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**Critical Elements for energetic transition:
development of innovative materials for new generation
Sodium Ion Battery**

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*A Bruna e Ambra,
i miei punti di riferimento*

ABSTRACT

The development of new technologies for electrochemical energy storage represents one of the most important challenges in the energy transition towards a more sustainable and greener world. In the batteries field, the main aim is to reduce dependence on lithium-ion batteries (LIBs), which have dominated the market since they were first commercialized. Among the post-Li batteries that have been investigated so far, sodium-ion batteries (SIBs) are certainly one of the most viable alternatives to LIBs. The main strengths of SIBs are: i) the high natural abundance of Na in nature, ii) their design does not depend on critical materials such as Co, Ni, or graphite, and iii) they can operate at low temperatures and in safer conditions. On the other hand, they will never be able to compete with LIBs in terms of electrochemical performance due to their lower energy density. For these reasons, SIBs are particularly interesting for large scale and stationary applications.

During my PhD, I mainly focused on the synthesis and characterization of new cathode materials for SIBs with a P2-layered structure (space group: $P6_3/mmc$). The study investigates the effect of substitution with Mg^{2+} , an electrochemically inactive cation, on the cycling stability of the P2- $Na_{0.67}Mn_{0.5}Fe_{0.5}O_2$ oxide. Conventional and advanced characterization techniques (*e.g.* operando XRD, PCGA, GITT) were employed to characterize all the materials. The best performing material was found to be the one with the composition P2- $Na_{0.67}Mn_{0.5}Fe_{0.3}Mg_{0.2}O_2$, which delivered capacities exceeding 110 mAh g⁻¹ after 100 cycles at 1C. In addition, I also evaluated the impact of synthesis conditions on the structural, morphological, and electrochemical properties of the cathode materials under investigation. In particular, I focused on conventional solid-state and the more promising spray-drying synthesis. Finally, through full-cell experiments, I was also able to investigate the performance of the best performing cathode by simulating the operation condition of a real commercial battery. Different pre-sodiation strategy were also investigated to increase the overall Na content in the battery, in particular the addition of Na_2CO_3 as sacrificial salt and the electrochemical Hard-Carbon anode presodiation. The latter demonstrated very promising results, showing a specific capacity increase of 90 mAh g⁻¹ after 100 cycles at 1C, with capacity retention exceeding 73%. In addition to P2-layered cathodes, in collaboration with the Department of Physics at the University of

Pavia, we also investigated the working mechanism and electrochemical performances of the polyanionic compound $\text{Na}_2\text{MnPO}_4\text{F}$ as a possible cathode for SIBs using both experimental and theoretical/computational approaches.

Finally, in the last chapter of the thesis, I will discuss the results obtained regarding the recovery of useful precursors from industrial wastewaters rich in Na and other elements useful for the synthesis of active materials for batteries. In particular, the procedures for the selective recovery of Ca^{2+} and Mg^{2+} by selective precipitation as $\text{Ca}_2\text{C}_2\text{O}_4$ and $\text{Mg}(\text{OH})_2$ are presented, along with preliminary results on Na^+ extraction via complexation with 15-crown-5.

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1. Introduction

1.1. Energy Transition

Climate change mitigation is one of the main goals of the European Green Deal, the strategy proposed by the European Union (EU) in 2019 to move toward a more sustainable and equal world. In particular, the achievement of climate neutrality by 2050 and the development of a circular economy model represent some of the main topics in view of a green energy transition. These two approaches represent the European contribution following the international Paris agreement (2015) on climate change. With this treaty, the United Nations (UN) has committed to limiting global heating to a maximum of 2 °C above pre-industrial levels.

Reaching climate neutrality means compensating for the emissions of human activities by developing new and greener technologies that can neutralize them. Concerning the circular economy, the idea is to move from a “produce-use-throw away” model to a new one in which the end-of-life devices can be recycled and reintroduced into the market. This approach means lowering the demand for additional critical raw materials (CRMs), generating less waste, and so reducing emissions.

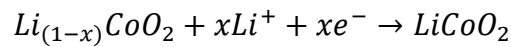
The energy production and consumption account for 75% of the greenhouse gas emissions, and Europe’s energy demand still strongly depends on imports, especially from Russia. In 2020, 58% of the energy consumed in Europe was produced in non-UE countries; in Italy, this dependency reached 73.4%. Following the Russian invasion of Ukraine in 2022 and the subsequent political alignment of the EU, this dependency triggered a severe energy crisis, with energy prices exceeding 300 €/MWh. Consequently, in the last few years, the EU adopted policies to diversify its fossil fuel (*e.g.*, gas, coal) suppliers from allied countries and, most importantly, accelerated the green transition and the development of sustainable energy sources. By 2030, the targets are to achieve 42.5% of energy demand through renewable sources and reduce by 55% greenhouse gas emissions.^{1,2}

In this challenging context, developing new storage systems for renewable energy, such as wind, solar, or hydro, is essential. Among these, the study of devices for electrochemical energy storage represents one of the most important and promising fields of research. The development of high-performance batteries is one of the major

challenges for the future, and the green transition in the automotive sector also depends on them. From 2035, the EU has established that it will only be possible to purchase zero-impact vehicles, which will then completely replace traditional combustion engines.

1.2. Lithium- and Post Lithium-Ion Batteries

Since their commercialization by Sony in 1991, Lithium-Ion Batteries (LIBs) have revolutionized the electronics market and become an integral part of everyday life. For this reason, in recognition of their pioneering contributions to this field, John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were awarded the 2019 Nobel Prize in Chemistry. Being secondary, *i.e.*, rechargeable batteries, LIBs operate based on the reversible movement of Li^+ between the anode and cathode, through a suitable electrolyte. Regarding the negative electrode, or anode, the most used active material is graphite. Its layered crystal structure is ideal for this application, as Li^+ can easily and reversibly insert itself between the layers during charge-discharge cycles. Regarding the positive electrode, or cathode, the first and most commercially successful material is lithium cobalt oxide (LiCoO_2 , or LCO), which was patented by John B. Goodenough between the 1980s and 1990s.³ Like graphite, LCO features a layered crystalline structure (space group: $R\bar{3}m$). This class of cathode materials is based on the concept of reversible lithium-ion intercalation within the host crystal structure, a principle first introduced by Whittingham in the 1970s.⁴ The electrochemical reaction driving the operation of LCO is:



The lithiation process from CoO_2 to LiCoO_2 occurs during discharge, while delithiation occurs during charge. In addition to layered oxides, those with a spinel-like structure (*e.g.*, LiMn_2O_4 , space group: $Fd\bar{3}m$) or olivine (*e.g.*, LiFePO_4 , space group: $Pnma$) are also very interesting and high-performance. As for the electrolyte, a dissolved lithium salt (LiPF_6 , Lithium bis(FluoroSulfonyl)Imide (LiFSI), Lithium bis-TriFluoromethaneSulfonImide (LiTFSI)) in a mixture of organic solvents, typically carbonates, is generally used.

However, all the components described above have some inherent critical issues, mainly related to sustainability, safety, or performance. For example, graphite and cobalt, which are fundamental for the synthesis of active materials, appear on the EU's list of Critical Raw Materials (CRMs),⁵ those elements or compounds whose use should be minimized due to the serious environmental, economic, and ethical problems associated with their extraction or production. Using metallic lithium as the anode would dramatically increase battery performance, as it would be possible to fully exploit lithium's theoretical capacity (3860 mAh g^{-1}), which is much higher than that of graphite (372 mAh g^{-1}). However, safety concerns due to the formation of dendrites during cycling limit its commercialization, as these can cause internal short circuits and thermal runaway. Non-aqueous organic electrolytes have additional safety risks, as the used organic solvents are highly flammable. Furthermore, meeting the ever-increasing market demand for electrochemical energy storage systems will become increasingly difficult by relying only on LIBs.

For all these reasons, designing suitable alternatives to LIBs is essential. Based on the same operating principle, over the last few years much of the scientific attention has moved to the study of so-called post-lithium batteries (PLIBs). It is important to remember that none of these technologies will completely replace Li-ion batteries, but they will certainly help to reduce their reliance and diversify the market.

Among these, some are still in the early stages of research, while others are already sufficiently established technologies to be commercially available or close to it. Regarding the first ones, multivalent batteries (*e.g.*, Ca^{2+} , Mg^{2+} , Al^{3+}) are very interesting. Their appeal lies in the possibility of having twice or more the mobile charge compared to Li^+ , and therefore considerably greater energy density. However, the development of electrolytes and electrode materials compatible with such large cations remains highly challenging. Solid-State Batteries (SSBs), by contrast, hold significant promise in terms of performance, particularly as they enable the use of $\text{Li}_{(\text{m})}$ as an anode. Nevertheless, designing solid electrolytes with properties comparable to those of conventional organic liquid electrolytes is very difficult and still relies on methods and expertise that are not yet sustainable at an industrial scale.

Concerning mature PLIBs, redox flow batteries represent one of the most established examples. Unlike LIBs, they operate based on a fundamentally different working

mechanism, which has attracted significant interest due to their high modularity and scalability. Nevertheless, their relatively large size and low energy density limit their application primarily to stationary energy storage systems.

Among PLIBs, however, the most promising candidates are Sodium-Ion Batteries (SIBs), which are already being commercialized by several leading companies worldwide. Their characteristics and properties will be discussed in detail in the following chapters.

1.3. Sodium Ion Batteries (SIBs)

1.3.1. Working Mechanism and theoretical concepts

One of the motivations driving the growing interest in Sodium Ion Batteries (SIBs) is the potential to leverage the knowledge and insights gained from the development of LIBs in their design. The operating principle of SIBs closely mirrors that of LIBs, relying on the reversible intercalation and deintercalation of Na^+ cations between the positive and negative electrodes during charge and discharge cycles (Figure 1).

The electrodes are physically separated by a separator, a highly porous material soaked in an electrolyte mixture containing a Na salt (usually NaPF_6 or NaClO_4). The role of the electrolyte is to ensure ionic conductivity and to prevent direct contact between the electrodes, which would otherwise cause a short circuit. The electrons movement needed to compensate for the Na^+ migration during the cycles is ensured by an external circuit.

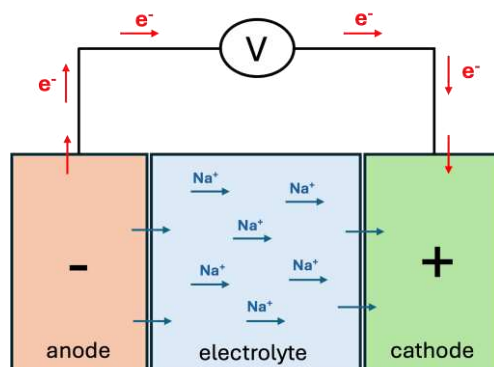


Figure 1. Schematic representation of a SIBs. The e^- and Na^+ flow is depicted in the direction of discharge, which is the spontaneous process. During the subsequent charge, the flow is reversed

From a thermodynamic perspective, the equation underlying the working principle of an electrochemical cell is:

$$\Delta G = -nFE_{cell}$$

Where ΔG is the change in free energy of the system (in Joule mol^{-1}), n is the number of moles of electrons exchanged, F is Faraday's constant (96485 C mol^{-1}), and E_{cell} is the electromotive force of the cell, calculated at equilibrium as the difference between $E_{cathode}$

and E_{anode} . As with all chemical reactions, a spontaneous reaction involves a negative ΔG . For electrochemical cells, this implies that the system can spontaneously generate electrical work, which can be harnessed to power devices or for other applications. Considering this equation, it is evident that the choice of the electrode materials plays a crucial role in determining battery performance. Specifically, to optimize the total energy of the system and increase E_{cell} , it is necessary to select cathodes and anodes that operate at increasingly higher and lower potentials, respectively. Another important material parameter to consider is their specific capacity (C_s), defined as the amount of electrical charge that the material can exchange during cycles per gram. Given the molecular weight (MW) and the number of electrons exchanged by the material during cycling in the desired potential range, C_s can be calculated as:

$$C_s = \frac{\Delta x \cdot F}{3.6 \cdot MW}$$

Since it is usually reported in mAh g^{-1} , a conversion factor ($= 3.6$) must be included in the formula to express Faraday's constant (F) in mAh mol^{-1} instead of C mol^{-1} .

From E_{cell} and the theoretical capacity, it is possible to evaluate the theoretical energy of the cell, calculated as:

$$\text{Specific Energy} \left[\frac{\text{Wh}}{\text{kg}} \right] = C_s \cdot E_{\text{cell}}$$

$$\text{Energy density} \left[\frac{\text{Wh}}{\text{l}} \right] = C_s \cdot E_{\text{cell}} \cdot \rho$$

Graphically, the energy density corresponds to the area under the curve in the plot of specific capacity vs. E_{cell} , as illustrated in Figure 2.

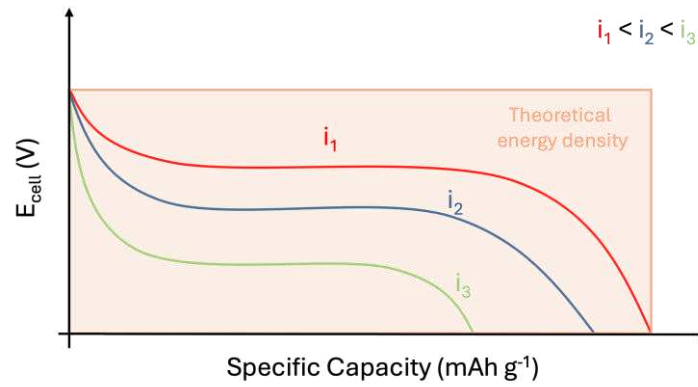


Figure 2. Schematic plot of the specific capacity vs. E_{cell} curves in ideal (orange) and real working condition at different current (i_1 , i_2 , and i_3)

However, the energy that can be obtained from the system during cycling is always lower than the theoretical value, as the working potential of the cells is always lower than the theoretical value (E_{cell}) due to the internal resistance of the components and overpotential caused by the current (i). Moreover, as the current increases, the achievable energy density will be increasingly lower, as these effects become more pronounced (Figure 2). As a convention, the cycling rate of a battery is typically expressed in terms of C-rate, that indicate the current required to fully charge or discharge the battery within a specified time. For example, cycling a battery at 1C means that the current is applied in such a way that the battery is fully charged or discharged within 1 hour. Similarly, 2C corresponds to a full cycle in 30 minutes, while 0.5C indicates a cycle time of 2 hours.

1.3.2. SIBs vs. LIBs

Sodium-ion batteries surely represent one of the most promising alternatives to LIBs, but we must pay attention to some intrinsic difference between Na and Li, that significantly influence the performance of the batteries. First, the energy density of SIBs will always be lower than LIBs because of the lower average E_{cell} . This difference can be ascribed to two main factors: i) The standard reduction potential of Na^+/Na (-2.71 V) is higher than that of Li^+/Li (-3.04 V) versus the Standard Hydrogen Electrode (SHE). Since this parameter thermodynamically limits anode optimization, SIBs will inherently exhibit a higher anode potential compared to LIBs. ii) The higher atomic mass of sodium (22.99 g mol^{-1}) compared to lithium (6.91 g mol^{-1}). As a result, the gravimetric and volumetric

capacities of SIBs are significantly lower than those of LIBs. Moreover, Na⁺ dimension is significantly higher than Li⁺, and so this makes intercalation processes more difficult and can cause greater volumetric expansion of electrode materials structure during cycling.^{6–8} Table 1 summarizes all these differences.

Table 1. Differences in the main chemical and physical properties of Na and Li

	Li	Na
E vs. SHE (V)	-3.04	-2.71
Ionic radius (Å)	0.76	1.02
Atomic weight (g mol ⁻¹)	6.91	22.99
Gravimetric capacity (mAh g ⁻¹)	3861	1165
Volumetric Capacity (mAh cm ⁻³)	2062	1131

For all this reason, it's easy to understand that SIBs will never compete with LIBs in term of performances. On the other hand, they can replace and be complementary to LIBs in some application field where high energy density is not needed (*e.g.*, smart grid, renewable energy storage systems).

However, Na batteries have also some important advantages in terms of sustainability, costs, and safety. Firstly, Na natural abundance is more than 1000 times higher than Li, and so it considerably reduces the overall cost of this element.⁹ Furthermore, the cathode materials most used for SIBs do not require CRMs such as Co and Ni for their development.

From a cost-reduction perspective, one particularly interesting aspect of SIBs is the possibility of using aluminum as the anode current collector, whereas LIBs require copper. This distinction arises from the chemical inactivity of sodium in contact with Al at low potentials, in contrast to lithium, which forms a Li-Al alloy below 0.1 V.¹⁰ This characteristic not only contributes to a reduction in overall device weight, but, more importantly, significantly lowers cost, since Al is far more abundant and less expensive than Cu. Moreover, the enhanced chemical stability afforded by this configuration ensures the safe transportation of SIBs even during complete discharge, at 0 V. This enhancement assumes particular significance when contrasted with LIB technology, wherein the partial dissolution of copper in such conditions can result in more hazardous outcomes.¹¹

1.3.3. Components

1.3.3.1. Hard-Carbon anode

Beyond the intrinsic differences between Na and Li above discussed, a major practical limitation in developing efficient SIBs lies in the fact that graphite cannot be employed as an anode material, unlike in LIBs. The difference in behavior is not simply due to the larger ionic radius of Na^+ (1.02 Å) compared to Li^+ (0.76 Å), which might suggest a greater difficulty for Na^+ to intercalate between the graphite layers during battery cycling. In fact, graphite can be successfully used as an anode material in potassium-ion batteries (KIBs), despite K^+ being even larger (1.38 Å) than Na^+ . To understand this apparent contradiction, one must consider the thermodynamic stability of the compounds formed between the intercalating cation and the layered graphite structure. According to thermodynamic principles, a chemical compound is considered stable when its Gibbs free energy of formation (ΔG_f) is negative. In this context, several studies have shown that graphite forms thermodynamically stable intercalation compounds with all alkali metal cations (Li^+ , K^+ , Rb^+ , Cs^+), except Na^+ . This explains why graphite is unsuitable as an anode material for sodium-ion batteries (SIBs).^{12,13}

The most widely used active material for SIB anodes is hard carbon (HC), a material with the same matrix or carbon composition as graphite but a significantly different crystalline structure. In fact, HC has a highly disordered structure, consisting of many graphite-like layered domains arranged randomly. Furthermore, the interlayer distance in the domains is greater than that of graphite (>0.37 Å vs. 0.34 Å), thus favoring the intercalation of Na^+ . Due to their disordered and almost amorphous structure, the XRD pattern of HC shows only two diffraction signals as very broad peaks from which it is not possible to obtain much information. For this reason, the characterization of HCs is usually carried out using SAXS to evaluate the size of the closed pores present, Raman spectroscopy to better assess the degree of structural disorder, or surface area and porosity analysis.

Hard carbons are produced through the high-temperature pyrolysis (> 1000 °C) of natural or synthetic organic precursors. This straightforward process not only lowers production costs but also enhances the sustainability of anode manufacturing compared to graphite-based alternatives, as HC can be derived from industrial waste or biomass.^{14–17}

Although the exact sodium storage mechanism in HCs is still not fully understood, most studies agree that it involves the interplay of two main processes: (i) intercalation of Na^+ ions between the graphitic layers, like the mechanism observed for Li^+ in graphite, and (ii) adsorption and pore-filling within the disordered structure, particularly in the voids between graphitic domains. The relative contribution of each process depends on the specific structural characteristics of the HC material. Figure 3 illustrates the most widely accepted models proposed to date for these storage mechanisms.¹⁸

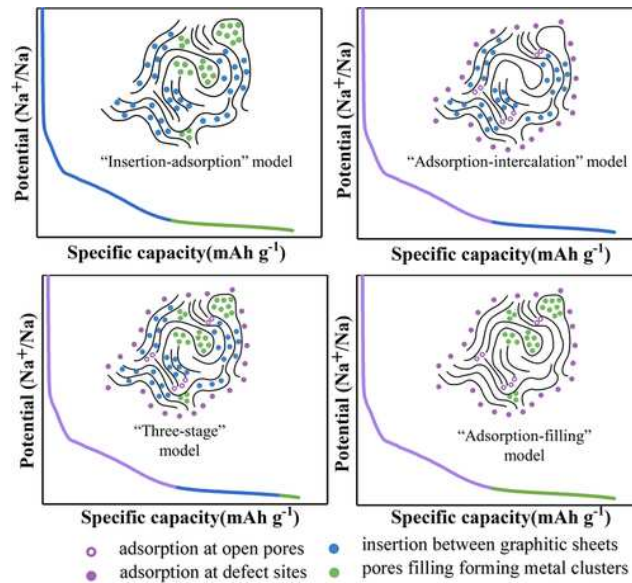


Figure 3. Schematic representation of the microstructure of the hard carbon and the main active sites with the ability to uptake of sodium ions. Reprinted from Ref [18]

One of the main limitations of HC is its low initial coulombic efficiency (ICE), which counts for the irreversible Na^+ loss between the first discharge and the subsequent charge. ICE is a critical parameter in the design of HC anodes, as it has a direct and significant impact on overall battery performance. This sodium loss is primarily attributed to the formation of the so-called solid electrolyte interphase (SEI) on the electrode surface. Although SEI formation has long been studied in Li-ion batteries, its formation mechanism remains debated, and no single theory has gained broad acceptance. What is well established, however, is that the SEI consists of electrolyte degradation products (including salts and solvents, whether Li- or Na-based batteries). Its formation and presence are essential for the proper operation of batteries, since it provides high ionic conductivity for the intercalating ion while blocking electron transport, thereby

preventing the continuous degradation of other cell components such as the electrodes and electrolyte.^{19,20}

Many strategies have been investigated to increase ICE, including the introduction of heteroatoms to increase Na^+ adsorption on the surface,²¹ structural modification to promote pore filling,²² and surface engineering.²³

1.3.3.2. Cathodes

The choice of cathode active material (CAM) is one of the crucial steps in the design of sustainable SIBs.²⁴ The most employed cathode active materials for sodium-based batteries include layered transition metal oxides, Prussian blue analogs, and polyanionic compounds. Each class exhibits distinct structural and electrochemical properties that render them more suitable for specific applications, depending on the performance requirements. This differentiation is clearly illustrated in Figure 4. For example, one of the main advantages of layered oxides is the possibility of achieving high energy densities by appropriately choosing their composition, even though this often goes at the expense of long-term stability.^{25,26} For polyanionic compounds, the trend is the opposite; because of their high molecular weight, they do not guarantee high energy densities, but they have high structural stability even after being stressed for many cycles. Prussian blue analogs, finally, have intermediate properties between the previous two in terms of energy density and stability but have the great advantage of having much lower production costs. On the other hand, their safety is still under debate.²⁷

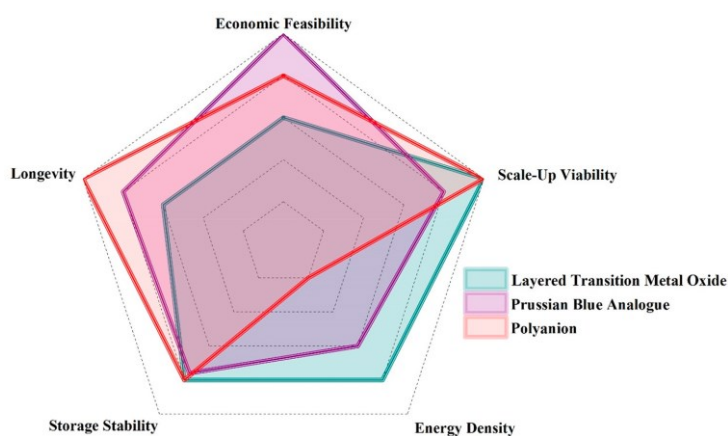


Figure 4. Comparison of existing cathode materials. Reprinted from Ref. [24]

The synthesis route plays a key role in the development of electrode materials, as depending on the precursors used and the synthesis conditions, materials with the same composition but different cathodic performances can be obtained due to different morphology, porosity, surface area, and microstructure. Spray-drying or spray-pyrolysis, for example, represents some of the most promising types of synthesis, as they are low-cost, highly reproducible, and easily scalable.^{28–30} In Figure 5 is shown a schematic representation of a spray-dryer instrument typically used in a Lab.

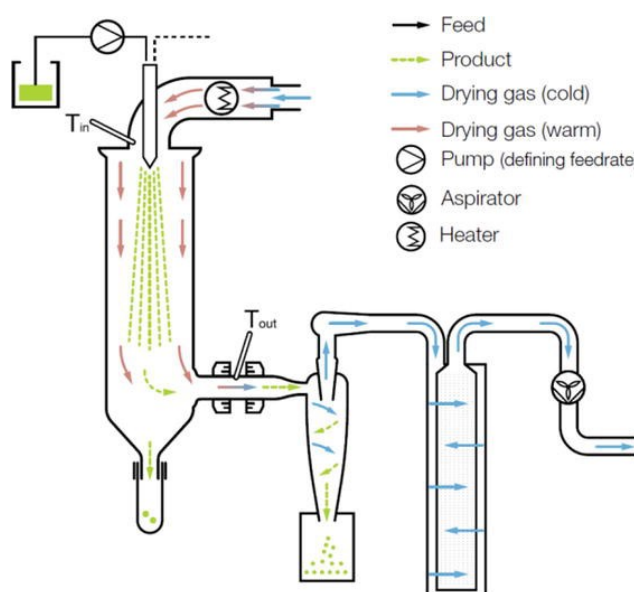


Figure 5. Schematic illustration of spray-drying process. Reprinted from Ref. [31]

Experimentally, spray-drying synthesis consists of three steps: i) atomization of the starting solution into fine droplets; ii) evaporation of the solvent (usually H₂O) by a hot gas flow; iii) recovery of the dry powder, with the desired composition and regular morphology. In many cases, final calcination at high temperatures (700–800 °C) is also necessary for the formation of the desired crystalline structure.

1.3.3.2.1. Layered Oxide

Unlike the most widely used cathode for lithium-ion batteries, lithium cobalt oxide LiCoO_2 (LCO),^{3,32} whose layered structure can only be of the O3 type (space group $R\bar{3}m$), layered cathodes for SIBs can be synthesized in different stacking sequences, among which the most important are the P2 (space group $P6_3/mmc$) and O3. As proposed by Delmas *et al.*,³³ the letters P and O represent the coordinative environment of Na^+ ions, prismatic and octahedral, respectively; the numbers indicate how many Na layers are present in each elementary cell. Figure 6 shows the main difference between the two structures.

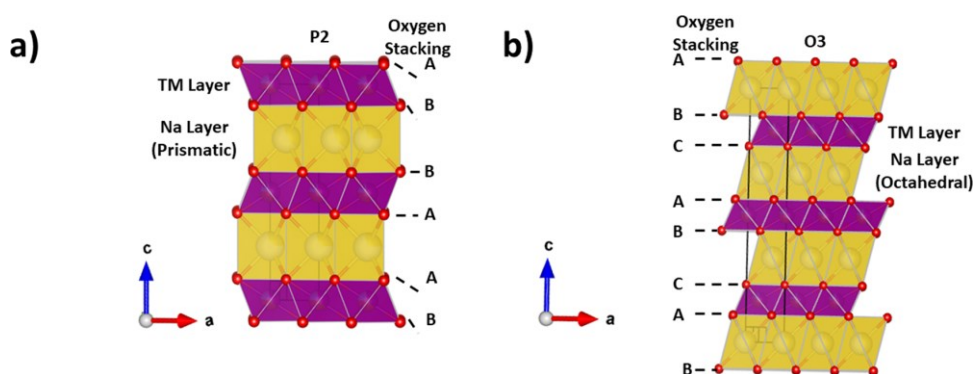


Figure 6. a) Crystal structure of the P2 phase b) Crystal structure of the O3 phase. Reprinted from Ref. [34]

These two phases have different initial sodium content and markedly different electrochemical performances. P2 generally offers higher ionic conductivity and structural stability than O3. However, at high potentials (> 4 V), it suffers from phase transitions to other phases (named O2, OP4, or Z in the literature), which are often electrochemically inactive.^{34,35} O3, by contrast, has a higher specific discharge capacity (due to its higher Na^+ content), but it has slower Na^+ diffusion kinetics and a lower average potential than P2. Even though this depends on the exact composition, all the layered structures are air-sensitive³⁶ but, in general, O3 phases suffer of more structural distortions than P2 ones when exposed to air or humidity.³⁷ As already mentioned, one of the main limitations to the development of P2 cathodes is the low Na content in the starting oxide, which obviously severely hinders its use in full cells. Several strategies have been developed to increase its content, as will be discussed in detail in Chapter 1.3.4.

In this context, accurately determining the sodium content in the as-synthesized P2-oxides is fundamental, as it has a significant impact on the lattice parameters and, consequently, on the electrochemical performance of the material.

One of the most promising research activities on layered oxides is trying to enhance their cathodic performance by modifying the elemental compositions, by introducing electrochemically inactive cations known for their stabilizing properties like Mg^{2+} , Ca^{2+} , or Ti^{4+} .^{38–40} Mg^{2+} sits on the lattice site occupied by the active cations on the transition metal layers and, because of this, can prevent the collapse and slippage of the planes during cycling.^{41–43} In addition, Mg^{2+} also allows for increased P2-layered oxide air stability by increasing the average oxidation state of the other cations in the structure.^{26,44} Among the various compositions studied and reported in the literature, $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ is certainly one of the most promising, due to its favorable electrochemical properties (theoretical energy density of 520 Wh kg^{-1}) and low production cost, resulting from the natural abundance of both Mn and Fe. However, the aforementioned phase transitions at high voltages limit its large-scale application. These P2-Z-phase transitions originate from the partial collapse of the P2 structure, which occurs during charging at high potentials due to the low sodium content. Because of these structural rearrangements, part of the Fe atoms located on the transition metal layers irreversibly migrate to atomic position typically occupied by Na. This migration leads to a reduction in the specific capacity during subsequent charge-discharge cycles, since Fe is now electrochemically inactive.^{45–47} Another critical aspect related to these undesirable phase transitions is the Oxygen redox activity, which typically occurs above 4 V. This contribution is usually irreversible and can trigger phenomena such as the loss and release of O_2 , leading to structural stability and electrochemical performance degradation. Strategies such as doping with electrochemically inactive cations (e.g., Mg^{2+}) or the partial substitution of O^{2-} with F^- have been shown to mitigate this activity,⁴⁸ although they can never fully suppress it. For this reason, a detailed understanding of the mechanisms underlying oxygen redox activation is of fundamental importance. In this context, advanced spectroscopic techniques such as Resonant Inelastic X-ray Scattering (RIXS) coupled with X-ray Absorption Spectroscopy (XAS) have proven to be highly informative and insightful.^{49–51}

Various synthesis strategies^{52,53} and cation substitutions have demonstrated that optimizing these two factors can significantly enhance cathode performance. For instance, a slight substitution with Ti^{4+} or Si^{4+} increases capacity retention by nearly 50% compared to the unsubstituted oxide after 100 cycles.^{54,55}

Recently, the development of layered cathodes with a P2/O3 biphasic structure has garnered significant attention, as this configuration combines the advantages of both phases, yielding higher-performance cathodes compared to pure P2 or O3. As an example, Faradion has successfully commercialized a P2/O3 biphasic cathode with the composition $\text{Na}_x\text{Ni}_{1-x-y-z}\text{Mg}_x\text{Mn}_y\text{Ti}_z\text{O}_2$, demonstrating enhanced electrochemical properties compared to their first pure O3 materials¹¹.

1.3.3.2.2. Polyanionic Compounds

Polyanionic compounds are an attractive alternative to layered oxides as potential cathodes for SIBs, thanks to their excellent properties in terms of structural stability, high working potential, and safety. However, their industrial application is limited by low ionic conductivity, caused by their rigid and complex 3D structure, formed by MO_x [$\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{V}, \text{Ti}, \text{Cr}, \text{etc.}$] polyhedral and $(\text{XO}_4)_m^{n-}$ or $(\text{X}_m\text{O}_{3m+1})^{n-}$ [$\text{X} = \text{B}, \text{P}, \text{S}, \text{Si}, \text{etc.}$] anion groups, which are connected by a corner and/or edge-sharing manner.^{56,57} In particular, the M–O bonds of redox-active polyhedra are not directly connected to each other but are instead linked through anionic groups (X–O). As a result, electrons must propagate along a more hindered pathway (M–O–X–O–M), rather than the direct M–O–M typically of, *e.g.*, layered oxides.⁵⁸

Among the various polyanionic compounds investigated in the literature, transition-metal fluorophosphates stand out as particularly promising. Their stable structural framework ensures high thermal stability and safety, while the strong electronegativity of fluorine elevates the redox potential, ultimately enabling higher energy densities.⁵⁹ Vanadium-based fluorophosphates are the most widely investigated systems in this context; however, concerns about toxicity and costs of V compared to transition metal ions such as Mn and Fe are making the investigation of fluorophosphates with general formula $\text{Na}_2\text{MPO}_4\text{F}$ ($\text{M} = \text{Fe}, \text{Mn}$) more pressing. Such systems show promising theoretical specific capacities, close to 125 mAh g^{-1} for the extraction of 1 Na ion per formula unit, and high intercalation

voltages, even up to 6 V, if two Na ions per formula unit were to be exchanged.^{59,60} In fact, the very high intercalating voltages for the M^{3+}/M^{4+} redox couple, outside the stability window of commonly used liquids electrolytes,⁶¹ practically limit at the moment their performances to the extraction of 1 Na ion per formula unit.⁶² The achievement of specific capacities close to the theoretical ones, as well as the stable operation over repeated cycling, are also limited by sluggish kinetics, which in turn is related to the Na-ion intercalation process in the crystal structure. The most common strategies to improve the electrochemical properties of these materials are thus carbon coating, cation doping, and particle size reduction.⁵⁹ Such strategies have proven to be successful for $\text{Na}_2\text{FePO}_4\text{F}$.^{63–65} The reported cathode active material was initially believed to be electrochemical inactive,^{66,67} and although improvements in synthesis and carbon coating have been tested in recent years, this material is still suffering from poor rate kinetics and poor capacity retention in comparison to its Fe-based counterpart.^{68,69}

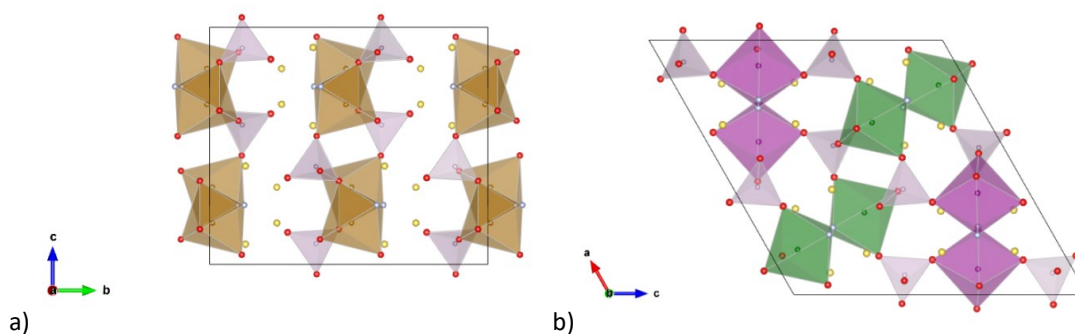


Figure 7. Crystal structure of a) $\text{Na}_2\text{FePO}_4\text{F}$ ⁶⁷ and b) $\text{Na}_2\text{MnPO}_4\text{F}$ ⁷⁰ highlighting the different arrangement of the coordination polyhedra. Na ions are shown in yellow, P tetrahedra in grey, Fe octahedra in brown, Mn octahedra in pink (Mn1) and green (Mn2).

$\text{Na}_2\text{FePO}_4\text{F}$ crystallizes in an orthorhombic layered structure (space group $Pbcn$) built from face-shared FeO_4F_2 octahedra bridged by PO_4 tetrahedra (Figure 7a), while $\text{Na}_2\text{MnPO}_4\text{F}$ presents a monoclinic structure (space group $P2_1n$), built from corner-shared MnO_4F_2 octahedra bridged by PO_4 tetrahedra to form a three-dimensional (3D) framework (Figure 7b). The different polyhedral arrangements likely support different diffusion behavior for the Na ion within the structure. While 2D diffusion were predicted and observed for $\text{Na}_2\text{FePO}_4\text{F}$ via density functional theory (DFT) calculations, molecular dynamics (MD) simulations and bond valence site energy (BVSE) analysis,^{71,72} the 3D

open structure of the $\text{Na}_2\text{MnPO}_4\text{F}$ compound is expected to allow 3D diffusion of the Na ion in the system.⁷³

1.3.4. Full-Cell

In recent years, world-leading companies in the field have been investing in developing sodium-ion batteries, in some cases already reaching large-scale production and commercialization. Prominent among these is China's CATL, which in 2021 presented its first battery based on Prussian White (cathode) and Hard Carbon (anode), with an energy density $>160 \text{ Wh kg}^{-1}$.⁷⁴ In Europe, an example is Britain's Faradion, which bases its battery on layered oxide-type cathodes and Hard Carbon-based anodes, with energy density $>120 \text{ Wh kg}^{-1}$ and an average life of more than 3000 cycles.¹¹ The French Tiamat uses polyanionic compounds as cathodes and patented batteries with energy densities of $90\text{-}120 \text{ Wh kg}^{-1}$, super-fast charge (5 minutes), and an average life of more than 5000 cycles with capacity retention $>80\%$.⁷⁵

However, numerous challenges associated with SIB materials still hinder their commercialization, particularly with regard to the parameters that must be optimized to achieve high performance. Even at the laboratory scale, when testing in a full-cell configuration, significantly more factors need to be considered than in half-cell experiments. This is readily explained by the presence of two active electrodes (anode and cathode) and the absence of a counter-electrode (metallic Na), which requires simultaneous precautions to prevent performance loss during cycling. The first parameter to optimize is the working potential range, which must simultaneously: (i) be as wide as possible to maximize the system's energy density; (ii) encompass the working potentials of both the cathode and anode to fully exploit their properties; and (iii) remain within the electrochemical stability window of the electrolyte mixture to avoid degradation. A second key factor is the proper balance between the charge available at the cathode and anode, commonly referred to as the N/P ratio,^{76–78} defined as:

$$\frac{N}{P} = \frac{Q_{\text{anode}} [\text{mAh cm}^{-2}]}{Q_{\text{cathode}} [\text{mAh cm}^{-2}]}$$

With Q derived from the specific reversible capacity of the active materials (mAh g^{-1}) after the first cycle, together with the loading of active material on the electrodes (mg cm^{-2}). Accurate evaluation of this parameter is of primary importance in the design of full cells, as it directly affects critical aspects such as coulombic efficiency, reversible specific capacity, and the long-term stability of all the cell components during cycling. Since the optimal value strongly depends on the nature of the electrode materials employed, no universal reference value can be applied. For example, in full cells combining a layered oxide cathode with a hard carbon (HC) anode, the optimal N/P ratio has been reported to be approximately 0.9.⁷⁸ This value enables simultaneous optimization of both electrodes' performance while mitigating issues such as sodium plating, dendrite formation, and the development of insufficiently stable interphases. In this type of cell, however, the main limitation arises from the intrinsically low sodium content of the cathode material ($\text{P2-Na}_{0.67}\text{MO}_2$), which constrains the achievable energy density and consequently hinders commercialization. This issue is further exacerbated by the substantial sodium loss associated with solid–electrolyte interphase (SEI) formation on hard carbon (HC) anodes, which is considerably higher than that observed for graphite anodes in lithium-ion batteries (LIBs). As a result, the use of a sodium-deficient cathode poses an even greater challenge. To address this problem and thereby increase the amount of mobile Na^+ available in full cells, several pre-sodiation strategies have been explored. Among these, the most promising approaches are the use of sacrificial salts^{79–82} (*e.g.* $\text{Na}_2\text{C}_2\text{O}_4$, Na_2CO_3 , NaN_3) and the electrochemical pre-sodiation of HC.^{83,84} The former is regarded as the most viable route for large-scale industrial implementation, owing to its simplicity and relatively low cost; however, it requires careful optimization of experimental parameters such as the amount and particle size of the sacrificial salt, electrode preparation conditions, and the control of by-product formation. The latter method, in contrast, has demonstrated superior effectiveness in terms of electrochemical performance, but its reliance on additional processing steps has limited its appeal for industrial applications.

2. Aim of the thesis

During my PhD, I worked on the synthesis and structural, morphological, and electrochemical characterization of new cathode active materials for sodium-ion batteries. The project was carried out in collaboration between the Department of Chemistry at the University of Pavia and ENI S.p.A. (Guido Donegani Institute, Novara). For this reason, in addition to the academic scientific interest derived from the study of new materials for post-Li electrochemical energy storage, it was necessary to consider the industrial feasibility of the various steps during each work stage. For this reason, we decided to work on materials based on Fe, Mn, and Mg, all elements that are abundant in nature and without supply problems. We focus the attention on the development of a new family of cathodic materials with the P2-layered structure and with the composition $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3$). Furthermore, during my time as a visiting student at the University of Bayreuth, I evaluated and optimized the possibility to use spray-drying synthesis instead of the more conventional solid-state synthesis, to significantly increase the economic and environmental sustainability of the synthesis conditions. The full characterization of these materials, together with the comparison of their performance obtained through different synthesis strategies, is presented in detail in Chapters 4.1, 4.2 and 4.3. The best-performing material was further evaluated in a full-cell configuration with a commercial Hard Carbon as anode, in order to reproduce realistic battery operating conditions and to assess its potential for industrial application (Chapter 4.4). To mitigate the issue of the low Na content of P2-layered materials, two pre-sodiation strategies were investigated: the addition of Na_2CO_3 as a sacrificial salt and the electrochemical pre-sodiation of the anode.

Moreover, in collaboration with the Department of Physics of the University of Pavia, we also evaluated the properties of $\text{Na}_2\text{MnPO}_4\text{F}$ as cathode materials for SIBs. In this work (Chapter 5), we performed several experimental and theoretical investigation, to establish correlation between what was expected based on calculation and what observed during electrochemical tests.

As highlighted in the first paragraph of the introduction, one of the European Union's strategic priorities for the coming years is the establishment of a circular and sustainable economic model. Within this framework, the recovery of precursors from the company's

wastewater, rich in Na and other important elements for battery development, represents a highly consistent and valuable approach. The methodologies optimized during the project, together with the results achieved in recovering selected elements (Na^+ , Ca^{2+} and Mg^{2+}), will be detailed in Chapter 6.

