode materials from the electrolyte [119]. As a result, EIS has been widely applied to study the SEI film since the deposition and dissolution processes are reflected as an increase and decrease of impedance respectively [120].

Appendix H - Material characterization

H.1 XRD patterns

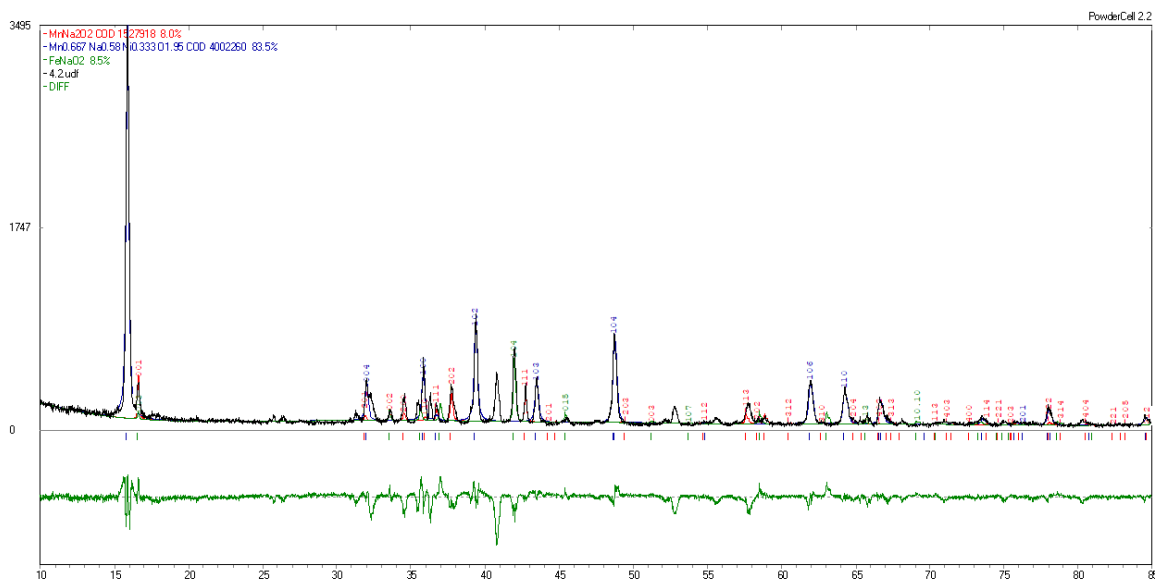


Figure H.1 - Rietveld refined XRD patterns of O3-NaMnTi_{0.1}Ni_{0.1}O₂.

