

Cathode Optimization for Application in Next- Gen All Solid-State Batteries

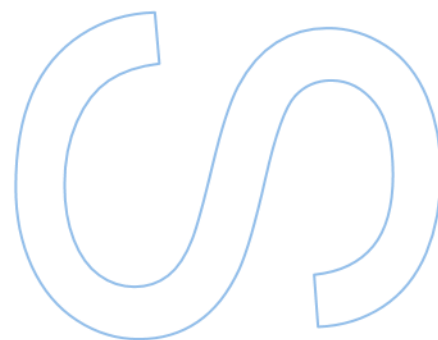
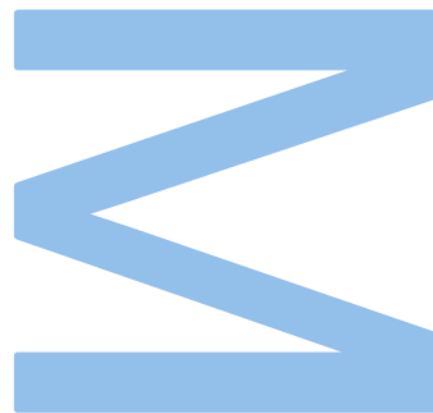
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2025



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Supervisor

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Dedicated to my family

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This journey was not always easy, and there were times when I doubted myself. But thanks to the people mentioned here, I always found reasons to keep going.

Resumo

Neste trabalho, foram sintetizados e otimizados cátodos à base de $\text{LiNi}_{0.90}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NMC955) para aplicação em baterias de estado sólido. A síntese foi estruturada para se alinhar com métodos escaláveis e com o objetivo de eliminar o uso de componentes tóxicos, nomeadamente fluoreto de polivinilideno (PVDF) como *binder* e N-metilpirrolidona (NMP) como solvente. Foram testados dois *binders* alternativos, poliisobutileno (PIB) e álcool polivinílico (PVA), e tolueno foi usado como solvente. Depois de sintetizados os cátodos foram incorporados em coin cells com eletrólito sólido $\text{Li}_5\text{PS}_6\text{Cl}$ e um ânodo de lítio metálico (Li^0). Estas células com estrutura NMC955/LPSCI/ Li^0 passaram por uma série de testes de caracterização eletroquímica que permitiram avaliar a sua performance e viabilidade: espectroscopia de impedância eletroquímica (PEIS), voltametria cíclica (CV), cargas e descargas galvanostáticas (GCD), e técnica de titulação intermitente galvanostática (GITT). Os melhores resultados foram obtidos para cátodos com 4% de *binder* na sua composição. Células fabricadas com um cátodo com PVA atingiram a capacidade teórica do NMC955 (192 mAh.g^{-1}) e foram capazes de manter um comportamento estável por mais de 100 ciclos eletroquímicos. Os cátodos com PIB foram usados em células que atingiram uma capacidade máxima de 145 mAh.g^{-1} a C/40, conseguindo manter esta capacidade mesmo depois de submetidas a ciclos mais exigentes a 1C. Caracterização dos cátodos através de medições de efeito de Hall e de *sheet resistance* revelou que ambos os *binders* não alteraram o comportamento condutivo do material ativo, necessário ao bom funcionamento das células. Análises de microscopia eletrónica (SEM/EDX) permitiram o estudo da superfície dos cátodos e monitorização da sua composição química. Este estudo demonstrou o potencial de ambos os binders, sustentáveis e não poluentes, para a produção de cátodos compatíveis com eletrólitos sólidos à base de enxofre, podendo contribuir para o desenvolvimento de baterias de estado sólido mais seguras e ecológicas.

Palavras-chave: All solid-state batteries, composite cathodes, *binders*, NMC

Abstract

In this work, $\text{LiNi}_{0.90}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NMC955) based cathodes were synthesized and optimized for application in solid-state batteries. The synthesis was structured to align with scalable methods and with the goal of eliminating the use of toxic components, namely polyvinylidene fluoride (PVDF) as a binder and N-methylpyrrolidone (NMP) as a solvent. Two alternative binders, polyisobutylene (PIB) and polyvinyl alcohol (PVA) were tested, and toluene was used as the solvent. After synthesis, the cathodes were incorporated into coin cells with $\text{Li}_5\text{PS}_6\text{Cl}$ solid electrolyte and a lithium metal (Li^0) anode. These cells with NMC955/LPSCI/ Li^0 structure underwent a series of electrochemical characterization tests to evaluate their performance and viability: potentiostatic electrochemical impedance spectroscopy (PEIS), cyclic voltammetry (CV), galvanostatic charging and discharging (GCD), and galvanostatic intermittent titration technique (GITT). The best results were obtained for cathodes with 4% binder in their composition. Cells manufactured with a PVA cathode reached the theoretical capacity of NMC955 (192 mAh.g^{-1}) and were able to maintain stable behavior for more than 100 electrochemical cycles. PIB cathodes were used in cells that reached a maximum capacity of 145 mAh.g^{-1} at C/40, managing to maintain this capacity even after undergoing more demanding cycles at 1C. Characterization of the cathodes through Hall effect and sheet resistance measurements revealed that both binders did not alter the conductive behavior of the active material, which is necessary for the proper functioning of the cells. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX) analyses allowed the study of the cathode surface and monitoring of its chemical composition. This study demonstrated the potential of both binders, which are sustainable and non-polluting, for the production of cathodes compatible with sulfur-based solid electrolytes, which could contribute to the development of safer and more environmentally friendly solid-state batteries.

Keywords: All solid-state batteries, composite cathodes, *binders*, NMC

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List of Abbreviations

CEI	CATHODE-ELECTROLYTE INTERFACE
CMC	CARBOXY METHYL CELLULOSE
EV	ELECTRIC VEHICLE
FCUP	FACULTY OF SCIENCES OF THE UNIVERSITY OF PORTO
FEUP	FACULTY OF ENGINEERING OF THE UNIVERSITY OF PORTO
ISE	INORGANIC SOLID ELECTROLYTE
LE	LIQUID ELECTROLYTE
LFP	LiFePO_4
Li^0	LITHIUM METAL
LIB	LITHIUM ION BATTERY
LMO	LiMn_2O_4
LMNO	$\text{LiMn}_x\text{Ni}_{2-x}\text{O}_4$
LPSCI	$\text{Li}_6\text{PS}_5\text{Cl}$
NMC	$\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$
NMP	N-METHYL-2-PYRROLIDONE
PAA	POLYACRYLIC ACID
PDADMA	POLY(DIALLYLDIMETHYLAMMONIUM)
PIB	POLYISOBUTYLENE
PVA	POLYVINYL ALCOHOL
PVDF	POLYVINYLIDENE FLUORIDE
SBR	STYRENE-BUTADIENE RUBBER
SEM	SCANNING ELECTRON MICROSCOPY
SOC	STATE OF CHARGE
SPE	SOLID POLYMERIC ELECTROLYTE
SSB	SOLID STATE BATTERY
SSE	SOLID STATE ELECTROLYTE
UP	UNIVERSITY OF PORTO
USD	UNITED STATES DOLAR
XRD	X-RAY DIFFRACTION

Introduction

1.1. Context

Since the 1980s, economic and population growth has created an ever-greater need for energy. Although fossil fuel energy production has enabled society to grow into the state known today, it will not be sustainable forever. It is essential to develop new forms of green energy production and storage that do not jeopardize the prosperity of future generations. Lithium-ion batteries (LIBs) have become a centerpiece of the energy transition. Currently, the LIB market is estimated at more than 50 billion dollars (USD) spread across industries such as electric vehicles and portable charging devices [1]. Despite LIBs nearing the limits of their technological potential, this has driven governments and nations to implement policies that encourage research, optimization, and innovation, to foster advancements that can revolutionize this energy storage technology [2,3].