3. Characterization techniques

3.1. Morphological-structural characterization

3.1.1. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most widely used structural characterization techniques for determining the crystallographic properties of crystalline solids. It is based on the physical phenomenon of diffraction, originating from the coherent scattering (or elastic scattering) undergone by X-ray photons when they encounter a crystalline structure. In the laboratory, X-rays are produced using metal anti-cathode X-ray tubes, consisting of a Tungsten (W) filament (cathode) and a metal target (anode). The production mechanism can be summarized as follows: i) thanks to the high potential and current differences used, the cathode emits electrons by thermionic effect; ii) following the collision with these electrons, the core electrons of the anodic material are excited to higher energy levels; iii) the electronic configuration achieved is stable, which is why the atom tends to return to its ground state through electronic relaxation; iv) the excess energy produced by relaxation can be released in the form of an X-ray photon or an Auger electron, in different percentages depending on the type of anode used. Since each element has a particular electronic structure, different types of characteristic X-rays will be obtained depending on the metal target used. The X-ray emission spectrum consists of two main components: continuous radiation (*Bremsstrahlung*), resulting from the deceleration of electrons when they encounter the electron cloud of the target atoms, and characteristic radiation, visible only when the incident electron promotes a core electron of the metal to higher energy levels. The latter consists of different types of radiation, which can be classified according to the core state from which the metal electron is extracted. For diffraction experiments, $K\alpha_1$ radiation (removal of an electron extracted from the K sphere and replaced by an electron from the L sphere) is usually used, as it is usually the most intense. Continuous radiation and all secondary characteristic radiation are eliminated by using special filters or monochromator crystals, which exploit the variation in the absorption coefficient of X-rays at specific wavelength values. For a Cu target ($Z = 29$), the monochromator used is Ni-based ($Z = 28$).

Bragg's law of diffraction is at the basis of the operation of all commercially available diffractometers. This law is based on the concept of diffraction intended as a simple phenomenon of reflection of X-rays following their scatter with the lattice planes of the sample to be analyzed. The planes are considered semi-reflective, allowing incident X-ray photons to be both reflected by the surface lattice planes and transmitted to the inner ones. Bragg's law is defined by the following equation:

$$2d \sin \theta = n\lambda$$

where d is equal to the interplanar distance, θ is the angle of incidence and reflection of the X-rays, and λ is the wavelength of the incident radiation. For a correct understanding of the results obtained using this formula, it is important to note that the diffraction angles θ at which the peaks fall in the pattern do not depend on the type of atoms composing the sample but exclusively on their spatial arrangement.

3.1.1.1. Rietveld Refinement

The Rietveld refinement method is widely used in materials science to obtain structural information from experimental powder diffraction patterns. Developed in 1969 by Hugo Rietveld⁸⁵ to analyze neutron diffraction (ND) data from polycrystalline materials, it can also be used to study patterns collected from XRD experiments. Starting from an initial structural model, the purpose is to minimize the difference between the experimental and theoretical patterns, calculated from the model, using a least squares minimization procedure. The application of this procedure yields a pattern that closely matches the experimental one, from which it is then possible to accurately extract different structural parameters of the material under investigation (*e.g.*, lattice parameters, crystallographic site occupancies, atomic positions, and thermal factors). Furthermore, for materials composed of multiple crystalline phases, the Rietveld refinement procedure also enables a quantitative analysis of the individual phases present in the sample.

3.1.2. Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX)

At the basis of scanning electron microscopes' (SEM) design is the idea of using a focused beam of electrons to light up the sample, unlike optical microscopes, which use a simple light source. The advantages of using electrons are due to their wavelength, which is much smaller than that of visible light ($0.1\text{-}0.005\text{ \AA}$ vs. $4000\text{-}7000\text{ \AA}$), thanks to which microscopes can be built that are much more powerful than optical microscopes. Performance is generally described in terms of i) resolution, understood as the minimum distance between two distinguishable points in the image (5 nm); ii) magnification, defined as the ratio between the distance between two points on the image and the same distance measured on the sample (up to 10^5); iii) depth of field, equal to the maximum distance between two points simultaneously in focus, measured in the direction parallel to that of observation. The values indicated in parentheses refer to those possessed by common SEMs. The magnified image of the sample is produced thanks to the signals emitted by the sample following interaction with the incident electron beam, produced using specific electron guns. The vacuum is necessary for all electron sources, as the beam produced must reach the sample without encountering any obstacles. In addition to the electron gun, the SEM also consists of i) a system of six electromagnetic lenses, necessary to make the beam hitting the sample as focused as possible; ii) a different detector for each type of secondary electron emitted by the sample; iii) a sample holder; iv) software to view the constructed images of the samples on a monitor.

There are different signals produced by the sample following interaction with the incident electron beam. The most used electrons for SEM analysis are secondary electrons (SE) and backscattered electrons (BSE). The former are produced because of the interaction between the incident electrons and the outermost electrons of the sample, which are ejected. In this case, we refer to inelastic scattering. Since they derive only from the most superficial atoms of the sample, important topographical considerations can be drawn from their detection. The emission yield for SE depends on various factors, the most important of which are the atomic number (Z) of the atoms present and the local curvature of the sample surface; in general, the number of secondary electrons emitted depends on the morphology of the sample. The result is an image that shows the surface of the sample illuminated in different ways depending on its surface characteristics. Backscattered

electrons, on the other hand, being formed by elastic scattering, have greater energy but are usually fewer in number than SE. They are equivalent to incident electrons that are reflected, following interaction with their own electron cloud, by the atoms of the sample. They are much more sensitive to composition than SE, which is why images produced using BSE are composed of areas that are bright depending on the composition. The brightness is proportional to the atomic number Z : the more an area is composed of heavy elements, the brighter the image. In addition to topographical information, therefore, important considerations about the chemical composition of the sample can be made from BSE analysis. In addition to the SE and BSE measurements, information can also be obtained from the analysis of the emitted X-rays, usually detected by a lithium-doped silicon (Si-Li) solid-state detector. The analysis of X-rays using an electron microscope is called EDX (Energy Dispersive X-Ray) analysis. Using this technique, it is possible to perform qualitative and quantitative analyses of the elemental chemical composition of the sample and obtain maps of the distribution of elements in a particular area of the sample.

3.1.3. Inductively Coupled Plasma Optical Spectroscopy (ICP-OES)

Inductively coupled plasma optical spectroscopy (ICP-OES) is an important analytical technique that can be used to perform qualitative and quantitative analyses of samples in solution. Compared to other analytical techniques, ICP-OES has two major advantages: it allows multiple elements to be analyzed simultaneously and makes it possible to determine concentrations of a few tens of ppb ($\mu\text{g L}^{-1}$).

ICP spectrometry is based on the so-called plasma, defined as a hot, electrically neutral but highly ionized gas, i.e., composed of positive ions and electrons in the gaseous phase. The ICP source is called a torch and consists of three concentric quartz tubes through which argon flows: in the innermost tube, the Ar flows at a rate of about 1 L min^{-1} , carrying with it the sample (in the form of an aerosol) from the nebulizer. The gas passing through the central tube serves to keep the hot plasma away from the end of the central injection capillary. Finally, in the outermost tube, the gas flow is very fast (10 L min^{-1}) and is essential for isolating the plasma from the external atmosphere and protecting the quartz tube. At the top of the torch, as shown in Figure 9, there is a solenoid powered by

a radiofrequency generator, which creates the alternating current needed to ignite the torch and ionize the argon. Ar^+ and e^- continuously interact with each other and with the oscillating magnetic field formed; they also manage to transmit some of their own momentum to the non-ionized argon particles with which they are in constant collision. As a result, the plasma reaches temperatures of around 9000 K. As already mentioned, the sample is introduced into the torch in the form of dispersed micrometric particles (aerosol), obtained using a nebulizer. Upon reaching the plasma, these particles undergo rapid atomization and subsequent ionization, giving rise to various ions that emit electromagnetic radiation at the specific wavelength of the starting element. Through an optical system consisting of a monochromator and several lenses, these rays reach the detector, which processes the light signal and allows the elements present in the sample to be quantified. The detectors usually used are photodetectors based on the use of semiconductors, which emit a signal whose intensity is proportional to the incident electromagnetic radiation; the most common are the so-called Charge Coupled Devices (CCD) and Charge Injection Devices (CID).

3.2. Electrochemical characterization

3.2.1. Galvanostatic Cycling with Potential Limitation (GCPL)

Conducting galvanostatic cycling with potential limitation (GCPL) means applying a specific current (both during charging and discharging) to the electrochemical system under examination and recording the potential evolution over time. The working potential window is appropriately defined based on the type of electrode to be investigated (anode or cathode) and its elemental composition. The modulation of this range is contingent upon the extent of the occurrence of the redox phenomena, with the objective being to encompass all electrochemically active contributions. A comprehensive analysis of the obtained charge-discharge curves enables the extraction of significant insights regarding the electrochemical properties of the materials. Tests performed at different C-rates (rate capability test) are highly significant, as they enable the evaluation of specific capacity variations at different current densities. Typically, the initial cycles are carried out at low C-rates to allow the material to stabilize. The current density is then progressively increased, and finally, to evaluate the structural stability of the material and the reversibility of the electrochemical processes, one or more recovery cycles are performed at intermediate C-rates between the initial and final values.

3.2.2. Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA)

Potentiodynamic cycling with galvanostatic acceleration (PCGA) is a widely used technique for the electrochemical characterization of electrode materials. This technique allows for a detailed evaluation of the intensity, contribution to total specific capacity, and reversibility of all redox phenomena occurring at the electrode during charge-discharge cycles.

Operationally, performing a PCGA means conducting a series of scans in potentiodynamic mode: a series of impulses with well-defined intensity (ΔV , in mV) and duration (Δt) are superimposed on the linear potential scan. In the subsequent stage of the analysis the differential capacity of the material under examination must be calculated. This is defined as the derivative of the specific capacity with respect to the potential (dQ/dV) and is expressed in $\text{mA g}^{-1}\text{V}^{-1}$. Plotting this value against the cell potential, the

resultant curves demonstrate peaks of distinct intensity and shape depending on the phenomena they represent, at discrete potentials. As already mentioned, by analyzing the shape and position of these peaks, significant conclusions can be drawn about the working mechanism of cathode materials. Furthermore, depending on their intensity, the amount of electronic charge involved in each of the observed phenomena can also be calculated. The information provided by these graphs can also be obtained from conventional Cyclic Voltammetry (CV), but with significantly higher precision and sensitivity, as the potential scan is less affected by noise from various sources and less influenced by parasitic currents that may slightly alter the measurements. For instance, the use of PCGA facilitates the effective separation of redox processes that occur at comparable potential; in a conventional CV, these processes would be amalgamated within a solitary signal.

3.2.3. Electrochemical Impedance Spectroscopy (EIS)

Conducting an electrochemical impedance spectroscopy (EIS) measurement in potentiometric mode involves the application of a sinusoidal potential to a system set at a fixed potential and analyzing its response, in the form of impedance, over an extended range of frequencies. The modulus of the imposed signal must be sufficiently small, usually within 10 mV, in order to ensure that the relationship between current (I) and potential (E) can be considered linear. In response to the sinusoidal input potential, $E(t)$, the current response, $I(t)$, will also exhibit a similar trend; the ratio $E(t)/I(t)$ is defined as impedance (Z).

Impedance is defined as a physical quantity that is associated with all the factors that hinder and limit the passage of current in the system under examination. In the context of sodium-ion batteries, numerous contributions oppose the flow of current. These include: i) resistance to charge transport in the electrolyte solution; ii) diffusion at the electrode of the Li^+ ; iii) double-layer capacity formed at the electrode-electrolyte interface; iv) intrinsic resistance of the electrolyte. The principal benefit of this technique is that it enables the separation/decomposition/segmentation and examination of these contributions, thereby facilitating a comprehensive analysis of overall impedance spectrum obtained. In order to accomplish this objective, it is imperative to conceptualise the electrochemical system as an electrical circuit comprising diverse components,

including resistors (R) and capacitors (C). The crucial step in EIS measurements consists of modeling the electrochemical system under examination in an electrical circuit (known as an ideal equivalent circuit). This must provide a simulated impedance spectrum very similar to the experimental one. As already mentioned, the spectra are collected in a fairly high frequency range, usually between 0.1 Hz and 10^4 Hz. Some contributions to inductance cannot be modeled as a simple combination of R and C. Among these, the most important are Warburg impedance (W) and the constant phase element (CPE). The Warburg element describes diffusion phenomena to and from the electrode surface, and it is particularly evident at low frequencies. Conversely, the CPE element considers the non-ideality of the electrodes.

The graph in Figure 1 is a so-called Nyquist diagram, which shows the real components Z' (X-axis) and imaginary components Z'' (Y-axis) of the impedance; the frequency increases from right to left.

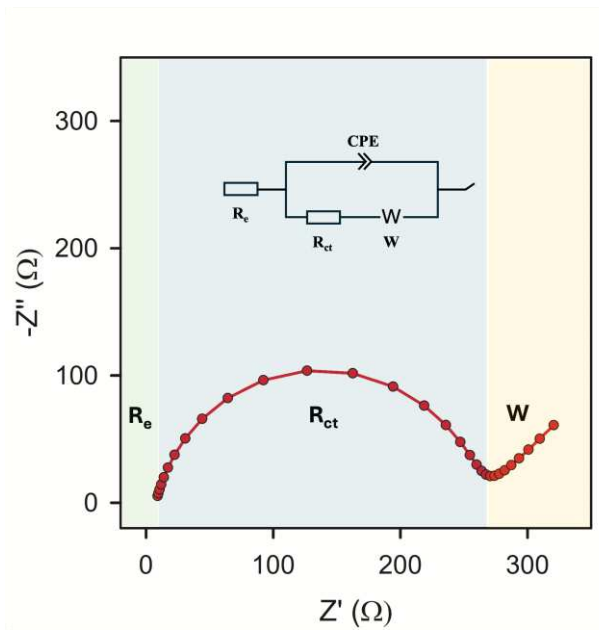


Figure 3. Example of a Nyquist diagram for an EIS measurement with the corresponding equivalent circuit for an ideal electrode interface, highlighting the different contributions derivable from the spectrum

This spectrum delineates the ideal behavior of an electrode interface. The semicircle describes a phenomenon of electron transfer with control over the transfer of matter and charge. The intersection of the semicircle with the X-axis at higher frequencies can be correlated to the ohmic resistance of the electrolyte solution (R_e), while that at lower

frequencies can be correlated to the charge transfer resistance (R_{ct}) at the electrode-electrolyte interface. Finally, the 45° line is typical of the presence of Warburg impedance (W).

3.2.4. Galvanostatic Intermittent Titration Technique (GITT)

The Galvanostatic intermittent titration technique (GITT) is an advanced technique widely used in the battery field to determine with high precision the diffusion properties of the materials (*e.g.*, anodes, cathodes, solid electrolytes) under investigation. For sodium-ion batteries, GITT is used to evaluate the Na^+ diffusion coefficient (D_{Na^+}) during cycling. Although D_{Na^+} can also be determined through EIS, the value obtained from GITT is generally more accurate, as it is derived from measurements performed under quasi-equilibrium conditions and does not rely on equivalent-circuit modelling, thus avoiding additional approximations. Furthermore, GITT enables the assessment of the D_{Na^+} evolution in the whole working potential range, whereas EIS provides only a single averaged diffusion coefficient value.

Experimentally, a GITT measurement is performed by cycling the material in a half-cell vs. $\text{Na}_{(m)}$. This process involves the repetition of two distinct steps: i) short current impulses (usually 10-15 minutes), corresponding to a slow C-rate (0.1C or lower), and ii) a long rest period (>1 hour), required to reach the equilibrium after each pulse. Figure 2 shows an example of an experimental charge-discharge curve obtained by GITT (in red), consisting of the sequence of the steps described above. Starting from Fick's law of diffusion, and under certain physical approximations, the diffusion coefficient can be calculated as:⁸⁶

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

Where τ is the current impulse duration, n_m and V_m refer to the moles of the cathode active material and the molar volume of the active material, respectively, and S indicates the electrode surface area.

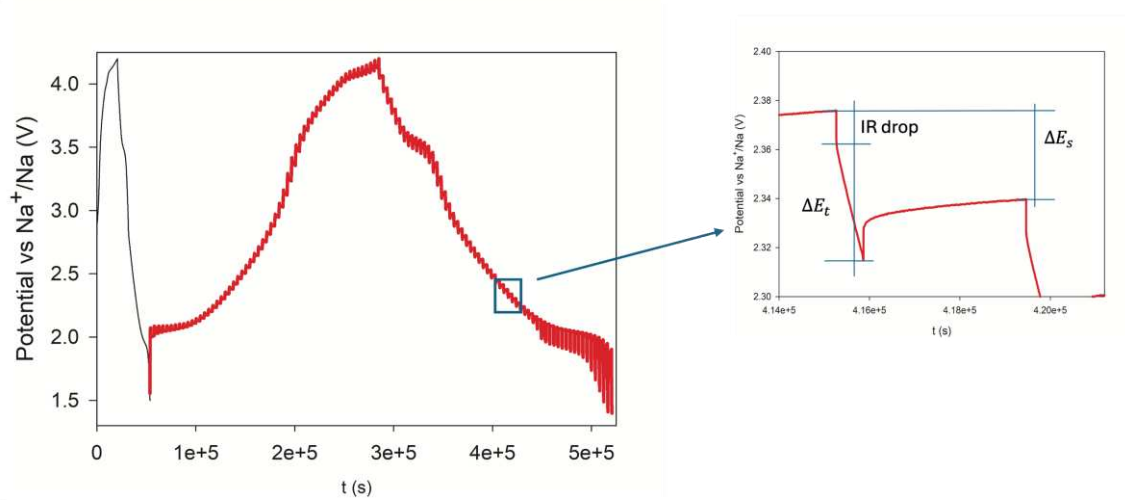


Figure 2. Example of charge-discharge curves recorded through GITT experiments (red curve). The box provides details on the shape and composition of one of the individual impulses that contribute to the overall curve

Note that S should represent the active surface area of the electrode material in contact with the electrolyte, but due to the difficulty in estimating the actual surface area in a composite with a binder and carbon, we approximate it by using the electrode surface. ΔE_s and ΔE_t represent the transient voltage change during the single current pulse and the equilibrium (steady-state) potential, excluding the IR drop (see inset of Figure 2). Another important parameter that can be obtained from GITT experiments is the overpotential (η), which can be evaluated as the difference between the potential recorded at the end of the current impulse and that at the end of the rest period. It is directly correlated to the electrochemical kinetics of the materials: the lower the η , the better the electrode kinetics of the system under examination.

4. P2-Na_{0.67}Mn_{0.5}Fe_{0.5-x}Mg_xO₂

4.1. Solid-State Synthesis

4.1.1. Materials and methods

4.1.1.1. Synthesis

P2-Na_{0.67}Mn_{0.5}Fe_{0.5-x}Mg_xO₂ ($x = 0, 0.1, 0.2, 0.3$) were prepared through solid-state synthesis, starting from commercial oxides and Na₂CO₃ in the proper stoichiometric ratio. All the precursors were first mixed in stainless steel jars by a planetary ball miller at 100 rpm for 3 h, to increase the contact area between the reagents. Sodium carbonate was introduced in 5 wt.% excess to compensate for the eventual loss of Na after high-temperature calcination. Subsequently, the resulting powder was sintered in pellets, using a uniaxial press, and treated in a tubular furnace at 1000 °C for 3 h (ramp rate of 5 °C min⁻¹), at the end of which the structure was quenched by quickly removing the product from the furnace to avoid phase transition during cooling time.

4.1.1.2. Cathode preparation and cell assembly

The cathode slurry for half-cell measurements were prepared by using 80 wt.% of active material (CAM), 10wt.% of Conductive Carbon black (Imerys, Ensaco 350P), and 10 wt.% of a binder (polyvinylidene fluoride, PVdF). The solid content of all slurries was kept between 28 wt.% and 30 wt.%. CAM and carbon powders were mixed in zirconia jars by a planetary ball mill at 150 rpm for 10 min twice, with a rest period of 5 min. Subsequently, the polymeric binder was added and mixed with a similar procedure. The as-prepared mixture was dispersed in N-methyl pyrrolidone (NMP) to obtain the slurry, which was cast on a carbon-coated Al foil using a doctor blade with a wet thickness of 300 µm. The casted slurry was dried under vacuum at 80 °C to avoid moisture and oxygen contamination. The cathode was finally cut into 2 cm² disks and stored in an Ar-filled glove box (MBraum, O₂, H₂O < 0.5 ppm) before the electrochemical measurements. All the functional tests were performed in coin cells (CR2032 - MTI Corp.) assembled in an

inert atmosphere (Ar) at room temperature (26 °C). metallic Na was used as the counter electrode. As a separator, we used two *Whatman* GF/A glass fiber, imbibed by 90 μL of liquid electrolyte, consisting of a solution of 1 M NaPF_6 in Ethylene Carbonate: Dimethyl Carbonate + 2 wt.% Fluoroethylene Carbonate (FEC).

4.1.1.3. Structural, elementary, and morphological characterization

Morphologies and elementary compositions of the materials were investigated through SEM and ICP-OES analysis. We used a Tescan Mira3XMU microscope operated at 20 kV and equipped with an EDAX EDX analysis system to collect SEM images. ICP-OES analyses were performed by an Avio 220 max (Perkin Elmer), equipped with an AVIO Glass Cyclonic Baffled spray chamber, a quartz torch, and a dual backside-illuminated charge-coupled device (DBI-CCD) detector. The TMs quantification was carried out on HNO_3 -digested solutions in the axial mode at 670.8 nm as wavelength, by an external standard calibration curve. ICP grade multi-elements standard (1000 mg L^{-1}) was diluted to 0.3–0.6–2.0–5.0–9.0 mg L^{-1} and then acidified to a final concentration of 2% nitric acid (from ultrapure 65% HNO_3). The measurement conditions were as in the following: nebulization gas flow: 0.7 L min^{-1} ; power RF: 1500 W; auxiliary gas flow: 0.2 L min^{-1} ; peristaltic pump: 1 mL min^{-1} ; frequency: 500 Hz. For Na quantification, we used an ultrapure H_2O for chromatography (Na <200 ppb).

XRD patterns of $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$ powder were collected with a STADI P diffractometer (STOE, Germany) with $\text{Mo-K}\alpha 1$ radiation ($\lambda = 0.70932 \text{ \AA}$, 50 kV, and 40 mA), in the $5\text{--}35^\circ 2\theta$ range and with 0.015° step. Rietveld and LeBail refinement was conducted using the FullProf Suite software.⁸⁷

4.1.1.4. Electrochemical characterization

The electrochemical performances of all the materials were investigated in half-cell configuration with a Bio-Logic BCS-810 through Galvanostatic Cycling with Potential Limitation (GCPL) at different C-rates, Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA), and Galvanostatic Intermittent Titration Technique (GITT) in the working potential window 1.5 V–4.2 V. Potentiometric Electrochemical Impedance

Spectroscopy (PEIS) spectra pre, during and post cycling were recorded between 0.1 Hz and 10^4 Hz.

4.1.2. Result and Discussion

4.1.2.1. Structural and Elementary Analysis

The XRD pattern reported in Figure 1a confirmed the successful synthesis yield. In particular, LeBail refinement confirmed that all the compositions were prepared with the desired P2-layered structure (space group: $P63/mmc$), accompanied by a small impurity of spinel-like phase ($MnFe_2O_4$, space group: $Fd-3m$). It's well established that, for these kinds of cathodes, c is the most important lattice parameter, because it can be correlated to the Na content in the structure, which, as mentioned in the introduction, represents one of the key points to investigate during the characterization of new layered materials. Moreover, the evolution of the c parameter upon Mg^{2+} -doping can be qualitatively evaluated by examining the 002 reflection in the XRD pattern, as clearly shown in the inset on the right of Figure 1a. Specifically, a shift toward lower diffraction angles indicates an expansion along the c -axis, which is attributed to a reduced Na content. This reduction increases electrostatic repulsion between the two O2-layers in the transition metal slab. Conversely, a shift toward higher angles suggests a contraction of the unit cell along the c -axis. Figure 1b shows the lattice parameter retrieved from the refinement. In particular, c decreases upon increasing Mg^{2+} content, from 11.2872(4) Å of $x = 0$ to 11.2304(2) Å of $x = 0.2$, while it increases to 11.2554(3) Å for $x = 0.3$.

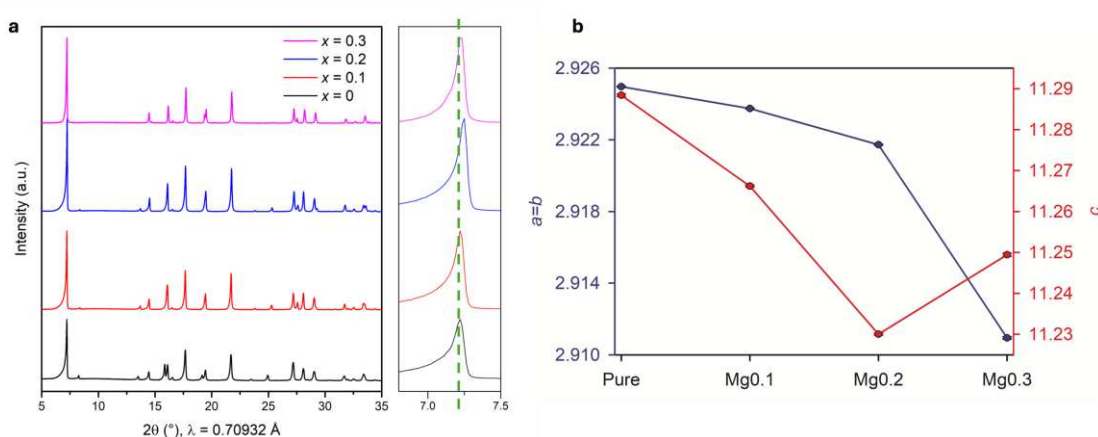


Figure 1. (a) experimental XRD pattern of $P2\text{-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3$). Impurity spinel-like phase main peaks are highlighted by stars (*). (b) Lattice Parameter obtained through LeBail refinement

Concerning the spinel-like impurity phase, it decreases by increasing the Mg(II) substitution, until it completely disappears for the $x = 0.3$ sample, for which we could perform a single-phase refinement. Indeed, Rietveld refinement reported in Figure 2 showed that the spinel phase decreases from 9.3(2) wt.% to 6.0(1) wt.% and 4.3(2) wt.% for $x = 0, 0.1$ and 0.2 , respectively.

This trend can be explained by taking into account: i) the stabilizing role of Mg(II) for this kind of structure and ii) its elementary properties of the cation. It is well established that Mg(II) doping enhances the structural stability of the layered structure by decreasing the presence of Mn(III) and consequently increasing the fraction of Mn(IV), which, unlike Mn(III), is not a Jahn-Teller active cation and partially suppress the orthorhombic distortion caused by it. Moreover, it is well established that Mg(II) preferentially occupies octahedral sites, in contrast to Fe and Mn, which can also favorably sit on tetrahedral sites. The presence of Mg(II) thus reduces the probability of Fe and Mn migration to tetrahedral positions, as Mg(II) hinders such cation rearrangements. This significantly limits the formation of more stable and highly symmetric crystalline phases than the hexagonal P2-layered structure, such as the cubic spinel one.

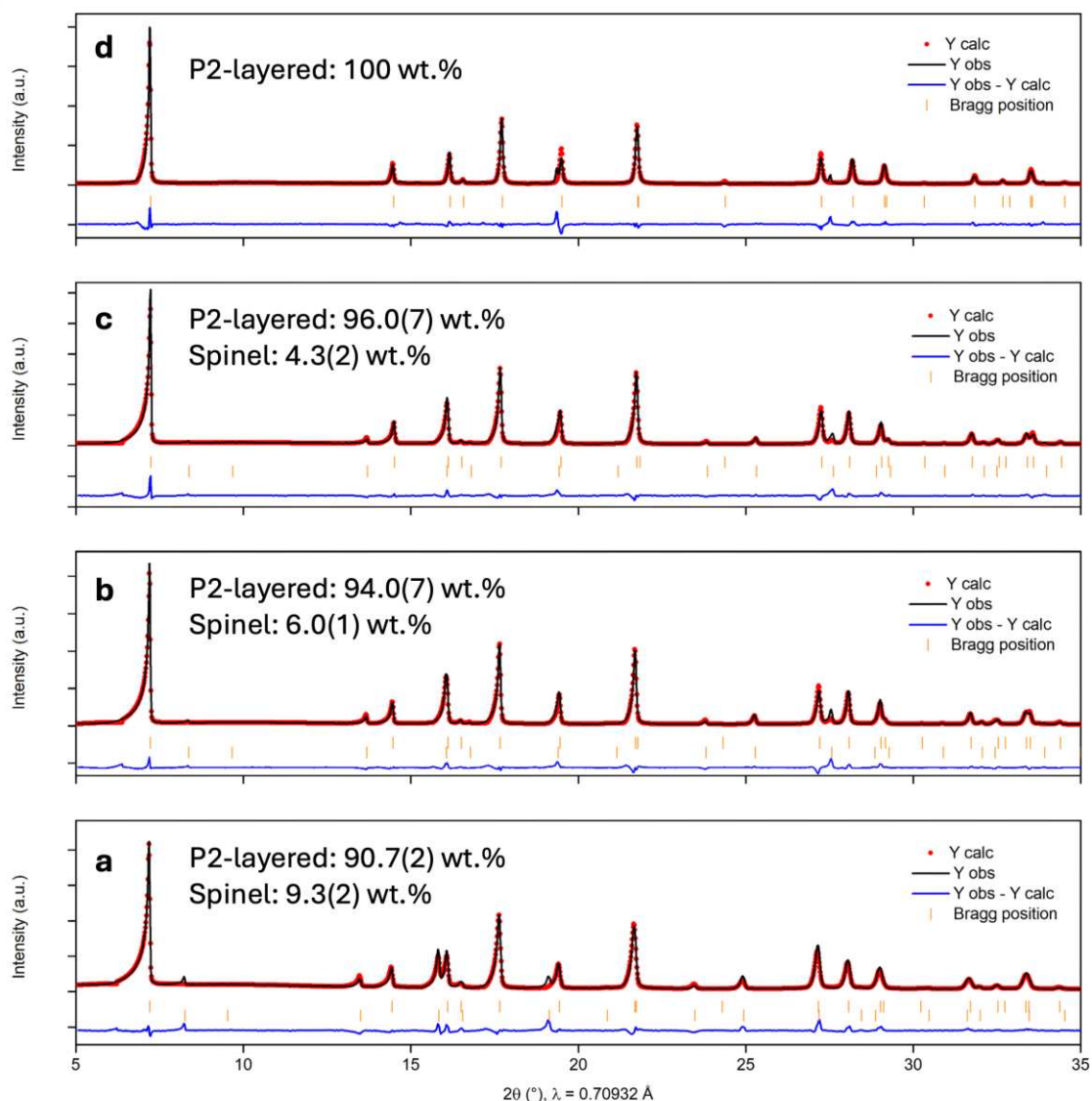


Figure 2. Le Bail and Rietveld Refinement for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$

Figure 3 shows the SEM images collected for the materials under investigation. Despite the difference in the elementary composition, all the P2-layered oxides have the same irregular and prismatic-like grains' morphology, with micrometric dimension, typical of the product of synthesis carried out at high temperature (1000 °C).

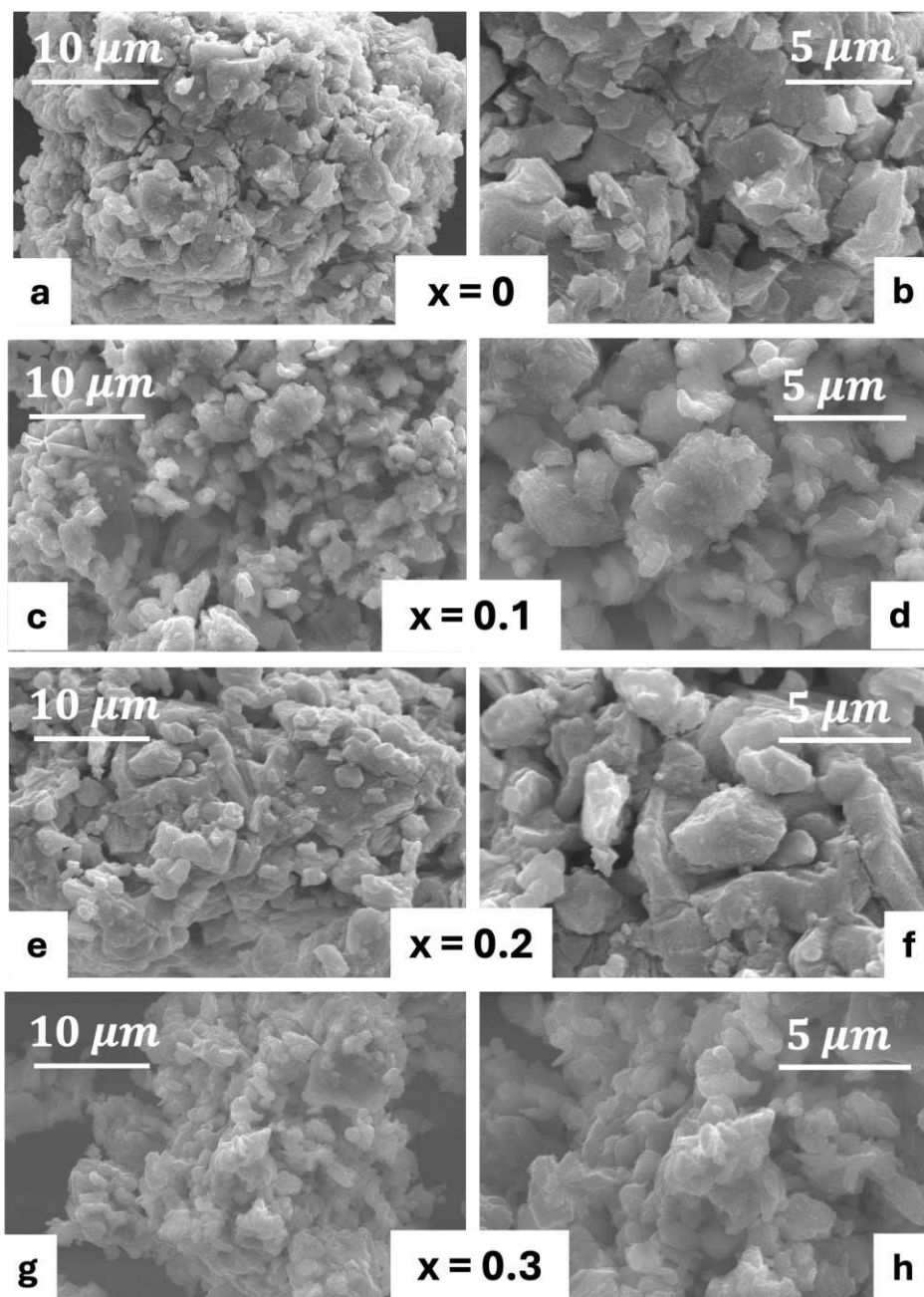


Figure 3. SEM images of (a-b) $x = 0$, (c-d) $x = 0.1$, (e-f) $x = 0.2$, (g-h) $x = 0.3$ composition, collected at different magnification.

Elementary compositions were investigated through ICP-OES analysis, whose results are reported in Table 1. Since comparing the ratios between the stoichiometric coefficients of the metals is more meaningful than considering the absolute values calculated for each element, we report the Fe/Mn and Fe/Mg ratios, along with the theoretical values (in brackets) expected from the elemental composition. As evidenced by the data, ICP-OES

analysis confirmed that all the materials have the expected stoichiometry, as the experimental ratios closely match the theoretical ones.

Table 2. Stoichiometric coefficient calculated through ICP-OES analysis for all the compositions. Theoretical values are reported in brackets.

	Fe/Mn	Fe/Mg	Na
$x = 0$	1.01 (1.0)	-	0.491
$x = 0.1$	0.79 (0.8)	4.33 (4.0)	0.511
$x = 0.2$	0.58 (0.6)	1.57 (1.5)	0.565
$x = 0.3$	0.38 (0.4)	0.68 (0.67)	0.525

Because of the difficulty in accurately assessing Na content, we decided to use the standard addition method for its quantification through ICP analysis. The reliability of the obtained results is further supported by comparison with the lattice parameter c (Figure 4), in strong accordance with the previously discussed correlation between the Na content and the dimension of the elementary cell along the c direction. In particular, as c decreases from $x = 0$ to $x = 0.2$, based on XRD patterns, the Na content progressively increases. Conversely, for $x = 0.3$, a decrease in Na content is evaluated, consistent with the increase in the c parameter.

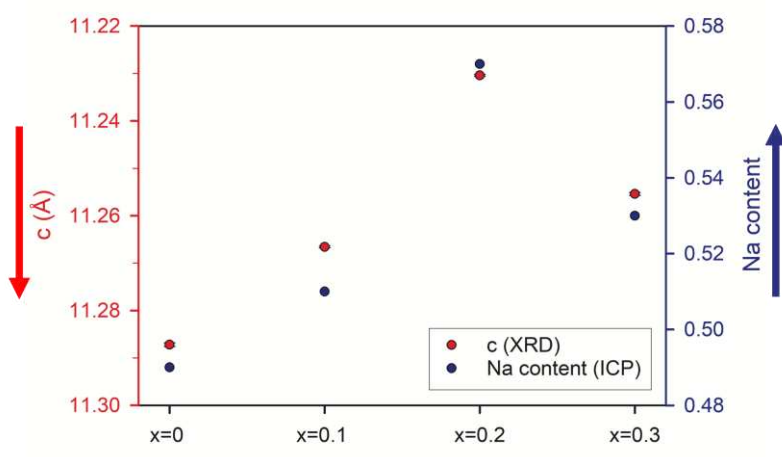


Figure 4. Correlation between the c parameter and Na content for all the compositions derived from Rietveld refinement and ICP analysis, respectively

4.1.2.2. Electrochemical Characterization

All compositions were fully characterized as cathodic materials for sodium-ion batteries in a half-cell configuration, employing Na_(m) as the counter electrode. This setup enables the investigation of the intrinsic electrochemical behavior of the materials under various conditions. To evaluate the active redox processes occurring within the operating voltage window (1.5 V-4.2 V), we employed Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA). This technique offers superior resolution and accuracy in identifying the individual redox contributions to the overall specific capacity, compared to conventional Cyclic Voltammetry (CV). While CV involves a continuous linear potential sweep at different scan rates (mV s⁻¹), PCGA incrementally increases the potential in small steps (5 mV). After each increment, the system is allowed to reach an imposed limiting current, corresponding to a defined C-rate (usually 0.07C or lower), before proceeding to the next step.

By differentiating the specific capacity achieved to the voltage (dQ/dV), differential capacity curves are obtained. Peaks in these curves correspond to voltage regions where charge-discharge profiles exhibit plateau (indicating two-phase transitions). Additionally, each peak can be associated with a specific redox-active couple present in the material.

Figures 5a-d show the experimental dQ/dV curves for all the compositions under investigation. As known in the literature,⁸⁸ peaks between 2 V and 2.5 V are related to the Mn(III)-Mn(IV) redox couple, which represents the main contribution to the specific capacity, being the most intense signals. Interestingly, since the hysteresis between the signal potential recorded in charge (oxidation) and discharge (reduction) is very low, this indicates that this redox pair has highly reversible behavior and does not cause significant stresses within the layered structure during cycling. On the other hand, the signals for the Fe(III)-Fe(IV) pair showed a significantly higher hysteresis, being the phenomena in charge and discharge separated by about 0.5 V (>4 V in charge and about 3.3 V in discharge). Keeping in mind this difference between the two redox couples and the problem, mentioned in the introduction, of Fe migration from the transition metal layers to those occupied by Na⁺ during cycling, we can easily conclude that the control and optimization of Fe activity is one of the key points to be developed to obtain performing

cathodes. The irreversibility observed for all compositions at high potentials (>4 V) between the first and subsequent cycles is due to both the partial degradation of the electrolyte and the possible redox activity of the oxygen present in the structure, as already documented in the literature for cathodes of this type.^{89,90} Electrolyte mixture degradation at high potentials is a well-known issue for sodium battery cathodes, and for that reason, a research line in the field is trying to develop new mixtures⁹¹ or new additives^{92,93} to be introduced to increase the stability of the electrolyte even at these potentials.