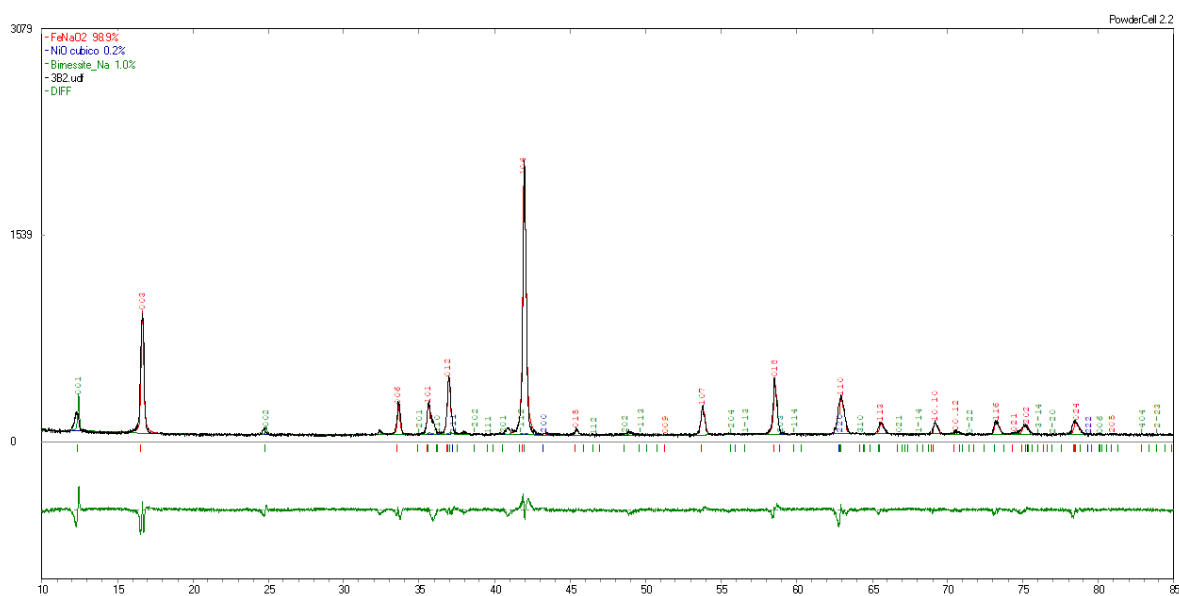


Figure H.2 - Rietveld refined XRD patterns of O3-NaNi_{0.5}Mn_{0.4}Ti_{0.1}O₂.

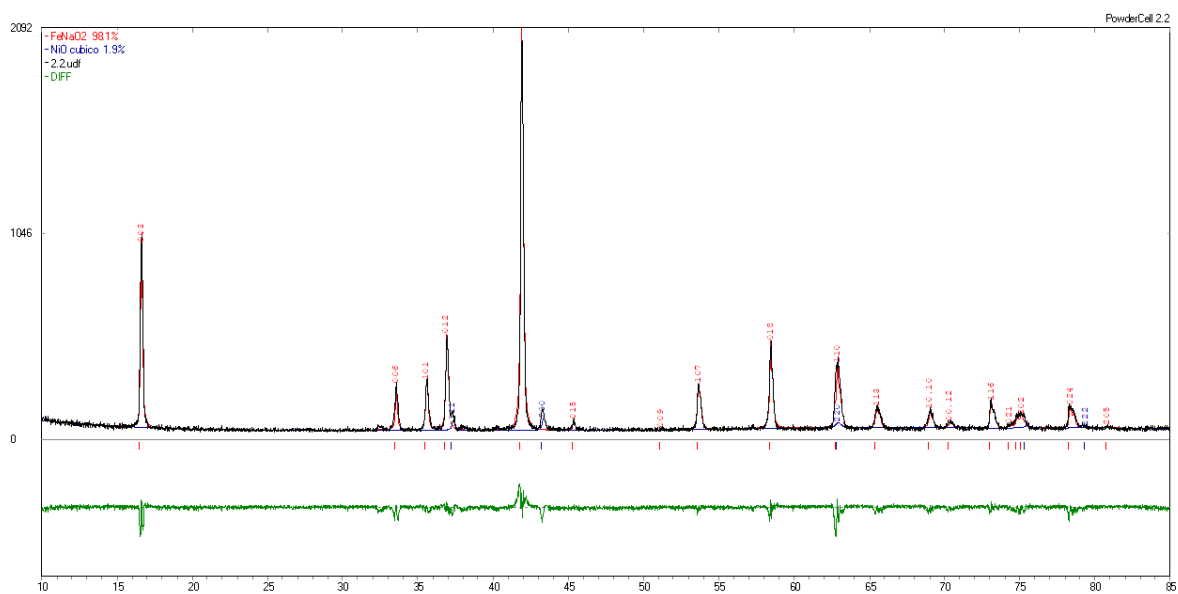


Figure H.3 - Rietveld refined XRD patterns of O3-NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O₂.