1.2. Motivation

The electric vehicle (EV) market has grown exponentially and attracted significant investment, becoming a centerpiece for reducing carbon dioxide emissions and mitigating climate change [4]. The success of this market relies on the development of batteries that provide high energy density, sufficient capacity, long lifespan, and affordability. Batteries have three main elements that significantly influence their performance: the cathode, the anode and the electrolyte. An important step in the evolution of batteries was the development of solid-state batteries (SSBs). Unlike in traditional LIBs where the electrolyte is liquid, SSBs employ solid-state electrolytes that are non-flammable and able to mitigate the formation of dendrites, virtually eliminating the risk of internal short-circuit and consequent battery failure. Additionally, solid-state electrolytes have a wider electrochemical window, which makes them more compatible with high-energy density cathodes and anodes [5–7].

The development of efficient cathodes that have increased stability and specific capacity is essential to achieve high energy density batteries. Cathodes have three main components: active material, binder, and conductive agent. The active material defines the cathode's capacity and therefore, it is a key element in its development. By 2022, the EV industry was dominated by three types of active materials: NMC, LFP and NCA [1,8,9]. NMC is highly promising since it offers a superior balance of energy density, cycle life, and thermal stability. Its structure and chemical composition allow for different stoichiometries of transition metals - Ni, Co, and Mn. Each of these elements offers

different advantages to battery performance, and their percentages must be optimized bearing in mind the ambitious goal set for the EV industry and its environmental impact [5,10,11]. The biggest challenge is to manage performance, stability, cost, and sustainability.

To consider batteries as a sustainable form of energy storage, it is necessary to evaluate their entire life cycle, from the extraction of minerals to the moment they are no longer usable. Currently, NMC cathodes contain cobalt (Co), which is not only toxic but also primarily sourced from the Democratic Republic of Congo. There, extraction occurs under inhumane labor conditions, and the ore is sold at high prices through unsustainable economic practices [12,13]. Naturally, the pressure to develop cathodes with reduced amounts of Co has increased considerably [10]. This shift toward more sustainable cathodes contemplates not only Co usage, but also the use of toxic binders and solvents during fabrication. The use of polyvinylidene fluoride (PVDF) as a binder in cathode synthesis is being restricted in the European Union due to concerns over environmental impact [14]. Additionally, the choice of sustainable solvents is essential. N-Methyl-2-pyrrolidone (NMP), a common solvent used to dissolve PVDF, is considered harmful to human health and the environment since its high water solubility increases the risk of aquatic ecosystem pollution. Safely disposing of NMP requires specialized processes to prevent environmental release, adding complexity and cost to waste management. Recent strategies have enabled the recycling or reuse of batteries and their components, promoting the growth of a circular economy [15–18].

1.3. Objectives

The objective of this thesis was to optimize $\text{LiNi}_{0.90}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NMC955) based cathodes for solid-state batteries, using environmentally sustainable binders and solvents compatible with solid electrolytes, eliminating the use of PVDF and NMP. To this end, two alternative binders, polyisobutylene (PIB) and polyvinyl alcohol (PVA) were studied using toluene as a solvent. The study developed in this thesis compared the electrochemical performance of different cathode formulations, incorporating the sulfide solid electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) in their composition, and integrating them into coin cells with a lithium metal (Li^0) anode.

To achieve these objectives, the following steps were followed:

1. Preparation of cathodes and assembly of coin cells:

- a. Synthesis of composite cathodes with different binder contents (2% and 4%) and two types of binder (PIB and PVA), incorporating LPSCI and C65, a carbon-based conductive agent.
- b. Fabrication of bilayers with a layer of cathode and a layer of LPSCI solid electrolyte.
- c. Assembly of NMC955/LPSCI/Li⁰ coin cells in a glovebox under an inert and controlled atmosphere.

2. Material characterization:

- a. Scanning electron microscopy (SEM) tests combined with X-ray energy dispersive spectroscopy (EDX) for microstructural and compositional analysis of the cathodes.
- b. Sheet resistance and Hall effect measurements to evaluate electrical behavior and charge carrier type and concentration.

3. Electrochemical testing of manufactured cells:

- a. Potentiostatic electrochemical impedance spectroscopy (PEIS) for analysis of bulk and interfacial impedances.
- b. Cyclic voltammetry (CV) for determining operating voltage windows and cycling reversibility.
- c. Galvanostatic charge-discharge (GCD) to determine cell's specific capacity, to evaluate its performance at different current rates, and its cycling stability
- d. Galvanostatic intermittent titration technique (GITT) to determine Li ion diffusion coefficients in the cathode.

1.4. Contributions

This thesis was carried out at the MatER Laboratory, at the Faculty of Engineering of the University of Porto. The experimental work was funded by a research grant awarded by the Department of Chemical and Biological Engineering (DEQB), entitled "Cathode optimization for application in next-gen all solid-state batteries".

Throughout this master's degree, various scientific contributions were made. Firstly, the results obtained were presented at two conferences:

- (1) **IRF 2025 - International Conference on Integrity, Reliability, and Failure**, where I had the opportunity to present my work during an oral-poster session, **Attachment A**.
- (2) **DCE25 - Doctoral Congress in Engineering 2025**, where I had the opportunity to present my work during an oral-poster session, **Attachment A**.

In addition, this collaborative work led to two scientific publications:

- (1) An experimental article, entitled “Nickel-Rich Cathodes for Solid-State Lithium Batteries: Comparative Study Between PVA and PIB Binders”, published in the journal MDPI Molecules (DOI:[10.3390/molecules30142974](https://doi.org/10.3390/molecules30142974)), with an impact factor 4.6 and Q1 in the corresponding area. In this article, in which I am first author, we studied the potential of PIB and PVA as suitable alternative binder to PVDF in cathode synthesis. My contribution included synthesizing cathodes, fabricating coin cells, structural and chemical characterization (SEM/EDX, Sheet resistance and Hall effect measurements), carrying out electrochemical tests (PEIS, CV, GCD, and GITT), processing and analyzing the data, as well as writing the manuscript.
- (2) A revision article submitted to Susmat (tentatively).

In this master thesis, I made experimental contributions to cell fabrication, electrochemical characterization experiments, microstructural analysis, and electric behavior analysis. Furthermore, I have developed the Python code to automatize the analysis of experimental results obtained from GITT and GCD tests (presented in **Attachment B** and **Attachment C**).

2. State of the Art

Modern LIBs have at last three key components: the anode, the cathode, and the electrolyte. Battery charging is a non-spontaneous process in which the negative electrode is reduced, and the positive electrode oxidized: lithium ions move through the electrolyte from the positive electrode to the negative electrode, which is typically carbon-based in LIB's technology. The discharge process is a spontaneous process, where the anode is oxidized, and the cathode reduced [19,20].

Liquid electrolytes (LEs), the traditional separators used in LIBs, present safety issues and are incompatible with high-energy density anode and cathode materials [6,21,22]. Consequentially, these batteries are reaching their peak performance as a technology and are struggling to meet the increasing energy demands of the market. Solid-state electrolytes (SSEs) were developed as a potential solution offering a wider electrochemical window while also mitigating safety concerns [6]. This broader range of accessible potential made the cathode a limiting factor to cell's performance. Considerable efforts have been made to produce cathodes with higher capacities to improve the cell's efficiency [10,11]. A cathode is composed of an active material, a binder, and a conductive agent [19].

2.1. Active Materials

Active materials can be categorized by their structural types into three main groups: layered oxides (e.g., NMC, LMO), spinel oxides (e.g., LNMO), and polyanion oxides (e.g., LFP), **Figure 1** [9,23]. Layered and spinel oxides exhibit higher energy densities and superior electronic conductivity compared to polyanionic cathodes [9,24]. Among these, layered cathodes stand out due to their broader range of possible compositions, making them a more attractive option than spinel structures [24]. The biggest disadvantage of layered oxides, like NMC, when compared to polyanionic cathodes like LFP, is the thermal instability and the presence of toxic Co in its composition [24,25]. Despite these issues, the higher energy density of NMC has driven researchers to develop new stoichiometries with minimal amounts of Co and increased stability [25–27].