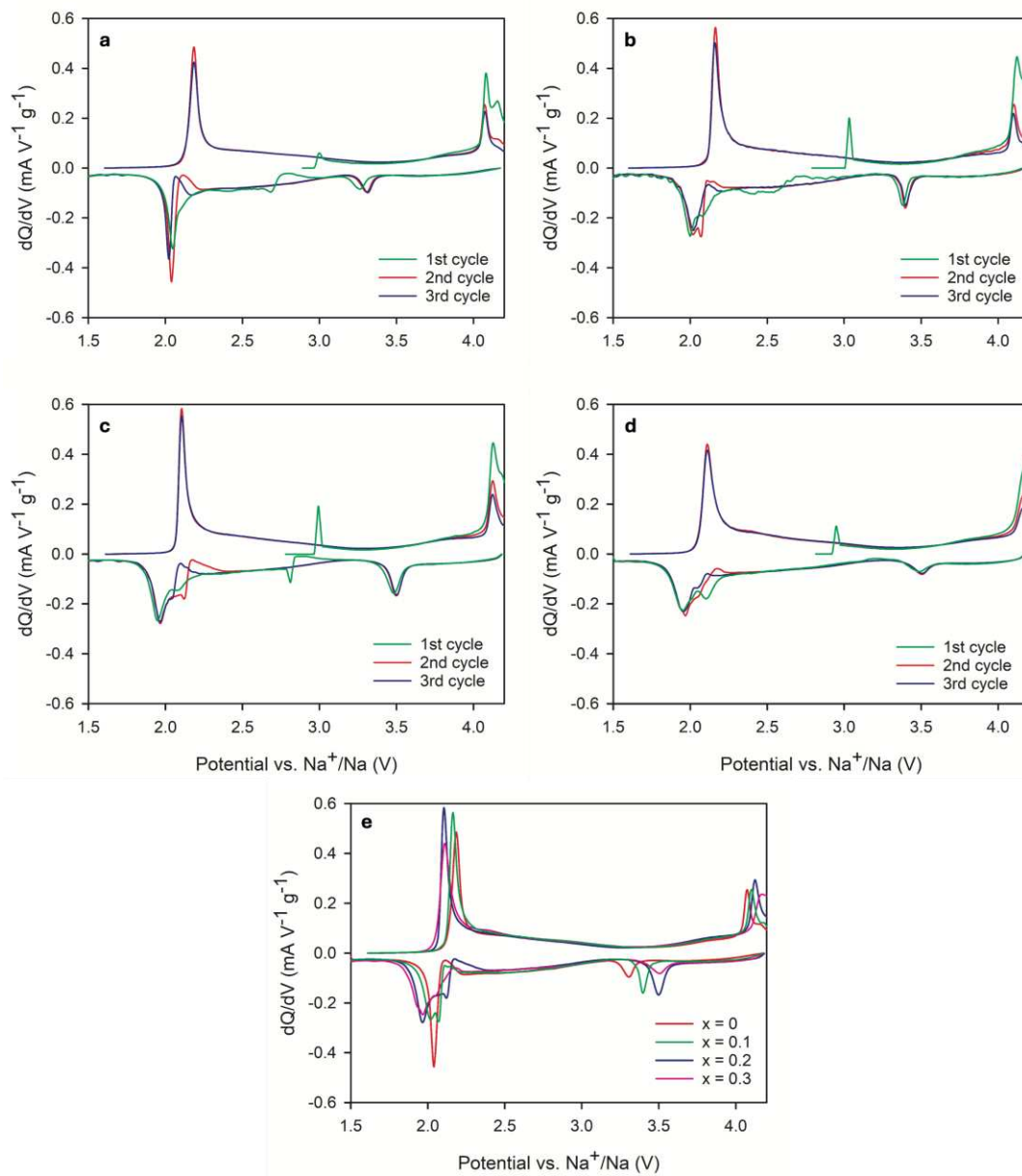


Figure 5. dQ/dV curves obtained through PCGA experiment for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ performed between 1.5 V and 4.2 V at 0.067 C vs. Na⁺/Na. (e) Comparison between the 2nd cycle dQ/dV curves for all the compositions

In this sense, the introduction of Fluoroethylene Carbonate (FEC) into the electrolyte used for all electrochemical tests only succeeds in limiting such degradation. In addition, as already introduced in the introduction of the thesis, the possibility of exploiting the redox contribution of Oxygen as well would be very interesting and would allow to greatly increase the performance of these materials. However, advanced RIXS and/or XAS experiments with synchrotron light are necessary for a proper and complete analysis of this complex problem, as these are the only techniques with which it is possible to detect any structural changes in the anionic sub-lattice. In this regard, an experiment is already planned to evaluate the mechanism by which Oxygen redox activity is activated and how different degrees of Mg(II) doping affect the overall electrochemical behavior of $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$. One last important consideration to be made based on the dQ/dV curves is that, as expected, Mg(II) is electrochemically inactive, as there are no additional peaks for $x = 0.1, 0.2$ and 0.3 compared to unsubstituted oxide (Figures 5b-d). In the 1st cycle, the peaks between 2.7 V and 3 V can be attributed to a polarization of the coin cell immediately after the start of the experiment.

As illustrated in Figure 5e, the second cycle dQ/dV curves for all compositions are presented for the purpose of facilitating a more comprehensive comparison of the observed differences and to assess the impact of Mg(II) doping on the performance characteristics. The decision was taken to report on the second cycle rather than the first, on the basis that it was considered to be more representative of the general electrochemical behavior of the materials. This comparison reveals that Mg(II) significantly affects the voltage for all the redox contributions observed. Looking at the Mn(IV)-Mn(III) reduction, it is clear that substitution leads to a clear modification of the process: the single peak observed for $x = 0$ splits into two distinct peaks in all doped samples. We hypothesize that this splitting results from a two-step reduction of Mn(IV), likely due to the presence of electrochemically inactive Mg(II) cations occupying the same crystallographic 2a sites, which alters the local environment and reduction kinetics. Regarding the subsequent Mn(III)-Mn(IV) oxidation, the redox peak progressively shifts to lower potential as the Mg content increases (from $x = 0$ to $x = 0.3$), suggesting that this reaction is thermodynamically favored by the presence of Mg. This shift also reduces the voltage hysteresis between the oxidation and reduction processes, thereby enhancing the overall reversibility. For the Fe(III)-Fe(IV) redox couple, during charge, oxidation to

Fe(IV) is shifted at higher potential as the substitution degree increases. However, since this trend is surely related to the Oxygen redox activity, which is at the same potentials, no definitive conclusions can be drawn about the role of Fe alone without clarifying oxygen's contribution. A similar trend is observed during the reduction to Fe(III), although the shift is more pronounced. As with Mn, Mg(II) doping leads to a decrease in voltage hysteresis for the Fe redox processes, further supporting the improved reversibility of the system. It is interesting to note that the curves for $x = 0.2$ and $x = 0.3$ are practically overlapping, indicating that the performance increase to substitution degrees correlation reaches a maximum for the P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ composition. This is an important consideration for both the upcoming electrochemical characterizations and, especially, from the perspective of a possible future scale-up. Indeed, with equal performance, it is certainly preferable to choose the composition with a lower degree of electrochemically inactive substitution.

Figure 6 shows the Na evolution during the first three charge-discharge cycles, derived from PCGA data. Starting from the nominal value ($x = 0.67$) at the Open Circuit Voltage (OCV) condition, all the composition de-intercalates Na^+ from the Na-layer until $x = 0.3$ - 0.4 , during the first charge. All the Mg(II)-doped compositions reach a slightly higher degree of desodiation compared to the pure P2-oxide. Then, from the subsequent discharge, they all reversibly intercalate 0.5 - 0.6 Na^+ equivalents, until $x = \sim 0.9$. This sodium excess compared to the initial value is due to the $\text{Na}_{(\text{m})}$ used as a counter-electrode, which ensures an almost infinite Na^+ source, leading to deep sodiation of the cathodes. These curves further highlight the marked irreversibility between the first charge and the following cycles. In particular, the change in slope above ~ 4 V is distinguishable between the region associated with the Fe(III)–Fe(IV) oxidation and the flatter region, which is likely related to oxygen redox activity and/or partial electrolyte degradation. The latter phenomenon is significantly reduced starting from the 2nd charge and is completely reversible.

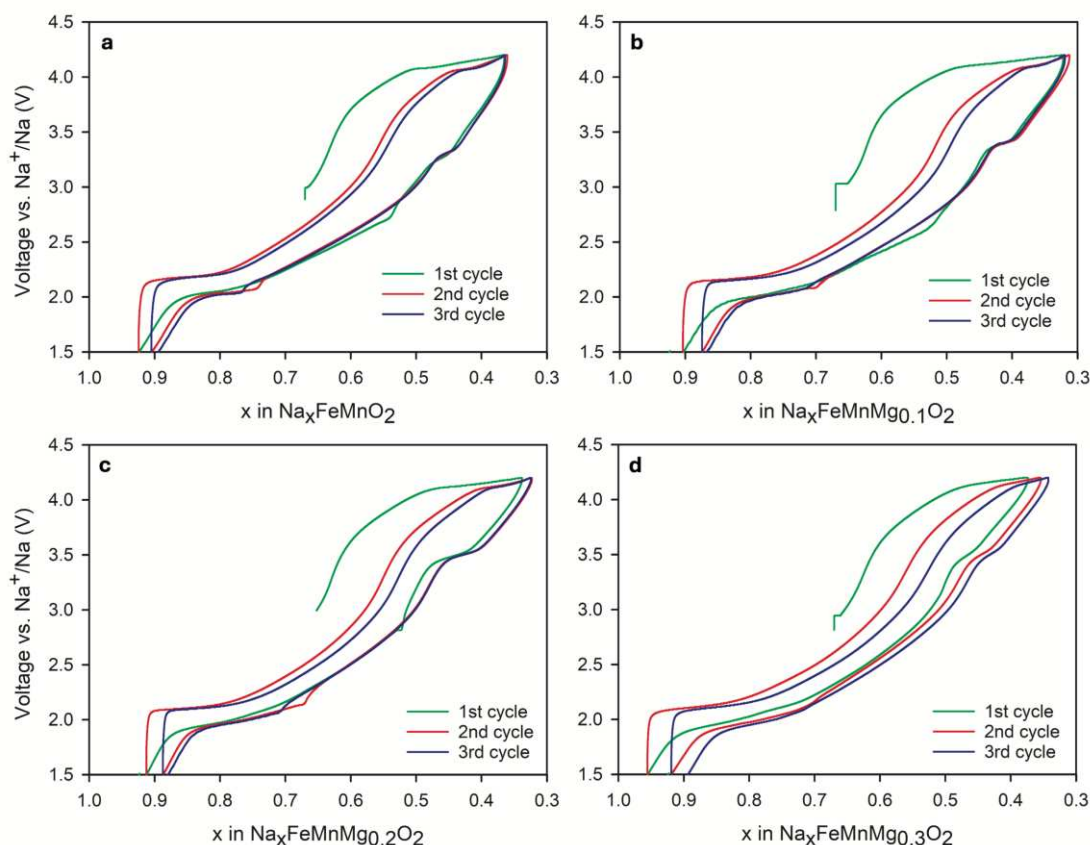


Figure 6. Voltage-composition profiles for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ during the first three charge-discharge cycles performed between 1.5 V and 4.2 V at 0.067 C vs. Na^+/Na .

We evaluated the rate performances of all the compositions through GCPL (Galvanostatic Cycling with Potential Limitation) experiments, performed in the working potential window 1.5 V-4.2 V at different current densities (C-rate). Figure 7a-d reports the results of these tests. All the cathodes recorded excellent coulombic efficiency, always higher than 95%, except for the first cycle and those where the C-rate changed (6, 11, 16, 21, 26).

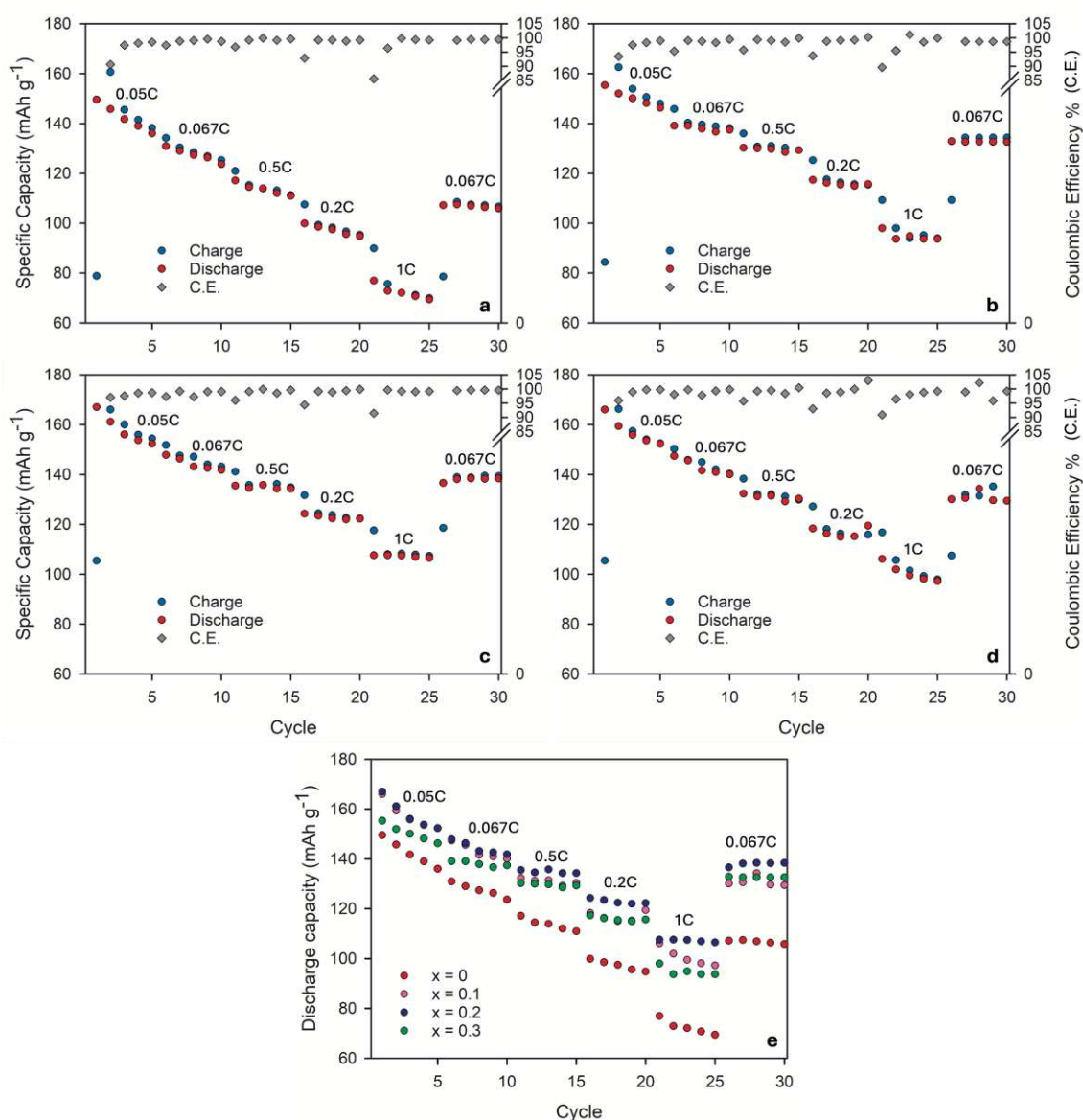


Figure 7. Rate capability tests for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ between 1.5 V and 4.2 V vs. Na⁺/Na at different C-rates. (e) Comparison between the discharge capacity recorded for all the compositions

Between cycles performed at the same current densities, capacity retention is very low for all the Mg(II) doped cathodes, while for $x = 0$, we observed a significant capacity loss. After cycling at 0.2C (cycle 20-25), we performed five cycles at low C-rate (0.067 C) to investigate the recovery properties of the cathodes, *i.e.*, how the P2-structure and the electrode behave following the stress caused by cycling at high current densities. Theoretically, the capacity should return to the values recorded in cycles 6-10, which were also carried out at the same C-rate. However, this is not fully observed experimentally, but the results clearly show that the recovery is always good, especially for materials in

which Mg(II) is present. In Figure 7e, the recorded discharge capacity for the four compositions is compared. Mg(II) substitution plays a crucial role in enhancing the discharge capacity, because we observe a significant improvement in both the capacity retention and the discharge capacity achieved at every C-rate for all the Mg(II)-doped samples compared to the pure one. Performances increase from $x = 0$ to $x = 0.2$, while $x = 0.3$ it's found to be intermediate between 0.1 and 0.2. For this reason, we could assume that $x = 0.2$ is the best-performing composition, although it's necessary to further investigate this trend with the employment of a new GCPL experiment. To investigate the long-term stability of the materials, we conducted some cycling tests for 100 cycles at 0.125C and 1C. We chose these two C-rates because we wanted to study the behavior of the cathodes under both low and high stressful conditions. In particular, at 1C, we can simulate the real-world operation. On the other hand, at 0.125C, we can better observe how the materials work in optimal conditions without the inference of overpotential, resistive effects, or other parasitic reactions caused by high current, which may affect the kinetics of the cathode. Figure 8 reports the discharge capacity and coulombic efficiency recorded for all compositions at both C-rates. As for the rate capability tests described above, we have confirmed that doping with Mg(II) is particularly effective in stabilizing cathodic performance, compared with unsubstituted oxide.

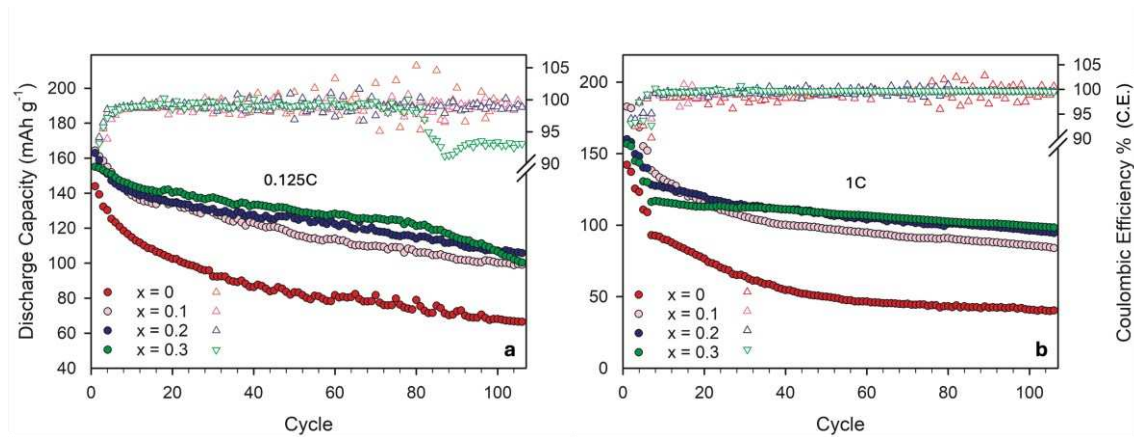


Figure 8. Comparison between the discharge capacity and the coulombic efficiency recorded during long-term cycling test between 1.5 V and 4.2 V vs. Na⁺/Na at (a) 0.125C and (b) 1C for all the compositions

This is particularly evident by also looking at the calculated capacity retention (between cycles 10-100), reported in Table 2. At low currents (Figure 8a), all three Mg(II)-doped compositions demonstrate remarkably similar capacity retention, indicating that the

kinetics during desodiation (discharge) of the materials remain unchanged, independent of the degree of substitution. However, it is also evident that $x = 0.1$ and 0.2 exhibit significantly greater stability compared to $x = 0$, for which the efficiency is much more variable, particularly in the second half of the cycling test (last 50 cycles).

Table 3. Calculated capacity retention after cycling (100 cycles) at 0.125C and 1C for all the compositions.

	Capacity Retention	
	at 0.125C	at 1C
$x = 0$	60%	45%
$x = 0.1$	72%	65%
$x = 0.2$	76%	76%
$x = 0.3$	74%	86%

On the other hand, at 1C, we observed an increase in capacity retention directly proportional to the level of doping. However, comparing the data in Figure 8b for $x = 0.2$ and $x = 0.3$, it appears that the retention difference is mainly due to the discrepancy in capacities recorded during the first 20 cycles, as the two compositions then exhibit an overlapping trend until cycle 100. The coulombic efficiency (C.E.) is consistently above 95%, except for the last 20 cycles at 0.125C for $x = 0.3$. However, since the discharge capacity values follow a trend comparable to that of the other compositions, we can conclude that during these last 20 cycles, the electrode and/or the material structure undergo degradation that hinder proper desodiation of the cathode. Furthermore, as shown in during the 1C test, the coulombic efficiency for all Mg-doped materials is nearly identical, while $x = 0$ again shows greater variability. The marked difference in trends between the two tests supports the earlier statement regarding the intrinsic difference between tests conducted at high and low current densities. Based on the results and considerations discussed above, we concluded that $x = 0.2$ exhibits the best performance among the cathodes studied. Consequently, we carried out a more in-depth electrochemical characterization of this material and compared it with the unsubstituted oxide, in order to better elucidate the stabilizing effect of Mg(II) observed in the long-term cycling tests.

Through Electrochemical Impedance Spectroscopy (EIS), it is possible to evaluate possible degradation mechanisms of materials after cycling. In particular, as described in Chapter 2, by modeling the experimental data as equivalent circuits, it is possible to differentiate between the various components that constitute the same spectrum. Figure 9a shows the circuit used to fit the experimental data collected after the long-term cycling tests performed. The circuit is composed by three resistances (R), two of which are connected in parallel with two Constant Phase Elements (CPE), and one Warburg element (Z_w), all connected in series. CPE accounts for the non-ideal behavior of the electrode-electrolyte interface, which can arise from practical factors such as electrode surface roughness, compositional inhomogeneity, or material porosity. R_e is the ohmic resistance due to the electrolyte solution, R_{sf} is related to the formation of the Cathode Electrolyte Interface (CEI) or other passivation layers formed on the electrode surface during cycling, and finally, R_{ct} is directly correlated to the difficulty of charge transfer during the redox reactions occurring on the electrode-electrolyte interface.

Figure 9b and c compare the experimental EIS spectra collected after 100 cycles at 0.125C and 1C, respectively, for both $x = 0$ and 0.2. In the tables are reported the Resistance values calculated from the Z fit (dotted red curve), performed through EC-Lab software (Bio-Logic). In general, the decrease in total resistance observed for $x = 0.2$ compared to $x = 0$ indicates that the previously discussed performance enhancement can be attributed to improved electrode-electrolyte interfacial properties. Furthermore, a detailed comparison of the different resistive contributions reveals additional important insights. Regarding R_e , the values calculated between tests performed at the same current density show no significant differences. This value cannot be correlated with the intrinsic properties of the cathode material. Therefore, it is expected that different cells with the same electrolyte and subjected to the same cycling stress, lead to similar R_e . The analysis of R_{sf} and R_{ct} shows a decrease in both resistance values following Mg(II) doping, confirming that the substitution exerts a stabilizing effect regardless of the C-rate. Interestingly, for a given composition, R_{sf} remains nearly unchanged between 0.125C and 1C, suggesting that the current density does not significantly influence the interfacial properties. As for R_{ct} , values measured at 0.125C are nearly four times higher than those at 1C for both compositions.

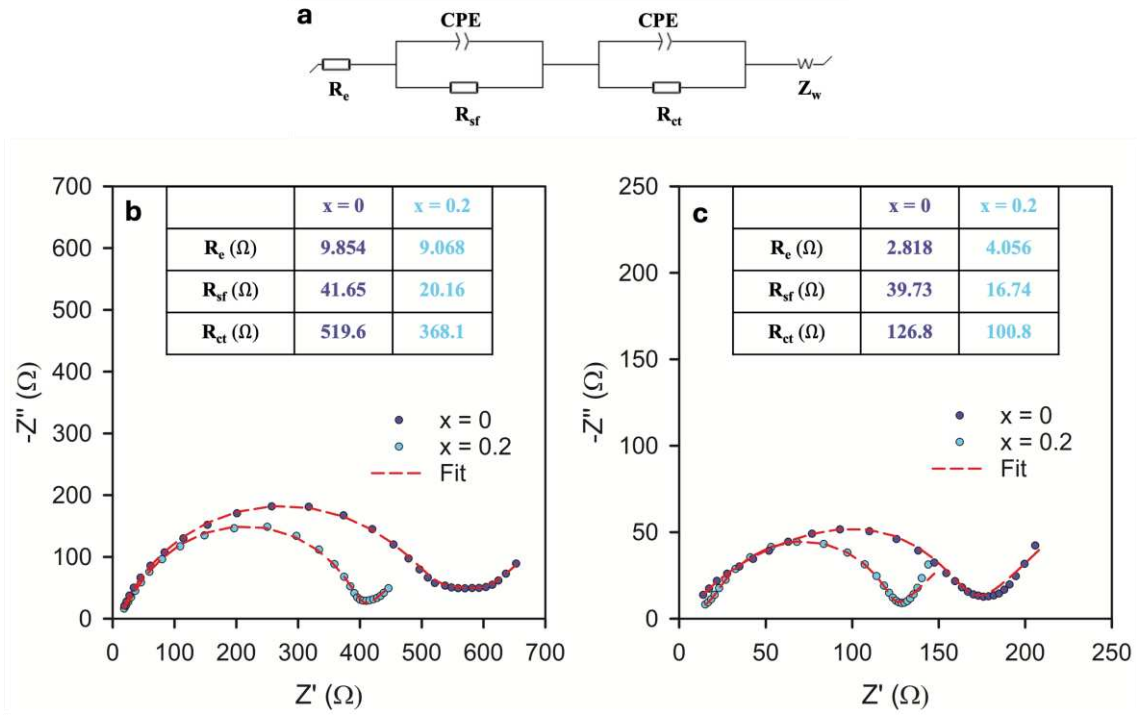


Figure 9. (a) Equivalent circuit model used to fit the experimental EIS spectra, collected for $x = 0$ and $x = 0.2$, after long-term cycling tests at (b) 0.125C and (c) 1C. Tables in the graphs report the results of the fitting

The stabilizing role of Mg(II) is further evidenced by comparing the reduction in R_{ct} between the two C-rates: approximately 30% (from 519.6 Ω to 368.1 Ω) at 0.125C and 20% (from 126.8 Ω to 100.8 Ω) at 1C. The larger difference observed at lower C-rates can be well explained by considering that, under slower cycling conditions, charge transfer is more limited and sluggish kinetic processes become more rate-determining. For this reason, the stabilizing influence of Mg(II) on the electrode's resistive properties becomes more pronounced.^{94–96}

Moreover, to further investigate the SEI formation and evolution during cycling, and correlate it with the discussed cathodic performance, EIS spectra were collected during the first 40 cycles (at 0.125C) for both the compositions under consideration. Figure 10 shows the results of these analyses. Up to the 10th cycle, $x = 0$ and $x = 0.2$ exhibit a similar evolution, characterized by a slight decrease in total resistance associated with SEI stabilization. From the 20th cycle onward, the EIS spectra of the Mg(II)-doped material appear nearly superimposed. In contrast, for the undoped sample, we first observe an increase in resistance (30th cycle) followed by a pronounced decrease (40th cycle). This unstable behavior indicates that, although interfacial phenomena (*e.g.*, SEI formation and

FEC degradation) appear similar for both materials in the initial cycles, the electrode-electrolyte interface of the $x = 0.2$ sample remains significantly more stable upon prolonged cycling, as reflected in its nearly constant resistance. On the other hand, the resistance variation observed for $x = 0$ suggests ongoing formation and/or decomposition of interfacial products derived from electrolyte or active material degradation. Therefore, the enhanced electrochemical performance previously discussed for P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ can be ascribed, at least in part, to the improved stability of its electrode-electrolyte interface compared to the unsubstituted counterpart.

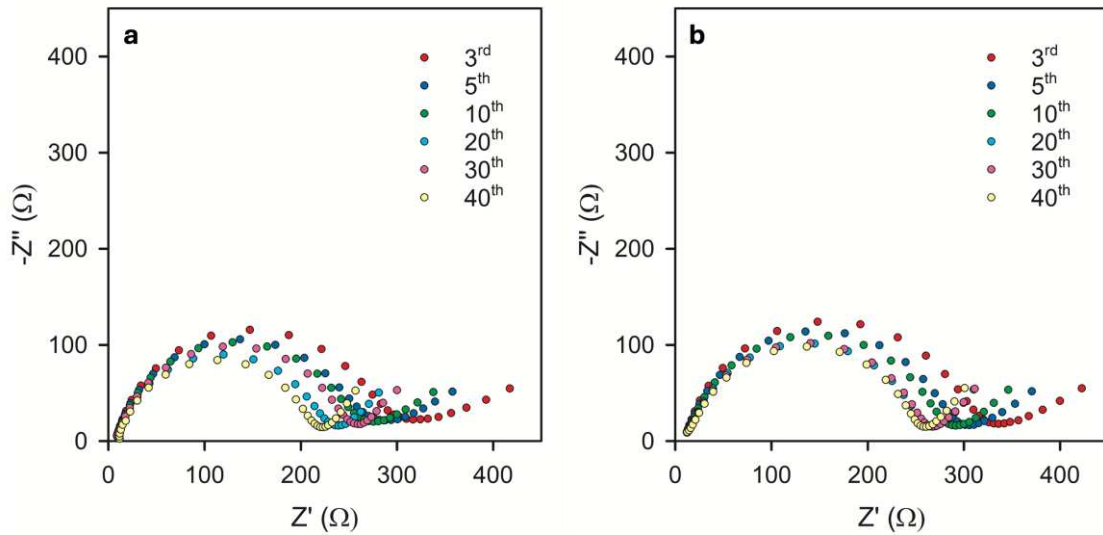


Figure 10. Experimental EIS spectra collected during the first 40 cycles of cycling at 0.125C for (a) $x = 0$ and (b) $x = 0.2$

Subsequently, we also evaluated the diffusive properties of these two compositions during the charge-discharge cycle, through Galvanostatic Intermittent Titration Technique (GITT). With this analysis, the goal is to further investigate the kinetic and diffusive properties of the materials, thereby establishing correlations with the different electrochemical performances discussed earlier. As discussed in Chapter 2, the GITT experiments are performed by charging and discharging the half-cells by setting current impulses consisting of: 1) a constant current (CC) step, with a current corresponding to a C-rate of C/15, for 15 minutes, and 2) a relaxation period, for 1 hour. In order to obtain meaningful results, it is important that, during step 2, the system is able to reach an equilibrium situation following step 1. For this reason, the duration of step 2 is four times

longer than step 1. From these experiments, the most insightful properties we can evaluate are the overpotential (η) and the Na^+ diffusion coefficient (D_{Na^+}) trend during cycling. The procedures used to calculate and analyze these parameters are discussed in detail in Chapter 2. It is important to emphasize that the approximations adopted for the calculation of D_{Na^+} are only valid when the material exhibits a solid solution-like behavior, that is, within the potential range where no active redox contributions are involved. For this reason, in Figure 11, the potential window where the Na^+ diffusion between the two materials can be properly evaluated is highlighted with an orange box; this corresponds to the voltage region in which the charge-discharge curves do not exhibit any plateau associated with redox processes. This limitation must also be considered when analyzing the overpotential, even though no approximated expressions are required for its determination. Indeed, in potential regions where the material displays biphasic behavior, the observed η may be significantly affected by the ongoing redox reaction, thus making the interpretation of the electrode kinetics less accurate. For these reasons, only the highlighted potential window was considered for the evaluation of the diffusive and kinetic properties of the cathode materials under investigation.

The overpotential can be easily evaluated by comparing the GITT charge-discharge curves (Figure 11a). Comparing the curves in the highlighted region, we can conclude that $x = 0.2$ has a higher overpotential compared to the $x = 0$ composition. This reflects in the lower kinetic properties of the material. This result is also confirmed by comparing the D_{Na^+} evolution during charge and discharge reported in Figures 11b and 11c, respectively. In both cases, $x = 0$ has higher Na^+ diffusion than the Mg(II)-doped oxide. Moreover, it's interesting to note that, for both compositions, the calculated D_{Na^+} is lower during discharge compared to the charge. These results mean that the sodiation process is slower than the de-sodiation, and so it can be considered as the limiting step of the entire electrochemical process.

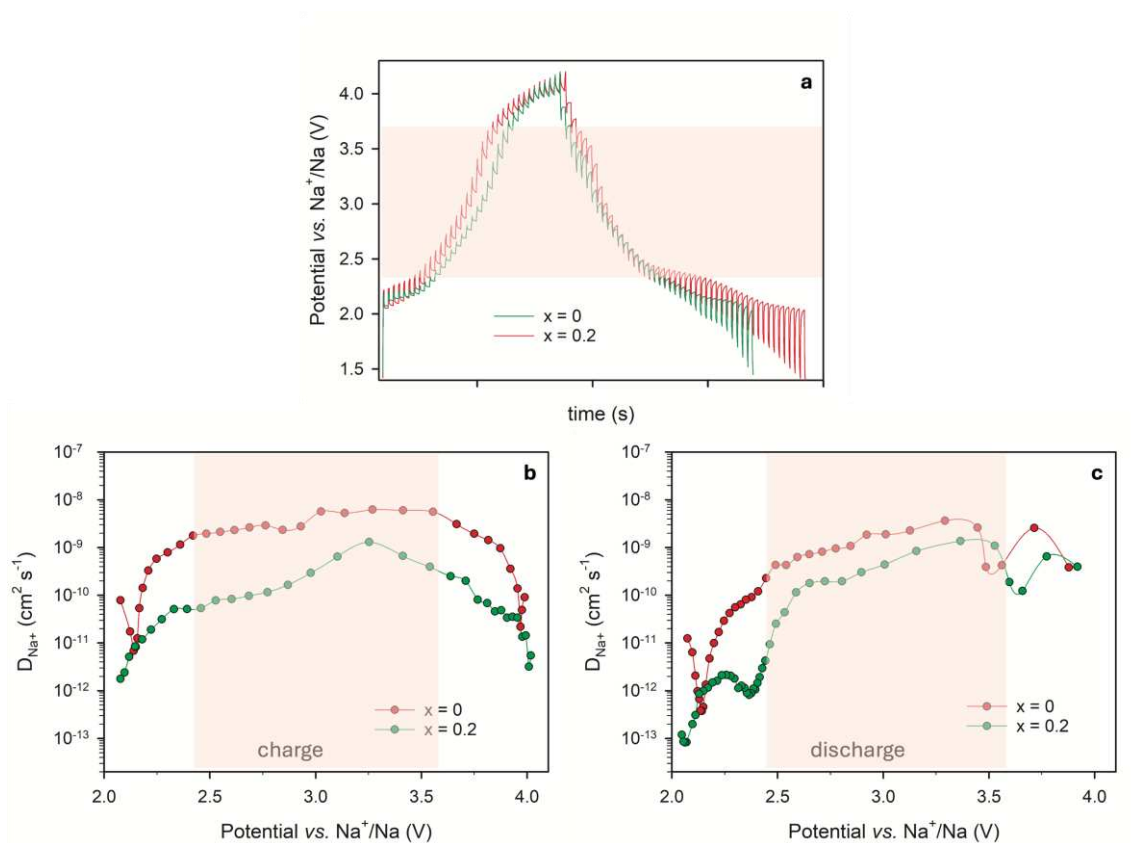


Figure 11. GITT experiment results. (a) Comparison of experimental charge-discharge curves (2nd cycle) of $x = 0$ and $x = 0.2$ composition. Calculated D_{Na^+} evolution trend during (b) charge and (c) discharge in the voltage range between 1.5 V and 4.2 V

In general, the results from these GITT experiments indicate that $x = 0$ exhibits superior kinetic and diffusive properties compared to the $x = 0.2$ composition. These findings are in contrast with the trend commonly reported in the literature, where doping with electrochemically inactive elements is typically associated with enhanced diffusive and kinetic properties of the materials.^{97–99} However, it is important to emphasize that an improvement in electrochemical performance does not necessarily imply an enhancement of the material's intrinsic kinetic properties. A comprehensive evaluation must also consider other factors, such as structural stability, electrode-electrolyte interfacial properties, and the reversibility of redox processes.

4.1.3. Conclusion

In conclusion, in Chapter 3.1 we fully characterized a new family of layered oxide cathode materials with composition P2-Na_{0.67}Mn_{0.5}Fe_{0.5-x}Mg_xO₂ ($x = 0, 0.1, 0.2, 0.3$). The

present study investigates the influence of Mg(II) substitution on transition-metal sites on the structural and, most importantly, the electrochemical properties of the materials. From the dQ/dV profiles and the rate capability test results, we determined that the best-performing composition is P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$. Long-term cycling at different current densities further demonstrated that Mg(II)-doping significantly enhances the performance in terms of capacity retention: from 60% to 76% after 100 cycles at $C/8$, and from 45% to 76% after 100 cycles at $1C$, for $x = 0.2$ and $x = 0$, respectively.

The observed differences in electrochemical performance, as well as the stabilizing role of Mg(II), were further investigated through GITT and PEIS. These analyses enabled the evaluation of differences in kinetic-diffusive and in the electrode-electrolyte interface properties, respectively. The results revealed that $x = 0.2$ exhibits slower kinetics compared to $x = 0$ (lower η and D_{Na^+}), but a less resistive electrode-electrolyte interface (lower R_{sf} and R_{ct}).

4.2. Spray-Drying synthesis

During my visiting period at the University of Bayreuth (Germany), I evaluated the possibility of synthesizing some of the cathode materials discussed above by spray-drying synthesis. This type of synthesis is very promising and interesting in the field of battery materials synthesis, as it simultaneously provides great sustainability, ease of process, large-scale scalability, and, in addition, leads to the formation of materials with optimal structural-microstructural properties for this type of application. In addition to the synthesis and characterization of these materials, this chapter will also compare morphological-structural properties with electrochemical properties between materials having the same elemental composition but synthesized via the two investigated synthesis routes (solid-state and spray-drying).

Part of the results that will be discussed in this Chapter 4.2 are contained in one of our papers published in Journal of Materials Chemistry A, titled “*Solid-state vs. Spray-drying synthesis for Mg-doped P2-Na_{0.67}Fe_{0.5}Mn_{0.5}O₂ as cathode material for Sodium-Ion Batteries*”.

4.2.1. Materials and Methods

4.2.1.1. Synthesis

P2-Na_{0.67}Mn_{0.5}Fe_{0.5-x}Mg_xO₂ (x = 0, 0.2) were synthesized by spray-drying synthesis (SD-0 and SD-02) followed by heat treatments. For the spray-drying process, we used a Buchi Mini Spray Dryer B-290, starting from a 0.2 M water solution made of commercial Fe(NO₃)₃ • 9H₂O, (CH₃COO)₂Mn • 4H₂O, Mg(NO₃)₂ • 6H₂O and CH₃COONa • 3H₂O. Since this synthesis allowed us to reduce the synthesis temperature, we didn't expect Na loss during the calcination process, so we didn't introduce Na excess. Table 1 shows the conditions imposed on the instrument for the spray process. After collecting the resulting spray-dried powder, we calcined it at 775 °C for 8 h (SD-0) and 800 °C for 10 h (SD-02) for the P2-layered phase formation.

Table 1. Experimental parameter for the spray-drying process

Solution concentration	0.2 M
T inlet	200°C
T outlet	143-145°C
Peristaltic pump flow rate	5%
Atomization gas flow rate	20%

4.2.1.2. Structural, elementary, and morphological characterization

Morphologies and elementary compositions of the materials were investigated through SEM and ICP-AES analysis. We used a ThermoFischer Scientific Phenom ProX microscope to collect SEM images. ICP-OES analyses were performed by an Avio 220 max (Perkin Elmer), equipped with an AVIO Glass Cyclonic Baffled spray chamber, a quartz torch, and a dual backside-illuminated charge-coupled device (DBI-CCD) detector. The TMs quantification was carried out on HNO₃-digested solutions in the axial mode at 670.8 nm as wavelength, by an external standard calibration curve. ICP grade multi-elements standard (1000 mg L⁻¹) was diluted to 0.3–0.6–2.0–5.0–9.0 mg L⁻¹ and then acidified to a final concentration of 2% nitric acid (from ultrapure 65% HNO₃). The measurement conditions were as in the following: nebulization gas flow: 0.7 L min⁻¹; power RF: 1500 W; auxiliary gas flow: 0.2 L min⁻¹; peristaltic pump: 1 mL min⁻¹; frequency: 500 Hz. For Na quantification, we used an ultrapure H₂O for chromatography (Na < 200 ppb).

XRD patterns of P2-Na_{0.67}Mn_{0.5}Fe_{0.5-x}Mg_xO₂ powder were collected with a STADI P diffractometer (STOE, Germany) with Mo-K α 1 radiation ($\lambda = 0.70932$ Å, 50 kV, and 40 mA) and a Mythen2K detector, in the 5-70° 2 θ range and with 0.015° step. Rietveld refinement was conducted using the FullProf Suite software⁸⁷. Operando XRD experiments were performed on a customized CR2032 coin cell with quartz glass windows (6 mm in diameter, 100 μ m in thickness). The cell was mounted on a rocking sample holder in the diffractometer mentioned above and measured in transmission geometry. Each scan was recorded for 15 min in 0.015° steps from 3° to 36°. The half-cell was cycled at 0.067 C.

4.2.1.3. Cathode preparation and cell assembly

The cathode slurry was prepared by using 80 wt.% of active material, 10wt.% of Conductive Carbon black (Imerys, Ensaco 350P), and 10 wt.% of a binder (polyvinylidene fluoride, PVdF). The solid content of all slurries was kept between 28 wt.% and 30 wt.%. Cathode Active Material (CAM) and carbon powders were mixed in zirconia jars by a planetary ball mill at 150 rpm for 10 min twice, with a rest period of 5 min. Subsequently, the polymeric binder was added and mixed with a similar procedure. The as-prepared mixture was dispersed in N-methyl pyrrolidone (NMP) to obtain the slurry, which was cast on a carbon-coated Al foil using a doctor blade with a wet thickness of 300 μm . The casted slurry was dried under vacuum at 80 $^{\circ}\text{C}$ to avoid moisture and oxygen contamination. The cathode was finally cut into 2 cm^2 disks and stored in an Ar-filled glove box (MBraun, O_2 , H_2O < 0.5 ppm) before the electrochemical measurements. The loading of the electrodes was $\sim 3 \text{ mg cm}^{-2}$. For *Operando* XRD experiments, we prepared the electrodes following a different procedure, as reported elsewhere¹⁰⁰. All the functional tests were performed in coin cells (CR2032 - MTI Corp.) assembled in an inert atmosphere (Ar) at room temperature (25 $^{\circ}\text{C}$). Metallic Na was used as the counter electrode. Electrodes were separated with two *Whatman* GF/A glass fiber separators, imbibed by 90 μL of liquid electrolyte, consisting of a solution of 1 M NaPF_6 in Ethylene Carbonate: Dimethyl Carbonate + 2 wt.% Fluoroethylene Carbonate (FEC).

4.2.1.4. Electrochemical characterization

The electrochemical performances of all the materials were investigated with a Bio-Logic VPM-3e through Galvanostatic Cycling with Potential Limitation (GCPL) at different C-rate. Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA), and Galvanostatic Intermittent Titration Technique (GITT) in the working potential window 1.5 V-4.2 V. The theoretical capacity was calculated as 260 mAh g^{-1} for $x = 0$ and 280 mAh g^{-1} for $x = 0.2$, based on the molecular weight of the respective compositions and assuming, in excess, the reversible extraction of one Na^+ equivalent for each half-cycle.

4.2.2. Results and discussion

4.2.2.1. Structural and Elementary Analysis

After the optimization of the spray-drying process experimental parameter for both $x = 0$ and 0.2, as well reported in the methods section, we checked the elementary composition of the resulting product by EDX. Figure 1 shows the EDX spectra and the atomic concentration of both samples. With this preliminary analysis, we confirmed that the dried powder resulting from the spray process has the desired composition, since both the Fe/Mn and Fe/Mg ratios are the expected ones based on the nominal stoichiometry of the cathodes.