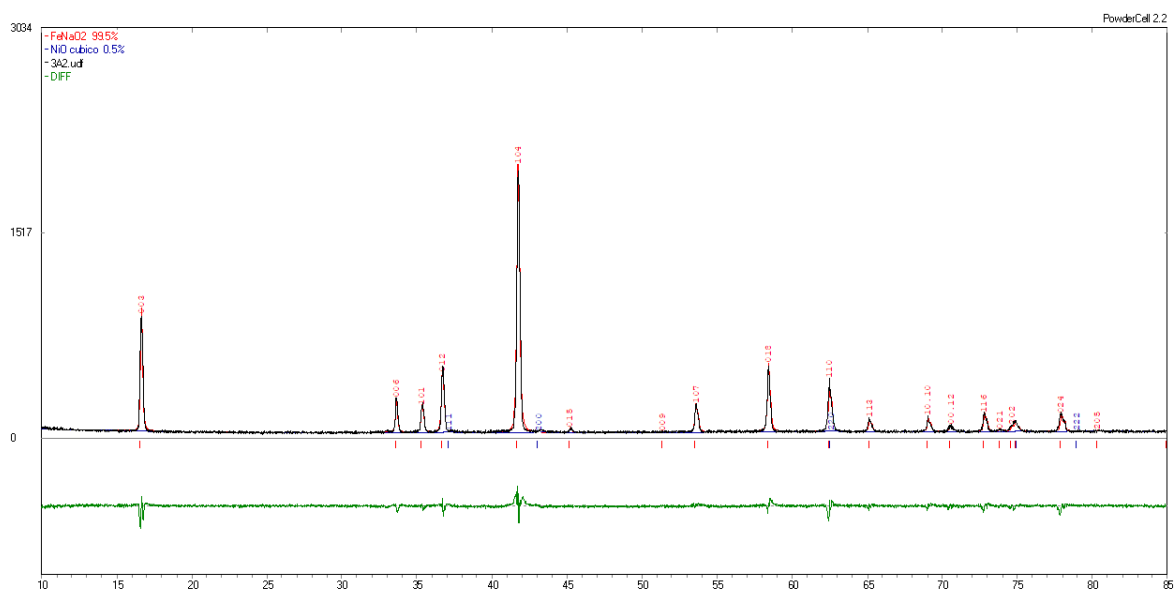
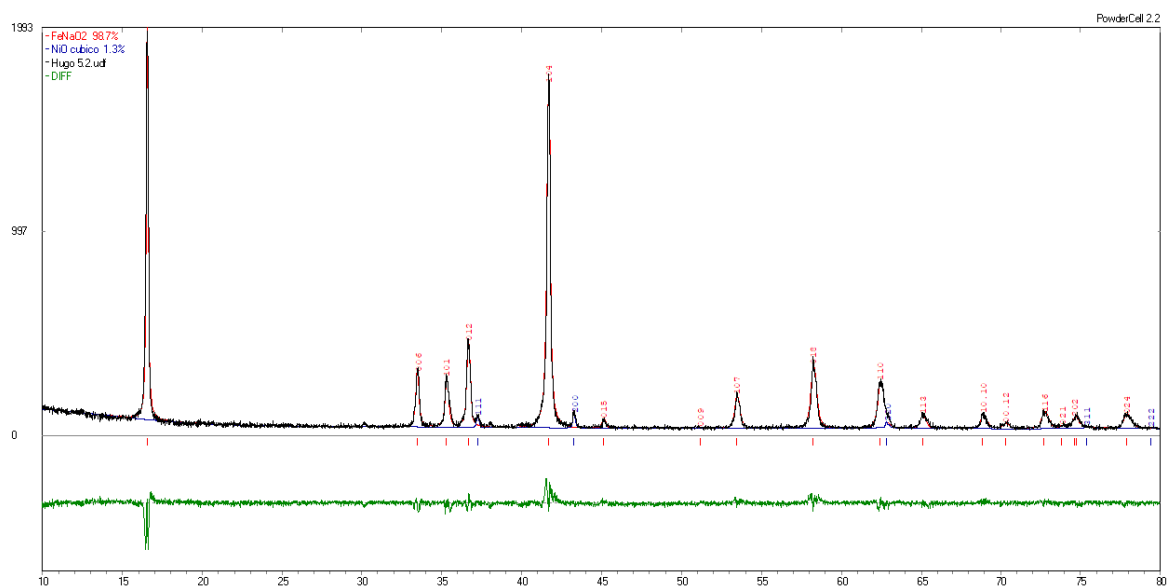
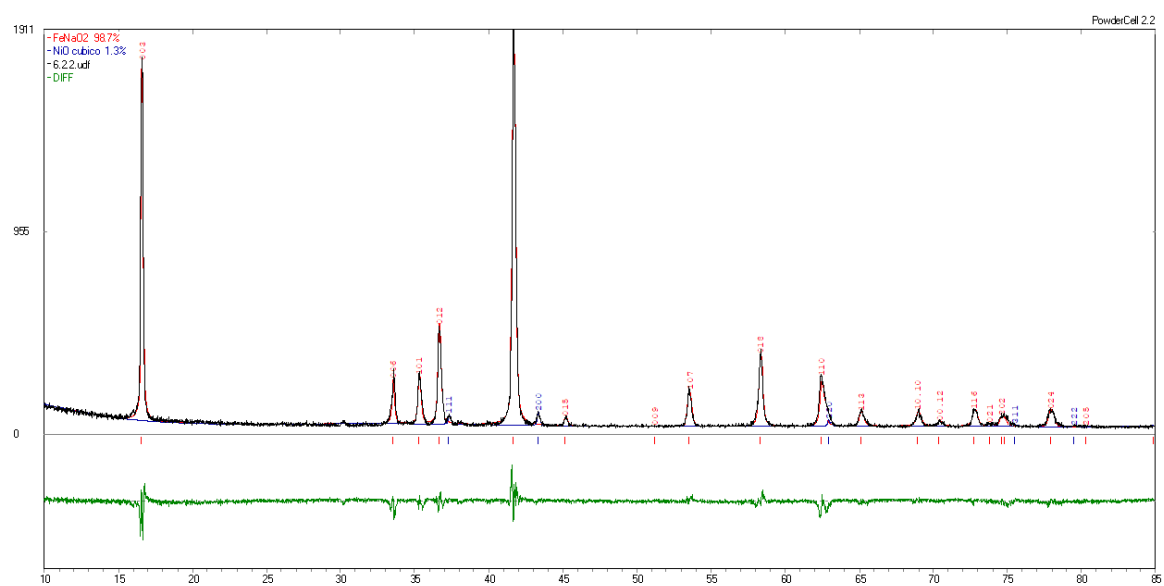