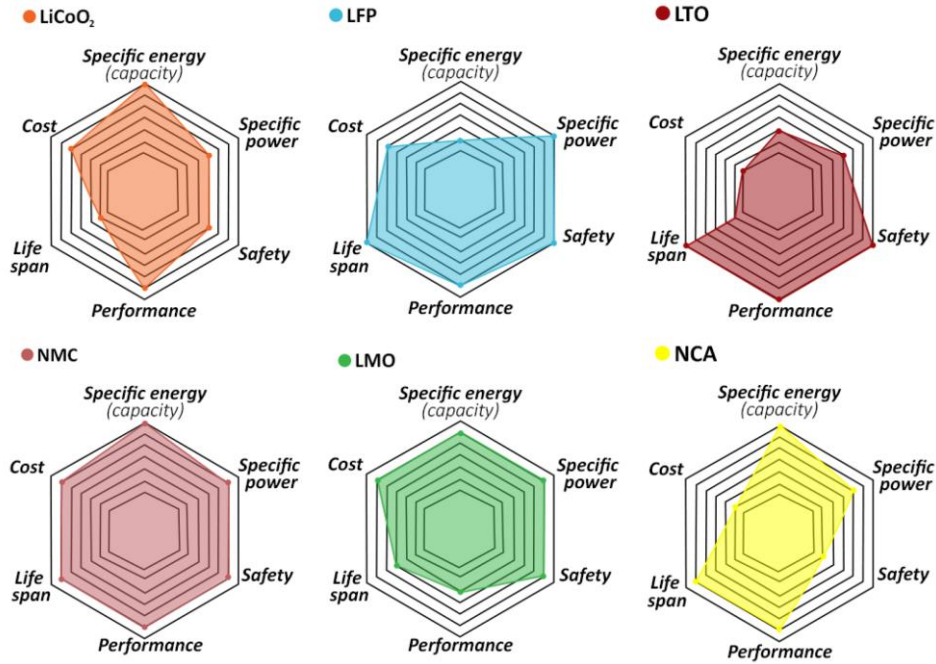


Figure 1: Comparison between different types of cathodes and their characteristics. Reproduced from reference [9] CC BY 4.0.

The first successful layered oxide synthesized was LiCoO_2 , where Li^+ and Co^{3+} cations are well ordered, improving ionic and electronic conductivity [28]. The crystalline structure stabilized in the $R\bar{3}m$ space group [29]. However, the overlapping band structure of Co and O_2 leads to the release of O_2 from the framework when Li stoichiometry drops below 0.5, restricting the cell's capacity to 140 mAh.g^{-1} at 4.2 V (vs Li/Li^+) [29]. To overcome this limitation, research has shifted to LMO_2 oxides, where M represents 3d transition metals Ni, Co, and Mn leading to the development of the first NMC cathodes [23].

LiNiO_2 emerged as a potential alternative due to its theoretically similar crystal structure and reduced overlap between Ni and O_2 energy bands. Despite cost-effectiveness and high achievable capacities, fabricating LiNiO_2 with the desired layered structure is challenging due to cation disorder. The similarity between Li^+ and Ni^{2+} ionic radius allows Li^+ to easily migrate to the transition metal layer [5]. This cation mixture induces a phase transition from a layered structure to an olivine structure, which is detrimental to the cell's efficiency, making it unsuitable for large-scale use [24,25].

In 2001, a cathode composed of equal parts Ni and Mn ($\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$) was successfully fabricated [27]. Characterization of this material revealed that Ni^{2+} is electrochemically active, while Mn maintains a +4-oxidation state during the charge and discharge cycles. This cathode demonstrated a significant improvement in stability, which was attributed

to the inclusion of Mn. However, a detailed analysis of the crystal structure detected Li in the transition metal layer, indicating ongoing cation disorder issues [27].

To take advantage of the positive contributions of each transition metal, ternary systems have been developed combining Ni, Mn, and Co in their structure [26,30]. The stoichiometry of these elements in an NMC cathode is decisive for its performance and properties. Each of them brings different benefits to the cathode. Ni and Co form a redox pair and are the main contributors to battery capacity [5,23]. Mn is electrochemically inert, so it does not define the specific capacity of the cathode, but it does improve its thermal and structural stability [5,23,24]. Although Ni alone can provide a high capacity, Co^{3+} is magnetically neutral and relieves the magnetic stresses induced by the mixture of Li and Ni cations. The inclusion of Co allows for high performances in terms of efficiency and an improvement in cycle stability [5,23,25,31]. Stoichiometries like NMC111 ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) and NMC523 ($\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$) have been developed to achieve capacities between 160 mA h g^{-1} and 200 mA h g^{-1} , and an average working voltage of 3.8 V (vs Li/Li⁺) [5]. NMC622 ($\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$) is commercially successful, achieving capacities of 170 mA h g^{-1} with a uniform particle size distribution [32]. Lipson *et al.* found that doping with Mg or Zr during fabrication significantly improves the thermal stability of NMC622 cathodes, though it slightly lowers capacity [33]. Electrode's stability is also affected by O_2 release from the crystal structure, which occurs once more than 80% of the Li ions are removed from the cathode's structure and is not a potential-driven process [34]. The pursuit of Co-free NMC cathodes led to the development of stoichiometries with even higher Ni content. NMC811 ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) was found to be able to deliver a capacity of 200 mA h g^{-1} and an average working voltage of 3.8 V (vs Li/Li⁺) as well [35]. However, the stability is compromised for charging above 4.2 V, which ends up limiting the cathode performance [35]. NMC955 ($\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$) was fabricated to achieve 220 mA h g^{-1} in the first discharge and to retain 78% of the capacity after 100 cycles (see **Figure 2**) [36].

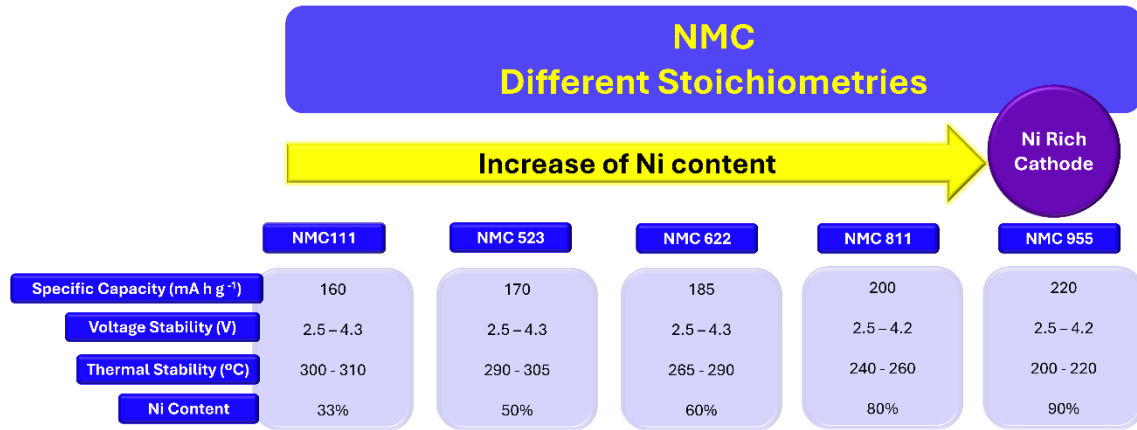


Figure 2: Different NMC stoichiometries towards Ni rich cathodes, with minimal amounts of Co and Mn, and their general characteristics. Data extracted from [5]

In LE batteries the electrolyte penetrates the cathode and saturates the active material ensuring a large contact surface area and therefore reduced impedance, **Figure 3A** [37]. In SSBs, solid interfaces form between the cathode and the electrolyte, inducing capacity losses, mechanical instabilities, and increasing the cell's impedance [38,39]. Interface-related problems occur due to poor electrode/electrolyte contact, volume changes of the cathode during charge and discharge cycles, and the degradation of the cathode-electrolyte interface (CEI), **Figure 3B-D** [37].