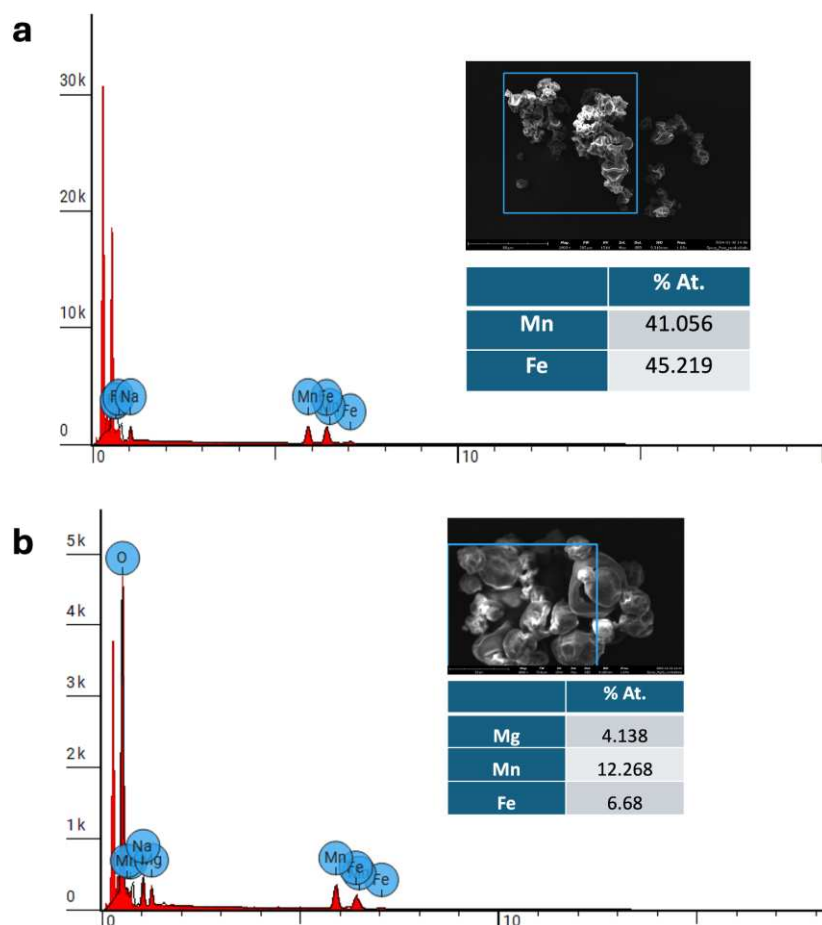


Figure 1. EDX spectra and elementary quantification of (a) $x = 0$ and (b) $x = 0.2$ precursor powder obtained after the spray-drying process

Subsequently, we attempted various calcination conditions to optimize the formation of the P2-layered structure. With the main aim of decreasing the temperature compared to the 1000°C needed for the solid-state synthesis, for $x = 0$, we started from 700°C and we increased it by 25°C until 800°C for a fixed time of 8h (ramp rate 5°C min⁻¹). Figure 2 shows the XRD patterns collected after each treatment. By comparing them, as the temperature increases, the pattern becomes progressively monophasic and ascribable only to the desired P2-layered hexagonal structure. Observing the trend of the peak highlighted by the orange arrow, which represents the major impurity observed in the various patterns, it is easy to understand why the treatment at 775°C for 8 hours yielded the best results. It is also important to note that, unlike solid-state synthesis, it was not necessary to compact the precursor powder into pellets to facilitate synthesis for these materials. This is a further advantage of this type of synthesis, as it avoids an experimental step that is also difficult to apply on an industrial scale.

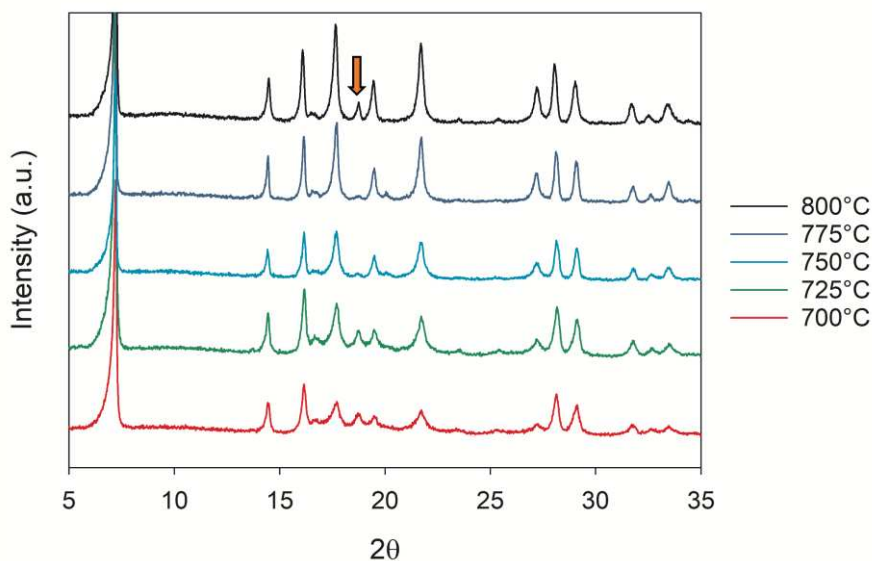


Figure 2. XRD patterns collected after different calcination treatments aimed at optimizing the synthesis of SD-0. The orange arrow highlights the main peaks of the impurity phase

Regarding $x = 0.2$, however, it was necessary to increase both the temperature and the treatment time, as after 8 hours at 775°C, the structure was not completely ordered. Figure 3 shows the attempts made for this composition, thanks to which we were able to optimize the parameters for this calcination at 800°C for 10 hours. We hypothesize that the

difference between the optimized heat treatments for the two compositions is attributable to the higher entropy on the transition metal planes and the greater steric hindrance for $x = 0.2$ compared to $x = 0$, caused by the presence of Mg(II), whose ionic radius (0.72 Å) is significantly larger than that of Fe (III), Mn(III), and Mn(IV), which are 0.64 Å, 0.64 Å, and 0.53 Å, respectively. The orange arrows here show the formation of a secondary phase relative to P2 after just 8 hours at 800°C. This impurity can easily be identified as the O3 phase, the other electrochemically active layered structure for SIBs. The inset in the figure reveals the presence of a small diffraction signal very close to the main peak of the P2 phase, which represents one of the fingerprints of the O3 phase.¹⁰¹

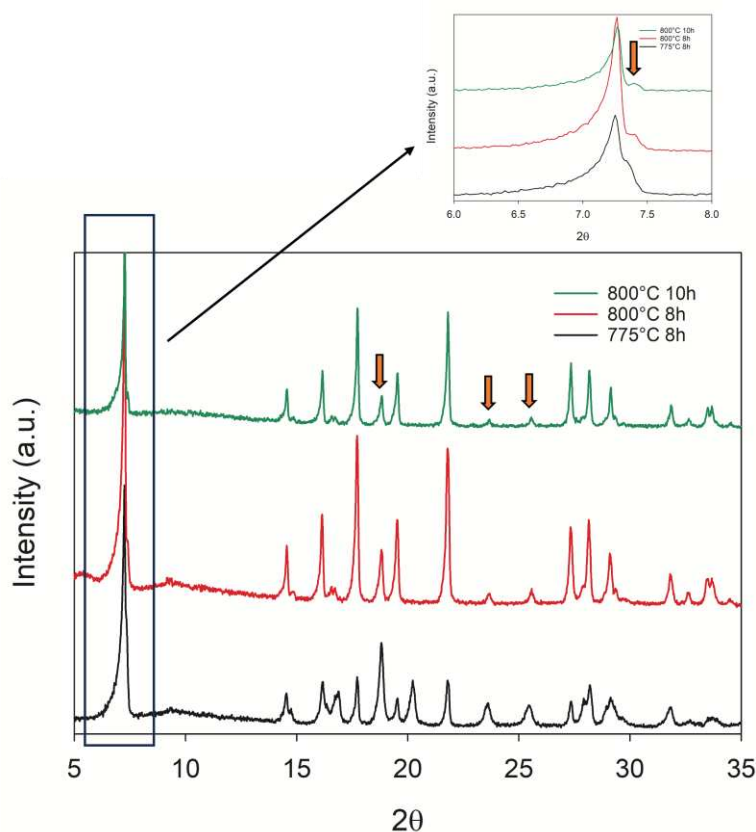


Figure 3. XRD patterns collected after different calcination treatments aimed at optimizing the synthesis of SD-02. The inset and the orange arrows highlight the main peaks of the secondary O3-phase

Figure 4 shows the SEM images collected for both the compositions after the spray process and after the final calcination. The morphology of the precursor powders in Figures 4a and 4c confirmed that the spray process led to the formation of particles with

very uniform dimensions, shape, and elemental composition. However, after calcination, this regular morphology is lost, as shown in Figures 4b and 4d, and the final materials have irregular grains like those of solid-state synthesized materials.

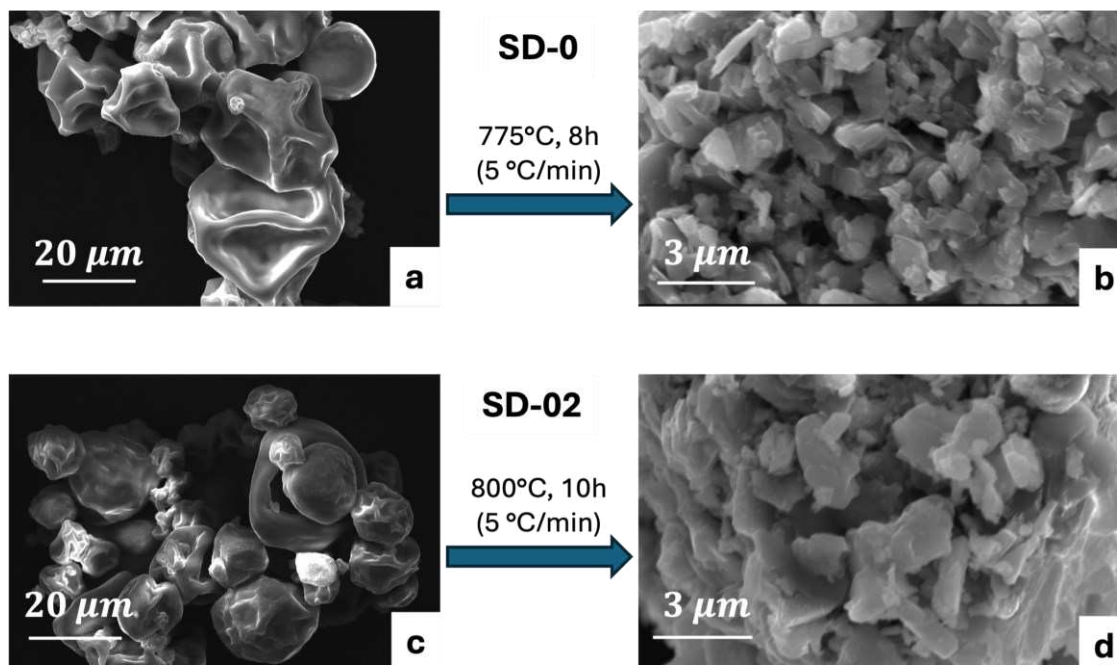


Figure 4. SEM images of (a-b) SD-0 and (c-d) SD-02 pre- and post-heat treatments

The elementary composition of the final P2-oxides was evaluated through ICP-OES analysis, which confirmed the good agreement between the nominal and experimental stoichiometric coefficients for all elements, except for Na. The results of these analyses are reported in Table 3. It is noteworthy that the low sodium content of SD-0 is likely to be significantly associated with the quality of the powder following the spray-drying process. This is likely attributable to inadequate incorporation of sodium acetate, resulting in a product with elevated hygroscopic tendencies. Consequently, the product becomes challenging to collect from the spray dryer. In contrast, for SD-02, none of these issues were experimentally observed, and in fact, the final powder exhibited a significantly higher sodium content.

Table 3. Stoichiometric coefficient calculated through ICP-OES analysis for all the compositions. Theoretical values are reported in brackets.

	Fe/Mn	Fe/Mg	Na
$x = 0$	1.04 (1.0)	-	0.449
$x = 0.2$	0.57 (0.6)	1.27 (1.5)	0.607

4.2.2.2. Electrochemical Characterization

All the materials were tested as positive electrode materials for SIB in half-cell vs. Na_(m). Based on the literature and the composition of the oxides under investigation, we studied the electrochemical performances between 1.5 V and 4.2 V. We introduced 2 wt.% FEC into the electrolyte mixture used to limit electrolyte degradation at high potentials (> 4 V) during cycling.^{102,103}

We evaluated the active redox phenomena from differential capacity curves (dQ/dV) obtained through PCGA analysis at low current density at 0.067 C (Figure 5a-b). As highlighted in the figures, two reversible active phenomena were identified in all the materials at potentials of 2 V-2.2 V and 3.3 V-4 V, corresponding to the Mn(III)/Mn(IV) and Fe(III)/Fe(IV) redox-active couple, respectively.⁸⁸ The irreversibility observed after the first charge at potentials >4 V can be attributed in part to the degradation of the electrolyte, which is only mitigated by the presence of FEC, but also possibly to the partially irreversible oxygen redox active contribution (O²⁻/O⁻),^{104,105} which we will also discuss later in the *Operando* XRD results section. In the 1st cycle, the peaks between 2.7 V and 3 V can be attributed to a polarization of the coin cell immediately after the start of the experiment.

We investigated the evolution of Na⁺ content in the P2 structure during the first three charge-discharge cycles for the two cathodes, aiming to assess the reversibility of the intercalation-deintercalation reaction (Figure 5c-d). Starting from the nominal value of Na⁺ in the cathodes ($x = 0.67$), during the first charge, both the materials are desodiated to a sodium content of $x = 0.2 - 0.4$. Over the next discharge, on the other hand, Na⁺ intercalation occurs to $x = 0.8 - 0.9$. This sodium excess compared to the initial value is due to the Na_(m) used as a counter-electrode, which ensures an almost infinite Na⁺ source, leading to deep sodiation of the cathodes. SD-02 (Figure 5d) intercalates less Na⁺ than

the other, but the process is almost completely reversible over the cycles investigated. As already known in the literature, the small phenomenon observed in discharge at potentials less than 2 V (circled in blue in Figure 5c-d) can be attributed to the reversible passivation of the $\text{Na}_{(m)}$ counter electrode due to the presence of EC in the electrolyte mixture.^{106,107} By comparing the cathodic performance of SD-0 and SD-02 at different current densities (Figure 6a), we confirmed the stabilizing effects of Mg^{2+} doping: at all the tested C-rates, $x = 0.2$ discharge capacity consistently exceeds that of $x = 0$. Moreover, coulombic efficiency (C.E.) remains above 95% across all the different current densities investigated. These findings provide conclusive evidence that Mg substitution enhances the electrochemical performance of the $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ cathode, independent of the synthesis method employed, whether solid-state, as previously reported, or spray-drying.

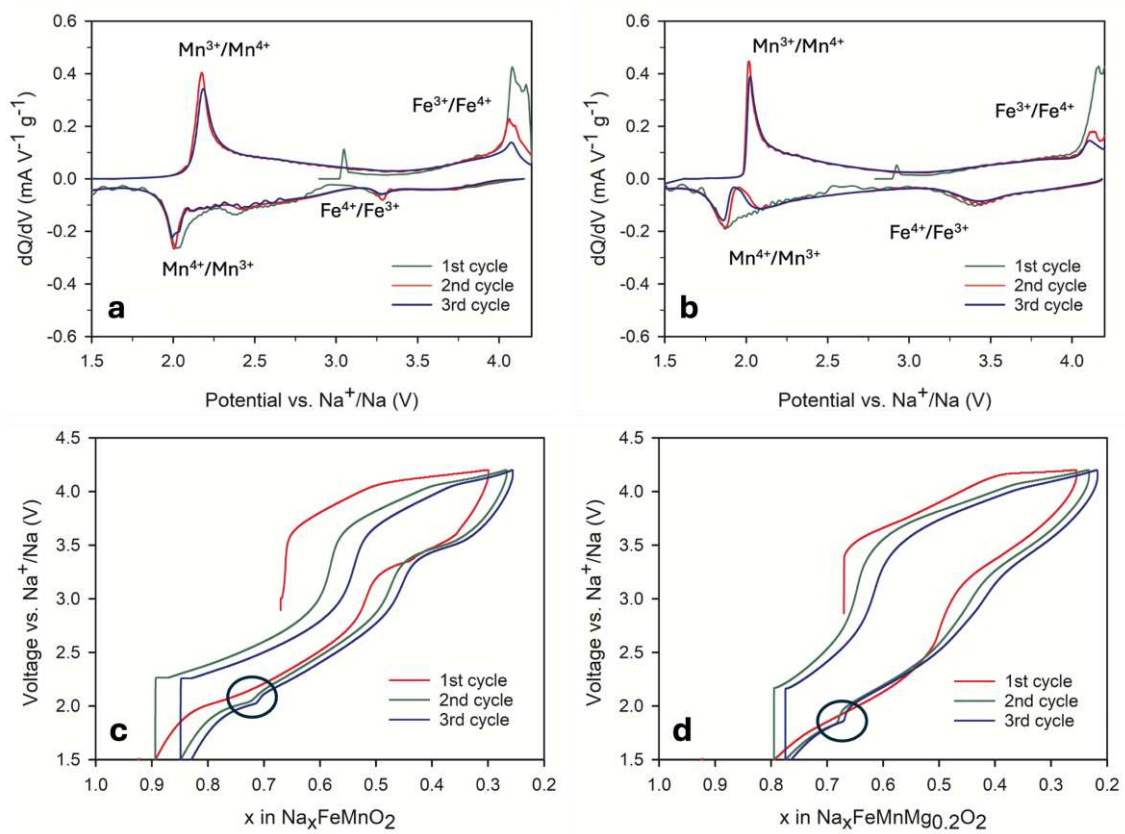


Figure 5. dQ/dV curves and Voltage-composition profiles obtained through PCGA experiment for (a-c) SD-0 and (b-d) SD-02, performed between 1.5 V and 4.2 V at 0.067 C vs. Na^+/Na .

In light of these findings, to further stress the electrochemical stability of the spray-drying materials, we extended to 200 cycles the stability test at 1C (Figure 6b): the capacity retention calculated after 200 cycles increases from 39% for SD-0 to 68% for SD-02. In

this regard, we confirmed what was reported by Zhou *et al.*¹⁰⁸ about the stabilizing role given by the co-existence of P2/O3 compared to pure P2-phase.

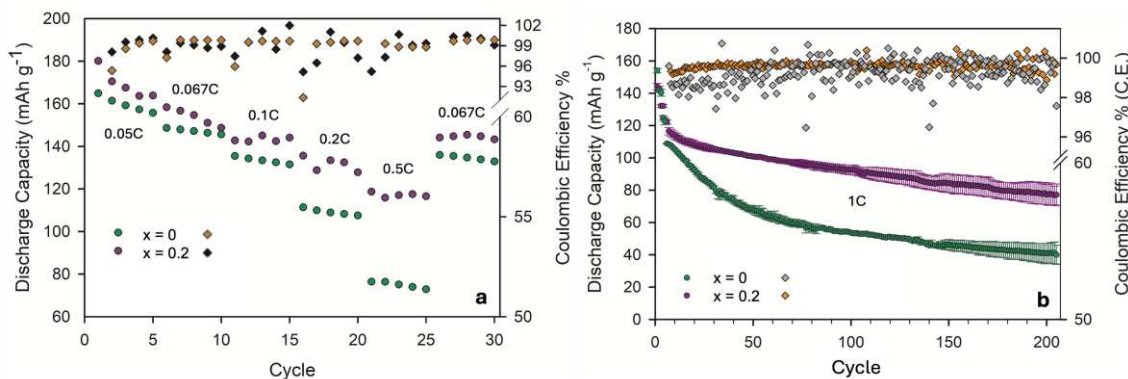


Figure 6. Comparison of discharge capacity and coulombic efficiency recorded during (a) rate capability and (b) long-term cycling test between SD-0 and SD-02, performed between 1.5 V and 4.2 V vs. Na⁺/Na

Subsequently, we also evaluated the diffusive properties of these two compositions during the charge-discharge cycle. This evaluation was undertaken using Galvanostatic Intermittent Titration Technique (GITT) (Figure 7). The objective of this analysis, the goal is to further investigate the kinetic and diffusive properties of the materials, thereby establishing correlations with the different electrochemical performances discussed earlier. As outlined in Chapter 2, the GITT experiments are performed by charging and discharging the half-cells by setting current impulses consisting of: 1) a constant current (CC) step, with a current corresponding to a C-rate of C/15, for 15 minutes, and 2) a relaxation period, for 1 hour. In order to obtain meaningful results, it is important that, during step 2, the system is able to reach an equilibrium situation following step 1. For this reason, the duration of step 2 is four times longer than step 1. From these experiments, the most insightful properties we can evaluate are the overpotential (η) and the Na⁺ diffusion coefficient (D_{Na^+}) trend during cycling. The procedures used to calculate and analyze these parameters are discussed in detail in Chapter 2. It is important to emphasize that the approximations adopted for the calculation of D_{Na^+} are only valid when the material exhibits a solid solution-like behavior, that is, within the potential range where no active redox contributions are involved. For this reason, in Figure 9, the potential window where the Na⁺ diffusion between the two materials can be properly evaluated is highlighted with an orange box; this corresponds to the voltage region in which the charge-discharge curves do not exhibit any plateau associated with redox processes. This

limitation must also be considered when analyzing the overpotential, even though no approximated expressions are required for its determination. Indeed, in potential regions where the material displays biphasic behavior, the observed η may be significantly affected by the ongoing redox reaction, thus making the interpretation of the electrode kinetics less accurate. Consequently, the evaluation of the diffusive and kinetic properties of the cathode materials under investigation was confined to the highlighted potential window.

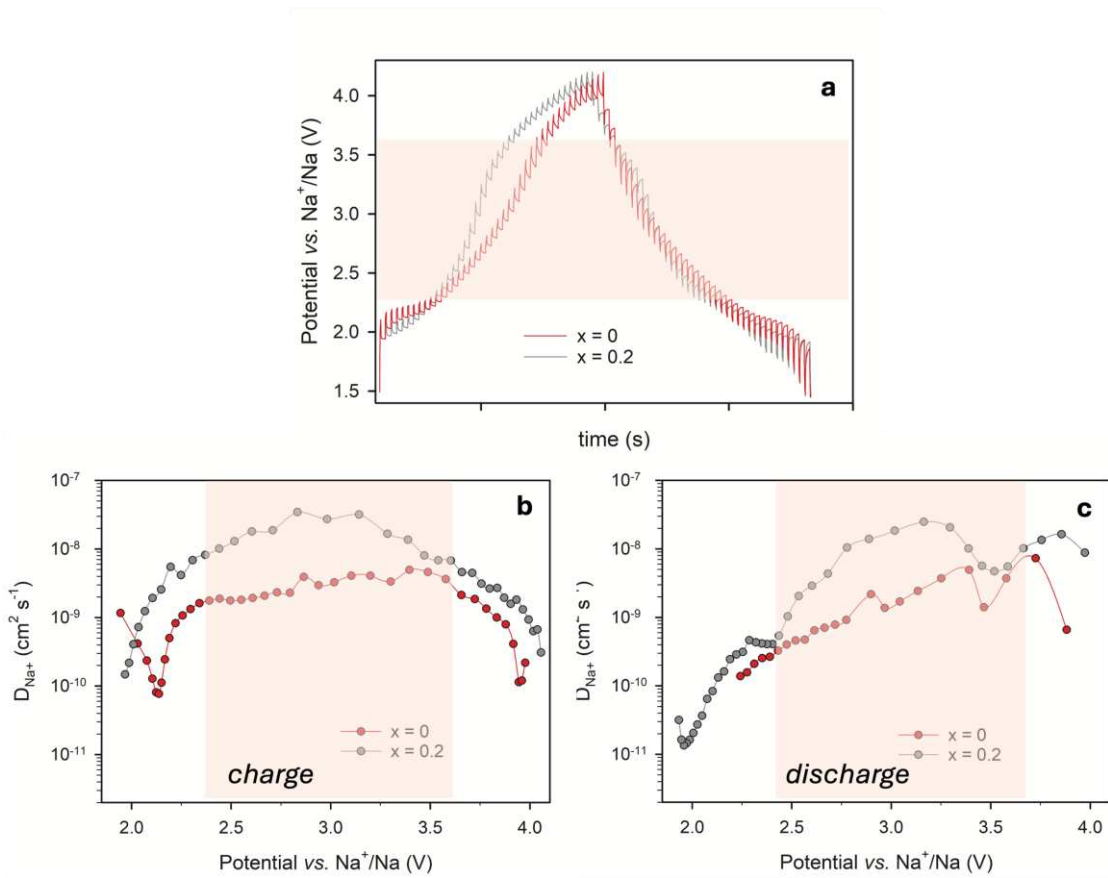


Figure 7. GITT experiment results. (a) Comparison of experimental charge-discharge curves (2nd cycle) of $x = 0$ and $x = 0.2$ composition. Calculated D_{Na^+} evolution trend during (b) charge and (c) discharge in the voltage range between 1.5 V and 4.2 V

Analysis of the charge–discharge profiles in Figure 7a clearly shows that the $x = 0.2$ composition exhibits lower overpotential values than $x = 0$ in both charge and discharge. This indicates that Na_{0.67}Mn_{0.5}Fe_{0.3}Mg_{0.2}O₂ composition has enhanced electrode kinetics. The trend of the Na⁺ diffusion coefficient further corroborates this observation: in both charge (Figure 7b) and discharge (Figure 7c), the calculated D_{Na^+} values are consistently higher for $x = 0.2$ than for $x = 0$. Discharge is confirmed to be the kinetically limiting

step of the overall electrochemical process, as reflected by lower diffusion coefficients for both compositions compared to the corresponding calculated charge values, in agreement with previous findings on materials synthesized through solid-state synthesis. Interestingly, the higher diffusive properties observed for $x = 0.2$ stand in marked contrast with those of solid-state synthesized materials (Chapter 4.1.2.2). This discrepancy can be rationalized by considering the distinct morphology and microstructure that arise from the two different synthetic routes employed. In addition, the coexistence of the secondary O3-type phase alongside the primary P2 phase is expected to play a key role in facilitating Na^+ ion transport. These aspects will be further examined in the following chapters, where the properties of materials with identical elemental compositions but prepared via spray-drying and solid-state synthesis will be directly compared and discussed.

4.2.2.3. Operando XRD

To investigate the structural evolution of the P2-layered structure during cycling and the Mg^{2+} stabilizing effect on the electrochemical properties, *Operando* XRD experiments were conducted on $x = 0$ and $x = 0.2$. The results in Figures 8a and b reveal that these materials exhibit different behaviors during the first two charge-discharge cycles, particularly at high potentials (>4 V). It is well-known that the biggest challenges for layered cathode materials for SIBs arise above 4 V, where the P2 structure undergoes phase transitions and structural rearrangements that, over cycling, can lead to a significant reduction of cathodic performance. These transitions occur because of the continuous Na^+ deintercalation-intercalation during cycling. This process can disrupt the structural periodicity and facilitate the formation of other inactive or unstable layered phases, such as P2', O2, and OP4.

An observation of the 002 reflections (but also 103, 104, 106), above 4 V, $x = 0$ undergoes the well-known P2-Z⁴⁹ phase transition, caused by the abovementioned layer sliding between the pristine P2 phase and a mixture of O2 and OP4 phases. In contrast, examination of the analogous reflections for $x = 0.2$ (Figure 8b) reveals a consistent solid-solution-like behavior across the entire working potential range, devoid of any phase transition. Our results corroborate those of Yang *et al.*,¹⁰⁹ who well explained that Mg^{2+} effectively suppresses this reversible P2-OP4 phase transition.

From the 002 reflection shift, it is possible to observe the evolution of the c parameter, which can be easily correlated with the evolution of Na content during cycling. In particular, upon desodiation, there is initially an increase in the c parameter (the peak shifts to smaller angles) due to the greater repulsion between the O^{2-} present on the metal planes. This results from the reduced shielding imparted by the Na^+ ions, which migrate toward the $Na_{(m)}$ counter-electrode. Beyond a certain state of charge, the 002 reflection abruptly shifts to higher angular values, which indicates the collapse of the Na interlayer and the onset of formation of the above-mentioned Z phase. During sodiation, for the opposite reason, c decreases as the Na^+ ions are re-intercalated between the P2-oxide layers. 100, 110, and 112 reflections have opposite trends to those observed for 002, and can be related to a and b unit cell parameters. These two parameters decrease during charge due to the increased oxidation of metal cations, which in turn shortens the M-O bond distance,^{110,111} leading to an overall contraction of the elementary cell along these directions. Figures 8a and 8b also show the refined lattice parameters, obtained through LeBail refinement, during the 1st and 2nd charge-discharge cycle for SD-0 and SD-02, respectively. We decided to not refine the lattice parameters in the Z-phase potential range for SD-0 because the peaks associated with the OP4 and P2 phases are broadened by stacking faults and have low intensity, making a proper refinement cumbersome.

Notably, the c parameter decreases during the first charge between 4.0 V and 4.2 V for both compositions. This behavior is well-documented in layered cathode materials for LIBs (e.g., LNO and NMC)^{112,113} and is typically attributed to a partial collapse of layers at low Li content, leading to an overall contraction of the unit cell. In other systems, this phenomenon also overlaps with the onset of partially irreversible oxygen redox activity at high potentials, which induces local structural rearrangements and may contribute to the contraction along the c -axis.¹¹⁴ It is worth noting that, during the second cycle, this c -axis contraction at high potential is no longer observed, resulting in a more symmetric evolution of this cell parameter during charge and discharge. Consistent with these findings, Jin *et al.* demonstrated that for $P2-Na_{0.75}Ca_{0.04}[Li_{0.1}Ni_{0.2}Mn_{0.67}]O_2$, the asymmetry in the 00l reflection shift (and thus in the c -parameter evolution), between the end of charge and the beginning of the subsequent discharge, is attributable to O_2 formation and release.¹⁰⁴ This has a deleterious effect on the performance of the materials concerned.

Conversely, for both $x = 0$ and $x = 0.2$, the absence of this contraction at high potentials during the second cycle lends support to the hypothesis that oxygen activity and/or collapse of the layers is significantly suppressed from the second cycle onwards.

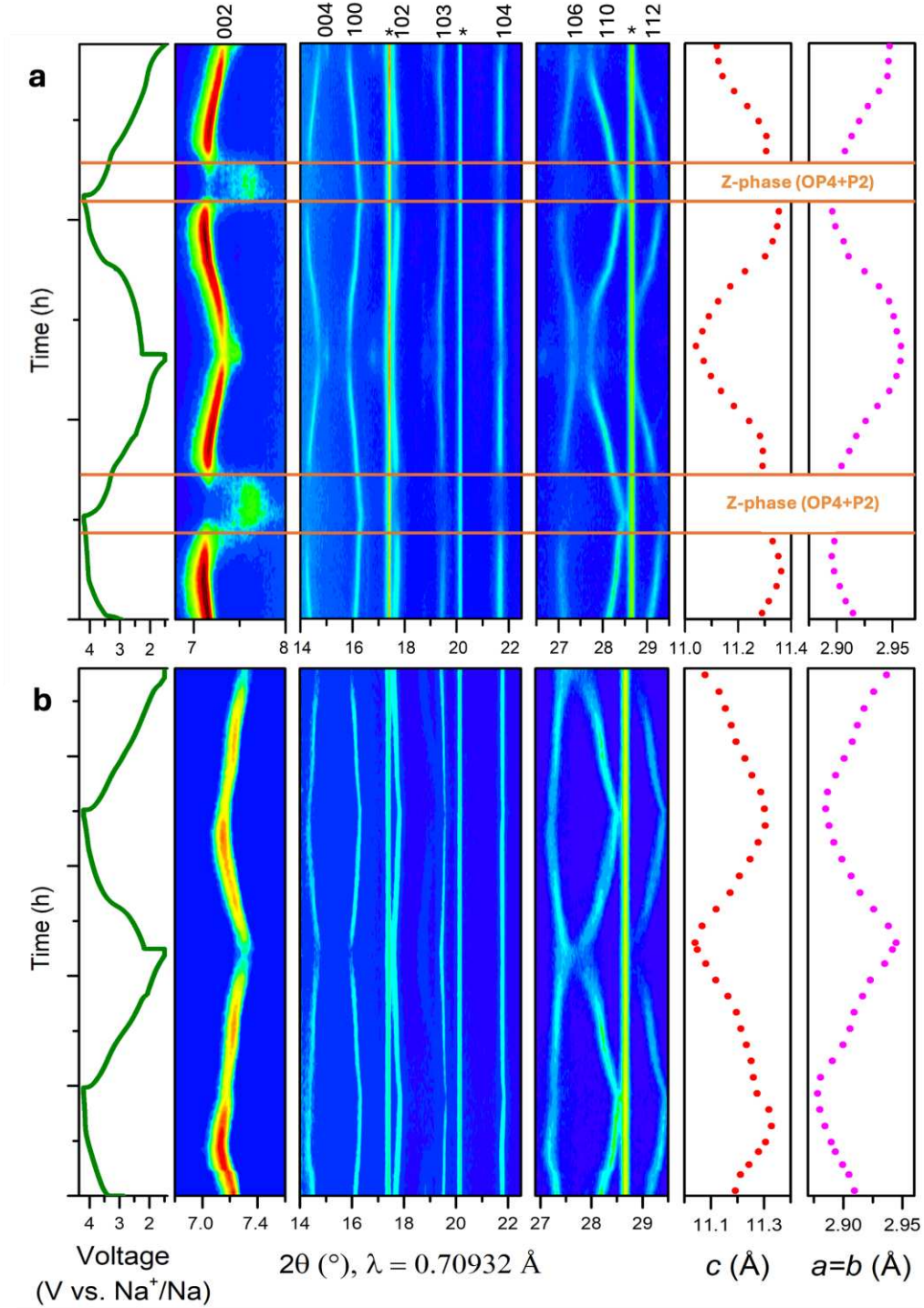


Figure 8. Operando XRD experiments performed between 1.5 V and 4.2 V for the first two charge-discharge cycles at 0.067 C and refined lattice parameters trend during the 1st and 2nd cycle for (a) SD-0 and (b) SD-02. Al (current collector) main reflections are represented by stars (*)

In accordance with the observations above, it is evident that for both $x = 0$ and $x = 0.2$, the evolution trend of c during the second cycle exhibits a greater degree of symmetry in comparison with the initial cycle, particularly with respect to the relationship between charge and discharge. This is particularly clear for $x = 0.2$: c reaches its maximum value at the end of the charge (4.2 V) rather than at ~ 4 V, indicating that during this cycle there is practically no more irreversible contributions. Nevertheless, in order to further verify this finding, advanced RIXS and XAS measurements are required.^{50,51} Furthermore, after the first and second discharge (1.5 V), a marked discrepancy in the values of c was observed between the two CAM under investigation: values ranging from 11.041(1) Å to 11.126(2) Å for $x = 0$ and from 11.041(1) Å to 11.078(1) Å for $x = 0.2$ were obtained. These differences are consistent with the observations presented in Figures 5c and 5d, as the cathodes internalized less Na^+ at the conclusion of the second discharge compared to the end of the first one. The huge divergence in these values for $x = 0$, compared to $x = 0.2$, further corroborates the enhanced reversibility of the Mg^{2+} -doped cathode.

4.2.3. Conclusion

In chapter 4.2, we discussed the properties and performance of cathode materials with composition $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$ ($x = 0, 0.2$) prepared by spray-drying synthesis. This synthesis method was chosen because of the significant advantages it offers over more conventional routes (e.g., solid-state) in terms of scalability, possibility to start with a water solution, and sustainability. SEM images collected after the spray-drying process confirm the formation of a precursor powder with the typical characteristics of this synthesis strategy: highly regular grains in terms of morphology, size, and elemental composition. XRD analysis confirmed the formation of the main P2-layered phase together with an O3-phase impurity, which is also electrochemically active. The $\text{Mg}(\text{II})$ doped material was confirmed to perform better than the not-substituted oxide: after 200 cycles at 1C, the capacity retention increased from 39% to 68%. GITT analysis revealed that, unlike materials prepared by solid-state synthesis (Chapter 3.1), $x = 0.2$ has superior diffusive properties (higher D_{Na^+}) compared to $x = 0$ in the whole working potential range. This is probably due to the presence of the active O3 phase in addition to the main P2 phase and to the different microstructure of the materials. Finally, operando XRD

experiments confirm the stabilizing effect of Mg^{2+} doping on the electrochemical performance of the layered oxide $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$, by suppressing the reversible P2–Z phase transition occurring over 4 V, during charge, for the non-substituted oxide.

4.3. Solid-state vs. Spray-drying synthesis

After analyzing the morphological, structural, and electrochemical properties of materials synthesized via conventional solid-state and the more promising spray-drying synthesis, we definitively confirmed the stabilizing effect of partially substituting Fe(III) with inactive Mg(II). The aim of the work was then to compare the properties of the cathodes prepared with the same elemental compositions ($\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ and $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$) but synthesized via the two different routes, to demonstrate how the choice of synthesis condition directly and significantly impacts the final material performance. To facilitate a clearer discussion of the results, an abbreviation was assigned to each of the four materials under study: SS-0 and SS-02 for the cathodes prepared via solid-state synthesis, while SD-0 and SD-02 for those obtained through the spray-drying procedure.

The results that will be discussed in this chapter 4.3 are contained in one of our papers published in Journal of Materials Chemistry A, titled “*Solid-state vs. Spray-drying synthesis for Mg-doped P2- $\text{Na}_{0.67}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as cathode material for Sodium-Ion Batteries*”.¹¹⁵

4.3.1. Structural-elemental properties

High-resolution XRD pattern analyses were performed to elucidate the structural differences between materials synthesized via solid-state and spray-drying routes.

Rietveld refinement reported in Figures 1a and 1b revealed that, for solid-state synthesized cathodes, the secondary impurity phase consists of electrochemically inactive spinel-like MnFe_2O_4 (space group: $Fd-3m$). For spray-drying compositions (Figure 1c and 1d), on the other hand, the secondary phase was found to be the electrochemically active O3-layered oxides structure (space group: $R-3m$). The presence of the O3 phase may be attributed to inhomogeneous mixing of sodium acetate during the spray process, which likely led to the formation of Na-rich and Na-poor domains, thereby favoring the formation of the O3 and P2 phases, respectively, during calcination. Tables 1 and 2 summarize the results obtained from the Rietveld refinement of structural models performed against the experimental powder XRD patterns. For these analyses, the

occupancy of Mn and Fe atoms was fixed at their stoichiometric values due to the inability of X-ray diffraction to differentiate between them. We applied the same constraint also for Mg-doped samples, assuming all Mg atoms substituted Fe on the $2a$ site. As indicated by the statistic factor reported under each table and the difference between the experimental and calculated profiles (blue line in Figure 1), the refinement quality for the two $x = 0$ cathodes is notably lower than that for the $x = 0.2$. This difference is attributed to stacking faults along the $\{10l\}$ family of planes in the $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ layered structure, as described by Yabuuchi *et al.*¹¹⁶ Because of this structural defect, we decided not to refine Na thermal factor (B_{iso}), instead fixing it at 3.0 for SS-0 and SD-0 (Tables 1a – 2c). This value was selected based on the B_{iso} refinement results for $x = 0.2$ (Tables 1b – 2d), which does not appear to suffer from a significant amount of stacking faults and thus allows us to refine Na B_{iso} with good accuracy. Contrary to the expectation that Mg^{2+} doping would increase the c lattice parameter due to its larger ionic size compared to Fe^{3+} , Mn^{3+} and Mn^{4+} (0.72 Å vs. 0.64 Å, 0.64 Å and 0.53 Å, respectively), we observed a notable reduction of this parameter from 11.2685(2) Å to 11.2356(2) Å and from 11.2921(4) Å to 11.2012(1) Å for solid-state and spray-drying synthesis, respectively. The decrease in the c parameter between the materials is not attributed to the $\text{Mg}(\text{II})$ substitution but, instead, to a different Na^+ content within the layers of the P2-layered structure, as we will discuss later regarding Na quantification results. In particular, a higher Na^+ positive charge can more effectively shield the O^{2-} negative charge located in the transition metal layers, enhancing the overall attraction between the layers and, thus, promoting the contraction of the elementary cell along the c axis. The $a=b$ parameter also decreases, which we can explain due to the increased oxidation state of Mn^{3+} following the introduction of Mg^{2+} , resulting in an overall reduction in the average ionic radius of the cations.