Figure H.4 - Rietveld refined XRD patterns of O3-NaNi_{0.45}Cu_{0.05}Mn_{0.3}Ti_{0.2}O₂.

Figure H.5 - Rietveld refined XRD patterns of O3-NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂.Figure H.6 - Rietveld refined XRD patterns of O3-NaFe_(1/3-x)Ni_{1/3}Mn_{1/3}Al_xO₂ (x=0.01).

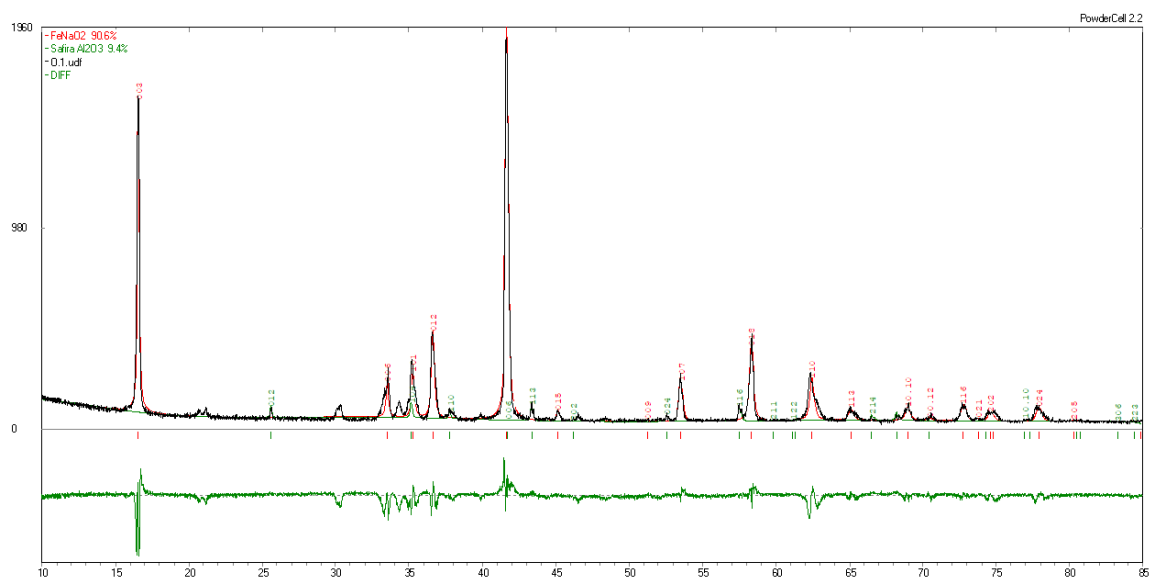


Figure H.7 - Rietveld refined XRD patterns of O3- $\text{NaFe}_{0.25}\text{Ni}_{0.25}\text{Mn}_{0.25}\text{Al}_{0.25}\text{O}_2$.

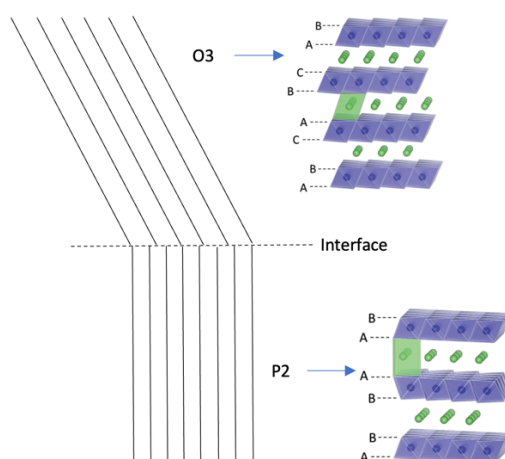


Figure H.8 - Schematic representation of intergrowth stacking of P2 and O3 structures at atomic scale.