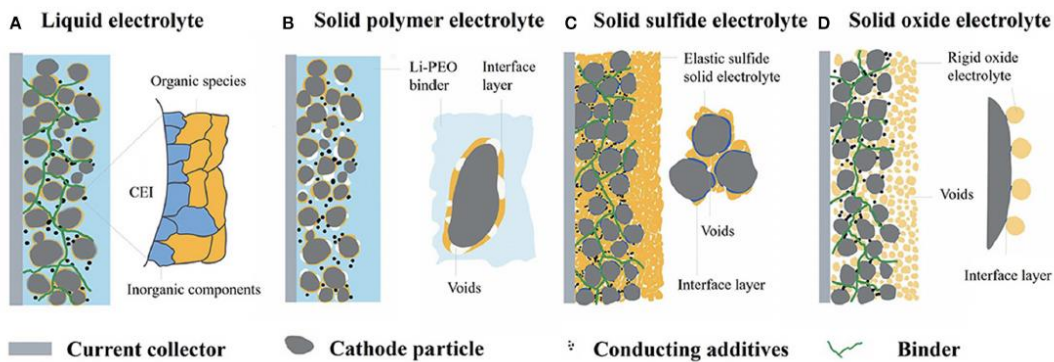


Figure 3. Morphology Models at the Cathode-Electrolyte Interface: (A) Cathode particles are fully immersed in a LE, forming a liquid-solid interface; (B) Cathode particles are embedded in a binder to ensure good contact, but interfacial reactions can lead to void formation; (C) Sulfide electrolytes exhibiting favorable mechanical properties, such as ductility and deformability, allow them to fit the SE. (D) Solid oxide electrolytes, being rigid ceramics, lead to poor contact with the cathode. Reproduced under CC BY 4.0. from [40].

Koerver *et. al.* [39] produced a cell with an NMC811 cathode that underwent electrochemical cycling. During the first cycle, an irreversible loss of capacity was observed and attributed to the formation of a resistive interphase in the cathode due to SE oxidation during charge, depending on the applied potential [39]. Although the major loss of capacity comes from this phenomenon, during the cycle-life of a battery,

expansion and contraction of the cathode material leads to CEI degradation due to differences in thermal expansion coefficients [41]. Wang *et al.* studied this effect on an NMC622 based cell and pointed it as a key factor for interface degradation and capacity loss [42]. In this study, the use of smaller NMC particles was found to alleviate mechanical stress and maximize capacity retention [42]. Phillip *et al.* [43] compared the stability of NMC622 cathodes with respect to solid and liquid electrolytes (LiPON and LiPF₆, respectively) highlighting the results cited above: for SE degradation was found to occur at potentials higher than 4.5 V (vs Li/Li⁺) and capacity fade was more significant, decreasing from 200 mA h g⁻¹ to 80 mA h g⁻¹ after 100 cycles [43]. Although the cathode's performance is theoretically limited by its capacity, in practice NMC cathodes are not able to perform under such potentials due to structural and thermal instabilities [34,39,42]. From the cited results, it is clear that optimization of the CEI is a crucial step to achieving high-performance and stable SSBs. As a result, multiple optimization strategies have been studied to improve the compatibility of NMC cathodes with the currently employed SEs (**Subsection 2.2**) [42,44].

SSEs are categorized into three types: inorganic solid electrolytes (ISEs), polymer electrolytes (SPEs), and solid organic-inorganic composite electrolytes [7,45]. SPEs offer flexibility but have reduced ionic conductivity and struggle to prevent dendrite growth [45]. ISEs provide high ionic conductivity, are non-flammable, and exhibit high mechanical strength, which helps inhibit dendrite growth and enhances safety. However, their rigidity often leads to interfacial incompatibilities [7,45]. Composite electrolytes strive to merge the benefits of both, but their performance is highly dependent on the precise integration of materials and processing techniques [45].

Different types of ISEs have been successfully developed in the past years. They can be divided based on their elemental composition into oxide, sulfide, and halide electrolytes [7]. Oxide SEs are electrochemically stable; however, they struggle with poor ionic contact with electrode materials and are unable to prevent the infiltration of liquid or polymer electrolytes [40,45]. Sulfide SEs provide significantly higher ionic conductivity but are highly susceptible to moisture, making them less stable [40,45]. Halide SEs demonstrate faster Li-ion conduction, but they typically contain scarce and expensive rare earth elements, which limits their commercialization [7,46].

Sulfur-based SEs (Li₆PS₅X, X = Cl, Br, I) are highly compatible for large-scale, cost-effective production. Among these, Li₆PS₅Cl (LPSCI) exhibits the highest capacity and better cycle stability [47]. Despite being a promising SE, LPSCI still faces stability challenges. During cycling, cation diffusion from the cathode leads to the formation of

mixed conductors with reduced ionic conductivity, which degrades the interface and increases its impedance [48]. A space charge layer is formed due to differences in Li chemical potential between the cathode and the SE [49]. Lastly, the microstructure of the interface and the grain orientation of the cathode can induce mechanical stresses that negatively affect the battery's performance [48,50].

2.2. Optimization of Cathodes for Solid-State Batteries

To improve the compatibility of cathodes and SSE, strategies to minimize the interface's impedance are currently being researched, such as: addition of buffer layers to reduce mechanical stresses [51,52]; application of pressure and thermal treatments to improve interfacial contact [53,54]; doping to boost interfacial stability [33,55]; and inclusion of the SSE itself on the cathode's composition [56,57].

Application of buffer layers, Table 1a. The cathode's surface is coated with a buffer layer that protects the electrode against interfacial parasitic reactions and reduces mechanical stresses at the interface, without jeopardizing the cell's electrochemical performance [5,52,58]. Ideally, the buffer layer is uniformly deposited and has a reduced thickness (in the order of some nm) [59]. Chae *et. al.* [52] fabricated a sulfonate-based interfacial layer on NMC811 via wet-coating and heat treatment. X-Ray diffraction (XRD) and scanning electron microscopy (SEM) analysis revealed that the buffer layer was successfully deposited and formed by sulfonate functional groups that retard electrolyte decomposition, retaining 97 % of the initial capacity (174 mA h g^{-1}) after 50 cycles. Although far from commercial requirements, this result poses a great improvement compared with the non-coated cathode, which retained only 86 % of the initial capacity (185 mA h g^{-1}) for the same number of cycles [52]. SiO_2 was used to coat NMC811 and found to form a uniform protective layer, which does not compromise the cell's capacity but improves its cyclability, retaining 30 % more than pristine NMC811. This improvement was justified by its ability to reduce the dissolution of metal ions and lithium leaching from bulk oxide, while also decreasing the polarization gap of electrodes and the charge-transfer resistance in electrochemical reactions [60]. Schipper *et. al.* [53] developed a novel strategy combining surface coating and doping of NMC811 with ZrO_2 . The coating was performed by a wet chemical method and followed by annealing, which promotes Zr diffusion through the bulk material. During diffusion, Zr^{+4} easily occupies Ni^{+4} sites near the interface, doping the material, and mitigating cation disorder. Nyquist-plots analysis obtained for both pristine and modified cathodes showed less impedance growth upon cycling for the modified electrode, indicating enhanced stability; mechanical properties were also improved since the coated/doped cathode presented a more stable

voltage hysteresis [53]. Alternatively, a coating compound containing Li ions can be employed [51,61,62]. Lee *et al.* [51] fabricated a $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode with Li_3PO_4 , leading to enhanced cyclability and thermal stability [51]. Zhao *et al.* [62] fabricated Li_2SiO_3 -coated NMC 811 cathodes resulting in reduced voltage decay and capacity fade upon cycling. Even though coated samples were more stable, they presented a lower initial discharge capacity [62].