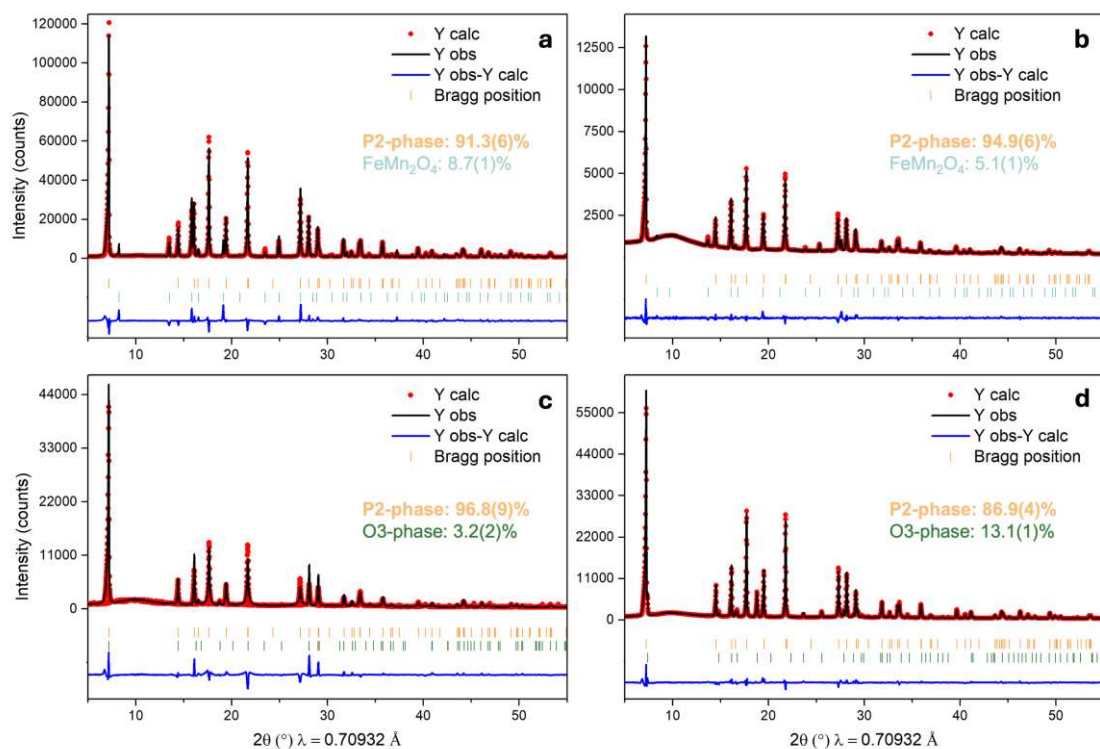


Figure 1. Rietveld refinement of the XRD pattern of (a) SS-0, (b) SS-02, (c) SD-0, and (d) SD-02. The quantification of the P2-layered oxide and the secondary phase, obtained through the refinement, is also reported for all samples

Table 1. Refined structural parameters of solid-state synthesized P2-layered oxides

a) SS-0						
Atom	Multiplicity	x	y	z	B	occ.
O	4f	1/3	2/3	0.0905(3)	0.64(7)	1.0
Fe	2a	0	0	0	0.50(2)	0.5
Mn	2a	0	0	0	0.50(2)	0.5
Na _f (1)	2b	0	0	1/4	3.0	0.200(5)
Na _c (2)	2d	1/3	2/3	3/4	3.0	0.385(6)
Space group: $P6_3/mmc$ (194), $a = b = 2.92557(3)$ Å, $c = 11.2685(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$						
Vol = 83.525(2) Å ³ . $R_p = 9.38\%$, $R_{wp} = 15.0\%$, $R_{exp} = 2.22\%$, Bragg R-factor = 6.32%						
b) SS-02						
Atom	Multiplicity	x	y	z	B	occ.
O	4f	1/3	2/3	0.0873(3)	0.92(6)	1.0
Fe	2a	0	0	0	0.60(2)	0.3
Mn	2a	0	0	0	0.60(2)	0.5
Mg	2a	0	0	0	0.60(2)	0.2
Na _f (1)	2b	0	0	1/4	3.2(2)	0.210(4)
Na _c (2)	2d	1/3	2/3	3/4	3.2(2)	0.391(5)

Space group: $P6_3/mmc$ (194), $a = b = 2.91543(3)$ Å, $c = 11.2356(2)$ Å, $\alpha = \beta = 90^\circ$,
 $\gamma = 120^\circ$
Vol = $82.705(2)$ Å³. $R_p = 4.44\%$, $R_{wp} = 6.13\%$, $R_{exp} = 4.62\%$, Bragg R-factor = 3.51%

Table 2. Refined structural parameters of spray-drying synthesized P2-layered oxides

c) SD-0

Atom	Multiplicity	x	y	z	B	occ.
O	$4f$	1/3	2/3	0.0831(4)	0.5(1)	1.0
Fe	$2a$	0	0	0	0.56(2)	0.5
Mn	$2a$	0	0	0	0.56(2)	0.5
Na _f (1)	$2b$	0	0	1/4	3.0	0.227(6)
Na _c (2)	$2d$	1/3	2/3	3/4	3.0	0.261(7)

Space group: $P6_3/mmc$ (194), $a = b = 2.91998(5)$ Å, $c = 11.2921(4)$ Å, $\alpha = \beta = 90^\circ$,
 $\gamma = 120^\circ$
Vol = $83.381(4)$ Å³. $R_p = 9.57\%$, $R_{wp} = 13.4\%$, $R_{exp} = 3.33\%$, Bragg R-factor = 8.76%

d) SD-02

Atom	Multiplicity	x	y	z	B	occ.
O	$4f$	1/3	2/3	0.0905(2)	1.04(4)	1.0
Fe	$2a$	0	0	0	0.66(1)	0.3
Mn	$2a$	0	0	0	0.66(1)	0.5
Mg	$2a$	0	0	0	0.66(1)	0.2
Na _f (1)	$2b$	0	0	1/4	2.5(1)	0.212(2)
Na _c (2)	$2d$	1/3	2/3	3/4	2.5(1)	0.380(3)

Space group: $P6_3/mmc$ (194), $a = b = 2.91269(2)$ Å, $c = 11.2012(1)$ Å, $\alpha = \beta = 90^\circ$,
 $\gamma = 120^\circ$
Vol = $82.297(1)$ Å³. $R_p = 5.30\%$, $R_{wp} = 7.36\%$, $R_{exp} = 3.06\%$, Bragg R-factor = 3.55%

The morphology of the materials has already been individually described in Sections 4.1.2.1 and 4.2.2.1. Since all samples are the product of high-temperature calcination (800 °C for SD and 1000 °C for SS), the grains exhibit a similar prismatic shape with micrometric dimensions. However, it is important to note that the starting precursors differ significantly between the two synthesis routes: commercial oxides were employed for the solid-state synthesis, whereas a powder derived from the spray process was used for spray-drying. For this reason, we hypothesize that the resulting microstructure and porosity are markedly different. In addition, the average grain size distributions reported in Figure 2 indicate that spray-drying (blue bars) yields smaller grains with a narrower

size distribution compared to solid-state synthesis (red bars), as further highlighted by the standard deviation associated with each result.

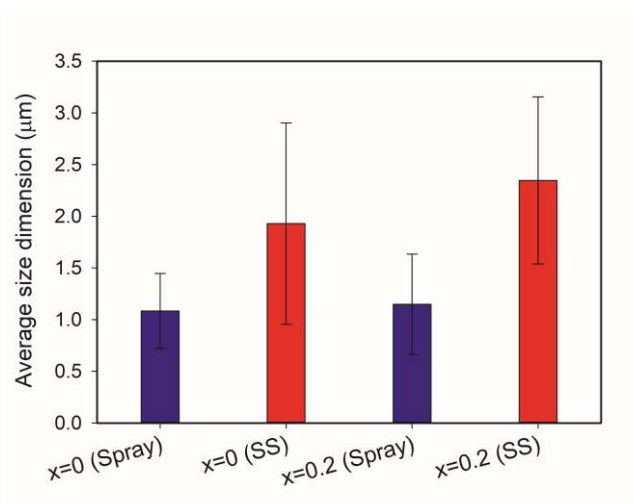


Figure 2. Average size dimension of materials synthesized by solid-state (SS) and Spray-Drying (Spray) calculated from SEM images

The elementary composition of the cathodes was evaluated and verified through ICP-OES analysis, whose results were previously discussed in chapter 4.1.2.1 and 4.2.2.1. However, since the Na content is recognized as one of the most influential factors affecting the structural-electrochemical properties of the P2-layered oxide cathode materials, we tried to accurately assess the stoichiometry of the cathodes by comparing ICP-OES and Rietveld refinement results for the Na quantification, as summarized in Table 3 and Figure 3.

Table 3. Comparison of Na content of all the cathodes under investigation derived from ICP-OES analysis and Rietveld refinements (XRD)

	Solid-State		Spray-Drying	
	ICP-OES	XRD	ICP-OES	XRD
$x = 0$	0.491	0.59(1)	0.449	0.49(1)
$x = 0.2$	0.565	0.601(9)	0.607	0.592(5)

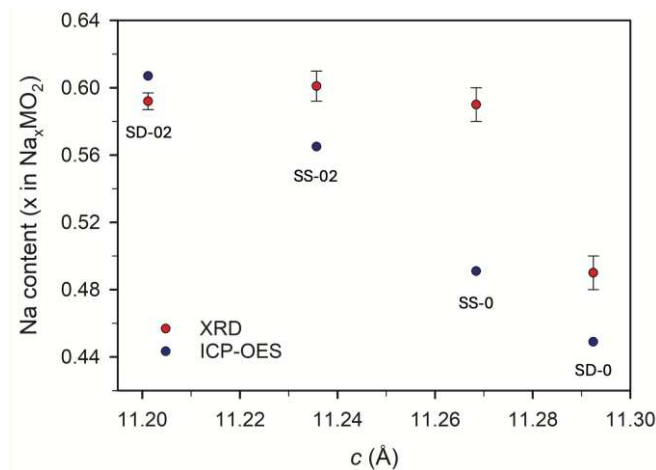


Figure 3. Comparison of Na content of all the cathodes under investigation derived from ICP-OES analysis and Rietveld refinements (XRD)

In general, we observe a reasonable agreement between ICP and XRD results, which improves, however, for SD samples over SS samples, and further for Mg-doped samples vs. undoped ones. The poor agreement in the case of undoped SD may be due to the stacking faults issue previously discussed, so that the Na quantification derived from the Rietveld refinement is expected to be less reliable than that obtained by ICP-OES, particularly for the $x = 0$ samples. Therefore, for all the electrochemical characterizations, we considered only the Na content obtained from ICP-OES analysis.

4.3.2. Electrochemical performances

To assess the influence of synthesis conditions on the electrochemical performance, we compared the cathodic properties between SS-0 and SD-0 and between SS-02 and SD-02 (Figures 4a and 4b, respectively). This comparison reveals that for both $x = 0$ and 0.2, spray-drying led to superior cathodic performance than solid-state synthesis. The good specific capacity recovery following cycles at 0.5C confirms the structural stability of all the materials, regardless of the type of synthesis. Interestingly, for the same elemental composition, the difference in capacity observed between the two synthesis methods is significantly more pronounced for $x = 0$ than for $x = 0.2$. This difference highlights that, for the unsubstituted oxide, whose composition is not optimized through Mg(II) doping, the choice of synthesis method leads to a marked performance improvement. As already mentioned in the introduction, the microstructure of spray-dried materials is indeed more

suitable for application in battery cathodes compared to that of solid-state materials. On the other hand, although $x = 0.2$ shows a lower performance enhancement between the two synthesis methods compared to $x = 0$, the discharge capacities achieved with both synthesis approaches are considerably higher. Therefore, it can be concluded that Mg(II) substitution exerts a generally more impactful stabilizing effect than the choice of synthesis route. However, it is essential to keep in mind that scan rate tests provide valuable insights during the early characterization of a material, particularly for understanding behavior at different current densities. Still, these tests alone are insufficient for the comprehensive evaluation of new material. In order to gain deeper insight into the material properties and to further stress the layered structure of the different cathodes, with the aim of better highlighting the stabilizing effect of Mg^{2+} over cycling and the differences in performances between different syntheses, we conduct long tests (100 cycles) at high C-rate (1C). Before cycling at 1C, we performed six pre-cycles at lower current densities (2 cycles at 0.13C, 2 at 0.25C, and 2 at 0.5C) to better stabilize the materials' structure and the cathode electrolyte interface.

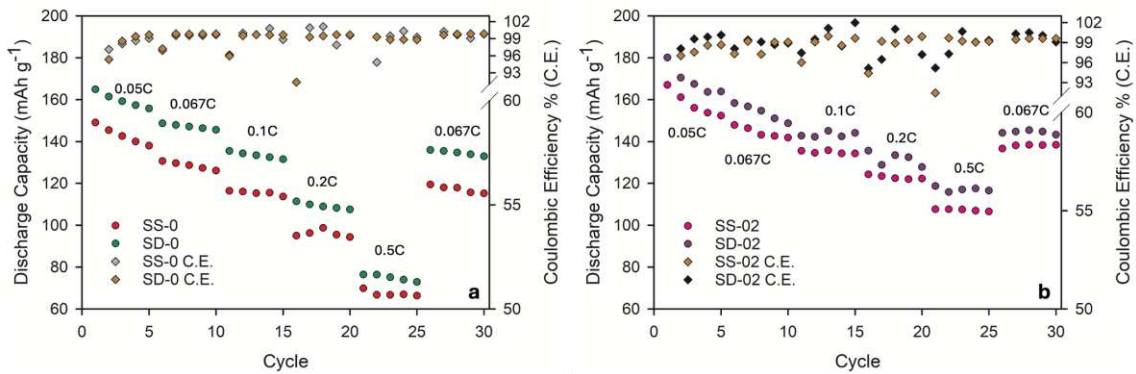


Figure 4. GCPL experiments results on the cathodes under investigation at different C-rates between 1.5 V and 4.2 V. Comparison of discharge capacity and Coulombic Efficiency (C.E.) between (a) SS-0 and SD-0 and (b) SS-02 and SD-02

Figure 5 compares the average discharge capacity and coulombic efficiency (calculated over two tests performed on each sample) for the two compositions prepared by both synthesis routes. For $x = 0$ (Figure 5a), the calculated capacity retention after 100 cycles is 50% for SD-0 and 44% for SS-0. Coulombic efficiency remained consistently high (>95%) for both cathodes. The differences for the Mg-doped oxides (Figure 5b) are more pronounced: after 100 cycles, capacity retention is 81% and 72% for SD-02 and SS-02,

respectively. Moreover, the coulombic efficiency was consistently maintained above 99% for both cathodes. The differences in discharge capacity across the two different synthesis methods employed, at the same compositions, corroborate that the Mg(II)-doping exerts a greater influence on cathodic performance than the choice of the synthesis route, in agreement with the rate capability tests results. In particular, for $x = 0.2$, the difference in capacity retention is nearly twice that of the undoped oxide, clearly indicating that the combination of an appropriate synthesis method with the stabilizing effect of Mg(II) represents a highly effective strategy for the development of high-performance cathode materials, as it leverages the advantages of both optimization approaches.

By comparing the results achieved for our best material (SD-02) with similar studies reported in the literature, we noticed that it's very promising in terms of performance. P2/O3 usually led to higher performances than single P2 or O3 phases. For example, P2/O3- $\text{Na}_{0.85}\text{Ni}_{0.34}\text{Mn}_{0.33}\text{Ti}_{0.33}\text{O}_2$ demonstrated a capacity retention of 80% after 200 cycles at 1C,¹¹⁷ while the High Entropy Oxide (HEO) with composition P2- $\text{Na}_{0.85}\text{Li}_{0.08}\text{Mg}_{0.04}\text{Ni}_{0.22}\text{Al}_{0.04}\text{Mn}_{0.62}\text{O}_2$ showed 72% retention after 200 cycles at 150 mA g^{-1} , due to the high configurational entropy that helps stabilize cathodic properties during cycling.¹¹⁸ The nature of the dopant cation also plays a crucial role in determining performance. For instance, $\text{Na}_{0.67}\text{Fe}_{0.5}\text{Mn}_{0.45}\text{Al}_{0.05}\text{O}_2$ exhibited excellent stability, maintaining over 90% of its initial capacity after 200 cycles at 1C,⁴⁶ mainly because of Al^{3+} -role in suppressing the Jahn-Teller distortion associated with Mn^{3+} presence. Overall, the electrochemical performance of SD-02 appears highly promising and in line with the best results reported in the literature.

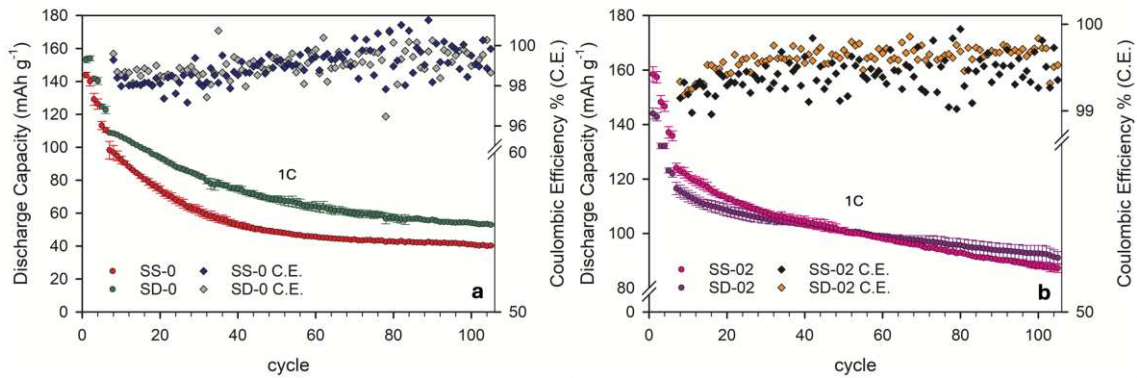


Figure 5. Long-term cycling test at 1C. Comparison between discharge capacity and coulombic efficiency for: (a) SS-0 and SD-0, (b) SS-02 and SD-02

We also conducted GITT experiments (see Figure 6) to gain a clearer understanding of the intrinsic differences between materials with identical compositions but prepared through different synthesis routes by examining the evolution of the sodium diffusion coefficient (D_{Na^+}) during cycling.

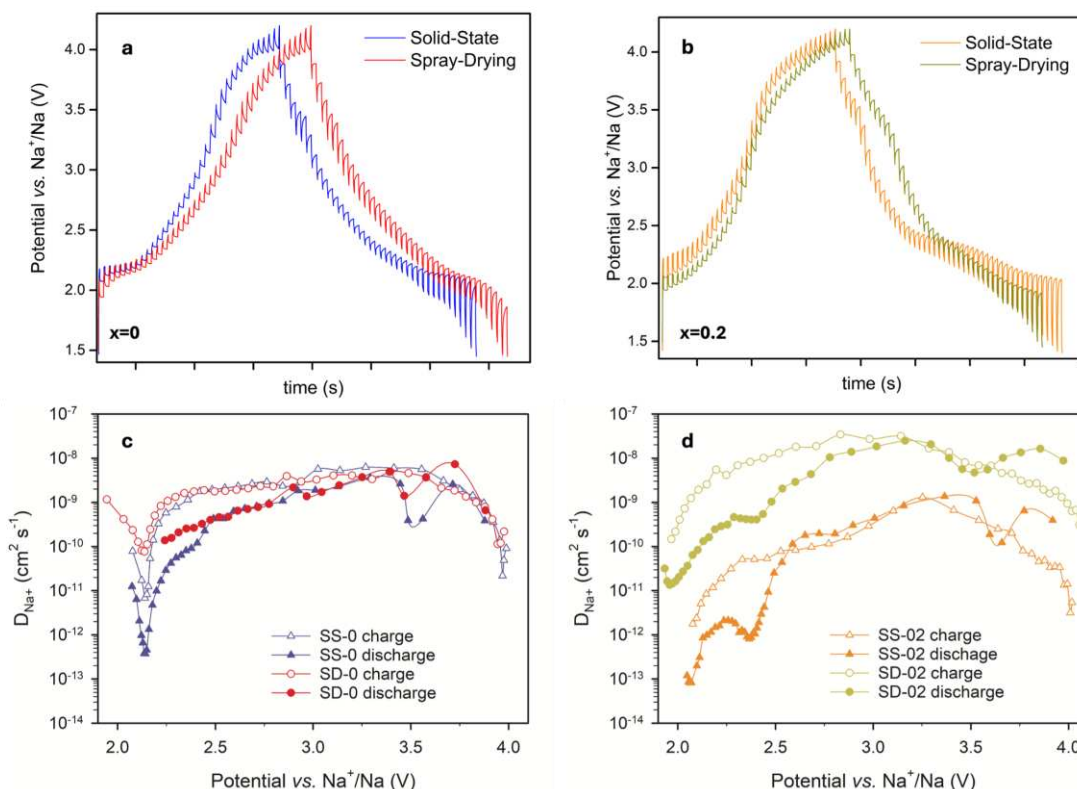


Figure 6. GITT charge-discharge curves (at 0.067 C) and calculated Na^+ diffusion coefficient (D_{Na^+}) for (a-c) $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ and (b-d) $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$

Figures 6a and 6b show the charge-discharge profiles (2nd cycle) recorded for the four materials under investigation. The analysis of these curves allows for a qualitative assessment of cathode kinetics by evaluating the overpotential (η), calculated as the difference between the potential at the end of the current pulse and the end of the relaxation period.^{119,120} This parameter is particularly insightful in the voltage regions corresponding to the Fe(II)/Fe(III) and Mn(II)/Mn(III) redox activity. Notably, the lower η observed in SD-02 compared to SS-02 indicates superior and faster kinetics.

As reported in Figures 6c and 6d, the diffusion coefficient trend shows significant decreases in the voltage regions where electrochemically active phenomena occur for all the materials under investigation. However, GITT cannot be deemed reliable at these potentials because the approximations made for calculating D_{Na^+} only apply when the

materials exhibit solid-solution-like behavior.¹²¹ In particular, Figure 6c shows that SS-0 and SD-0 exhibit similar D_{Na^+} during charge. However, during discharge, SD-0 demonstrates a slightly higher Na^+ diffusion, which may account for the improved performance discussed above. Nonetheless, since D_{Na^+} is consistently lower during discharge than charge, we can conclude the Na^+ intercalation process is the rate-limiting step in the electrochemical reaction. For P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ (Figure 6d), the D_{Na^+} differences between the two syntheses are significantly enhanced compared to the non-substituted oxides. Interestingly, even for this composition, Na^+ insertion appears to be slower than Na^+ extraction. The most interesting result, however, is the D_{Na^+} increase by more than two orders of magnitude for SD-02 compared with SS-02. This remarkable increase can be explained by considering: i) the different microstructure of spray-drying materials compared to solid-state ones, which is inherently more suitable for the design of high-performance electrode materials; ii) the different surface area of the two electrodes, which significantly influences the D_{Na^+} calculation; iii) the presence of an electrochemically active impurity phase in SD-02 (O3-layered phase) compared to the inactive FeMn_2O_4 of SS-0, whereby only the former would contribute to the overall sodium diffusion during cycling; iv) the coexistence of mixed P2/O3 phases for SD-02 compared to the pure P2 phase of SS-02. As previously mentioned in the introduction, the co-existence of both P2 and O3 can, in some cases, lead to enhanced Na^+ diffusion compared to pure P2 or O3 materials, because the advantages of both phases can be fully exploited.¹²² The presence of multiple interfaces in the grains composed of both P2 and O3 phases offers additional channels and active sites for enhancing the Na^+ diffusion upon cycling.¹²³ For this reason, Na^+ ions can move to and from the P2/O3-layered structure with faster kinetics and increased diffusion rate during cycling.

4.3.3. Conclusion

In Chapter 4.3, the impact of varying synthesis conditions on the electrochemical and structural characteristics of novel cathodic materials for sodium-ion batteries was examined. The present study investigates the potential of spray-drying synthesis as a promising method for the preparation of new cathodes. This approach offers advantages over conventional solid-state synthesis in terms of both sustainability (lower calcination

temperature and a water-based process) and functional properties. The GITT study allowed us to study the intrinsic kinetics and diffusion properties of the materials under investigation and correlate them with the observed electrochemical performance. The results of these tests, in particular concerning the η and the D_{Na^+} evolution trend analysis, allowed us to justify the significant increase in performance of the material synthesized by spray-drying compared to the solid-state synthesized material. Based on these findings, SD-02 demonstrated superior structural and electrochemical performance compared to the other materials. Moreover, we confirmed that the mixed P2/O3 phases in SD-02 are beneficial for the cathodic performances, as it allows for the exploitation of the distinct properties inherent in the crystal structures. The synergic effect between spray-drying synthesis and the doping of P2– $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_2$ with electrochemically inactive Mg^{2+} offers a highly effective strategy for advancing the design of new and promising cathodes. In conclusion, this integrated approach between the correct choice of the synthesis routes and the optimization of the elementary composition underscores the potential for enhancing the functional properties of the electrode materials and provides a robust framework for the development of advanced materials with improved performance. This methodology represents a promising direction for future research and commercialization of next-generation batteries.

4.4. Full-Cell configuration

In light of the detailed characterization carried out in Chapter 4.1, it has been confirmed that the most promising and high-performing material among those investigated as potential cathodes for sodium-ion batteries (SIBs) is the layered oxide with composition $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$. For this reason, based on the structural and functional properties previously discussed, we decided to evaluate the performance of this material in a full-cell configuration, simulating the behavior of a real battery system. This step is crucial for assessing the true development and scale-up potential of a material, as full-cell assembly requires consideration of multiple additional parameters compared to half-cell testing, which has already been extensively described in the introduction. These parameters include the presence of the anode, the charge balance between the two electrodes (N/P ratio), and the optimization of the operating voltage window. Moreover, the amount of sodium in the cathode material becomes a critical factor, as it represents the only source of Na in the full-cell configuration. This contrasts with half-cell systems, where the Na metal counter electrode acts as an almost unlimited reservoir of Na^+ ions during cycling.

To address these challenges, we prepared various full-cells with different N/P ratios to identify the optimal operating conditions. We also investigated different electrode pre-sodiation strategies, previously reported in the literature for other materials, including electrochemical pre-sodiation of the anode and the use of sacrificial salts.

4.4.1. Materials and methods

4.4.1.1. Hard-Carbon pre-treatments

A commercial hard carbon (HC) was used as the anode material, specifically Kuranode type II from Kuraray, which is widely reported in the literature for SIBs. Using a commercial HC helped eliminate the variability that could arise from using a lab-prepared material. Before use, the HC was dried in a vacuum oven at 60 °C overnight to remove any surface-adsorbed impurities and/or residual moisture (H_2O).

4.4.1.2. Cathodes preparation

For full-cell configuration tests, we aimed to increase the CAM mass loading (mg/cm^2) on the electrode. To achieve this, we used an 85:7.5:7.5 ratio between the three components, instead of the 80:10:10 ratio used for half-cell experiments, with a 40% solid content in the slurry. Elsewhere, the cathodes were prepared following the procedure described in Chapter 4.1.1.2.

For the tests carried out using Na_2CO_3 as a sacrificial salt, the slurry was prepared with a composition of 85- x :7.5:7.5, where $x = 10$ wt.% of Na_2CO_3 .

4.4.1.3. Anodes preparation and full-cell assembly

The anode slurry was prepared by using 90 wt.% of HC, 5wt.% of Conductive Carbon black (C65), and 5 wt.% of a binder composed of a water-based solution of Carboxymethyl Cellulose (CMC) and Styrene-Butadiene Rubber (SBR) 1:1 m/m. The solid content of all slurries was ~ 26 wt.%. Initially, CMC was dissolved in an appropriate volume of deionized water. Subsequently, the HC active material was incorporated into this solution and stirred for 30 minutes. Following this step, an SBR aqueous suspension (50 wt.% concentration) was added dropwise to the mixture under continuous magnetic stirring until a homogeneous product was achieved (~ 2 h). The obtained slurry was cast on an Al (current collector) foil using a doctor blade with a wet thickness of $250\ \mu\text{m}$, and then it was dried for 30' under vacuum (500 mbar) at $45\ ^\circ\text{C}$ to prevent moisture and oxygen contamination. The anode was finally cut into $2\ \text{cm} \times 2\ \text{cm}$ disks and stored in an Ar-filled glove box (MBraum, O_2 , $\text{H}_2\text{O} < 0.5\ \text{ppm}$) before the electrochemical measurements. The full-cells were assembled following the same procedure used for the half cells tests, with the only difference being the replacement of the Na metal counter-electrode with the HC anode prepared as above. As electrolyte, a 1 M NaPF_6 solution in Ethylene Carbonate: Dimethyl Carbonate + 2 wt.% Fluoroethylene Carbonate (FEC) was employed.

4.4.1.4. Structural, elementary, and morphological characterization

Morphologies of the pristine HC powder and the electrodes (both anodes and cathodes) pre- and post-cycling were investigated through SEM analysis. We used a SEC SNE-4500 M Plus microscope equipped with a EDX analysis system to collect SEM images. XRD patterns were all collected with a Bruker D8 Advance diffractometer, equipped with Mo-K α 1 radiation ($\lambda = 0.70932 \text{ \AA}$, 50 kV, and 40 mA), in the 5-30° 2 θ range and with 0.02° step.

4.4.1.5. Electrochemical characterization

HC was preliminarily characterized in half-cell configuration with a Bio-Logic BCS-810 through Galvanostatic Cycling with Potential Limitation (GCPL) at different C-rates, in the working potential window 0.01 V-1.5 V. In particular, HC was charged in Constant Current (CC) and discharged in Constant Current-Constant Voltage (CC-CV) mode, with CV step limited when current drops to 5% of the initial value applied during the constant current (CC) step.

Regarding full-cell, based on recent literature on similar materials, we choose as the working potential window the range between 1 V and 4 V.⁷⁸ The electrochemical performances of the batteries were investigated in CC-CV mode during charge, while in CC during discharge. A CV step at the top of the charge is required to complete the desodiation of the P2-layered cathode, thereby maximizing battery performance. This step is considered complete when the current measured by the potentiostat drops to 5% of the initial value applied during the constant current (CC) step.

Electrochemical pre-sodiation of the HC electrodes was performed by assembling half-cells vs. Na_(m) and discharging them in CC-CV mode down to 0.01 V. At this point, the half-cells were disassembled in a glovebox (inert atmosphere, Ar), the pre-sodiated electrode was recovered, and then used in a new full cell.

4.4.2. Structural and Elementary Analysis of Hard Carbon

Figure 1 shows the XRD pattern collected on the HC powder. Both indexed peaks are very broad, as expected from the quasi-amorphous structure typical of hard carbon, as also mentioned in the Introduction (Chapter 1.3.3.1). Unlike graphite, which exhibits a highly ordered crystalline structure, hard carbons feature a highly disordered structure composed of many small and ordered domains randomly oriented with respect to each other. As a result, hard carbon is practically amorphous over long-range order. Additionally, the position of the (002) reflection (d_{002}) provides information about the interlayer distance within the ordered domains, which is significantly larger than that of graphite ($d_{002} = 0.335 \text{ \AA}$). In this specific hard carbon, d_{002} is approximately $3.9 \text{ \AA}$.

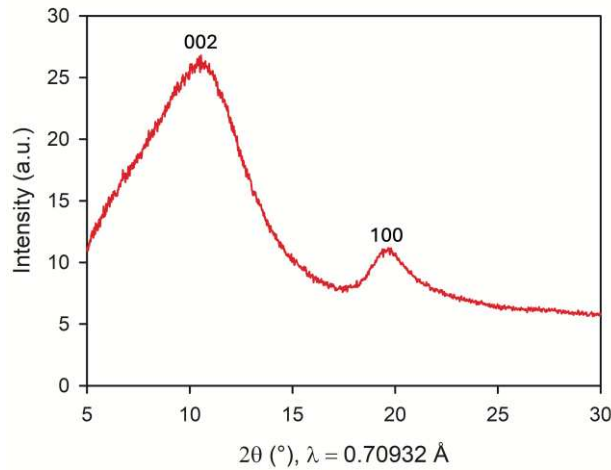


Figure 1. XRD pattern on Kuranode type II Hard Carbon powder

The morphology of HC powder was evaluated through SEM analysis. Figure 2 indicates that Kuranode type II has irregular and prismatic-like grains, with micrometric dimensions. Since HC is the product of calcination at very high temperature ($>1200 \text{ °C}$) of carbon-based materials, the features mentioned above are expected.

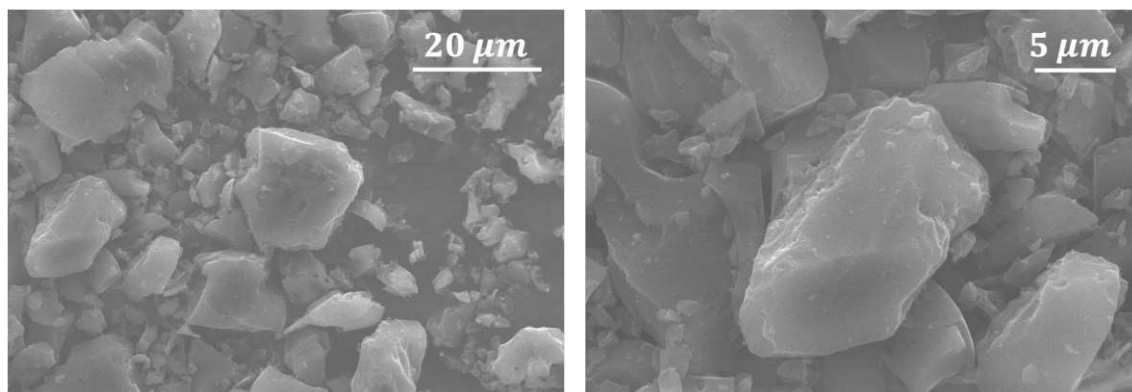


Figure 2. SEM images collected on Kuranode type II Hard Carbon powder at different magnifications

4.4.3. Electrochemical Characterization

4.4.3.1. Hard Carbon

Prior to its utilisation as an anode within a full-cell configuration, the electrochemical performance of the HC was evaluated in a half-cell configuration in comparison to Na^+/Na . This preliminary characterization enabled the subsequent optimization of operational parameters and enhancement of performance in full-cell tests. Initially, the electrode preparation procedure was optimized, with particular emphasis on solid loading and the ratios between active material, binder, and conductive carbon.

Since the slurry could be prepared in water, we opted for this more sustainable route compared to the use of NMP, which is instead required for the cathode. However, since the solid loading of aqueous slurries plays a crucial role in ensuring good adhesion to the Al current collector, several tests were conducted under different experimental conditions to optimize this parameter. As illustrated in Figure 3, even minor alterations in solid loading can yield substantial variations in outcomes. A solid loading of 26% yielded optimal results in terms of both slurry homogeneity and adhesion to the Al current collector.



Figure 3. Experimental photos collected after casting anodic slurry with a 90:5:5 (HC:binder:carbon) composition, prepared with different solid loadings, on the Al current collector

Regarding the ratios between the electrode components, three different compositions were tested, all with decreasing conductive carbon content: (i) 90:5:5, (ii) 92.5:2.5:5, and (iii) 95:5. As mentioned in the Introduction (Chapter 1.3.4), one of the key parameters to assess for HC anodes is the Initial Coulombic Efficiency (ICE), which accounts for the amount of Na^+ loss between the end of the first discharge (fully sodiated HC) and the end of the first charge (desodiated HC). This Na^+ loss is primarily due to the formation of the Solid Electrolyte Interphase (SEI), which is essential for the stable operation of the battery. HC with higher ICE is preferred, as they ensure higher performance and lower Na loss. While this aspect is uncritical in half-cell, where the metallic Na used as a counter-electrode acts as a quasi-infinite sodium reservoir, it becomes crucial in full-cell configurations, where all Na^+ cations come from the cathode. These considerations also apply to LIBs, but they are even more critical for SIBs, as one of the main limitations to the P2-layered oxides cathodes commercialization is the low sodium content of the pristine material. Thus, minimizing initial Na^+ consumption due to SEI formation is fundamental to ensuring good performance over cycling.

Figure 4 shows the first three cycles recorded for all the different electrode compositions, with the respective calculated ICE. For 95:0:5 (Figure 4a), it was impossible to calculate it because the material didn't reach the top of the charge (1.5 V) during the first cycle, and the voltage didn't have a linear behavior like the other reported. For these reasons, we considered 95:0:5 not suitable for our purpose and excluded it from the following characterization and comparison with the other compositions.

No significant differences were observed when comparing the charge-discharge profiles of the 90:5:5 (Figure 4b) and 92.5:2.5:5 (Figure 4c) compositions. The variation in slope observed between the 1st and 2nd discharge, particularly in the 0.6 V-0.8 V range, can be

attributed to the effect of FEC addition in the electrolyte mixture. During the first sodiation step, FEC decomposes at these potentials along with the NaPF_6 salt and the carbonate forming the electrolyte, leading to the formation of a more stable SEI on the HC electrode surface compared to that formed using an additive-free electrolyte.^{102,124–126}

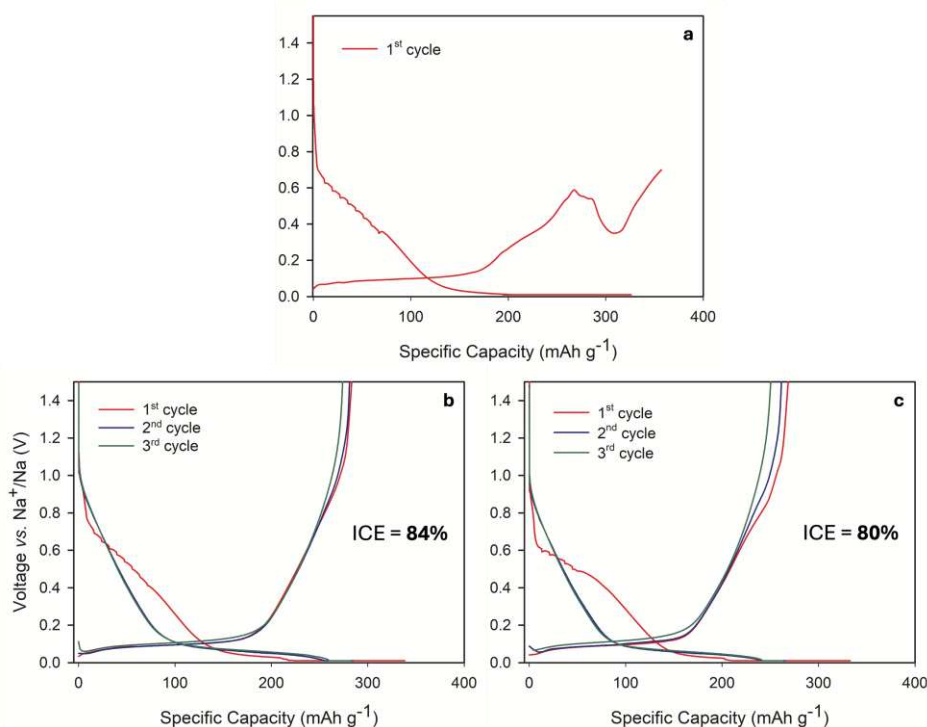


Figure 4. First charge-discharge cycle recorded for anode prepared with different HC:conductive carbon:binder compositional ratio: (a) 95:0:5, (b) 90:5:5, and (c) 92.5:2.5:5 cycled between 1.5 V and 0.01 V vs. Na^+/Na at 0.03C

From the second cycle onward, no further decomposition processes are expected, and indeed, the voltage profiles become more reversible and ascribable only to the insertion of Na^+ ions in the HC structure, particularly: (i) between the graphitic layers within the ordered domains, and (ii) into the pores formed between the domains, as also discussed in the introduction (Chapter 1.3.3.1). Concerning ICE, 90:5:5 proved to be the most promising composition, with an initial efficiency of 84% compared with 80% calculated for 92.5:2.5:5. In addition, the charge-discharge curves are also more overlapping during the 2nd and 3rd cycles, indicating higher reversibility in electrode processes and less capacity loss during cycling.

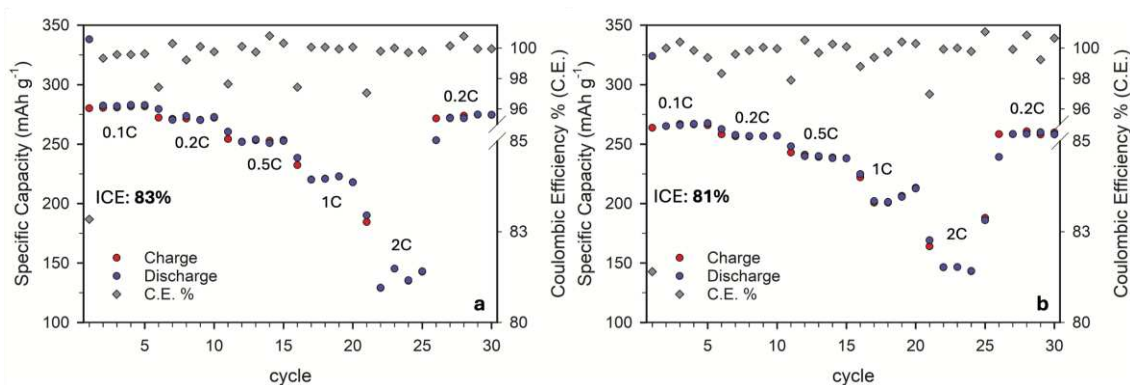


Figure 5. Rate capability test recorded for anode prepared with different HC:conductive carbon:binder compositional ratio: (a) 90:5:5, (b) 92.5:2.5:5 cycled between 1.5 V and 0.01 V vs. Na^+/Na at different C-rates in CC-CV (discharge) and CC (charge) mode

To definitively confirm that the electrode with a 90:5:5 composition is the most effective, rate capability tests were conducted to evaluate potential differences in behavior at varying current densities. The results of this analysis are presented in Figure 5. The calculated ICE is consistent with the values previously discussed, with a specific capacity loss of about 60 mAh g^{-1} for both the compositions after the first discharge. Considering the difference in C-rates used for the first cycles for the two tests (0.03C and 0.1C), we can conclude that, for this HC, the ICE remains stable regardless of the applied current density. Although both compositions exhibit consistently high coulombic efficiency, the 90:5:5 electrode demonstrates lower variability across all cycles, maintaining values consistently above 99%. Furthermore, the recorded discharge capacities for both compositions are comparable, with no significant differences observed. The results of the study, when considered as a whole, provide further confirmation that the composition of 90:5:5 is optimal for this HC anode. Consequently, this anodic composition will be used for all subsequent full-cell configuration tests.

4.4.3.2. Full-Cell

4.4.3.2.1. N/P ratio optimization

Despite the electrochemical performances of $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ being already fully characterized and discussed in Chapter 4.1.2.2. Before testing it in a full-cell with HC anode, we performed a rate capability test under the same conditions used for HC and

described in the methods section. The results of this analysis are shown in Figure 6. This test was crucial to evaluate the behavior of the P2-type structure during charging and discharging in CC-CV and CC mode, respectively, as for a real battery. In addition, since we cycled the full cells up to 4.0 V instead of 4.2 V (as in previous half-cell tests) to avoid capacity fading and instability related to the irreversible oxygen redox activity and the electrolyte decomposition at high voltage, this test also allowed us to assess cathode performance within the 1.5 V- 4.0 V working potential range.