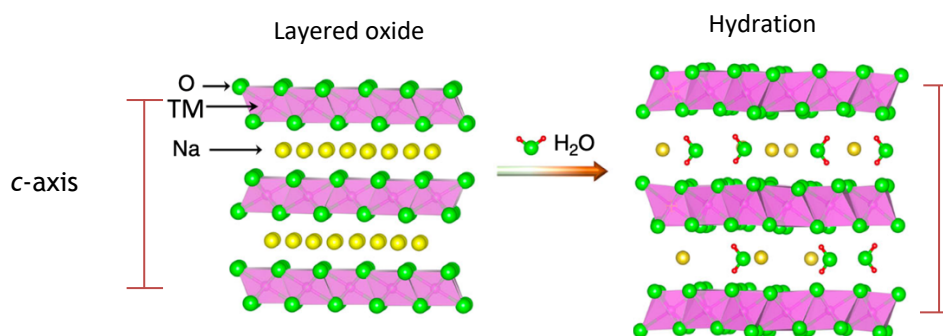
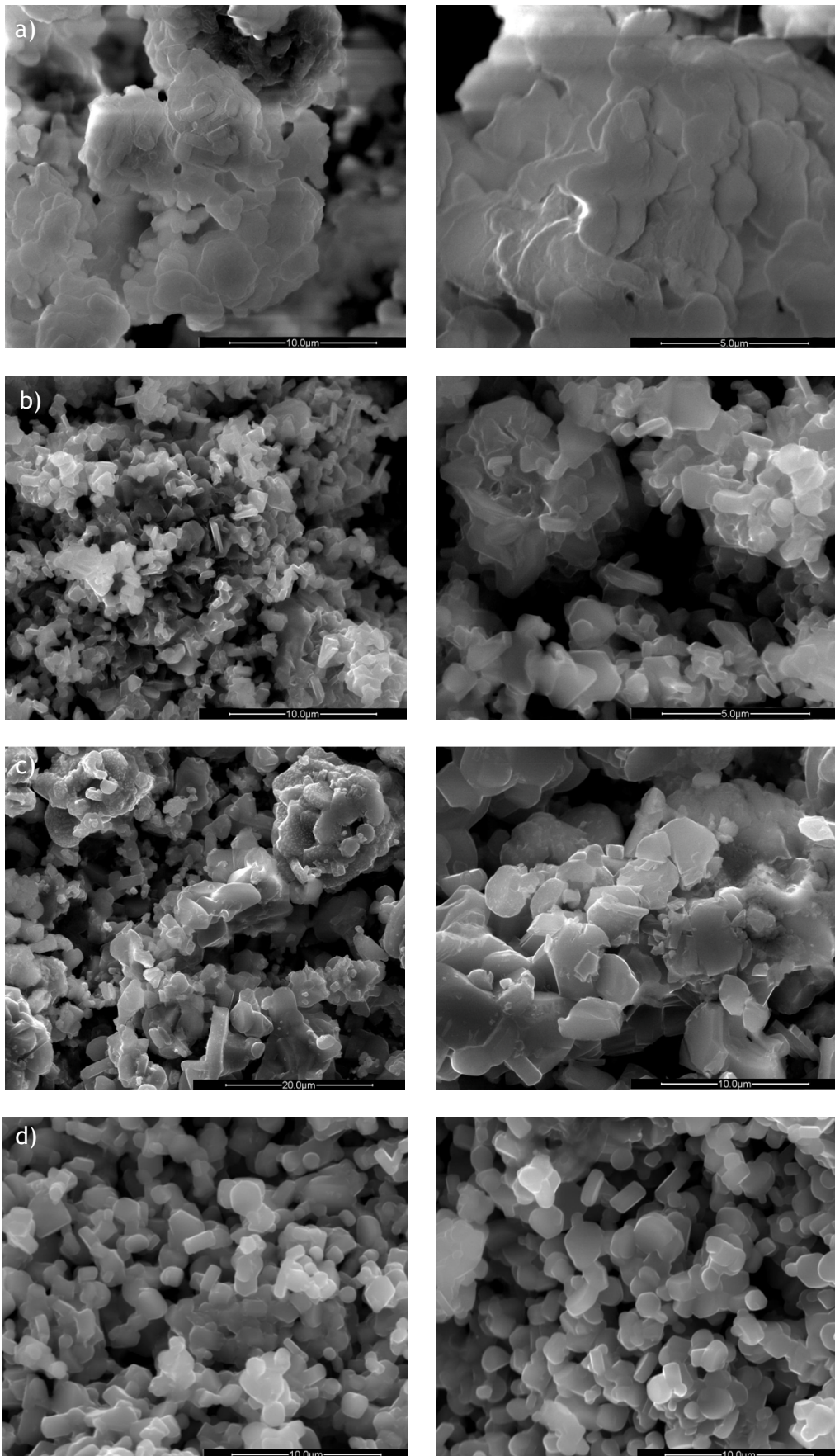