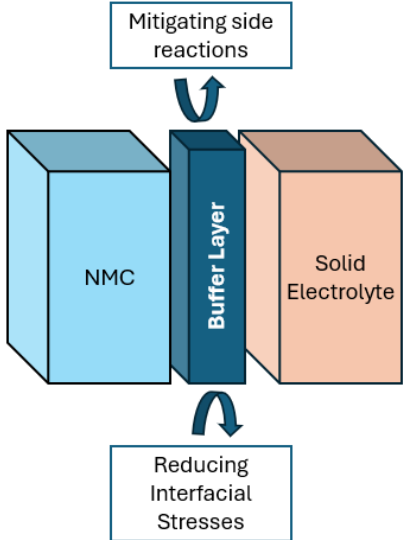
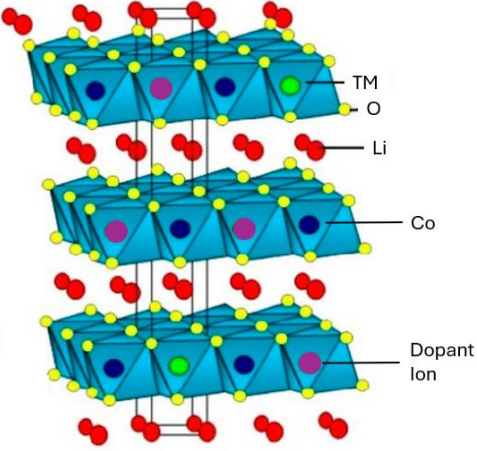
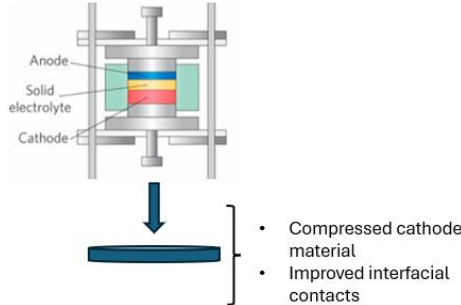
Doping, Table 1b. NMC doping can reduce cation disorder between Li and Ni, improve interfacial stability, and enhance electrochemical performance by lowering O_2 atomic activity, suppressing lattice distortion at high delithiated states, or increasing Li-ion diffusion dynamics [61,63,64]. O_2 evolution contributes to electrolyte oxidation and can be a safety hazard [34,65]. This phenomenon can be mitigated by adding metal ions (e.g. Al, Zr, Nb) that form strong covalent bonds with O_2 atoms, reducing their reactivity [63,66,67]. Guo *et al.* [66] doped $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$ with Nb^{+5} achieving a capacity of 211 mA h g^{-1} in the first discharge and 150 mA h g^{-1} after 100 cycles. The retention of high capacities under high voltage operation was attributed to the absence of intragranular cracking due to lattice stabilization by the Nb ions. Additionally, Nb doping promoted the development of an interfacial structure that improved the CEI mechanical stability [66]. NMC goes through phase changes during electrochemical cycling which will impose structural stress, especially in deep charging scenarios [68]. Ou *et al.* [67] developed an Al/Zr co-doped $\text{LiNi}_{0.88}\text{Co}_{0.09}\text{Mn}_{0.03}\text{O}_2$ cathode. Al ions diffused into the NMC lattice, while Zr ions stayed on the interface. Li-ion mobility was enhanced, internal strain reduced, and cation disorder mitigated, leading to improved performance. The Zr-rich surface established a stable cathode-electrolyte interface, which prevented undesirable reactions and Ni dissolution. The group fabricated a pouch cell with a graphite anode that achieved a 200 mA h g^{-1} capacity and 98 % retention after 200 cycles between 2.75 and 4.55 V [67]. It is possible, either by co-doping or by surpassing the solubility limit of a certain ion during fabrication to achieve doping and coating at the same time [25,53,55,67,69]. Mu *et al.* [69] co-doped a Co-free LiNiO_2 cathode with Mg and Ti. Mg diffuses through the lattice and Ti forms a coating layer at the CEI. The authors attributed to these dopants the mitigation of phase transitions, reduction of cation disorder, and stabilization of the CEI, which provided better rate capability, higher thermal stability, and self-discharge resistance [69].

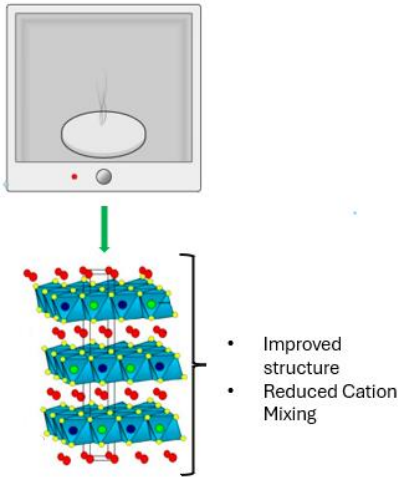
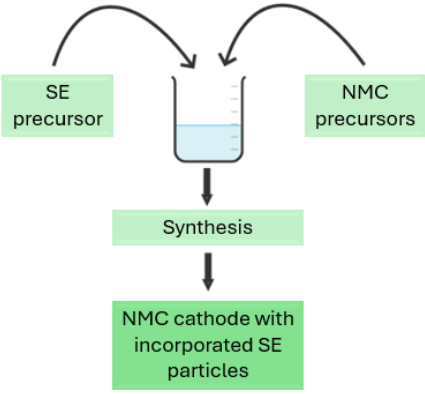
Pressure and thermal treatments, Table 1c-d. Some studies use pressure and thermal treatments before cell assembly to reduce its impedance [35,53,63,67]. Uniaxial pressure is applied to compact the cell and improve interfacial contacts [35,70]. Laufen

et al. [71] studied the effect of applied pressure on an NMC Li-ion pouch cell, finding that optimal external pressures between 100 and 300 kPa minimized cell impedance. They also found that for states of charge (SOC) in the range of 80–100% the NMC cathode dominates the cell's strain, while in other regimes it is dominated by the graphite anode [71]. Although in [71] an optimal pressure range for impedance reduction was established, the cell's stability was not evaluated. However, applying a pressure of 300 kPa during cycling was found to minimize the effects of particle cracking in NMC pouch cells with a lithium-titanium-oxide (LTO) anode, reducing capacity losses up to 42% [54]. Thermal treatments can improve cell performance through diverse mechanisms [33,52,72–74]. During the fabrication of NMC 622 cathodes, higher sintering temperatures were found to increase the average particle size [33]. Slower heating ramps improve the development of the CEI [52]. As already explained, cation mixing between Li and Ni negatively impacts performance. Post-synthesis longer thermal treatments at 500 °C to NMC111 were reported to reduce cation mixing in the final material [73]. Shim *et al.* [72] found that treating cells in an oxygen-rich atmosphere enhances capacity retention. Cells with a $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ cathode treated in an oxygen atmosphere retained a capacity of 185 mA h g⁻¹ after 50 cycles, while the ones treated in air retained only 172 mA h g⁻¹ [72]. NMC 622 and NMC811 can establish nonstoichiometric interfaces, which can have unpredictable consequences. White *et al.* [74] after demonstrating this effect, showed that thermal treatments can adjust stoichiometry, aligning it more closely with the bulk material [74].

Inclusion of SSE in the cathode's composition, Table 1e. Multiple works have been done where SSE powders were mixed with cathode precursors during fabrication [56,57,75,76]. NMC622 and NMC811 cathodes were prepared with a 3% weight ratio of $\text{Li}_6\text{PS}_5\text{Cl}$ and used in cells with an innovative Sn-based anode, achieving energy densities of 200 Wh kg⁻¹ and 220 Wh kg⁻¹, respectively [56]. Doerrer *et al.* [75] fabricated a $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ and $\text{Li}_6\text{PS}_5\text{Cl}$ cathode with a discharge capacity of 210 mAh g⁻¹. The inclusion of SE in the cathode's composition was shown to reduce interface debonding, which is usually partially mitigated through the application of pressure, since even under low pressures the performance remained satisfactory [75]. Alternatively, instead of including SSE particles in the bulk of the NMC cathode material, Han *et al.* [57] applied a 500 nm layer of $\text{Li}_6\text{PS}_5\text{Cl}$ and a buffer layer of LiNbO_3 to an NMC811 cathode. The obtained composite achieved a reversible capacity of 197 mA h g⁻¹ and an 86% retention after 100 cycles at 2C, which also reflects the enhancement of stability by the buffer layer [57].