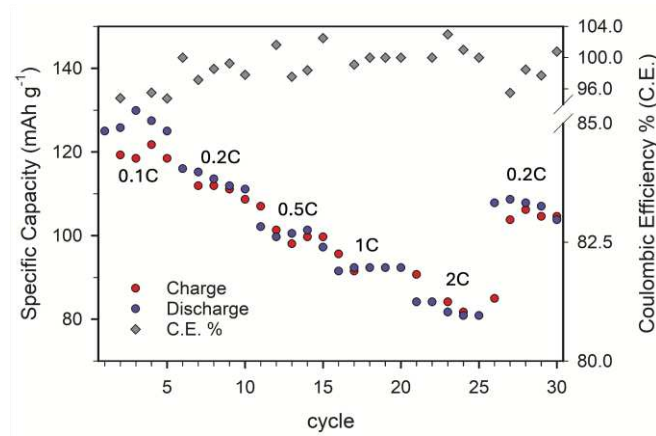


Figure 6. Rate capability test for P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ cathode between 1.5 V and 4 V, vs. Na^+/Na at different C-rates in CC-CV (charge) and CC (discharge) mode

At this stage, having thoroughly characterized and discussed the performance and properties of both electrodes under investigation, we proceeded to assemble full cells using $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ as the P2-type cathode and HC as the anode. However, compared to the previously discussed half-cells, the design and optimization of full cells requires consideration of a greater number of parameters. Among these, the proper balance between the capacity available at the anode and that at the cathode is undoubtedly one of the most critical. This factor is commonly referred to as the N/P ratio, and is calculated as:

$$\frac{N}{P} = \frac{\text{specific capacity per unit area (Anode)} [\text{mAh cm}^{-2}]}{\text{specific capacity per unit area (Cathode)} [\text{mAh cm}^{-2}]}$$

N/P ratio represents one of the key parameters that must be optimized during the characterization of full-cell batteries, regardless of the chemistry (e.g., LIBs, SIBs, solid-

state batteries), because it directly influences the stability, the lifetime, and the energy density of the battery. For all these reasons, we assembled four different coin cells with different N/P ratios. Table 1 reports the experimental parameters for every test, in particular: i) the mass of active material (in mg) of P2-layered cathode and HC on the electrode; ii) the specific capacity per unit area (in mAh cm⁻²) on both the anode and the cathode, and iii) the calculated N/P ratio. The theoretical capacity of the electrodes was evaluated based on the average reversible capacity achieved during the first five cycles at 0.1C, as shown in Figures 5a and 6.

Table 4. Summary of Cathode and Anode experimental parameters used for N/P Ratio optimization tests

C _{theo} (cathode) = 130 mAh g ⁻¹ C _{theo} (anode) = 280 mAh g ⁻¹ electrode area = 2.01 cm ²					
	P2-Na _{0.67} Mn _{0.5} Fe _{0.3} Mg _{0.2} O ₂		Hard Carbon		N/P
	mg	mAh cm ⁻²	mg	mAh cm ⁻²	
1	22.015	1.42	7.89	1.1	0.77 --> 0.8
2	12.257	0.78	5.301	0.74	0.95 --> 1
3	15.1725	0.98	8.35	1.16	1.18 --> 1.2
4	8.1515	0.53	5.256	0.73	1.37 --> 1.4

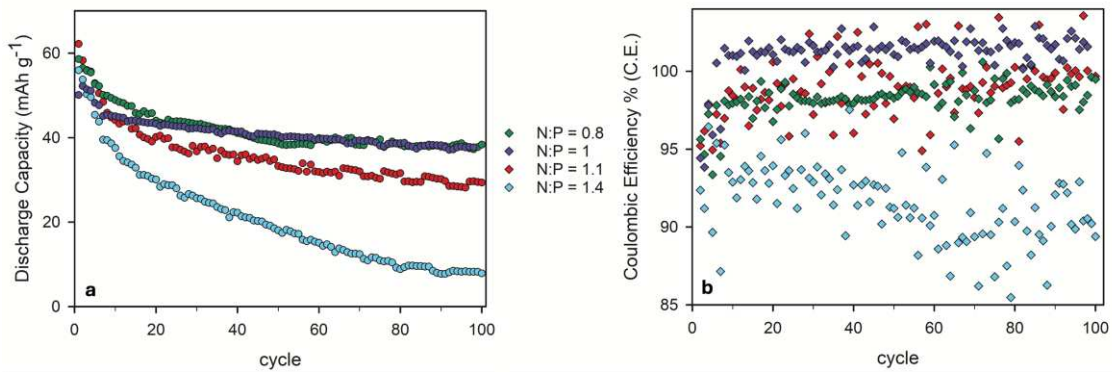


Figure 7. Comparison of (a) discharge capacity and (b) coulombic efficiency % for full-cell assembled with different N/P ratios, in the working potential window 1 V- 4 V

Figures 7a-b compare the discharge capacity and the calculated coulombic efficiency for all the different N/P ratios tested. The analysis of these results confirmed the findings reported by Song *et al.*⁷⁸ regarding the performance as a function of the N/P ratio in a

full-cell with configuration: O3-layered oxide | HC. Now, we can extend these conclusions to P2-layered cathode structures as well. In particular, N/P ratios greater than 1 were confirmed to be detrimental to battery performance. In such cases, the areal capacity of the anode significantly exceeds that of the cathode, forcing the latter to operate beyond its stability window to compensate for the excess capacity on the anode side. This leads to phase transitions and active material loss, resulting in an overall decline in performance, clearly observable by comparing the capacity retention after 100 cycles (Figure 7a) for the different N/P ratios. The best-performing N/P ratio was found to be equal to 1, with a capacity retention of 80% and a stable specific capacity of approximately 40 mAh g⁻¹. For N/P = 0.8, additional considerations must be made, as the limiting electrode is now the cathode rather than the anode. Under these conditions, the main issue may be sodium plating on the surface of the anode, as the HC sites are insufficient to accommodate all the Na⁺ ions extracted from the cathode.

A comparison of the capacity trends in Figure 7a for N/P = 0.8 and 1 shows that the difference in the capacity retention (74% and 80%, respectively) can mainly be attributed to the first 20 charge-discharge cycles. Beyond that point, the performance become nearly identical. Furthermore, the analysis of the coulombic efficiencies reported in Figure 7b shows that the cell with N/P = 1 exhibited a value closer to 100% throughout all cycles and significantly lower variability compared to the other cases. In light of these results and considerations, we may conclude that the full-cell with N/P ratio = 1 is the best performing one, and so we decided to adopt it for all the next tests we'll discuss in the next chapter.

After cycling, we conducted some post-mortem analysis on both the electrode to evaluate whether the different N/P ratios directly modify the structural and morphological properties of the material. In particular, we focused on N/P = 0.8 and 1.2. We first investigate the morphology of the HC anode after cycling. Figure 8 shows SEM images, at different magnifications, collected on the anode's surface and cross-section for both the N/P ratios under investigation. To better highlight changes in morphology before and after cycling, we also acquired the same images on a pre-cycling electrode (OCV). In contrast to the pristine electrode, two distinct morphologies were detected on the surface of both cycled electrodes, highlighted in orange and red in the figures. The red-marked regions correspond to HC grains, consistent with the morphology observed on the OCV electrode

and the powder shown in Figure 2. In contrast, the orange-highlighted regions appear only on cycled electrodes, indicating that they represent reaction by-products formed during cycling. Given their markedly different morphology and size compared to the HC grains, we hypothesize that these zones consist of organic products, likely originating from electrolyte degradation. This consideration is supported by EDX spectra collected on electrode cross sections (reported in Figure 9), whereby, for the cycled electrodes (b, c), clear signals from P and F are observed, two key elements from the electrolyte salt (NaPF_6) and additive (FEC). Furthermore, the difference in the Na signal is expected, since the analysis was performed on cycled electrodes at 1 V (end of discharge), when the anode is fully sodiated. In contrast, the OCV electrode shows no Na signal, as the HC contains no sodium.

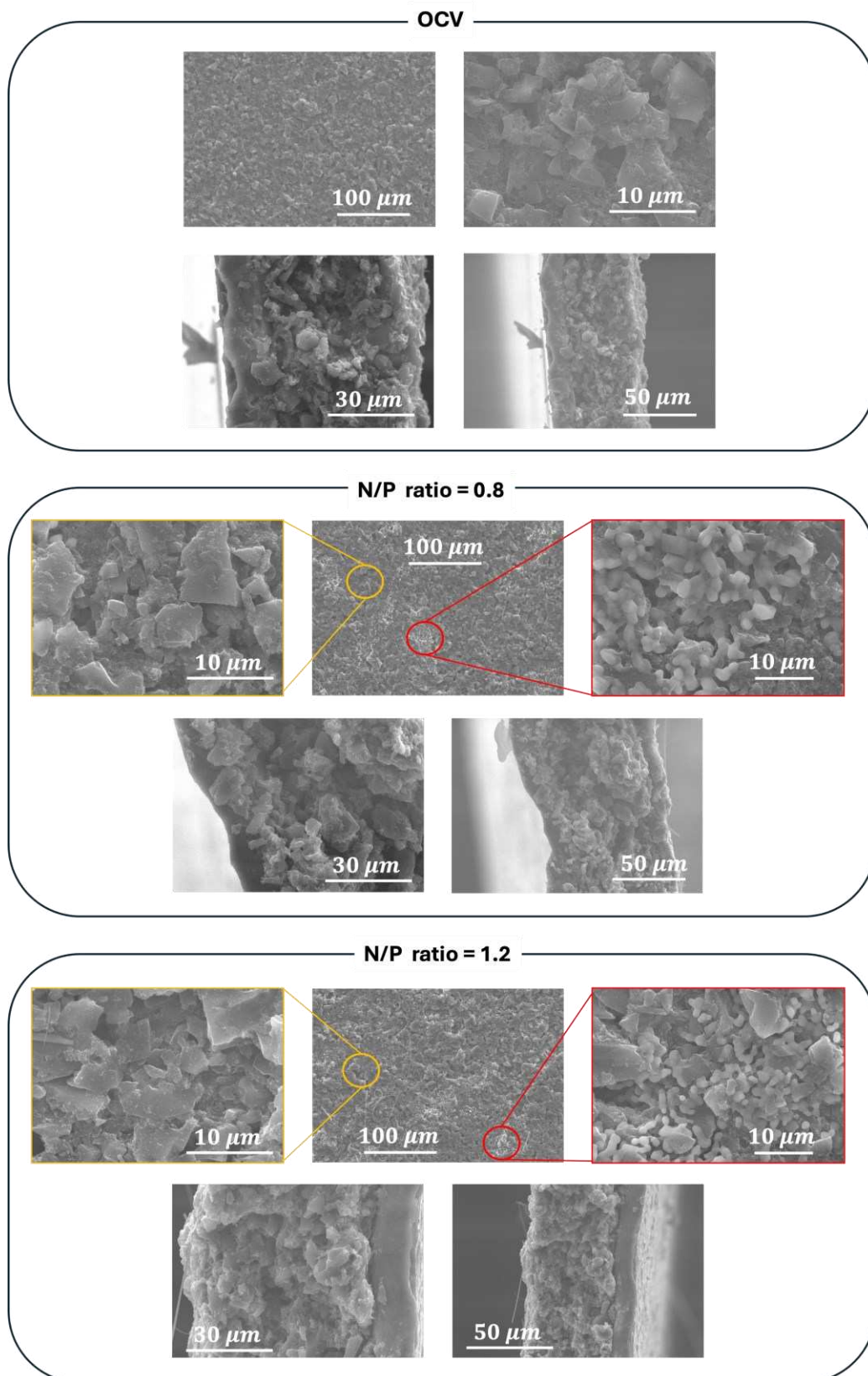


Figure 8. SEM images collected on HC anode, pre- (OCV) and post- (N/P = 0.8 and 1.2) cycling at different magnifications, on both the electrode surface and in cross-section

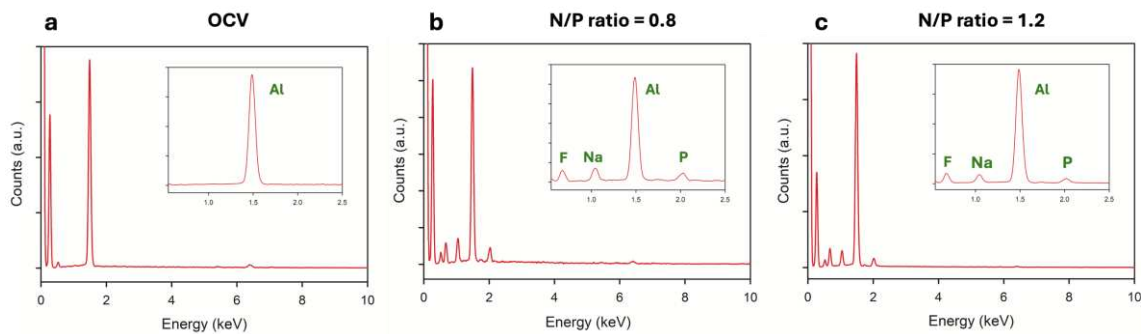


Figure 9. EDX spectra collected on HC anode cross-section (a) pre- (OCV) and post- (N/P = (b) 0.8 and (c) 1.2) cycling

For the cathode, on the other hand, we checked the structural stability of the P2-layered structure after cycling through XRD analysis.

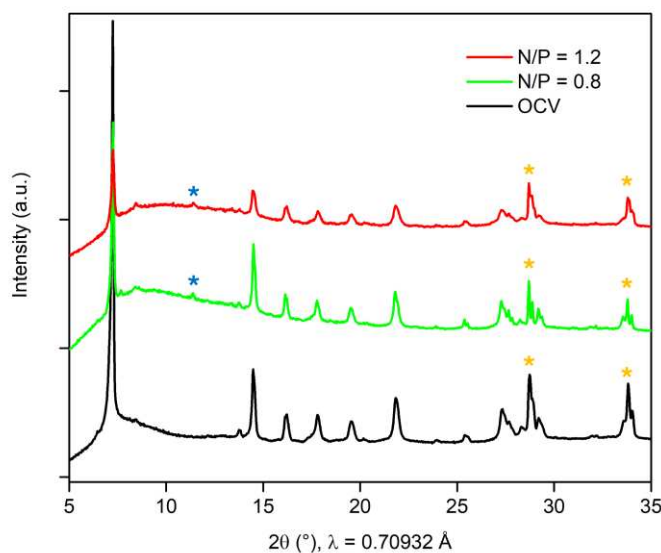


Figure 10. ex-situ XRD pattern collected on P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ cathodes pre- and post- (for N/P = 0.8 and 1.2) cycling

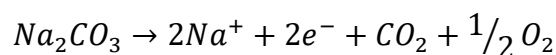
Figure 10 presents the XRD pattern obtained from the $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ cathodes after cycling. To provide a reference, a diffraction pattern was also collected on an electrode before cycling (OCV). The comparison of the diffraction patterns presented in the figure indicates that the P2-layered structure remains intact during cycling. This is evidenced by the post-cycling pattern, which exhibits no additional reflections beyond those present in the pristine electrode. This finding suggests that there has been no secondary phase formation or structural degradation. The peaks marked with a yellow

asterisk correspond to the current collector (Al), which was used as an external reference to analyze potential shifts in the diffraction signals. The signal highlighted with a blue asterisk, present only in the post-cycling patterns, has also been observed and discussed in our previous studies on completely different cathode materials.¹²⁷ It is therefore hypothesized that this signal originates from electrolyte decomposition products formed during cycling.

4.4.3.2.2. Pre-sodiation strategy

Following a thorough evaluation and discussion of the significance of N/P ratio optimization in battery design, the investigation proceeded to examine various pre-sodiation strategies with the objective of enhancing the overall Na content within the full-cell. As already mentioned, the low sodium (Na) content is a primary constraint on the commercialization of P2-layered oxide as a cathode in sodium-ion batteries (SIBs).

Firstly, we tried to introduce a new source of Na using Na₂CO₃ as a sacrificial salt. As reported by Matsuzaki *et al.*,⁸² sodium carbonate decomposes at high potentials (>4 V), during the first charge, according to the reaction:



thus, releasing Na⁺ cations that, from the first discharge, will be added to those initially present in the cathode. In this pioneering study, it was also verified that the other decomposition products do not affect the electrochemical performance of the battery, as they are present in very low concentrations. Before being used during cathode preparation, we optimized a ball-mill procedure to reduce the grain size of commercial Na₂CO₃ as much as possible. The presence of nanosized grains enhances the efficiency with which the sacrificial salt fulfills its role as a Na source.

Figure 11 reports the XRD patterns obtained after the different ball-milling procedures performed. Compared to the commercial powder (black curve), the samples ground at 550 rpm for 4 and 8 hours with steel jars (red and green curves, respectively) do not exhibit significant grain size reduction, as evidenced by the absence of significant peak broadening in their diffraction patterns. Indeed, it is well established that the full width at

half maximum (FWHM) of XRD peaks is inversely proportional to the average crystallite size. Conversely, the sample ground at 600 rpm for 4 hours (blue curve) with ZrO_2 jars clearly shows substantial peak broadening, indicating a marked reduction in grain size compared to the pristine powder, a finding that is corroborated by the comparison between the reported SEM images.

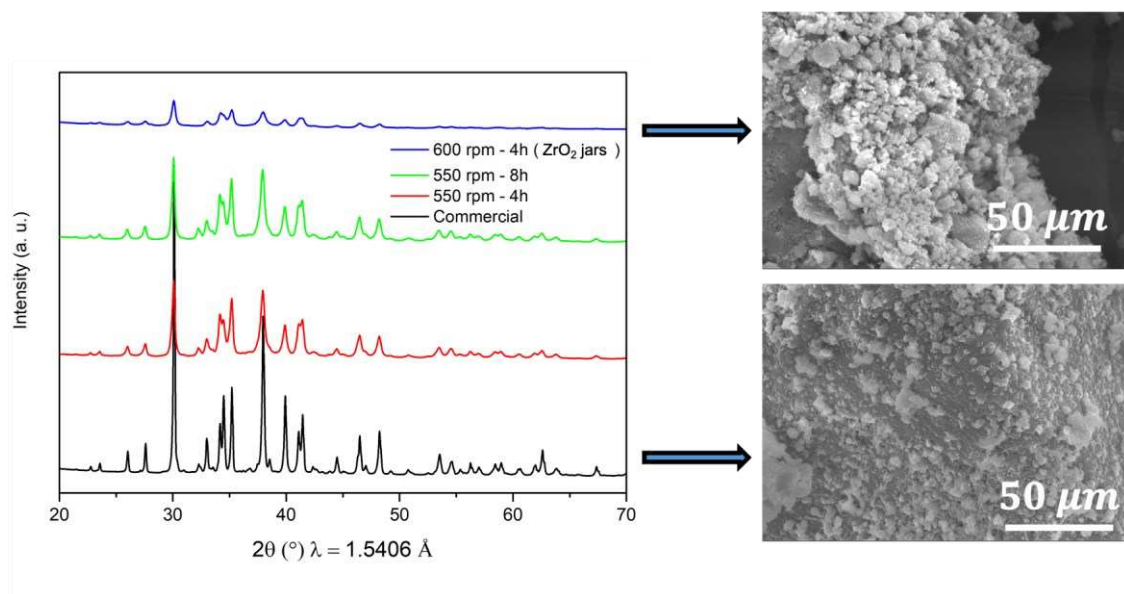


Figure 11. XRD pattern and SEM images collected before and after Na_2CO_3 grinding with different ball-milling protocols

After the grinding step, Na_2CO_3 was added to the slurry during cathode preparation. In accordance with the procedure reported in the previously mentioned study, 10 wt.% was incorporated relative to the total electrode mass. Thus, the composition of the positive electrode for these tests was as follows: 75 wt.% CAM, 10 wt.% Na_2CO_3 , 7.5 wt.%, PVdF and 7.5 wt.% of conductive carbon. Since the decomposition of sodium carbonate to Na^+ occurs only at potentials higher than 4 V, we increase the upper limit of the working potential window, compared to the previously discussed N/P optimization test performed, from 4 V to 4.2 V. Figure 12a shows the 1st cycle charge-discharge curves for the full-cells assembled with (violet) and without (green) addition of the sacrificial salt. Notable finding was the confirmation of effective decomposition of Na_2CO_3 through a comparison of the two charge curves. This was evidenced by the significantly higher capacitance levels recorded in the violet curve (182 mAh g^{-1}) in comparison to the green curve (119 mAh g^{-1}), corresponding to a 35% increase. It is also interesting to note that the trend of

the two curves begins to diverge significantly from about 3.5 V, that is, when Na_2CO_3 begins to decompose. Consequently, even during the subsequent discharge, we observe an increase in the specific capacity recorded.

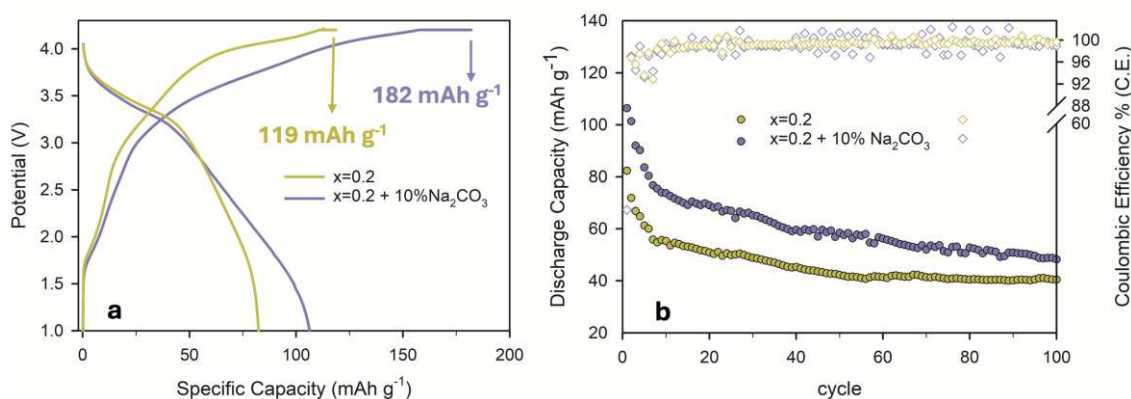


Figure 12. Comparison of (a) 1st cycle charge-discharge curve and (b) electrochemical performances registered for full-cell assembled with (green) and without (violet) the addition of 10wt.% of Na_2CO_3 as sacrificial salt on the cathode, in the working potential window 1 V-4.2 V

Figure 12b, on the other hand, compares the long-term performance of the two cells under consideration, thereby enabling an assessment of the impact of the addition of Na_2CO_3 on battery's performance after 100 cycles. Capacity retention between cycles 10 and 105 is slightly lower for the cell with Na_2CO_3 addition compared to the other one: 66% and 71%, respectively. From the comparison of the discharge capacities, we can definitively conclude that the addition of Na_2CO_3 as sacrificial salts improves battery performance and represent a promising strategy to employ and further investigate to increase the Na content for SIBs using P2-layered oxides as cathodes. Nevertheless, this represents only an initial assessment of the proposed pre-sodiation strategy: with proper optimization of all the involved experimental parameters, improved results could be expected in terms of performance and stability.

The second approach aimed at increasing the Na content in full-cells we investigated is the electrochemical pre-sodiation of Hard Carbon anode. Experimentally, this strategy requires more steps than using sacrificial salts, as it is necessary to: i) assemble a half-cell with HC vs. $\text{Na}_{(m)}$, ii) discharge it at 0.01 V in CC-CV mode to allow Na^+ to fit between the graphite domains and layers, (iii) disassemble it in an inert atmosphere (Ar),

and, (iv) use this pre-sodiated HC as anode in a full-cell with a P2- $\text{Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.3}\text{Mg}_{0.2}\text{O}_2$ -type cathode.

In the first two steps, the electrolyte mixture (1 M NaPF_6 in EC:DMC 1:1 v/v) was prepared without FEC. Since this additive decomposes during the initial discharge to form a stable SEI, its exclusion prevents the deposition of surface products on the anode that could compromise the performance of the full cell assembled with pre-sodiated HC. This approach ensures that SEI formation in the first charge–discharge cycle of the full cell occurs naturally, without artifacts related to the prior sodiation state of the hard carbon. The effect of FEC on cell behavior was confirmed experimentally by comparing the first discharge profiles of two half-cells, one with and one without the additive, which exhibited distinct electrochemical features. As shown in Figure 13, these profiles diverge significantly around ~ 1 V, the potential at which FEC decomposition begins, in agreement with previous reports.¹²⁵

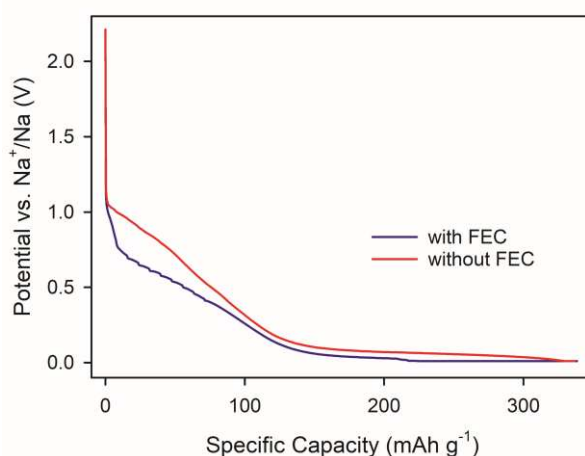


Figure 13. Comparison of the first discharge curves recorded for HC half-cells assembled with (blue) and without (red) the addition of 2 wt.% of FEC to the electrolyte mixture.

To optimize battery performance, an experimental investigation was conducted in which three different levels of hard carbon (HC) pre-sodiation in full cells were tested: 200 mAh g^{-1} , 300 mAh g^{-1} , and 340 mAh g^{-1} . The highest value corresponds to the maximum specific capacity of the HC used, while the lowest approximates the theoretical capacity required to fully use the capacity of the cathode. This value also accounts for the irreversible Na loss due to SEI formation ($\sim 60 \text{ mAh g}^{-1}$). Figure 14a provides a comparison of the initial first charge-discharge curves of full cells assembled with and

without pre-sodiated anodes. The first difference is in the open-circuit voltage (OCV). Without HC pre-sodiation, the OCV is approximately 10 mV, reflecting the low Na^+ content in the cell (zero at the anode and low at the cathode), and therefore a negligible chemical potential difference between the two electrodes. In contrast, with a pre-sodiated anode, the OCV increases to ~ 2.7 V, as the presence of extra sodium in the anode introduces a significant chemical potential difference across the electrodes. The second difference regards the specific capacity registered at the end of the discharge: as expected, the cell with the pre-sodiated HC recorded more than double the capacity of the other cell (130 mAh g^{-1} vs. 60 mAh g^{-1} , respectively). This result is very promising since it allows us to conclude that, through this pre-sodiation strategy, during the first discharge we can achieve the same specific capacity recorded by the cathode in the half-cell configuration vs. $\text{Na}_{(\text{m})}$ (see Figure 6), in the same potential range and at the same current densities.

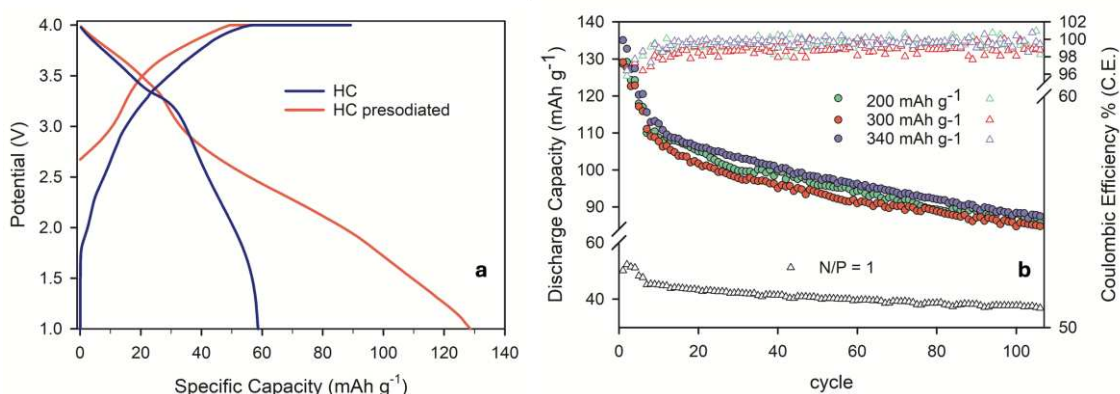


Figure 14. Comparison of (a) 1st cycle charge-discharge curve of full-cell with (red) and without (blue) electrochemical pre-sodiated HC anode, and (b) electrochemical performances registered of full-cell with different HC pre-sodiation level. For reference, the performance of a full-cell without HC pre-sodiation is also reported (white)

Figure 14b compares the electrochemical performance of all full cells assembled with different pre-sodiation levels of the HC anode. No significant differences were observed between the tests in terms of both discharge capacity and coulombic efficiency. However, the HC pre-sodiated at 340 mAh g^{-1} led to slightly higher performance, with a very promising capacity retention of 73% and a discharge capacity higher than 90 mAh g^{-1} after 100 cycles at 1C. To better highlight the significant improvement in the functional performance of the full-cell with pre-sodiated HC, Figure 14b additionally illustrates the

discharge capacity achieved from the previously examined full-cell with N/P ratio = 1 without pre-sodiation.

4.4.3.3. Conclusion

In conclusion, electrochemical Hard Carbon pre-sodiation and the use of Na_2CO_3 as sacrificial salts have been confirmed to be very promising strategies to increase the Na content of these kinds of SIBs using P2-layered oxide as the cathode. The first approach yielded the most promising results in terms of electrochemical performance. However, the multiple experimental steps required for hard carbon sodiation currently limit its feasibility from an industrial perspective. In contrast, the second strategy did not result in a comparably substantial enhancement in performance but appears considerably more attractive in terms of potential scalability, as it involves fewer and simpler processing steps. For these reasons, further optimization of both strategies will be of considerable interest in future studies to overcome the current limitations. For instance, exploring the chemical sodiation of hard carbon using solution-based agents,¹²⁸ or tuning the type and quantity of sacrificial salts may offer viable pathways for improvement.

5. $\text{Na}_2\text{MnPO}_4\text{F}$

In addition to layered oxides, during my PhD I also studied polyanionic compounds as cathodes for sodium batteries. Among these, fluorophosphates are one of the most promising types in terms of predicted high intercalation voltages and high theoretical capacities. However, their practical applications are limited by effective capacities lower than the theoretical ones and by high-capacity fading, particularly at high C-rate.

For this reason, in collaboration with the Department of Physics of the University of Pavia, we published a paper in the Journal of Energy Storage in which we investigated the electrochemical and structural properties of $\text{Na}_2\text{MnPO}_4\text{F}$, entitled: “*Intercalation voltages and ion diffusion in Mn-based transition metal fluorophosphates as cathode materials for Na-ion batteries: a synergistic experimental and theoretical approach.*” I was responsible for the synthesis and all the morphological-structural and electrochemical characterization of the material, while Marco Ravalli and Lorenzo Marti took care of the computational analyses.

5.1. Materials and methods

5.1.1. Cathode active material synthesis

$\text{Na}_2\text{MnPO}_4\text{F}$ was prepared by a solution synthesis,¹²⁹ starting from an aqueous solution of NaF (>99%, Sigma-Aldrich), NaH_2PO_4 (>99%, Sigma-Aldrich), and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%, Thermo Scientific) in the proper stoichiometric ratio. Citric acid (>99.5%, Sigma-Aldrich) was both a fuel for the combustion process and a carbon source. Once the fuel was added to the precursors, the solution was heated at 120 °C under magnetic stirring until the solvent evaporated completely. The resulting powder was compacted into a pellet and treated in a tubular oven at 600 °C for 6h (ramp rate 5 °C min⁻¹) under Ar flow, to prevent Mn(II)-Mn(III) oxidation at high temperature.

5.1.2. Cathode preparation and cell assembly

The cathode slurry was prepared with an 80:10:10 wt.% ratio of active material, conductive carbon black (Imerys, Ensaco 350P) and polymeric binder (polyvinylidene fluoride, PVDF), respectively, with a solid content kept between 28 wt.% and 30 wt.%. The cathode active material (CAM) and carbon powders were initially mixed in zirconia jars by a planetary ball miller (Fritsch Pulverisette 7 Premium Line) at 150 rpm for 10 min twice, with a rest period of 5 min. The ball-to-active material ratio used was 77:1 in weight ratio. Subsequently, the polymeric binder was added and mixed with a similar procedure. The as-prepared mixture was dispersed in N-methyl pyrrolidone (NMP) to obtain the slurry, which was then cast on a carbon-coated Al foil (MTI corp.) using a doctor blade with a wet thickness of 300 μm . The casted slurry was dried under vacuum at 80 °C. Finally, the cathode was cut into 2.01 cm² disks and stored in an Ar-filled glove box (MBraun, O₂, H₂O < 0.5 ppm). All the functional tests were performed in coin cells (CR2032 - MTI Corp.) assembled under inert atmosphere (Ar), using metallic Na (Sigma-Aldrich) as the counter electrode. Electrodes were separated with one Whatman GF/D glass fiber separator, imbibed by 180 μL of liquid electrolyte, consisting of a solution of 1M NaClO₄ in Ethylene Carbonate (EC): Propylene Carbonate (PC) + 2wt.% Fluoroethylene Carbonate (FEC).¹⁰²

5.1.3. Experimental characterization

XRD pattern of the active material powder was collected on a Bruker D8 diffractometer in Bragg-Brentano geometry equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA), collecting the diffraction signal in the 10-80° 2 θ range. XRD patterns on electrodes pre- and post-galvanostatic cycling were collected on a Bruker D8 Advance diffractometer equipped with Mo-K α radiation ($\lambda = 0.70932 \text{ \AA}$, 50 kV, and 40 mA) in Bragg-Brentano configuration in the 5-40° 2 θ range. Rietveld refinement was performed using the FullProf software.⁸⁷ SEM images were collected with a SEC SNE-4500M Plus microscope. Samples were made conductive by coating them with a carbon thin film, deposited by a Cressington 208 carbon coater. The electrochemical performance of Na₂MnPO₄F was investigated with a Bio-Logic VPM-3e through Galvanostatic Cycling

with Potential Limitation (GCPL) and Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA) in the 1.5 V-4.5 V working potential range. The C-rate has been calculated by using the following equation (eq.1):

$$C_{rate} = \frac{I_d(Ag^{-1})}{C(Ahg^{-1})} \quad \text{eq. 1}$$

where I_d represent the charging or discharging current density and C is the theoretical capacity of the cathode active material ($C = 125 \text{ mA h g}^{-1}$ for 1 Na ion per formula unit), normalized to the mass content of the cathode active material.

Electron paramagnetic resonance (EPR) measurements were performed at room temperature by using an X-band (at about 9.46 GHz) Bruker spectrometer, in the static magnetic field range between 30 and 630 mT, with microwave power of 18.6 mW and peak-to-peak modulation field of 0.1 mT. Particular care was paid to determining the samples position in the resonator. The EPR spectra of the investigated samples have been compared referring the data to the sample unit mass.

5.1.4. Computational modelling

The ab initio calculations of the present work were all performed using the plane-wave pseudopotential implementation of density functional theory contained in the QuantumESPRESSO (QE) package.^{130,131} Specifically, we used an exchange-correlation functional constructed within the Generalized Gradient Approximation (GGA) and with the PBEsol parameterization.¹³² To model the interaction of valence electrons with the atomic cores of the various species entering the composition of the systems studied here we employed Ultrasoft (US) and Projector Augmented Wave (PAW) pseudopotentials^{133,134} obtained from the Standard Solid-State Pseudopotentials (SSSP) library (efficiency version 1.2.1).^{135,136} Kinetic energy cut-offs of 75 and 640 Ry for the plane-wave expansion of wavefunctions and charge-density, respectively, were found high enough to converge the total energies, forces and stresses of our system. For all the considered compositions the Brillouin zone was sampled through a uniform 3x6x3 Monkhorst-Pack grid, which amounted to 20 k-points in its irreducible portion.

Since Mn is a paramagnetic ion featuring, in all the considered compositions, a non-zero net spin from its 3d electrons, we initially considered various collinear arrangements of the magnetic moments. Comparing their total energies, the ferromagnetic one resulted to be the most stable and is adopted throughout this work. To improve the localization of valence electrons on Mn 3d states (which is crucial to capture the shift in the oxidation state of this species during the charge/discharge processes) we adopted Hubbard corrections to the approximate GGA exchange-correlation energy; in particular we employed the so called DFT+U+V¹³⁶ functional, containing both on-site (U) and inter-site (V) interactions.^{137,138} The Hubbard functional was constructed employing a basis set of orthogonalized atomic orbitals, that was used consistently for calculations of both total energies and its derivatives (*e.g.*, forces and stresses).¹³⁹ The effective interaction parameters of the Hubbard corrective functional were computed (on the same atomic basis set) from linear-response theory¹⁴⁰ using the Density Functional Perturbation Theory¹⁴¹ (DFPT) implementation contained in the hp.x code.^{142–144} More specifically, we adopted a self-consistent procedure for this calculation^{143,145} where the effective Hubbard interaction parameters and the equilibrium crystal structure are recomputed from the DFT+U+V ground state until the value of U's and V's and the structural parameters result fully converged. The Hubbard parameters that are obtained this way are in full consistency with both the equilibrium crystal structure of the system at various compositions and the electronic structure of the corresponding ground state. The DFT+U (albeit with semi empirical Hubbard parameters) is by now the standard approach for calculations of electronic properties in cathode materials,^{146–149} as it has been proved to significantly improve the energetics of materials containing oxidation-state-shifting species. The use of the extended DFT+U+V was introduced much later¹⁵⁰ and is still more sporadic for this type of calculations; however, recent works in literature prove that it is capable to further refine the prediction of the intercalation voltages of electrode materials and of their crystalline structures.^{146,151–153} Part of this improvement is due to the use of inter-site interactions between transition-metal (TM) ions and the anions in their coordination shells; part to the automatization of the calculation of the Hubbard parameters with the hp.x code that allows us to update their values accurately and efficiently in dependence of the chemical composition and for all the inequivalent TM species of the considered systems.

BVSE analysis was performed on different stoichiometries in the $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ ($x = 0; 0.5; 1$) system. The structural models employed for the analysis were obtained from the DFT-level geometrical optimization described above. Usually, BVSE analysis employs experimental crystallographic data, which describes the vacancy concentration as averaged over one or more crystallographic sites; as DFT models do not account for this possibility, and the vacancies must be included explicitly in the structure, different structures with different arrangements of sodium vacancies (for $x = 0.5$) were optimized by DFT and subsequently analyzed by BVSE in order to get an average description of their diffusion pathways and energetics. The analysis was performed on the softBV software,¹⁵⁴ which utilizes Morse type force-fields; the resulting isosurfaces were visually analyzed by the VESTA software,¹⁵⁵ and the migration barriers for the different stoichiometries were obtained by plotting the calculated pathway's energy profiles. To make the different compositions and structural models comparable, a screening factor of 0.65 was used for all the BVSE calculations.

The LAMMPS code¹⁵⁶ was employed to conduct MD simulations; to model the ion-ion interactions, the pretrained universal machine learning (ML) interatomic potentials MACE-MP0 (version 2023-12-10-mace-128-L0_energy_epoch-249) was used, making it possible to perform preliminary DFT-level MD simulations and investigate the diffusion mechanism of the Na ion in the system in a relatively fast and accurate way. The simulations were performed on the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition; the simulation box was a 1x5x1 supercell (340 atoms) built up from the minimum energy structure obtained from the DFT calculations. The system was allowed to equilibrate in the isothermal-isobaric ensemble (NPT) for 5 ps at the target temperature (300 K, 500 K, 650 K, 750 K and 850 K) to determine the equilibrium cell volume. From this data, canonical ensemble runs (NVT) were conducted for at least 100 ps. The Nosé-Hoover thermostat and the Velocity-Verlet algorithm were used for both the ensembles, with a 1 fs integration timestep. The resulting trajectories were analyzed by the OVITO software.¹⁵⁷

5.2. Results and discussion

Rietveld refinement results reported in Figure 1a confirm that the synthesis adopted in this work led to the formation of the desired polyanionic monoclinic structure (space

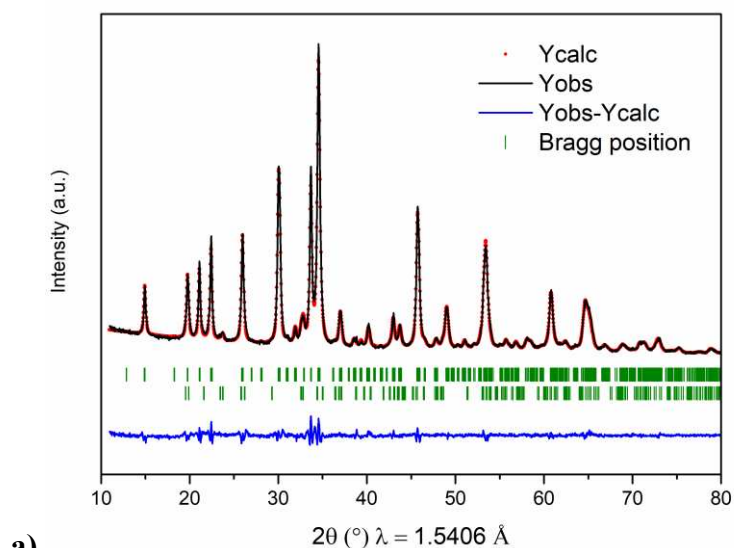
group: $P2_1/n$), with minor impurities (approximately 6%) identified as NaMnPO_4 .¹⁵⁸ The refined structural parameters of the main phase (reported in Table 1) are in very good agreement with experimental literature data on the same composition.⁷⁰

Table 1. Rietveld refined data for the $\text{Na}_2\text{MnPO}_4\text{F}$ nominal composition in the $P2_1/n$ space group

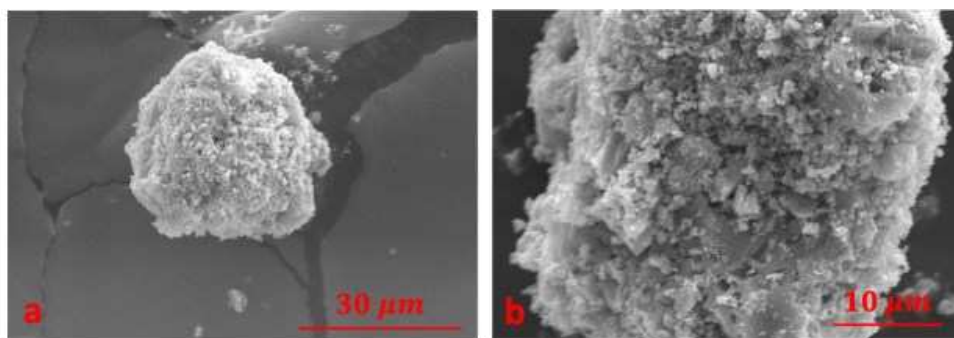
Atom	x	y	z
Mn1	0.10109	0.27532	0.67757
Mn2	0.32318	0.24140	0.40287
P1	0.07891	0.20965	0.41797
P2	0.41015	0.72909	0.57301
Na1	0.58481	0.23614	0.67134
Na2	0.16687	0.73568	0.58639
Na3	0.33192	0.23827	0.67405
Na4	0.15679	0.74757	0.32772
F1	0.23296	-0.03260	0.24204
F2	0.22962	0.00609	0.75327
O1	0.34780	0.84102	0.45138
O2	0.13245	0.29513	0.53936
O3	-0.02351	0.36302	0.36152
O4	0.40634	0.43728	0.56513
O5	0.54181	0.77751	0.64663
O6	0.34824	0.79115	0.63045
O7	0.06624	-0.09882	0.42117
O8	0.15270	0.27084	0.36105

Space group: $P2_1/n$. Lattice parameters $a = 13.700(1)$ Å, $b = 5.3211(1)$ Å, $c = 13.7088(9)$ Å, $\beta = 119.716(2)^\circ$; $V = 867.99(9)$ Å³; $R_p: 8.50$, $R_{wp}: 8.80$, $\chi^2: 2.52$

Figure 1b shows the SEM images collected at different magnifications of the as-prepared powders of nominal composition $\text{Na}_2\text{MnPO}_4\text{F}$, indicating that the sample is characterized by the presence of micrometric particles, likely constituted by aggregates of irregular grains with residual internal porosity. The smaller and lighter particles visible on the surface are likely residual carbonaceous material originating from the citric acid used as fuel in the initial synthesis stage, which might not be fully decomposed during pyrolysis under inert (Ar) atmosphere.



a)



b)

Figure 1. (a) Experimental XRD pattern of $\text{Na}_2\text{MnPO}_4\text{F}$ (black line) and corresponding calculated profile computed by Rietveld refinement (red circle) based on the monoclinic $P2_1/n$ structure (upper green bars). The difference curve (blue line) is shown below. Lattice parameters $a = 13.700(1) \text{ \AA}$, $b = 5.3211(1) \text{ \AA}$, $c = 13.7088(9) \text{ \AA}$, $\beta = 119.716(2)^\circ$; $V = 867.99(9) \text{ \AA}^3$; $R_p: 8.50$, $R_{wp}: 8.80$, $\chi^2: 2.52$. (b) SEM images of the synthesized $\text{Na}_2\text{MnPO}_4\text{F}$ powder at different magnifications.