Figure H.9 - Schematic representation of the formation of a hydration phase [61].

H.2 SEM images



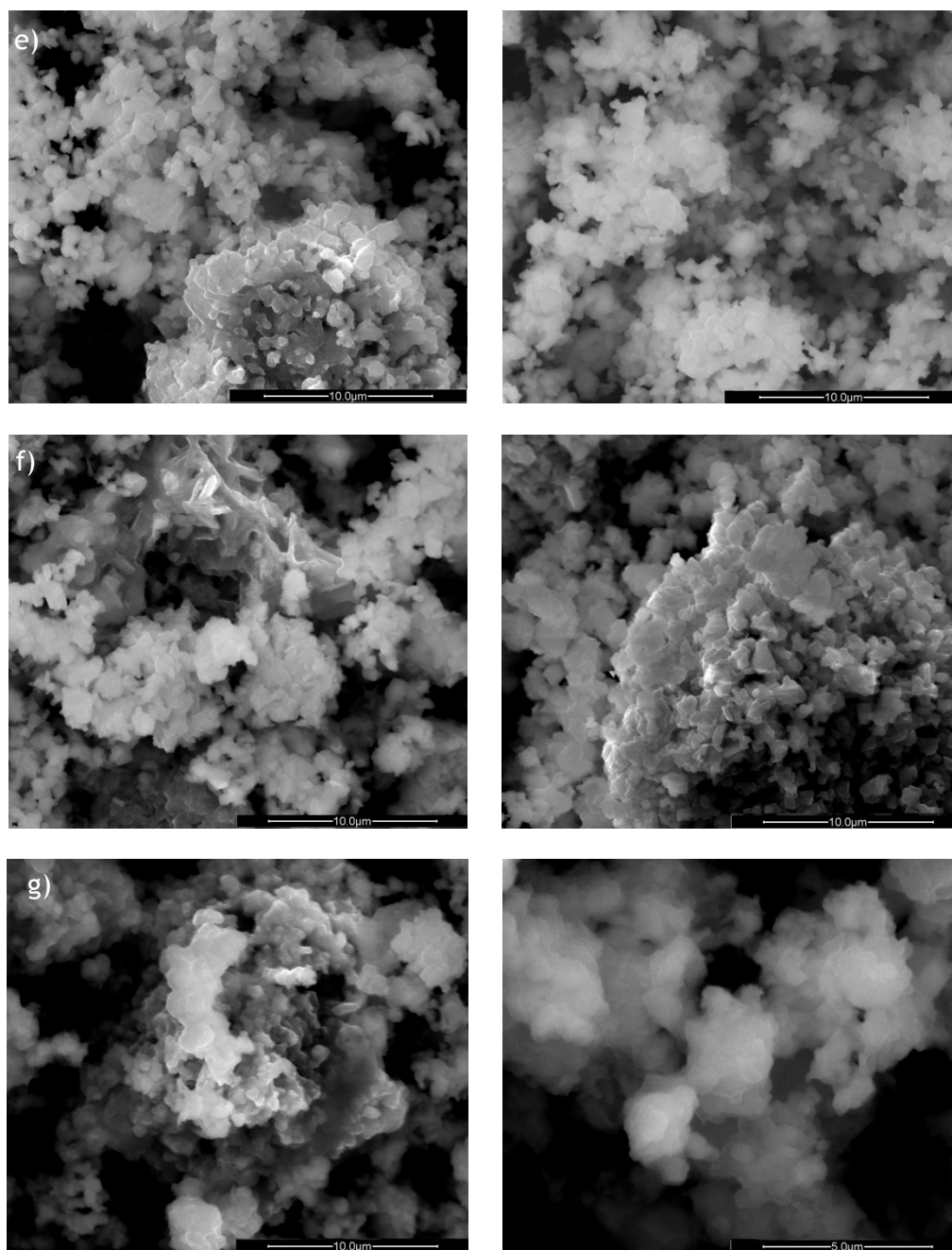


Figure H.10 - SEM images for the materials a) 1.2, b) 2.2, c) 3.2, d) 4.2, e) 5.2, f) 6.2, g) 7.2.