Table 1. Optimization strategies for cathodes in ASSBs: physical principle, benefits and challenges. (b) adapted from [77]. (c) adapted from [78]. All under CC BY 4.0.

Strategy	Mechanism	Benefits	Challenges	Scheme
Application of Buffer Layers	Coat cathode's surface with a protective layer that reduces mechanical stress and mitigates interfacial parasitic reactions	Improved stability of the interface, resulting in longer lifetimes [51–53]	May increase interfacial impedance, thus reducing cell's capacity [52]	(a) 
Doping	Incorporation of foreign ions into the NMC lattice	Reduces cation disorder, improves interfacial stability, suppresses lattice distortion, enhances Li-ion diffusion dynamics [63,64,68,69]	Safety concerns due to high voltages, complex fabrication processes	(b) 
Pressure Treatment	Apply uniaxial pressure to improve interfacial contacts	Impedance reduction and minimization of particle cracking [35,54,70].	Depending on cell's geometry and material structure. Difficult to generalize.	(c)  - Compressed cathode material - Improved interfacial contacts

Thermal Treatment	Varying the thermal treatment parameters permits to fine tune the properties of the cathode material	Define particle size, reduce cation mixing, enhance capacity retention, improve interfaces [33,52,73].	Not reproducible across all materials	(d)  - Improved structure - Reduced Cation Mixing
Inclusion of SE in Cathode's Composition	SE powders are mixed with the cathode's precursor during fabrication.	Reduce interface debonding, improved stability. [57,75]	Obtain the desired benefits without jeopardizing cell's electrochemical performance.	(e) 

2.3. Common Synthesis Methods for NMC Active

Nickel-Manganese-Cobalt cathodes can be manufactured using multiple methods. Each synthesis technique has different key parameters, which will influence the characteristics of the manufactured cathode, namely its morphology and electrochemical characteristics [79,80].

In the SSB industry, NMC cathodes are primarily produced using wet processing techniques. This involves dissolving a precursor in a solvent to create a uniform solution, which is then thermally treated to remove the solvent and precipitate the desired material [81]. Oppositely, dry-processing techniques can be employed (e.g., ball-milling, reactions under autogenic pressure at elevated temperature), which involve a mechanical mixing of the necessary materials, followed by thermal treatment [82]. The later require both intense mechanical mixing and long hold time at high temperatures, making them less attractive for large-scale applications when compared to wet-processing methods [31].

The most common wet-processing methods are co-precipitation, sol-gel and hydrothermal. Although sol-gel preparation is a well-established technique that can achieve better characteristics than traditional solid-state reactions, it is a long and complex process that is difficult to scale [83,84]. Hydrothermal fabrication techniques produce highly crystalline cathodes with tunable morphology, but it is already considered as a method for treatment and optimization due to its inability for bulk production [31,85]. Nowadays, co-precipitation is the most used method in industry due to its simplicity, scalability and relative low cost. Additionally, co-precipitation can produce cathodes with a good morphology, homogeneous mixing at the atomic scale, and good electrochemical characteristics [31,86,87].

Co-precipitation, Figure 4a. This method is a widely utilized synthesis technique known for its ability to control morphology and achieve atomic level homogeneity [88,89]. It involves two steps: co-precipitating transition metals and sintering them with a lithium source, using precursors like hydroxides or carbonated salts [90,91]. Key parameters influencing the process include pH, sintering temperature, chelating agent type, and stirring rate [81]. Experimentally, pH, stirring rate, and chelating agent were found to control particle size and morphology, while sintering temperature affects particle uniformity and electrochemical properties, with studies reporting discharge capacities exceeding 150 mA h g^{-1} and cycle retention in the order of 90% [86,91]. While co-precipitation is scalable and cost-effective, it faces challenges like impurity control and optimization of parameters [31].

Sol-Gel, Figure 4b. This method is significant for achieving high atomic-level mixing and crystallinity, and the formation of small, uniformly sized particles, which lead to enhanced electrochemical performance and structural stability when compared to dry-processing techniques [92]. Metal precursors are dissolved in distilled water, and a lithium compound that has been previously dissolved in a chelating agent, usually citric acid, is added slowly. A controlled pH of approximately 8 is maintained to form a gel, which is then dried and sintered [31]. Drying and sintering parameters, along with chelating agent concentration, affect the morphology, size, and crystallinity of the resulting material [93,94]. Sol-gel does not require high-temperature processing and allows for precise stoichiometry control. However, longer processing times, poor reproducibility, and expensive raw materials make the sol-gel process less suitable for commercial production [84]. Low Co NMC811 cathodes were produced achieving an average capacity of 188 mA h g^{-1} but poor stability [95]. A more stable NMC111 cathode achieved a 190 mA h g^{-1} capacity and a retention rate larger than 90% [96].

Hydrothermal, Figure 4c. The hydrothermal method utilizes high-pressure and high-temperature conditions to produce precursors with a uniform particle size and morphology. This process involves dissolving transition metal precursors in a solvent and placing the solution in an autoclave, which is then placed in an oven. The final cathode material is obtained by mixing the resulting precursor with a Li salt and subjecting the mixture to thermal treatment [31,84]. Key factors influencing particle size and morphology include the autoclave temperature, reaction time, and choice of precipitating agents [97]. This method enhances electrochemical performance due to improved crystallinity, but high equipment costs and limited production capacity [14] hinder large-scale manufacturing. Due to this limitation, hydrothermal techniques are often combined with other fabrication methods to enhance the quality of the cathode materials [98,99]. NMC111 cathodes prepared using hydrothermal and co-precipitation methods and different synthesis parameters showed capacities between 150 mAh g⁻¹ and 185 mAh g⁻¹, but a significant decay after only 30 cycles [100].

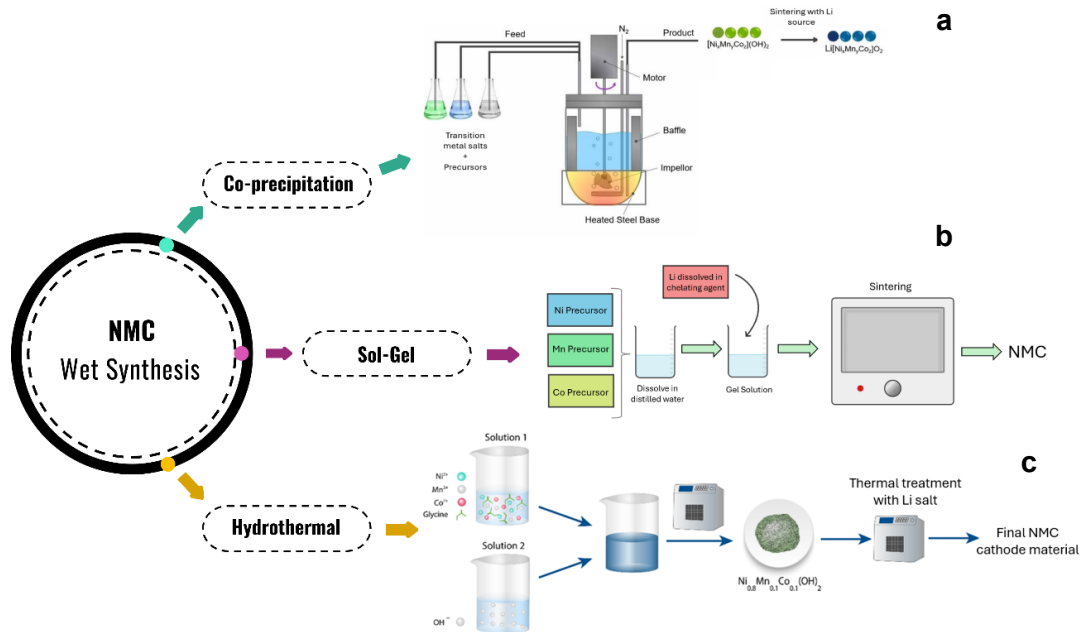


Figure 4. Wet synthesis approaches of NMC – three main methods. Co-precipitation scheme adapted from [101] and Hydrothermal scheme adapted from [102]. Both under CC BY 4.0.