The Rietveld refined structural data of $\text{Na}_2\text{MnPO}_4\text{F}$ were used as starting point for the subsequent DFT-based calculations. Starting from this initial unit cell, a structural optimization of the crystal structures was performed for various sodium concentrations, namely those corresponding to $x = 0, 0.5, 1$, and 2 in $\text{Na}_{2-x}\text{MnPO}_4\text{F}$. Each phase contains two crystallographically inequivalent Mn ions, as discussed in Chapter 1.3.3.2.2.

While for the $\text{Na}_2\text{MnPO}_4\text{F}$ and MnPO_4F cases only one spatial configuration exists (see Figure 2a and Figure 2d), at intermediate sodium concentrations Na atoms only occupy a fraction of the available sites and many arrangements are possible. Unfortunately, the calculation of all the possible microstates with different combinations of sodium cations becomes rapidly prohibitive at the DFT level, even with the single unit cells considered

here. Given this limitation, for NaMnPO_4F we selected four possible configurations of Na atoms that, based on the symmetry of the crystal, seemed to guarantee a more even distribution of these cations, as similarly done elsewhere.^{73,159} This resulted in the deintercalation of eight sodium cations per unit cell, achieved by the removal of two groups of non-equivalent sodium sites. The most energetically favorable de-intercalation route led, through a structural optimization, to the configuration in Figure 2c. From this Na arrangement at $x = 1$, we re-intercalated four Na^+ cations per unit cell, to study intermediate $x = 0.5$ phases. The most stable configuration resulted to be the one displayed in Figure 2b.

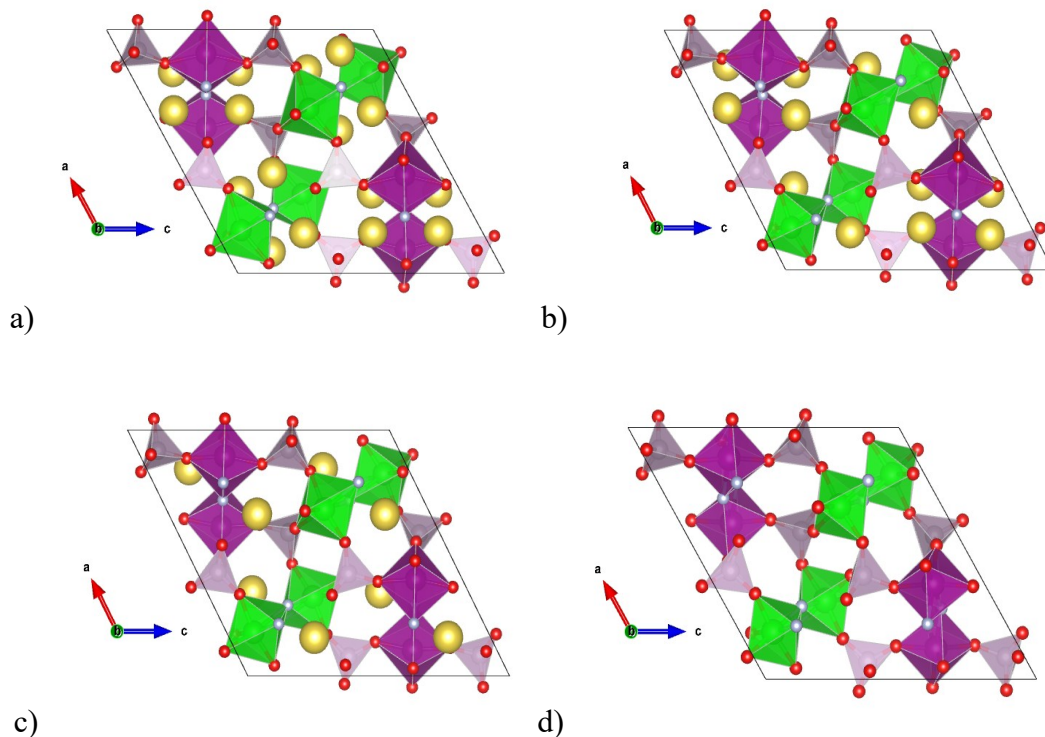


Figure 2. The $x = 0$ NMPF phase, namely $\text{Na}_2\text{MnPO}_4\text{F}$ (a), the $x = 0.5$ NMPF phase ($\text{Na}_{1.5}\text{MnPO}_4\text{F}$) (b), the $x = 1$ NaMnPO_4F (c) and the totally desodiated phase, MnPO_4F (d). Mn (violet), F (gray), O (red), Na (yellow), P (lilac)

A similar procedure could be employed to obtain the crystal structure for $x = 1.5$, which also presents multiple possible configurations of Na. However, given the instability of available electrolytes at voltages corresponding to high oxidation states of Mn and the consequent difficulties in characterizing systems at high concentrations of Na vacancies, this has not been done here and the study of the $x = 1.5$ phase will be the object of future work. Figure 3a shows the total energies of the stable phases in dependence of Na

concentration, referred to a mixture of the $x = 0$ and $x = 2$ phases (convex hull). As evident from the graph, our computational results suggest that at least two phases are stable in the compositional range investigated, as shown in Figure 4a, predicting the existence of at least three biphasic regions during charging and discharging of a cell based on $\text{Na}_2\text{MnPO}_4\text{F}$ as a cathode. These will be $\text{Na}_2\text{MnPO}_4\text{F}/\text{Na}_{1.5}\text{MnPO}_4\text{F}$, $\text{Na}_{1.5}\text{MnPO}_4\text{F}/\text{NaMnPO}_4\text{F}$, and $\text{NaMnPO}_4\text{F}/\text{MnPO}_4\text{F}$. Figure 4b shows the variation of the unit cell volume along with composition as derived from the DFT+U+V calculations on the most stable structures, along with the data extracted from a previous work¹⁶⁰ and a direct comparison to the experimental data derived in this study for the nominal $\text{Na}_2\text{MnPO}_4\text{F}$ composition. Table 2 reports all the calculated lattice parameters.

Table 2. Calculated lattice parameters and unit cell volumes as obtained from the self-consistent DFT+U+V structural for $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ ($x = 0, 0.5, 1, 2$)

	$\text{Na}_2\text{MnPO}_4\text{F}$		$\text{Na}_{1.5}\text{MnPO}_4\text{F}$		NaMnPO_4F		MnPO_4F	
	This work	Ref. ¹³²	This work	Ref. ¹³²	This work	Ref. ¹³²	This work	Ref. ¹³²
a (Å)	13.70	13.77	13.05	13.19	12.95	13.08	12.54	12.72
b (Å)	5.33	5.36	5.27	5.31	5.25	5.30	4.95	5.013
c (Å)	13.73	13.80	13.87	13.89	13.25	13.22	12.60	12.86
β (°)	119.50	119.68	118.82	119.00	118.09	118.23	120.53	120.00
V (Å³)	872.54	884.39	835.47	850.35	795.28	813.37	674.17	710.15

Thanks to a more flexible description of electronic localization, achieved through the inclusion of intersite interactions in the Hubbard functional, our DFT+U+V calculations show excellent agreement with the experimental data, with an equilibrium volume that is within 1% from the one obtained from Rietveld refinement. Unfortunately, to the best of our knowledge, no experimental data is available on the cell volume of the desodiated phases in the $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ system, therefore a direct comparison is not possible for these phases. The computational data presented in Figure 3b indicates an expected volume contraction of approximately 9% when 1 Na ion is removed (from $\text{Na}_2\text{MnPO}_4\text{F}$ to

NaMnPO₄F), and a volume change as large as approximately 22% for the complete desodiation of the sample (from Na₂MnPO₄F to MnPO₄F). Such values, although not unusual for intercalation cathode materials, especially for NIBs,¹⁶¹ suggest that the high-volume changes expected upon cycling may have a negative impact on the electrochemical performances, especially if more than 1 Na per formula unit were to be exchanged during the process. In fact, large volume changes upon cycling affect the stability of the cathode layer, with potential delamination and separation of the CAM particles from the conductive carbon particles. For comparison, experimental data on the Na₂FePO₄F system revealed a 3.5 % volume variation upon removal of 1 Na ion per formula unit,¹⁶² considerably lower than the 9% predicted in this study for the Mn-based counterpart.

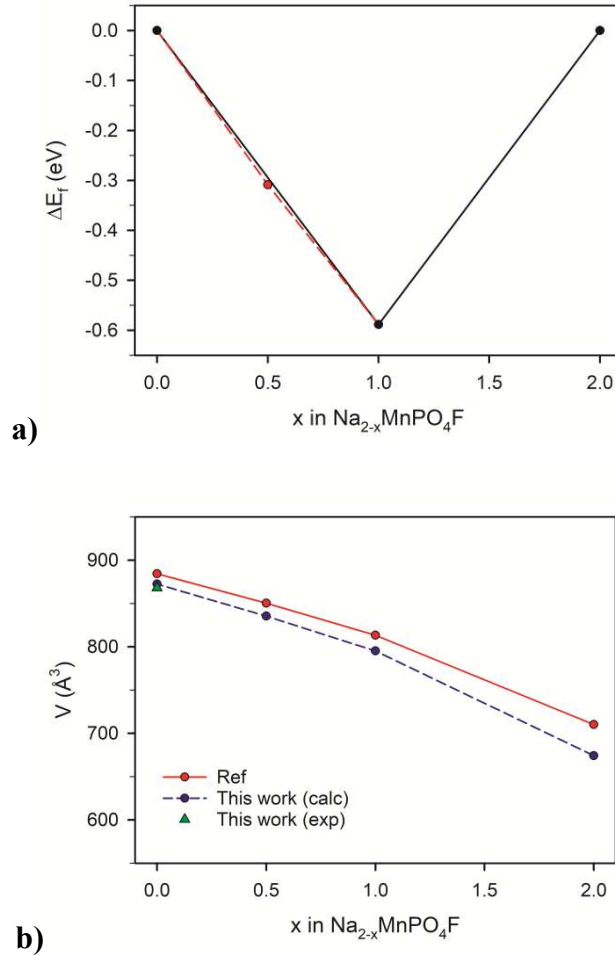


Figure 3. (a) Convex hull phase diagram showing the difference in formation energies calculated in the Na_{2-x}MnPO₄F ($0 \leq x \leq 2$) system for different sodium configurations, suggesting the presence of two stable intermediate phases during cell cycling. (b) lattice variation along with composition for the calculated stable phases, together with those of ref. [53]

Besides the equilibrium lattice parameters and cell volumes, it is interesting to investigate how the local crystalline environment of Mn cations evolves during sodium deintercalation. In Table 1 the Mn-O/F distance for the two inequivalent manganese ions are reported, together with an octahedral distortion parameter, D , based on bond lengths and defined as follows (eq.2):

$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}} \quad \text{eq.2}$$

where l_i is the distance from the central atom to the i th coordinating atom and l_{av} is the average bond length for the specific octahedron.¹⁶³

The results presented in Table 3 indicate that the average Mn-anion bond lengths for both the Mn sites decreases along with the Na content, a result consistent with the contraction of the lattice parameters visible in Figure 4b. In general, in the fully sodiated phases the MnO_4F_2 octahedra are distorted, with one of the two Mn-F distance particularly elongated compared to the other bond lengths. The relative difference between Mn-O and Mn-F distances increases in particular for $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ and NaMnPO_4F , as testified by the calculated distortion parameter, D , reported in Table 3. D assumes the lowest values, 0.012, for MnPO_4F , in which Mn^{4+} is nominally present, and it is just lightly higher for $\text{Na}_2\text{MnPO}_4\text{F}$, in which only Mn^{2+} is nominally present. For NaMnPO_4F , which nominally contains only Mn^{3+} , D is considerably higher (approximately 0.08), indicating that the Mn-O/F octahedra are thus quite significantly distorted from their ideal symmetry, likely due to (or at least enhanced by) the Jahn-Teller activity often featured by Mn centers in the Mn (III) oxidation states. For $\text{Na}_{1.5}\text{MnPO}_4\text{F}$, consistently with the expected disproportionation of the Mn cations in Mn (II) and Mn (III) states, half of the Mn centers feature distance distributions from the nearest anions like those of the Mn^{2+} in $\text{Na}_2\text{MnPO}_4\text{F}$, the other half, instead, is more comparable to the Mn in the NaMnPO_4F .

Table 3: Nearest-neighbors' distances from Mn ions for different phases in the $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ system, as derived from DFT+U+V calculations. On the right, the spin-resolved Hubbard occupations of 3d orbitals of Mn ions are reported

		d F ^a (Å)	d F ^b (Å)	d O ^a (Å)	d O ^b (Å)	d O ^c (Å)	d O ^d (Å)	<d> (Å)	D	n (↑)	n (↓)
$\text{Na}_2\text{MnPO}_4\text{F}$	Mn1	2.15	2.37	2.13	2.14	2.16	2.18	2.18	0.02 79	4.98	0.23
	Mn2	2.18	2.32	2.14	2.14	2.16	2.18	2.18	0.02 12	4.98	0.23
$\text{Na}_{1.5}\text{MnPO}_4\text{F}$	Mn1	2.12	2.25	2.12	2.13	2.16	2.16	2.16	0.01 66	4.98	0.24
	Mn2	1.89	2.65	1.91	1.93	1.93	2.07	2.07	0.10 09	4.46	0.52
NaMnPO_4F	Mn1	1.87	2.37	1.91	1.91	1.93	2.02	2.02	0.07 43	4.44	0.53
	Mn2	1.89	2.49	1.91	1.92	1.93	2.04	2.04	0.08 55	4.45	0.52
MnPO_4F	Mn1	1.90	1.94	1.84	1.86	1.89	1.87	1.87	0.01 28	4.10	0.80
	Mn2	1.91	1.93	1.86	1.86	1.87	1.89	1.89	0.01 20	4.11	0.79

To further corroborate this hypothesis, and validate our structural modeling, the occupation of Mn 3d states in dependence of the Na concentration in the crystal were analyzed. This quantity, displayed in Table 3, is obtained as the trace of the occupation matrices that are also employed in the construction of the Hubbard corrective functional. These matrices are defined as follows (eq.3):

$$n_I^\sigma = \sum_{\mathbf{k},v} f_{\mathbf{k}v}^\sigma \langle \psi_{\mathbf{k}v}^\sigma | P^I | \psi_{\mathbf{k}v}^\sigma \rangle \quad \text{eq.3}$$

where I is the ionic index, $\psi_{\mathbf{k}v}^\sigma$ are the Kohn-Sham states, $f_{\mathbf{k}v}^\sigma$ represent their Fermi-Dirac occupations, and P^I are the projectors on the atomic orbitals of the I^{th} atom (e.g., Mn 3d). It is important to stress that, in order to eliminate the finite overlap between states of neighbor atoms (and the consequent overcounting of electrons on atomic orbitals), in our calculations we construct the Hubbard corrective functionals on an orthogonalized atomic basis set, so that we have: $P^I P^L = \delta^{IL} P$. The same orthogonalised atomic basis is also

used in the optimisation of the crystal structure and in the calculation of the Hubbard effective parameters. Although the variation of the numerical value of these occupations does not conform to the integer shift in the nominal oxidation state of Mn ions upon changing Na concentration, it is important to note that they represent a valid and consistent descriptor of the Mn oxidation states. In fact, for $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ the two crystallographically inequivalent Mn ions feature occupations that resemble very closely those of Mn^{2+} ($\text{Na}_2\text{MnPO}_4\text{F}$) and Mn^{3+} (NaMnPO_4F), respectively, thus confirming the charge disproportionation occurring at intermediate Na concentrations. This internal consistency between the total occupation of the transition-metal ions' d states and their nominal oxidation state, albeit usually not based on numerical coincidence,¹⁴⁵ is in fact crucial to capture charge-disproportionated ground states and to predict accurate average intercalation voltages and formation energies.

Table 4: Calculated voltages for the different stable phases, compared to previously reported computational [53] and experimental results [13]. All our calculations were performed from DFT+U+V total energies

	Computational (this work) (V)	Computational [53](V)	Experimental [13] (V)
$\text{Na}_2\text{MnPO}_4\text{F} \rightarrow \text{Na}_{1.5}\text{MnPO}_4\text{F} + 0.5 \text{ Na}$	3.64	3.71	3.55
$\text{Na}_{1.5}\text{MnPO}_4\text{F} \rightarrow \text{NaMnPO}_4\text{F} + 0.5 \text{ Na}$	3.71	3.76	3.75
$\text{NaMnPO}_4\text{F} \rightarrow \text{MnPO}_4\text{F} + \text{Na}$	4.82	4.76	-

Consistently with abundant literature,^{145,152,159,161} the deintercalation voltages (vs Na/Na^+) were calculated using the following formula (eq.4):

$$V = - \frac{E(x_1) - E(x_2) - (x_2 - x_1)E(\text{Na})}{(x_2 - x_1)e} \quad \text{eq.4}$$

where $E(x_i)$ stands for the DFT+U+V total energy of (a single formula unit of) $\text{Na}_{2-x_i}\text{MnPO}_4\text{F}$, while $E(\text{Na})$ is the total energy (per Na atom) of bulk sodium. The resulting voltages are reported Table 4, showing an overall good agreement with available data from similar computational studies. It is important to remark here that, at variance

with other similar studies, our voltages are computed from total energies obtained from composition-specific Hubbard parameters and no averaging procedure (over x) was involved. The average voltages pertaining to the $\text{Na}_2\text{MnPO}_4\text{F} \rightarrow \text{Na}_{1.5}\text{MnPO}_4\text{F} + 0.5 \text{ Na}$ and to the $\text{Na}_{1.5}\text{MnPO}_4\text{F} \rightarrow \text{NaMnPO}_4\text{F} + 0.5 \text{ Na}$ half-reactions show slightly lower values than those computed previously,¹⁵⁹ while the voltage computed for the full desodiation of the cell ($\text{NaMnPO}_4\text{F} \rightarrow \text{MnPO}_4\text{F} + \text{Na}$) is slightly higher than the one achieved in other computational works.

The prediction of the stability of the phase with composition $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ (Figure 4a) suggests that at least three phenomena should be detectable during cycling of cells based on $\text{Na}_2\text{MnPO}_4\text{F}$. To confirm the computational prediction, the sample of nominal composition $\text{Na}_2\text{MnPO}_4\text{F}$ was used to conduct electrochemical tests, as described in Chapter 5.1.3. Figure 4 shows the results obtained from the galvanostatic cycling test at different current densities.

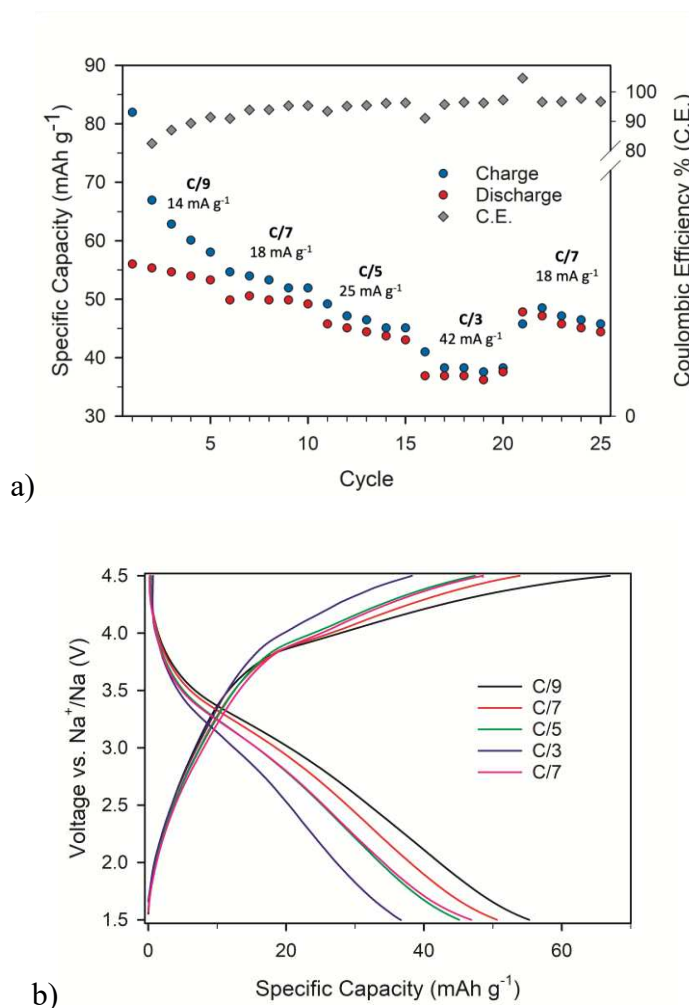


Figure 4. a) $\text{Na}_2\text{MnPO}_4\text{F}$ rate performance between 1.5 V - 4.5 V at different C-rates. b) Examples of voltage profiles for the galvanostatic cycling at different C-rates

As usually observed for intercalation cathodes, with increasing C-rates the specific capacity decreases; also, it is common to observe a capacity fading over subsequent cycling. Several factors affect such behavior; nano-structuring or nanoengineering of the electrode, together with efficient C-coating and metal doping, are among the main strategies to achieve high-rate capability, and stable cycle life of the electrode materials. The same procedures also allow to achieve, in general, superior specific capacities, close to the theoretical, by increasing the specific surface area and the readily accessible Na^+ storage sites.¹⁶² As shown in Figure 1b, the sample employed in this study was not morphologically optimized to improve rate performances. As a consequence, the recorded capacities are considerably lower than the theoretical value (125 mAh g⁻¹ one Na^+ extracted) and somewhat lower than the values reported in the literature for morphologically optimized samples of this composition,^{163,164} although not significantly different from earlier reports.¹⁶⁵ It is also important to note that the simple solution-based synthesis employed in this study allowed to obtain electrochemically active samples in contrast to the preliminary investigations in which $\text{Na}_2\text{MnPO}_4\text{F}$ was believed to be electrochemically inactive.^{66,166} Figure 4 also shows that the material can work quite reversibly during cycling. Apart from the first few cycles, the coulombic efficiency is greater than 90%, indicating good structural stability of the cathode material under investigation, as testified by the comparison of the XRD patterns collected on the pre- and post-cycling electrodes (Figure 5). The structural stability of the CAM is further supported by the significant capacity recovery registered during cycles carried out at a slower C-rate (0.14 C, cycles 21-25) after high stress cycles at 0.33 C.

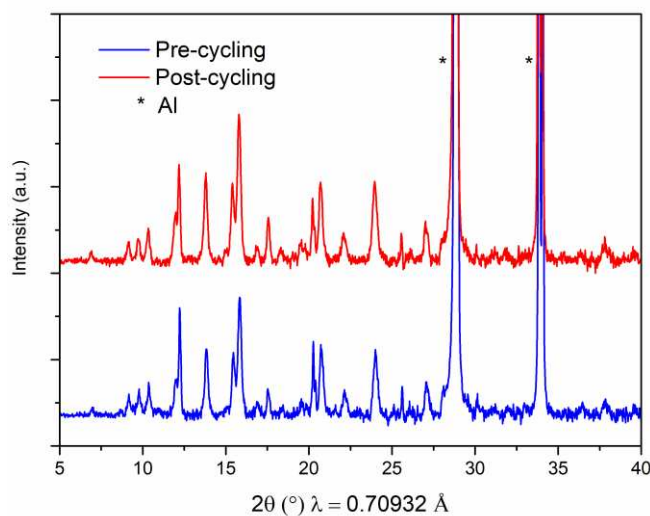


Figure 5. XRD patterns collected on the electrode pre- and post-cycling. The peaks marked with the star are those of the Al foil used as current collector; taken as an internal standard reference to better compare the patterns

Figure 6 shows the differential capacitance (dQ/dV) curves recorded at 0.067 C. Based on these results, it is possible to evaluate the electrochemically active phenomena within the working potential window that contribute to the specific capacity. The curve clearly confirms the presence of two partially reversible signals, both of which can be ascribed to the Mn (II)-Mn (III) redox couple. As expected, based on the DFT calculations, the two redox phenomena happen at very close voltage values and are the consequence of the first two reactions reported in Table 4 and ascribed to the $\text{Na}_2\text{MnPO}_4\text{F} \rightarrow \text{Na}_{1.5}\text{MnPO}_4\text{F} + 0.5\text{Na}$ and $\text{Na}_{1.5}\text{MnPO}_4\text{F} \rightarrow \text{Na}_1\text{MnPO}_4\text{F} + 0.5\text{Na}$ desodiation steps. This experimental result thus confirms the presence of the stable intermediate phase of composition $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ shown in Figure 4a, in agreement with previous literature.⁶⁹ In the 1st charge, in particular, it is evident how the dQ/dV signal is formed by two consecutive peaks at different potentials, which can be attributed to the desodiation of the cathode from Na_2 to $\text{Na}_{1.5}$ and from $\text{Na}_{1.5}$ to Na_1 . In the 2nd charge, this difference is not so well defined, but the broadening of the signal certainly indicates that the peak again cannot be ascribed to a single phenomenon. At high potentials (>4.2 V), the irreversible contribution observed during both charges (highlighted by the red star in Figure 6) is due to the partial degradation of the electrolyte mixture. In particular, the irreversible electrochemical degradation of the carbonates and NaClO_4 contributes to the increase in charge capacity and, consequently, lowers the coulombic efficiency, consistently with the results

presented in Figure 4. Unfortunately, the competing degradation of the electrolyte does not allow to achieve the removal of more than 1 Na ion per formula unit, since the expected intercalation voltages (Table 4) for the subsequent desodiation steps are higher than 4.5 V; the limited electrolyte's electrochemical stability window does not allow to gain full advantage of the potentiality of the CAM. The partial degradation of the electrolyte at each cycle can be counted among the factors that induce the capacity fading over cycling, contributing to the partial irreversibility of the intercalation/deintercalation process.

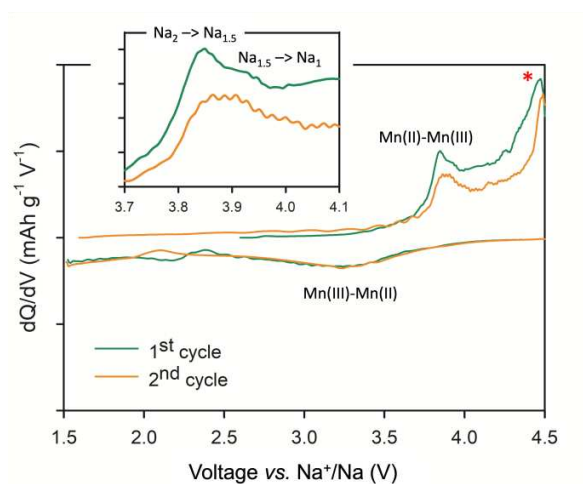
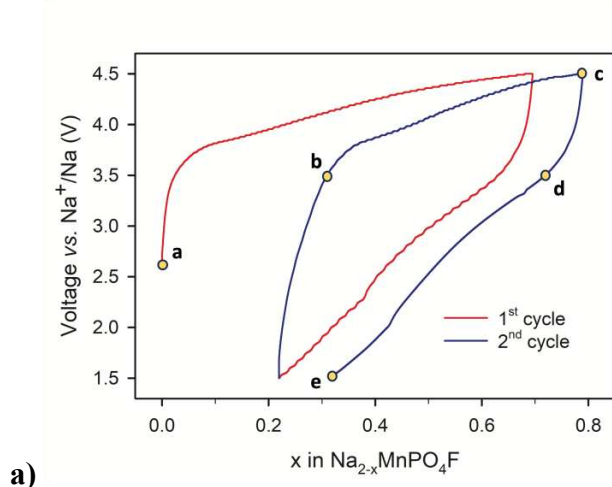


Figure 6. dQ/dV curves for $\text{Na}_2\text{MnPO}_4\text{F}$ collected in the working 1.5 V – 4.5 V voltage range employing PCGA experiments at 0.067 C; the red star marks the irreversible contribution due to the partial degradation of the electrolyte mixture

In order to monitor the reversibility of the Mn (II) – Mn (III) reduction-oxidation process at various cycling steps, room temperature EPR measurements have been performed on the NMPF-based cathode samples quenched at different voltages during the second charge-discharge cycle according to the scheme reported in Figure 7a (b, c, d, and e samples). The $\text{Na}_2\text{MnPO}_4\text{F}$ uncycled cathode (OCV, the a-sample in Figure 7a) has been also investigated as a reference starting sample. In this last compound manganese nominally only exhibits an oxidation state of Mn (II). Indeed, it is known that in crystalline systems a unique intense signal centred at $g \sim 2$, just greater than 2, is expected from undiluted Mn^{2+} ions, with unresolved hyperfine structure. Quite the opposite, a signal from Mn^{3+} ions is generally hardly observable^{167,168} and, in particular, Mn^{3+} is reasonably expected to be EPR inactive in the X-band at room temperature, as in the

present case. A comparative plot of the derivative EPR spectra recorded for all the investigated samples is reported in Figure 7b. All the spectra disclose a main signal with a very similar almost symmetrical lineshape and with central magnetic field value corresponding to $g \sim 2$. The peak-to-peak linewidth increases passing from the OCV sample (about 15.5 mT) to the highest quenching voltages (about 18 mT) and then it turns to decrease during the discharge process, reaching a relative minimum value for the 1.5 V quenched cathode (about 17 mT). A different signal intensity can be appreciated for the different samples. The most intense signal pertains to the OCV sample, *i.e.* the one with the expected highest Mn^{2+} amount. The inset of Figure 7b shows the estimated relative EPR intensity values (area of the absorption signals) reported as a function of the successive steps in the quenching during the charge-discharge process. Again, the value pertaining to the OCV sample is reported as a reference value. The EPR signal intensity values clearly correlate to the electrochemical cycling procedure. Indeed, for the data shown in the inset of Figure 7b a qualitatively congruent trend is observed with the expected Mn^{2+} amount at the different cycling quenching voltages. A noticeable feature is the strong decrease of the EPR spectra intensity passing from the uncycled sample to all the cycled ones suggesting the partially irreversible character of the process. This is also supported by the EPR linewidth value achieved for the 1.5 V quenched cathode (e-sample), markedly higher than what observed for the OCV sample, denoting a decreased order degree for the Mn^{2+} environment after cycling. This result is consistent with the observed capacity fading upon cycling and the large difference between charge and discharge capacity recorded over the first few cycles (Figure 4a and Figure 7a).



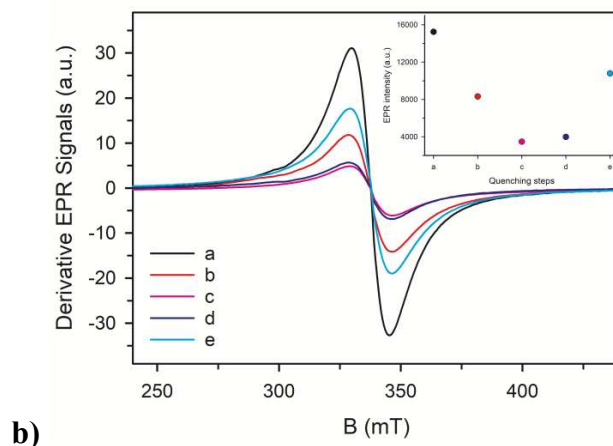


Figure 7. a) Voltage vs Na content related to the 1st and 2nd charge-discharge cycles for Na₂MnPO₄F collected at 0.08 C. Circles on the graph indicate the potential at which samples for EPR investigation have been quenched; b) Comparison between EPR spectra acquired from the different quenched cathodes (b, c, d and e samples of figure 7a) and from the uncycled one (a-sample of figure 7a). Inset: EPR signal intensity values vs the quenching steps

As anticipated, the capacity fading with increasing C-rate observed in Figure 4, as well as the electrochemically inactivity of Na₂MnO₄F described in earlier reports,¹⁶⁶ can be partially ascribed to the kinetic limitation to Na-ion intercalation in the host structure, which is directly related to the Na-ion conduction mechanisms and energetics within the host structure. To investigate this aspect, BVSE analysis on the Na_{2-x}MnPO₄F system was performed and used as a reference point for subsequent MD simulations. Based on the DFT energy minimized structures, it was possible to visualize the most likely sodium ion diffusion pathways and to estimate the associated migration energies. Three different vacancy-driven pathways were identified in the Na₂MnPO₄F structure, which together can account for the expected 3D diffusion Na-ion diffusion in the system. These are separately presented in Figure 8 and can be described as follows:

- i) A-type (Figure 8a), resulting in a 1D-diffusion channel delineated by corner-sharing Mn1 octahedra and running parallel to the F-ion chain, along the *b* axis. It has a calculated activation energy of 0.718 eV, the highest;
- ii) B-type (Figure 8b), having the same characteristics as the A-type, but involving the Mn2 octahedra, with a calculated activation energy of 0.572 eV;
- iii) C-type (Figure 8c), when sodium-ion hops between A- and B-type channels, interconnecting them, making the diffusion in the material effectively 3D. The hopping happens parallel to the *ac*-plane and has the lowest calculated

activation energy, 0.450 eV. This type of hopping is auxiliary to the diffusion in the 1D-channels, as it cannot guarantee by itself long range diffusion within the system. Therefore, even if it exhibits the lowest energy barrier, it cannot be the dominant diffusion process in the material.

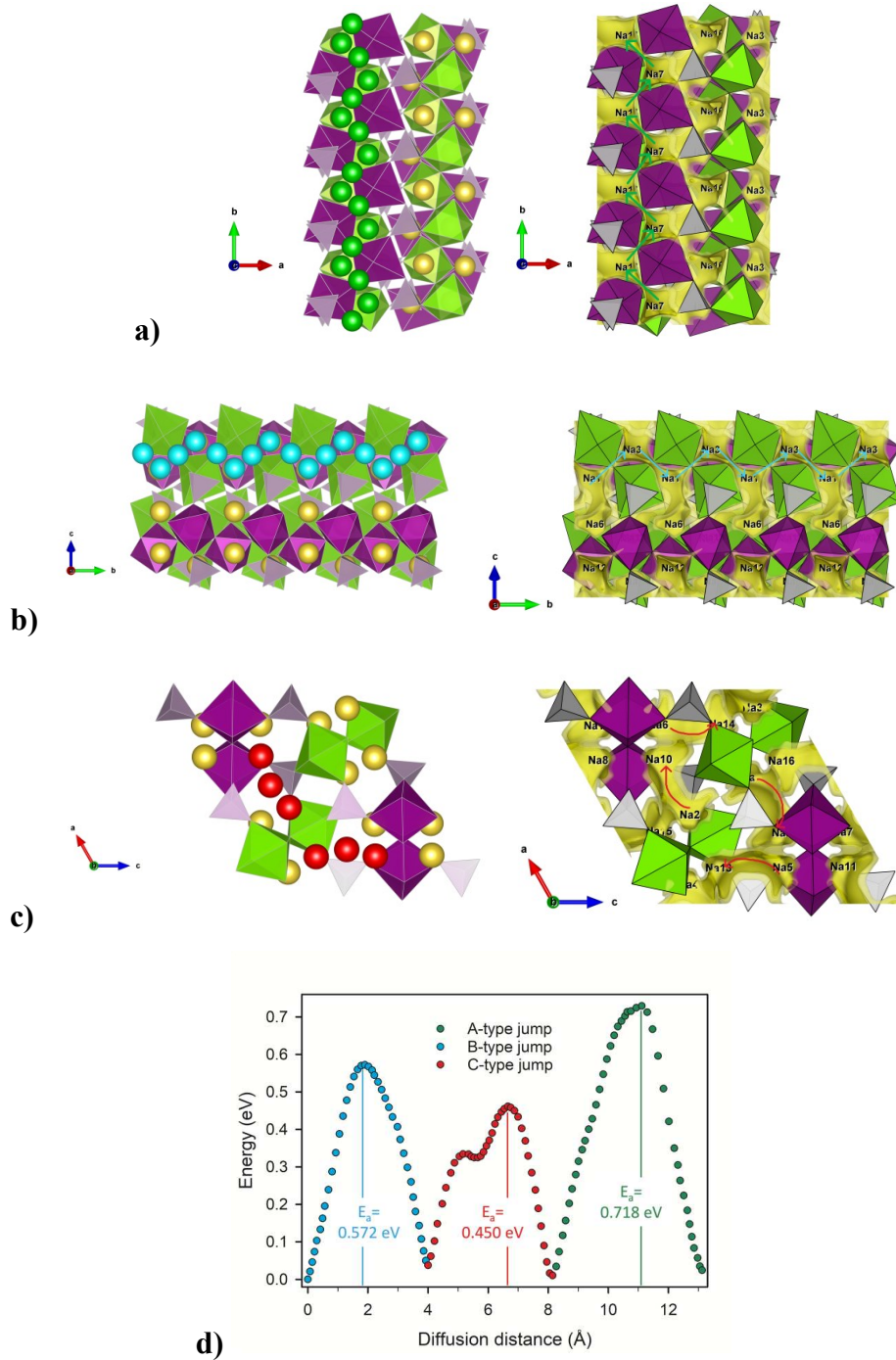


Figure 8. Schematic representation of the migration pathways and the corresponding BVSE calculated isosurfaces for (a) the intra-channel A path, involving Na2 - Na3 hopping; (b) the intra-channel B path, involving Na1 - Na4 hopping and (c) the interchannel C-path, together with the complete energy profile (d), showing the calculated activation energies for the three distinct hopping phenomena

Summarizing, the A- and B-type diffusion pathways support 1D diffusion along the b axis but they are characterized by relatively high activation energies for sodium-ion diffusion at room temperature; the lower energy C-type pathway within the ac plane makes the sodium-ion network effectively 3D and aids its diffusion during the intercalation/de-intercalation processes. The lower calculated activation barrier for the B-type diffusion pathway, close to the Mn2 ions, compared to the A-type path close to the Mn1 ions, is consistent with the shorter Na-Na hopping distance along the respective 1D diffusion channel. The results from the BVSE analysis are in good agreement with DFT-based Nudged Elastic Band (NEB) calculations present in the literature on the same composition,⁷³ with calculated energy barriers slightly overestimated due to the nature of the BVSE technique, which doesn't allow local relaxation around defective sites. On the other hand, the low computational cost of BVSE analysis allows to investigate several compositions and vacancy configurations, which would not be easily accessible through DFT-based NEB. This aspect allows us to get insight into the sodium kinetics during the material's cycling, and to investigate correlation between activation barriers for Na-ion diffusion and lattice distortions induced in the system as a consequence of Na de-intercalation. To this end, the same analysis was carried out also on the two stable phases shown in the convex hull presented in Figure 3a, namely $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ and NaMnPO_4F . The calculated activation energy for the most stable configurations in the $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ system decreases along with the Na content, from 0.60 eV to 0.55 eV when considering the $\text{Na}_2\text{MnPO}_4\text{F}$ and NaMnPO_4F compositions. As shown in Figure 9, the calculated activation barriers for the three different migration paths follow different trends; in particular, while the energy barrier for the A-type hopping reaches a maximum value for the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition, the energy barrier for the B-type hopping reaches a minimum value for the same composition, hinting that the distortion of the Mn2 polyhedra, as evident from Table 3, may enhance Na-ion diffusion.