H.3 EDS qualitative analysis

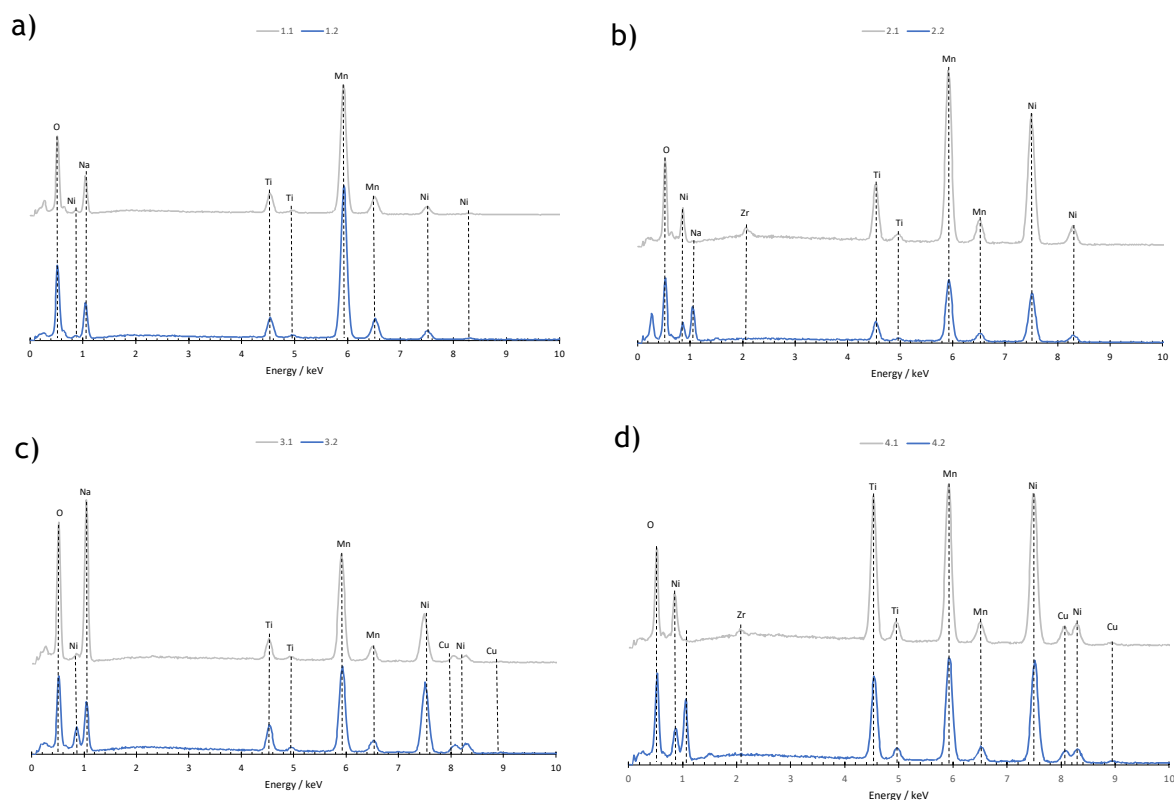


Figure H.11 - Comparison of the EDS spectra for the materials a) 1.1 and 1.2, b) 2.1 and 2.2, c) 3.1 and 3.2, d) 4.1. and 4.2.