2.4. Binder Materials

After NMC synthesis, the final cathode can be obtained using wet or dry methods. The assembly of the cathode involves putting together the active material, a binder, and a conductive agent. Wet methods use solvents to dissolve the active material, binder, and conductive agent. A current collector is then coated with the obtained slurry and dried for an extended period of time [36,51–53,69,75,103]. In contrast, dry methods do not use

solvents. The powdered materials are mechanically mixed using a ball mill or a mortar and pestle, and the mixture compressed into pellets of with the desired dimensions [33,39,42,56,73,75].

Binders, though used in small concentrations, play an important role in battery performance, and are required to have: a wide electrochemical window; high thermal stability; low reactivity with other cell components; elasticity to avoid cracking from volume changes during cycling; high ionic conductivity; and capability to form homogeneous slurries [104].

If the cathode is manufactured using a dry method, the binder is directly mixed with the other powders and incorporated into the final pellet. By contrast wet methods require the use of a solvent. This solvent must therefore be chosen considering the compatibility with the binder material and the other components of the final cathode. Several binder/solvent pairs with different characteristics can be found in the literature [19,105,106]. These pairs can be categorized as having low or high polarity, and this characteristic makes them more or less compatible with SEs (see **Figure 5**) [107].

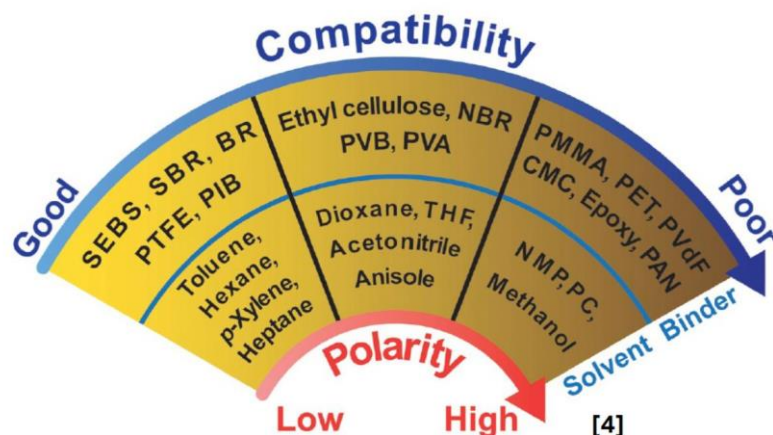


Figure 5. Different binder/solvent pairs and their compatibility with solid electrolytes. Reproduced from reference [107] CC BY 4.0.

PVDF is the most used binder material, since its highest occupied molecular orbital is lower than the typical cathode's chemical potential [19]. Nevertheless, PVDF has significant drawbacks: it is expensive, non-recyclable, and poses health and environmental hazards [19,105]. This binder is currently under much attention due to environmental concerns and UE policies aiming to ban materials containing fluorine [14,105]. Additionally, using PVDF in the cathode, in wet synthesis, requires the use of N-methyl-2-pyrrolidone (NMP) as a solvent, which is even more toxic and pollutant

[19,108]. These compounds present high polarity, meaning they can easily react with SSEs like LPS and LPSCI [106].

Alternatively, styrene-butadiene rubber (SBR) can also be used as a binder, in which case toluene is used as the solvent. This binder/solvent pair has a lower polarity, which makes it more compatible with sulfide based SEs. However, it is equally problematic from an environmental and health point of view [106]. Consequently, researchers are exploring environmentally friendly binder and solvent pairs that maintain battery performance. In particular, water-soluble binders attracted much attention as a possible solution for this issue.

Carboxy Methyl Cellulose (CMC) is a water-soluble binder, cheaper than PVDF, which can be synthesized from cellulose, and was already reported to be compatible with NMC111 and NMC442 cathodes [109,110]. Xu *et al.* [109] conducted a comparative study between PVDF and CMC with NMC111 cathodes: CMC was found to offer lower discharge capacity at low discharge rates, but better stability and cyclic performance than PVDF [109]. Accordingly, Chen *et al.* [110] did a similar study using NMC422 cathodes instead. The performance of cathodes binded with CMC was superior, showing higher capacity at high C-rates, and better thermal and cycling stability. These results were attributed to faster Li ion diffusion and lower electrode polarization in the cathodes fabricated with CMC [110].

Other water-based binders are being studied: polyacrylic acid (PAA) was used in an NMC811 cathode that achieved a capacity of 189 mAh g⁻¹ [111]; poly(diallyldimethylammonium) (PDADMA) was used in an NMC532 cathode with improved performance when compared with one produced using PVDF [112]; a novel environmentally friendly and natural binder extracted from brown-algae was developed and its application in NMC111 cathodes also revealed a better performance when compared with PVDF [109].

Furthermore, it is necessary to include a binder material in the composition of the SSE to ensure mechanical integrity [107,113]. Given the chemical instability of SSEs, the choice of binders and solvents is restricted to weakly polar compounds. The polarity of the compound, which is defined by the functional groups present in its molecular structure, is the main factor influencing its compatibility with the SSE [107,113,114]. The challenge is similar to that of using binders in cathodes: to obtain a stable material and maximize conductivity, while minimizing environmental impact and health risks.

The use of the most common binders, namely PVDF, has not been able to meet the necessary requirements [113,114]. Wang et al. showed that PVDF does indeed fill the gaps in the SSE membrane, improving its cyclability, but at the cost of a reduction in ionic conductivity due to its thickness of 100-120 μm [115]. However, the high polarity of PVDF guided research into the use of binders and solvents with low polarity, with the use of rubbers such as SBR, together with toluene or xylene, being quite common. These low polarity compounds suffer from weaker adhesion to the electrolyte material, which is an obstacle for wet slurry processing [107,116].

To address the aforementioned obstacles, several strategies have been experimented. These include optimizing the molecular weight of the binder in slurry synthesis processes [117]; manufacturing cells without binders in their final composition [118]; and developing innovative binders that can create thin membranes with high ionic conductivity [113,115,116]. These new chemical formulations could ideally be applied to the cathode, with the expectation that using the same binder in both the cathode and the electrolyte will enhance their compatibility.

3. Experimental Procedures

This chapter details the entire process from cathode synthesis to battery evaluation. The materials used are listed, the full assembly procedures outlined, and the characterization techniques explained.

3.1. Materials

LiNi_{0.9}Mn_{0.05}Co_{0.05}O₂ (NMC955). NMC955 was used as the active material in the synthesized cathodes. The powder was supplied from Huayou New Energy Technology, Quzhou, China.

Li₆PS₅Cl electrolyte. Lithium argyrodite Li₆PS₅Cl was used as a solid electrolyte and was provided by NEI Corporation. This electrolyte was incorporated in the cathodes and used as a bilayer with the cathode material.

C65. This carbon-based powder was used in the composite cathodes as a conductive agent. Purchased from TIMCAL.

Polyisobutylene. Polyisobutylene (PIB) was used as binder agent in the cathodes. It was purchased from Sigma Aldrich. The used PIB has 500000 molecular weight.

Poly (vinyl alcohol). Poly (vinyl alcohol) (PVA) was used as binder agent in cathode synthesis. It was purchased from HiMedia. The used PVA has 140000 molecular weight.

Toluene. This was the solvent of choice for the wet synthesis process. It was supplied from Honeywell, with a purity $\geq 99.7\%$.

3.2. Methods

Cathode Synthesis. The prepared cathodes were initially synthesized for a total mass of 5 g with the following component percentages: 57% of active material, (40-x)% of solid electrolyte, 3% of conductive agent, and x% of binder material, with $x = 2\%$ or $x = 4\%$. Due to material shortages cathode's mass was later reduced to 1 g, keeping the same ratios between their components. Firstly, the desired amount of binder material was added to 5 ml of toluene and magnetically stirred for 24 hours; secondly, NMC and C65 were added to the solution and mixed for another 24 hours; lastly the electrolyte was added to the mixture, and it was left to stir for another 24 h period. Using a film depositor, the resulting slurry was deposited in a pre-heated Al foil coated with carbon and left to dry overnight. The prepared cathode material was cut into discs with a 10 mm diameter with the help of a disk drilling machine from TMAX-CN. The full procedure was realized inside an Argon filled GS Glovebox ($O_2 < 1$ ppm and $H_2O < 1$ ppm).