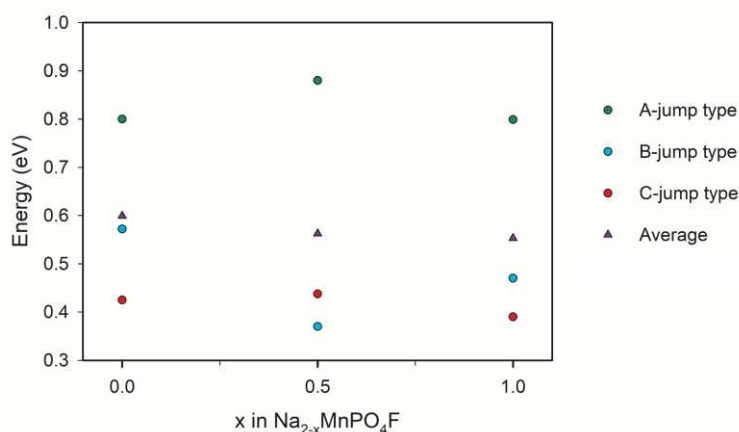


Figure 9. Energy barriers for Na-ion diffusion as derived from BVSE analysis on the DFT energy minimized structures in the $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ system

This result is particularly interesting because the lowest energy configuration calculated for the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition (Figure 2b) indicates a preference for the deintercalation of Na ion close to the Mn2 site. For the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition different Na vacancies configurations were tested. Analysis of the results revealed another important aspect to consider, *i.e.* the high variance of the different calculated activation energies. Each structure, characterized by different vacancies arrangements, presents different local distortions around Na vacant sites and this can either aid the diffusion or disrupt it. The calculated activation energy for the B-type diffusion phenomena for the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition can range from 0.2 eV, when the vacancies are localized near the Mn2 site and, consequently, the nearest MnO_4F_2 polyhedron is highly distorted, up to 0.8 eV, when the vacancies are localized far from the Mn2 channel, and consequently the nearest MnO_4F_2 polyhedron is less distorted. As discussed with reference to Table 3, such octahedral distortions are related to the presence of Mn^{3+} ions instead of Mn^{2+} , which in turn is a consequence of the introduction in the model of Na vacancies in specific positions. To clarify this point, Figure 10 shows two selected examples of configurations for the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition; the calculated distortion parameter, D , and the corresponding activation energy, E_a , are reported for different environments, highlighting the described trend, which is the combined result of octahedral distortion and the presence of Na ion vacancies. For the intermediate compositions, it is likely to have situations in which the presence of vacancies greatly aid one 1D-channel over the other (*i.e.* A- versus B-type pathway): in such cases, the C-type hoppings are essential because, by promoting

the diffusion between adjacent channels, allow for the sodium diffusion in the structure to follow the easiest accessible route following local distortions.

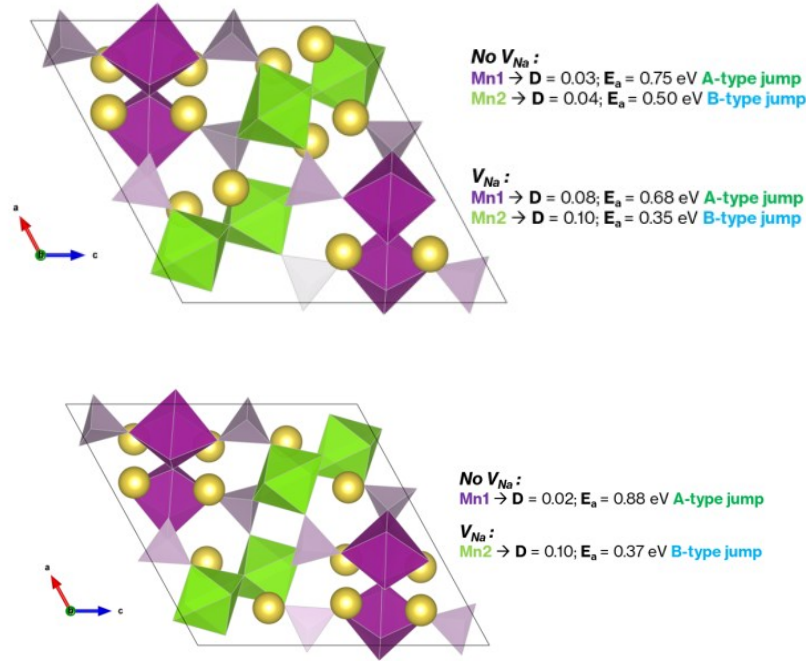


Figure 10. Representation of two configurations of the $Na_{1.5}MnPO_4F$ composition, selected as examples to show the relation between octahedral distortion and calculated activation energy for Na-ion diffusion

To get further insight into the diffusion mechanism and energetics of Na-ion transport in this system, MD simulations based on machine learning interatomic potentials, were performed on the $Na_{1.5}MnPO_4F$ system at different temperatures in the 300-850K temperature range. The potential model employed successfully reproduced the experimental structure reported in Table 1, with the polyhedral framework maintained also at high temperature. Figure 11 compares the trajectory plots at different simulation temperatures, namely 300 K (a), 650 K (b) and 850 K (c). The visual inspection of these plots indicates that long range diffusion of Na-ion is not detectable at room temperature (Figure 11a) over the timescale employed in this study, consistently with the relatively high activation barriers predicted for this composition and the low degree of Na under stoichiometry. At intermediate temperatures (Figure 11b), Na-ion hoppings are visible, mainly those recognizable as type-C and type-B, in line with the activation barrier presented in Figure 8d; at the highest temperature (Figure 11c) all the hopping phenomena predicted on the basis of the BVSE analysis are present and long-range diffusion in the

structure is clearly appreciated. As shown in the zoomed region presented in Figure 11d, the three types of possible hoppings are represented and, when the diffusion of Na-ion along one of the 1D channels along the b crystallographic axis is impeded (either by the high activation energy and/or the lack of a suitable vacant site), the 1D channels are linked by the C-type hopping and sodium diffusion is preserved along the nearest channel.

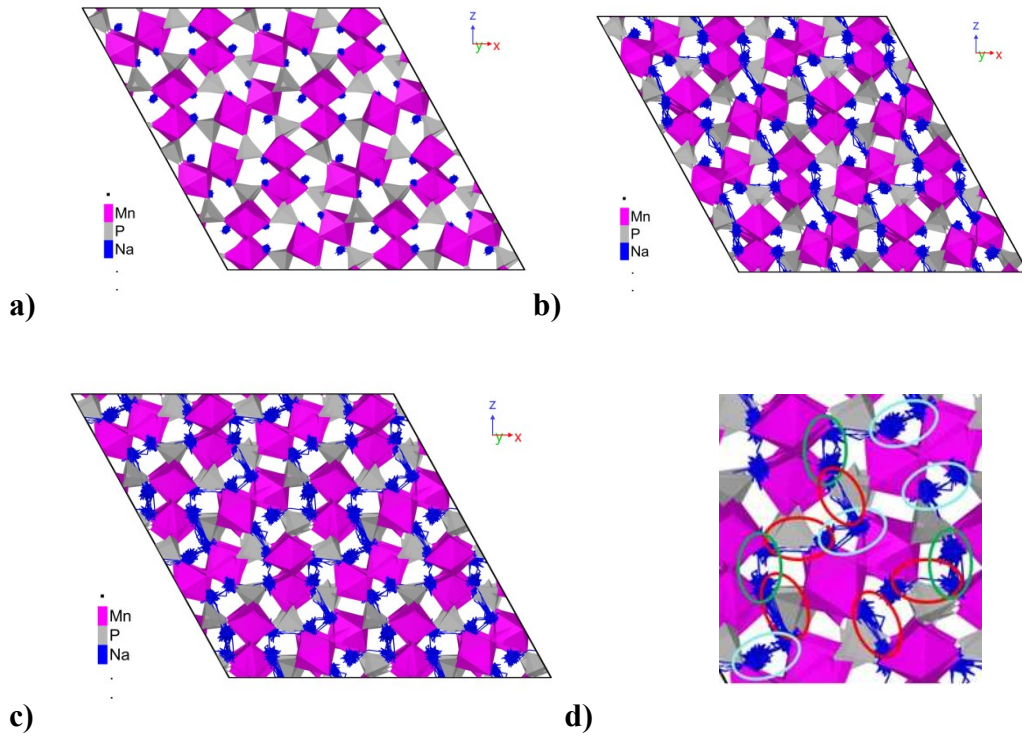


Figure 11. Na-ion trajectory plots derived from MD simulations at 300K (a), 650K (b) and 850K (c) for the composition $\text{Na}_{1.5}\text{MnPO}_4\text{F}$; d) enlarged region showing the interconnection of the different pathways (path A – green, path B – cyan, path C – red)

Figure 12b reports an example of mean square displacement (MSD) of ions as a function of time derived at 750K, clearly showing how Na is the only species achieving long range diffusion within the system, while all the other atoms vibrate around their equilibrium position over the simulation time. From the MSD vs time plots, the Na-ion diffusion coefficients (D_{Na}) at the higher simulation temperatures were calculated by linearly interpolating the data according to the Einstein relation. From these data, reported in Figure 12a, it was possible to extrapolate the diffusion coefficient (D_{Na}) at 300K (room temperature, RT), the usual operating temperature for the final device; the calculated activation energy for Na-ion diffusion in the system is 0.60 eV. This result is in line with

the average activation energy derived from BVSE in this study and close to the values calculated for several Na-ion intercalation cathodes. As a reference, the activation energy for Na-ion diffusion is 0.58 eV in $\text{Na}_2\text{MnP}_2\text{O}_7$.¹⁶⁹ Under the conditions employed in this study, the extrapolated diffusion coefficient at room temperature is $2.57 \times 10^{-10} \text{ cm}^2\text{s}^{-1}$, in line with computationally simulated ones for intercalation cathodes for NIBs.^{170,171} Experimentally derived values for $\text{Na}_2\text{MnPO}_4\text{F}$ are considerably lower, ranging between 10^{-13} to $10^{-16} \text{ cm}^2\text{s}^{-1}$.^{69,163,164}

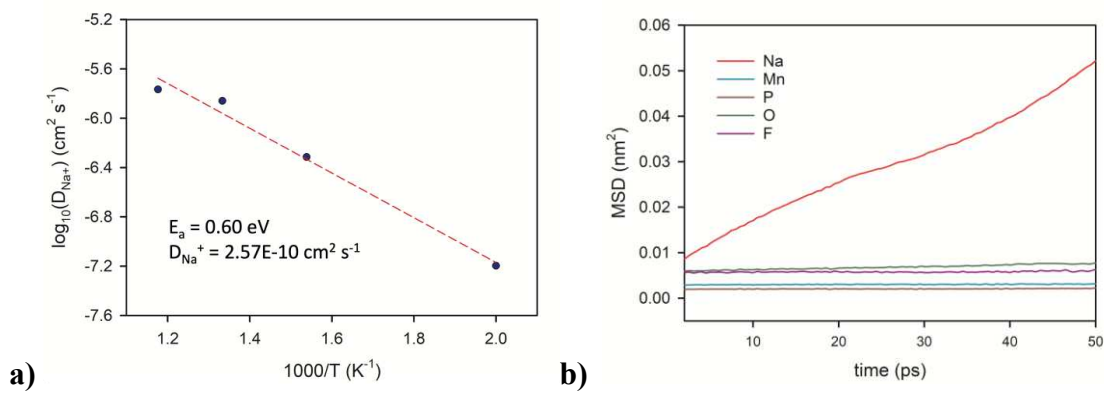


Figure 12. a) Arrhenius plot of diffusion coefficients for $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ as derived from MD-simulations in the NVT ensemble. b) Example of mean square displacement parameter (MSD) vs time plot for the $\text{Na}_{1.5}\text{MnPO}_4\text{F}$ composition as derived from MD simulations at 750K, showing that the only species with appreciable long range diffusion over the simulation time scale is Na

While differences between calculated and experimental values are not unusual, with the most common phenomena that inhibit sodium diffusion (*e.g.*, grain boundaries, particle morphology, cathode/electrolyte interface, cathode slurry composition, cycling rate) being the most frequent causes, we cannot exclude that point defects, such Na/Mn anti-site, may play an important role in determining the materials intercalation properties. This aspect has not been considered in the present computational modeling and warrants further investigation. The presence of anti-site defects, the exchange of the alkali and the transition metal ions in their respective sites, is known to be detrimental to the intercalation properties of phosphate-based alkali-metal cathodes,^{172–174} including $\text{Na}_2\text{FePO}_4\text{F}$.¹⁷⁵

5.3. Conclusion

Transition metal fluorophosphates with general formula $\text{Na}_2\text{MPO}_4\text{F}$ (M = transition metal) are interesting cathode materials for NIBs, thanks to predicted high intercalation voltages and high theoretical capacities. However, the practical applications of several compositions in this family of compounds are limited by effective capacities lower than theoretical ones and by high-capacity fading, particularly at high current densities.

Thanks to the synergy of a broad spectrum of experimental and theoretical techniques, we have completed an extensive characterization of the electrochemical behavior of the prospect cathode material $\text{Na}_{2-x}\text{MnPO}_4\text{F}$ ($x = 0, 0.5, 1$ and 2). The computational part of this study was based on *ab initio* calculations that were performed using Hubbard-corrected Kohn-Sham DFT according to the DFT+U+V scheme, with composition-specific effective Hubbard parameters evaluated (from linear-response theory) in full consistency with each crystal structure. This approach allowed us to capture charge disproportionation at intermediate compositions (*i.e.*, the differentiation of Mn ions in different oxidation states), which is crucial to achieve an accurate prediction of the average voltages at various stages of charge/discharge, and the readjustments that the crystal structure of the considered systems undergo upon changing the concentration of Na in its interior. The calculated intercalation voltages for the $\text{NaMnPO}_4\text{F}/\text{MnPO}_4\text{F}$ couple are confirmed to be outside the stability window of conventional liquid electrolytes, and this aspect limits the electrochemical performances to the extraction of 1 Na-ion per formula unit. In this context, the EPR technique turned out to be a successful tool for monitoring the reversibility degree of the Mn (II) - Mn (III) reduction-oxidation process during the cycling of $\text{Na}_2\text{MnPO}_4\text{F}$.

To investigate the role of Na-ion diffusion on the electrochemical properties of this system, BVSE analyses and molecular dynamics were used to correlate the kinetic energy barriers along the main diffusion paths with the availability of diffusion channels and with the distortion of Mn-O/F octahedra in the vicinity of Na vacancies at various Na concentrations. The calculations allowed to identify three main diffusion paths for Na ions, two of which are substantially one-dimensional, long-range and parallel to the b axis of the cell, the third being instead oblique and transverse to the first two. The latter, characterized by the lowest kinetic barrier overall, although short in nature, turns out to

be essential for the diffusion as it allows Na ions to migrate between the one-dimensional channels and to maintain diffusion even when one of them is impeded. The computational evaluation of the Na-ion diffusion coefficient confirms the high level of ionic conductivity that may characterize this system compared to similar ones. This result suggests that the experimentally observed performances, lower than expected particularly at high charging rates, can only marginally be referred to the difficulties in Na-ion diffusion in the system. At an atomistic level, other aspects not included in our computational model, such as the formation of anti-site defects, may limit Na-intercalation in the structure and thus warrant further investigations with the aim to achieve high performances in a sustainable Mn-based cathode.

6. Recovery of precursor from industrial wastewater

During my PhD, I had the opportunity to conduct part of my research activity at the ENI Renewable, New Energies and Material Science Research Center in Novara. During this period, I focused on optimizing procedures for the selective recovery of specific elements from company's wastewater, which is particularly rich in sodium and other constituents. The goal of the project was to employ the recovered precursors for the synthesis of new materials for SIBs. In this final chapter, I therefore present the optimized recovery procedures together with the first preliminary results obtained.

Since the direct use of production water was not permitted for safety reasons, we prepared “standard” solutions reproducing the composition of the original water. These solutions were obtained from water-soluble precursors and subsequently used to investigate the selective recovery of the target components. The composition employed in all tests was as follows (pH = 6.6):

Table 1. Elementary composition of the standard solution prepared

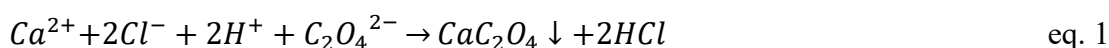
	ppm
Na (NaCl)	2930
K (KBr)	306
Mg (MgSO ₄)	206
Ca (CaCl ₂)	726
Sr (SrCl ₂ • 6H ₂ O)	43

Considering that the recovery of Na and K by simple selective precipitation is very difficult due to the high solubility of their compounds in water, our strategy was to first recover the other cations through selective precipitation. Subsequently, we explored the possibility of recovering Na via complexation, employing highly selective crown ethers.

6.1. Selective precipitation of Ca²⁺ and Mg²⁺

After preparing the model solution, we first proceeded with the selective precipitation of Ca²⁺ using oxalic acid (H₂C₂O₄). The selection of oxalate as the precipitating agent was

made based on the observation that calcium oxalate (CaC_2O_4) is characterized by a low level of solubility in water, thus resulting in its facile precipitation without the necessity for any experimental precautions. Furthermore, among all divalent cation oxalates, CaC_2O_4 has the lowest solubility product. Therefore, if used properly, it is possible to avoid the simultaneous precipitation of other cations present in the solution, including Mg^{2+} , which will then be separated through another strategy. The Ca^{2+} precipitation reaction is as follows (eq. 1):



However, based on the literature, it is necessary to add oxalic acid in large excess (x2 mol) to obtain quantitative precipitation of Ca^{2+} . To increase the yield and quality of the precipitate, all operations were carried out at a temperature of ca. 50-60 °C. This promotes the precipitation of calcium oxalate monohydrate over other more hydrated oxalates, which is easier to separate by simple vacuum filtration on a Buckner. To promote the growth of the precipitate particles, after adding $\text{H}_2\text{C}_2\text{O}_4$, the solution obtained was stirred for 40 minutes under magnetic stirring.

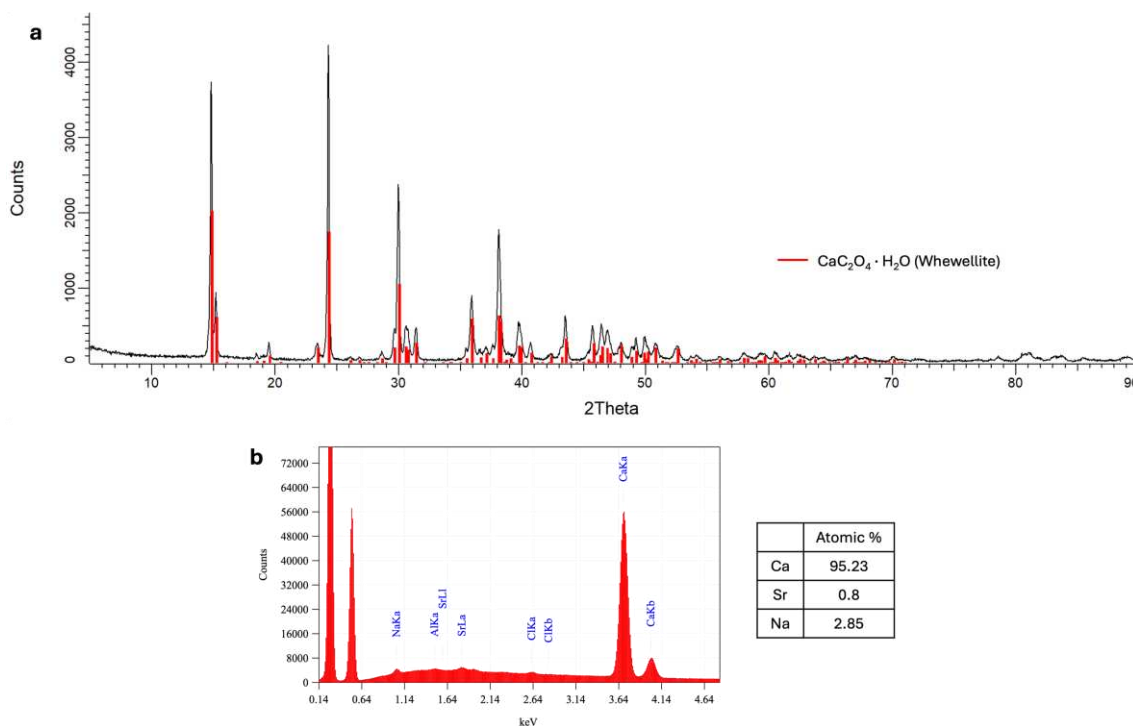
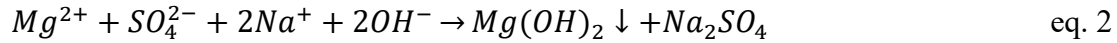


Figure 1. (a) XRD and (b) EDX analysis of the powder collected after selective precipitation of Ca^{2+} with $\text{H}_2\text{C}_2\text{O}_4$

The XRD pattern shown in Figure 1a was collected on the precipitate recovered after filtration and subsequent oven-drying. By comparing the experimental data (black curve) with the reference signals of CaC_2O_4 (red bars), it was possible to conclude that the precipitate is monophasic. Nevertheless, EDX analysis (Figure 1b) revealed the presence of a minor Sr impurity, consistent with its occurrence in the starting solution. This can be explained considering that SrC_2O_4 and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ crystallize in the same structure (monoclinic system, space group: $P21/c$) and are therefore indistinguishable by XRD. By considering the significantly higher solubility of the Sr compound compared to that of Ca (5.6×10^{-8} vs 1.8×10^{-9} at 18°C), further purification of the precipitate could be achieved by washing with water. However, since these two cations are not directly relevant for the synthesis of the cathode materials investigated in the previous chapters ($\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$), no additional purification steps were carried out.

After removing Ca and Sr from the solution, we attempted to recover Mg^{2+} as hydroxide by precipitation with NaOH. The reaction involved in this step is (eq. 2):



However, due to the very acidic pH of the solution ($\text{pH} = 1.3$) obtained after the previous step, caused by the formation of many H^+ ions from oxalic acid (eq. 1), it was necessary to add a large amount of NaOH to neutralize the acidity and reach a suitable pH to start precipitation ($\text{pH} = 9-10$). Furthermore, the whitish precipitate formed afterwards was very fine and very difficult to isolate. Figure 2 shows the XRD pattern collected on the precipitate. In addition to the desired phase, this analysis also showed the presence of a significant amount of CaC_2O_4 impurity (about 20%), also observable in the EDX spectrum.

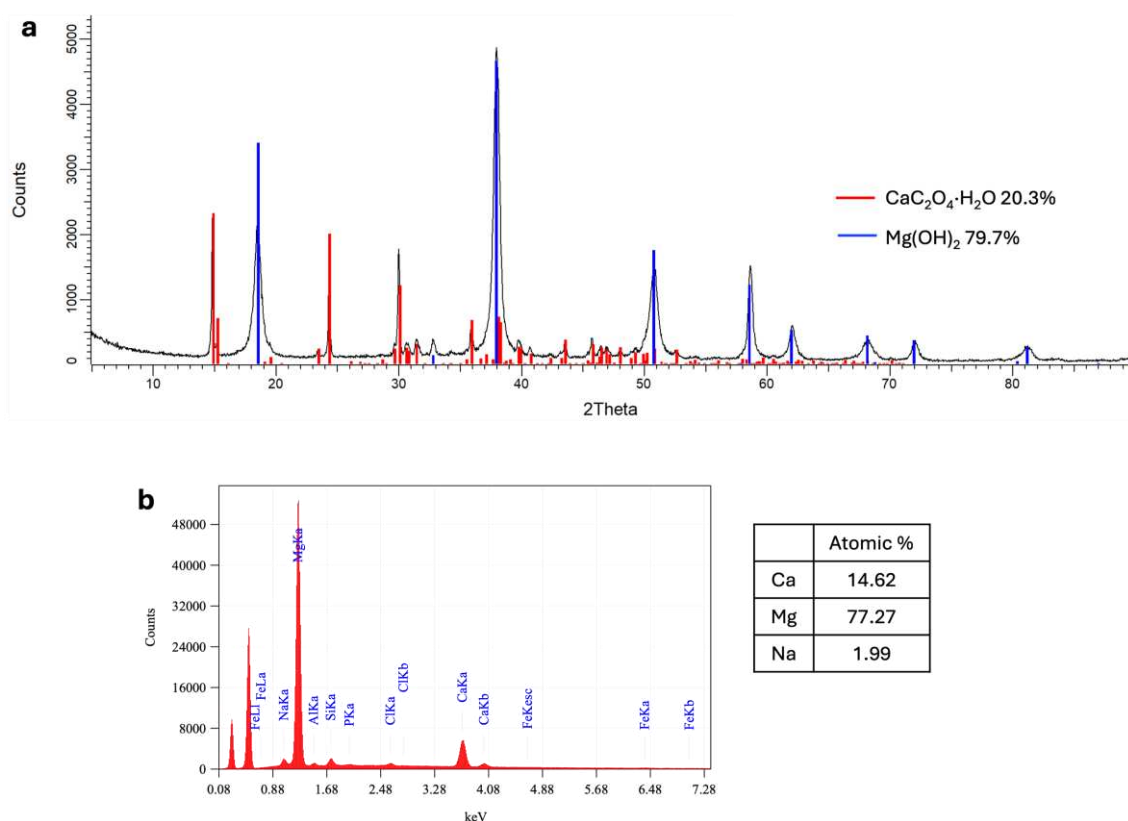


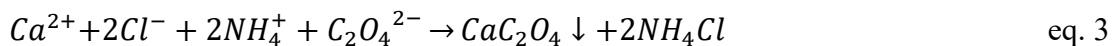
Figure 2. (a) XRD and (b) EDX analysis of the powder collected after selective precipitation of Mg^{2+} with NaOH

This impurity is most likely due to the precipitation of Ca oxalate when the addition of NaOH to basify the solution brought the pH back into the optimal range for oxalate precipitation.

Considering these results, we decided to modify the experimental conditions in order to limit the pH drop observed after Ca^{2+} precipitation with $\text{H}_2\text{C}_2\text{O}_4$. As a first attempt, we employed a buffer solution to stabilize the pH during the precipitation. Given the desired pH range, a 1:1 mixture of citric acid and sodium citrate was selected. All other experimental conditions were kept unchanged. Under these conditions, the CaC_2O_4 precipitate exhibited markedly improved properties compared to the previous case (larger particle size), and the solution pH remained stable after precipitation (pH = 4.8).

Nevertheless, the adjustment of the buffer range to achieve the requisite pH for $\text{Mg}(\text{OH})_2$ precipitation necessitated the incorporation of substantial quantities of concentrated NaOH (in pellet form), which compromised the reproducibility of the procedure. Furthermore, due to the probable formation of highly soluble Mg^{2+} -citrate complexes, no precipitation of $\text{Mg}(\text{OH})_2$ was observed even at very basic conditions (pH > 13).

To overcome these issues, we decided to replace the Ca^{2+} precipitating agent $\text{H}_2\text{C}_2\text{O}_4$ with $(\text{NH}_4)_2\text{C}_2\text{O}_4$. As shown in the reaction involved (eq. 3), this approach deletes the formation of H^+ in solution.



By employing these conditions, the precipitation yield of CaC_2O_4 was practically quantitative ($> 95\%$), and the pH of the solution remained almost unchanged. As can be seen from the XRD pattern shown in Figure 3, the only difference compared to the previous cases is that two oxalates with different degrees of hydration are now formed. In addition, almost 2% NaCl was also detected, but this could be easily removed by washing in H_2O .

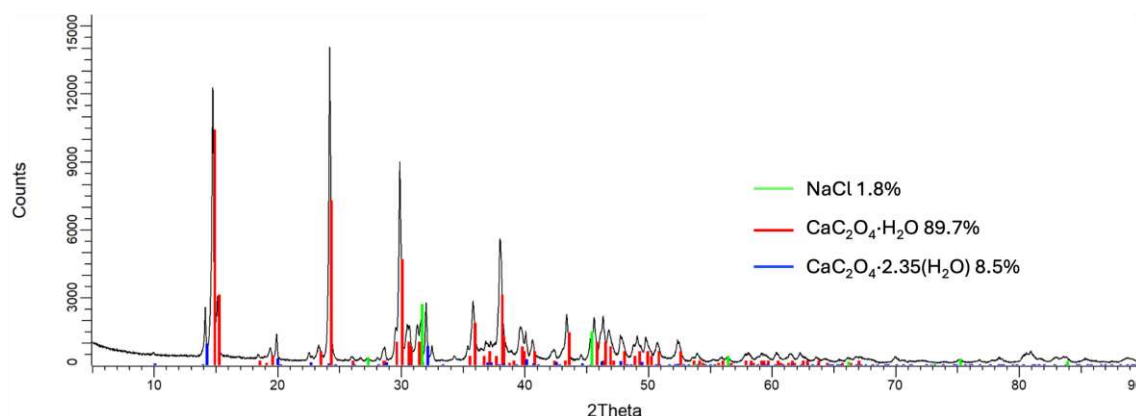


Figure 3. XRD analysis of the powder collected after selective precipitation of Ca^{2+} with $(\text{NH}_4)_2\text{C}_2\text{O}_4$

Concerning the precipitation of Mg^{2+} , it was sufficient to add 0.5 M NaOH drop by drop to reach the pH necessary for the precipitation of $\text{Mg}(\text{OH})_2$ to begin (eq. 2). After 30 minutes of stirring, the precipitate obtained was a very fine white powder, and therefore a centrifugation step (20 min, 4000 rpm) was necessary to recover it. Figure 4a shows the XRD pattern collected after these steps. It is important to note that, unlike the results shown in Figure 2, the hydroxide is now practically pure ($\text{CaC}_2\text{O}_4 < 1\%$). The impurities observed were easily eliminated by washing with H_2O , as shown by the pattern in Figure 4b. This is an excellent result, as we were able to obtain a pure precursor that could

potentially be used for the synthesis of cathode materials, which I worked on during my PhD.

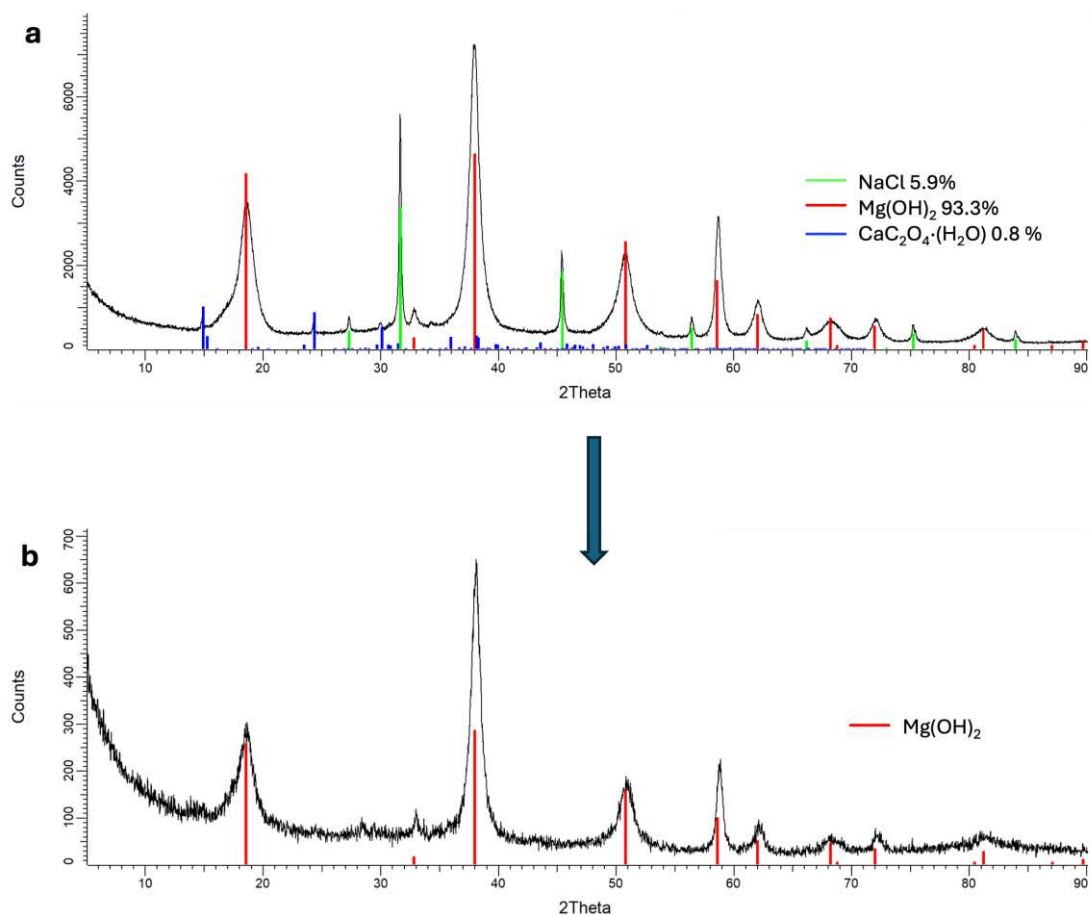


Figure 4. XRD and of the powders collected after selective precipitation of Mg^{2+} with NaOH (a) before and (b) after washing step with H_2O

In conclusion, through ICP analysis of the solution obtained after precipitation, we evaluated the amount of Ca^{2+} and Mg^{2+} still in solution. The results in Table 2 clearly show that the precipitation of both elements occurred quantitatively.

Table 2. ICP-OES analysis results after Ca^{2+} and Mg^{2+} precipitation

	ppm
Ca	< 0.3
Mg	2.4

6.2. Na⁺ recovery through complexation with Crown ethers

Recovering Na⁺ from wastewater is the most challenging task, because unlike other cations, it is not possible to precipitate any Na compounds due to their high solubility in H₂O. For example, Na oxalate, which is one of the less soluble Na salts, has a solubility at room temperature of approximately 37 g L⁻¹. By contrast, Ca oxalate, discussed above, has a solubility of 7 mg L⁻¹. For this reason, to selectively recover sodium, we decided to investigate the possibility of using highly specific organic complexing agents. Among these, the 15-crown-5 (15C5) crown ether is certainly one of the most widely used and interesting. Crown ethers are a class of cyclic organic compounds discovered in the 1960s by Charles Pedersen,¹⁷⁶ and they immediately gained great attention in coordination chemistry due to their great ability to selectively complex alkali cations. Li⁺, Na⁺, and K⁺ have an ideal ionic radius to be accommodated within the cavity of 12C4, 15C5, and 18C6, respectively. The number after the C indicates the number of oxygen atoms present on the ring, linked together by ethylene bridges; the number before the C, on the other hand, is equal to the sum of the C and O atoms.

Experimentally, the procedure was carried out as follows: (i) formation of the Na⁺-15C5 complex; (ii) extraction into the organic phase, thereby isolating it from the rest of the solution; (iii) dissociation of the complex by acid treatment, allowing Na⁺ to return to the aqueous phase; and (iv) recovery of a Na precursor, such as NaCl or NaNO₃, by evaporation. However, during the months spent at the ENI Research Center we were only able to focus on optimizing the first two steps of the process described above. As will be detailed in the following paragraphs, two different complexing agents with distinct physicochemical properties were employed, with the aim of identifying the most suitable one and the optimal operating conditions for Na⁺ complex formation.

6.2.1. Na⁺-(NitroBenzo-15Crown5)

The first crown ether used was 4'-NitroBenzo-15C5 (NB15C5), whose structure is shown in Figure 5.

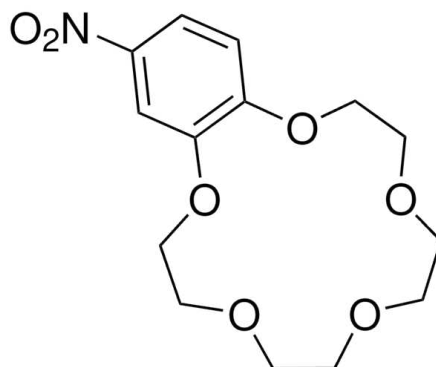
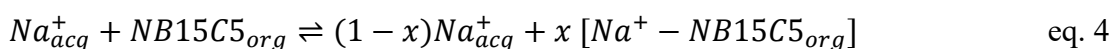


Figure 5. Chemical structure of 4'-Nitrobenzo-15-crown-5 (NB15C5)

The choice of this compound was motivated by the need for a complexing agent with specific solubility properties. It had to be highly soluble in the organic phase but insoluble in the aqueous phase. The nitro-phenyl group on the 15C5 ring strongly reduces its solubility in water. The extraction was carried out using a two-phase system. The Na-rich aqueous solution was brought into contact with dichloromethane (CH₂Cl₂, DCM) containing the selected complexing agent. As the crown ether is insoluble in water, it was deemed unnecessary to consider the possibility of its transfer into the aqueous phase during the extraction process. The reaction involved in this extraction is (eq. 4):



To minimize reagent consumption, in particular crown ether, we used small volumes of dilute solutions. Specifically, 5 mL of a 1 M NaCl aqueous solution and 10 mL of a 0.01 M NB15C5 solution in CH₂Cl₂. The organic phase was used in excess to increase the extraction efficiency. The two phases were put in contact and stirred vigorously overnight under magnetic stirring, and then separated with a separating funnel. The Na content in the organic phases, both before and after extraction, was analyzed by ICP-OES. The results did not match expectations, since the Na concentration increased only from <10 ppm to 54 ppm. This shows that only a very small fraction of Na⁺ was complexed and

transferred to the organic phase, in agreement with the expected mechanism. To confirm the key role of the crown ether, the experiment was repeated under identical conditions but without NB15C5 in the organic phase. ICP analysis showed no change in Na concentration (<10 ppm), confirming that no extraction occurs in the absence of the crown ether.

To improve the Na extraction from aqueous solution, we doubled the concentration of NB15C5 to 0.02 M. ICP analysis confirmed a significant increase in Na concentration in the organic phase after extraction compared to the previous extraction, reaching 332 ppm. This result confirmed both the validity of the process and the direct proportionality between the amount of complexing agent and that of Na⁺ extracted from the aqueous phase. Nevertheless, the extraction yields are still unsatisfactory, and further optimization is required.

6.2.2. Na⁺-(15Crown5)

The second complexing agent investigated for Na⁺ recovery from wastewater was the unsubstituted 15-Crown-5 (15C5), represented in Figure 6.

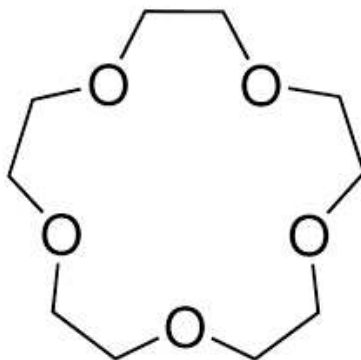


Figure 6. Chemical structure of 15-crown-5 (15C5)

This ligand was selected because, unlike NB15C5, it is also soluble in water. This property allowed us to separate two processes that previously occurred simultaneously: Na⁺ extraction into the organic phase and subsequent complex formation.

Experimentally, 10 mL of a 0.01 M aqueous solution of 15C5 were added to 5 mL of a 1 M NaCl aqueous solution and stirred for 2 h. Then, 10 mL of CH₂Cl₂ were introduced,

and the system was stirred overnight to promote the transfer of the Na^+ -15C5 complex into the organic phase. The two phases were then separated with a separating funnel, and the Na^+ content in the post-extraction organic phase was evaluated by ICP analysis, which gave 387 ppm. This result is remarkable since a solution of 0.01 M 15C5 extracted nearly the same amount of Na^+ as 0.02 M of NB15C5 (332 ppm). Therefore, the 15C5-based protocol appears to be the most effective approach for optimizing Na^+ recovery from water.

6.3. Conclusion

In conclusion, during my time at the ENI research center, I was able to optimize procedures for the selective recovery of Ca^{2+} and Mg^{2+} from the company's production water. Specifically, Ca^{2+} was quantitatively recovered as oxalate through selective precipitation with $(\text{NH}_4)_2\text{C}_2\text{O}_4$, while Mg^{2+} was recovered as $\text{Mg}(\text{OH})_2$ through the addition of NaOH. EDX analysis performed on the recovered calcium oxalate revealed a small impurity of Sr, one of the cations present in minor quantities in the pristine wastewater. The presence of this cation is easily explained, as Sr^{2+} precipitates simultaneously with Ca^{2+} as oxalate. Regarding Mg^{2+} , however, we were able to optimize a procedure that allowed us to obtain highly pure $\text{Mg}(\text{OH})_2$, which could potentially be used as a precursor of Mg in the synthesis of cathode materials, which is the subject of my PhD project. Finally, regarding Na^+ , I discussed the preliminary results collected on the use of 15-crwon-5 as complexing agent for its selective recovery. In particular, 15C5 proved to be more effective than NB15C5, as it allows the same Na content to be extracted but with half the concentration. However, the yields obtained are not satisfactory, although they provide a solid basis for future optimization.

CONCLUSION

As outlined in the preceding chapters, the primary focus of my PhD research was the synthesis and characterization of novel materials for emerging Na-ion batteries. In particular, the investigation focused on two distinct categories of cathode materials: the subject of this study is P2-layered transition metal oxides and polyanionic compounds. In Chapter 4, I discussed the properties of a family of materials with the composition $\text{P2-Na}_{0.67}\text{Mn}_{0.5}\text{Fe}_{0.5-x}\text{Mg}_x\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3$) from a structural, morphological, elemental, and, above all, electrochemical perspective. During this study, noteworthy correlations were identified between the recorded cathodic performance and the elemental properties of the different compositions. The stabilizing role of Mg^{2+} was confirmed by long-term cycling, EIS and *operando* XRD experiments. The process of spray-drying synthesis has been shown to hold considerable promise for utilization within battery applications. The principal merits of this method can be summarized as follows: firstly, it is easily scalable; secondly, it is significantly more environmentally sustainable than conventional solid-state synthesis. Moreover, this promotes the formation of materials with microstructures and morphologies that are perfectly in line with the standards of active materials in batteries. The best-performing material was also evaluated in a full-cell configuration with a commercial anode (HC). To solve the problems of low Na^+ content in P2-layered oxides and low ICE of the HC-based anode, we tested two pre-sodiation strategies: the addition of Na_2CO_3 as a sacrificial salt and the electrochemical pre-sodiation of HC anode. The second pre-sodiation approach yielded particularly encouraging results in terms of electrode structural stability, energy density, and capacity retention after 100 cycles conducted under real-world battery operating conditions (slow charge and fast discharge). In Chapter 5, we presented the results of a study, conducted in collaboration with the Department of Physics at the University of Pavia, on the electrochemical properties and the redox behavior of $\text{Na}_2\text{MnPO}_4\text{F}$ as a cathode for SIBs. Through a dual experimental and theoretical/computational approach, we were able to predict the diffusion mechanism of Na^+ ions during cycles in the polyanionic structure and the working potentials. Furthermore, we confirmed the possibility of monitoring the behavior of the Mn (II)-Mn(III) redox couple through ex-situ EPR spectroscopy experiments, since Mn (II) is an EPR-active cation.

In Chapter 6, I discussed the selective recovery procedures of Ca^{2+} , Mg^{2+} , and Na^+ from industrial wastewaters rich in these and other elements. In particular, the most interesting result is the optimization of a procedure that enabled the nearly quantitative recovery of Mg^{2+} from solution through hydroxide precipitation with NaOH. $\text{Mg}(\text{OH})_2$, in fact, could be directly employed as a precursor for the synthesis of electrode materials for SIBs. For Na^+ , preliminary results showed its complexation with 15-crown-5, followed by biphasic extraction from the aqueous solution. This procedure still requires further optimization to provide a fully recycled Na source for new and more-sustainable syntheses.

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