H.4 Slurry preparation and coating

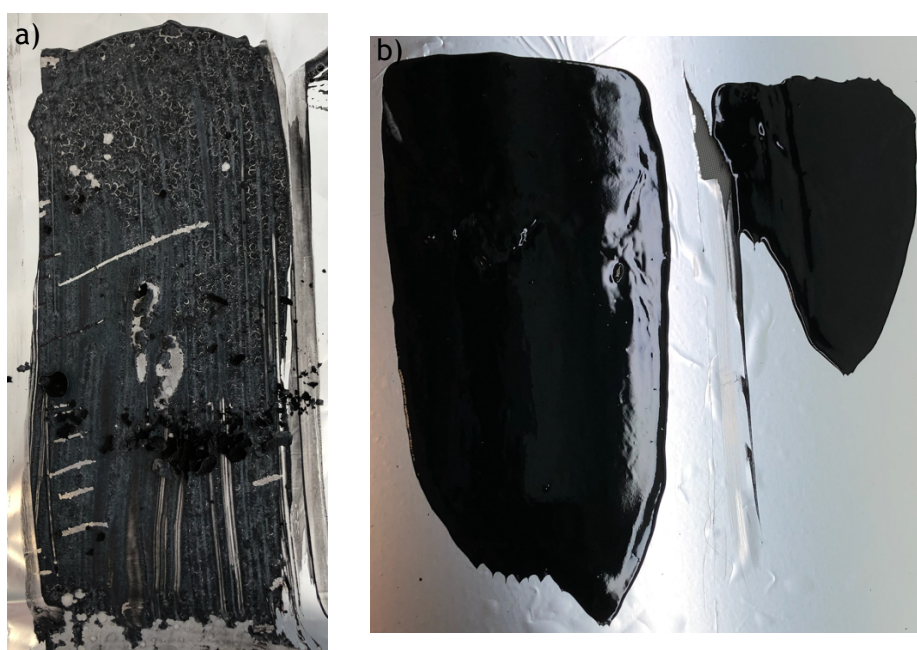


Figure H.12 - Effect of mixing strategy in the PVDF electrodes a) manual mixing, b) magnetic stirring.

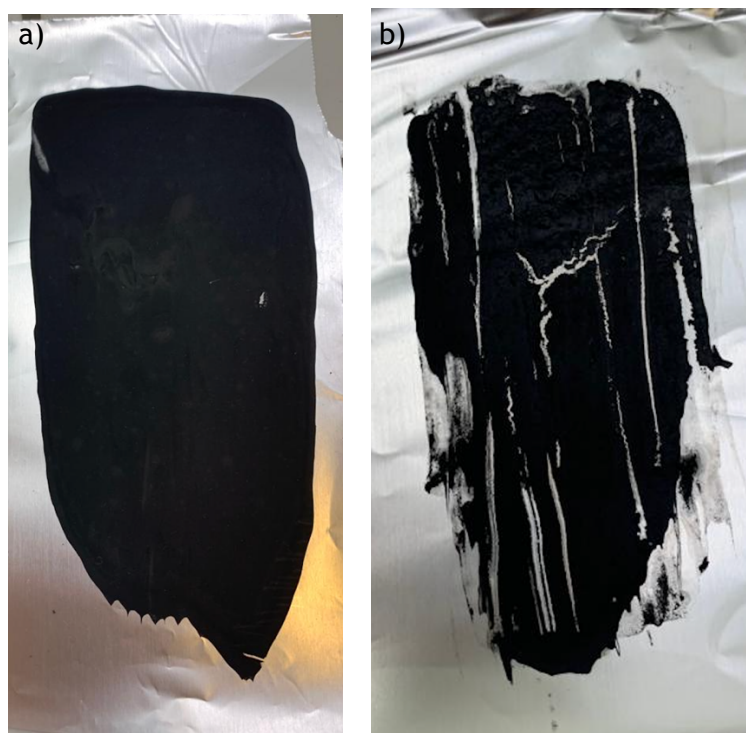


Figure H.13 - Solvent evaporation rate on PVDF electrodes a) room temperature, b) placed on a hot plate at 75 °C.

H.5 Theoretical capacity of each cathode material

Table H.1 Theoretical capacity of each cathode material.

Numerical designation	Cathode material	$Q_{\text{Theo,cat}} / \text{mAh}\cdot\text{g}^{-1}$
1	$\text{O3-NaNi}_{0.1}\text{MnTi}_{0.1}\text{O}_2$	222.26
2	$\text{O3-NaNi}_{0.5}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$	241.24
3	$\text{O3-NaNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$	240.71
4	$\text{O3-NaNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{0.3}\text{Ti}_{0.2}\text{O}_2$	242.25
5	$\text{O3-NaNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$	240.41
6	$\text{O3-NaNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{(1/3-x)}\text{Al}_x\text{O}_2$ ($x=0.01$)	241.03
7	$\text{O3-NaNi}_{0.25}\text{Mn}_{0.25}\text{Fe}_{0.25}\text{Al}_{0.25}\text{O}_2$	257.45