Coin Cell Assembly and Electrochemical Characterization. A bilayer of the previously prepared cathode material and $\text{Li}_6\text{PS}_5\text{Cl}$ was formed. To do so, 100 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ were pressed onto the cathode disk for 2 minutes at 1 ton, using a mold with a 10 mm diameter and the SPECAC press machine. The coin cells were fabricated by stacking the anode on top of the SE sheet of the bilayer, followed by a spacer and a spring. The used anode material was Li metal with a thickness of 200 μm and 8 mm diameter. The cells were closed using a pressure-controlled electric crimper for coin cells MSK-160E. The areal capacities of the cathodes were calculated based on the active area of the cathode, which is constrained by the size of the anode and considering the theoretical capacity of 192 mAh.g^{-1} . The anode was made smaller than the cathode to avoid short circuits by possible contact at the disk's edge. Three types of electrochemical tests were performed to evaluate the fabricated cells. Potentiostatic electrochemical impedance spectroscopy (PEIS) tests were performed to determine the internal resistance. Cyclic voltammetry (CV) tests were done to determine the capacity of the obtained cell. Both were done using a Biologic VMP-300 potentiostat. Lastly, galvanostatic charge-discharge (GCD) was performed to evaluate the cyclability and behavior of cells at different C-rates and specific energy. The galvanostatic cycling tests were performed in a Neware-CT-4008Tn-5V-20mA battery tester with 2.6 and 4.1 V cut-off voltages.

3.3. Characterization Techniques

Potentiostatic Electrochemical Impedance Spectroscopy, PEIS. Electrochemical impedance spectroscopy studies the behavior of electrochemical systems by applying a small, sinusoidal signal over a range of frequencies and measuring the resulting current. In PEIS specifically, the overall cell potential is held constant while the response to the varying frequency input is acquired. PEIS can provide an understanding of electrochemical kinetics, charge transfer dynamics, and system characteristics, showing how the system responds at different frequencies, and thus time scales [119].

The resulting curves are represented in the form of Nyquist plots, and depend significantly on the battery's material and structure, making proper interpretation necessary for achieving meaningful conclusions. Fitting the PEIS data with an equivalent electric circuit simplifies the interpretation of electrochemical processes by modeling them as ideal electrical components. By quantifying these components, the fit helps identify weaknesses in the cell, track degradation over time, and compare different materials or cell designs. As an example, a typical curve of a solid-state cell is presented in **Figure 6** and can be interpreted as follows. R_1 is the intercept at higher frequencies

and represents asymmetric processes occurring at both electrodes of the cell; it can be modelled by an ohmic resistor. R_2 , the radius of the first semicircle, corresponds to the bulk resistance of the SSE layer between electrodes. The diffusion process of ions through the electrolyte is effectively represented by a resistor in parallel with a capacitor, capturing the dielectric behavior of the solid electrolyte. R_3 reflects the charge transfer resistance at the electrode–electrolyte interface, which is influenced by the reaction kinetics of lithium ions, also being modeled as a resistor in parallel with a capacitor. W , known as Warburg element, represents the Warburg impedance, associated with Li ion diffusion within the electrode materials or across interfaces. In the scope of this thesis, PEIS tests were done with a Biologic VMP-300 potentiostat (Seyssinet-Pariset, France), in a frequency range from 7 MHz to 100 mHz,

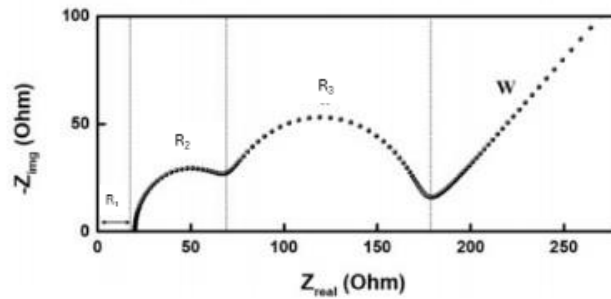


Figure 6: Theoretical PEIS curve used as an example. Each region is related to different phenomena occurring in the cell. Adapted from [119], under CC BY 4.0.

In this thesis, PEIS is used to evaluate the performance and behavior of battery materials, helping to understand how synthesis choices affect the internal resistance, charge transport, and overall efficiency of the system.

Cyclic Voltammetry. Cyclic voltammetry (CV) is an electrochemical technique used to analyze the properties of electrochemical cells or electrodes [120]. The potential difference between both electrodes varies between two limits at a constant rate and the resulting current is measured. During cycling, reduction and oxidation may occur, and these processes appear as characteristic peaks in the CV curves. In the context of batteries, these peaks correspond to lithiation and delithiation phenomena in the cell's electrodes, helping to identify the voltage ranges where these take place and to determine suitable voltage windows for the system to stay stable. The voltage range and scan rate are chosen based on experimental objectives and CV results vary depending on the analyzed system. A reference curve is presented in **Figure 7** as an example: oxidation and reduction peaks are clearly visible. The consistency between cycles reflects the reversibility of the system, going from a delithiated cathode (charged) to a

lithiated cathode (discharged) state and back [120]. For all the reported experiments, the CV tests were performed between 2.0 V and 4.1 V, at a scanning-rate of 50mV/s, using a Biologic VMP-300 potentiostat (Seyssinet-Pariset, France).

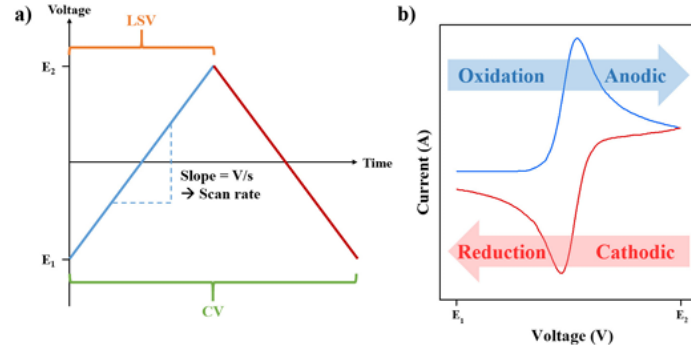


Figure 7: Voltage vs. time profile (left) and typical cyclic voltammetry plot showing oxidation and reduction peaks (right) of the cathode. Picture reproduced from [120] under CC BY 4.0 terms.

Galvanostatic Charge and Discharge (GCD). GCD evaluates battery performance and long-term stability. The battery is charged and discharged repeatedly by applying a constant current. During charge, Li ions are driven into the negative electrode, increasing cell's voltage to a maximum. Once charged, the opposite process occurs, and a negative current drives Li ions back to the positive electrode, reducing the voltage to a minimum pre-defined threshold. This method determines specific capacity at various C-rates, coulombic efficiency, and if the cell is able to maintain a stable operation for numerous cycles. By submitting the cell to higher C-rates it is possible to assess if the system is capable of handling high power demands. The performance is influenced by the battery's composition and structure, with voltage limits mainly set by the cathode's active material. It is important to consider electrolyte degradation at high potential. All these limits can be determined from the CV curve analyses, identifying the voltage at which the current exponentially increases [120,121]. Ideally, the discharge capacity should approach the theoretical capacity of the active material. In **Figure 8** GCD profiles are presented for coin cells with a LE and LFP cathode (left), as well as for coin cells with SSE and NMC based cathode (right). A distinct difference can be observed between the two systems. The LFP cell with a LE exhibits a voltage plateau, which is characteristic of a two-phase equilibrium (between $LiFePO_4$ and $FePO_4$) occurring during cycling. In contrast, the NMC cell does not display a plateau. Instead, the voltage profile shows a smooth slope, consistent with the reaction mechanism in such systems, where lithiation and delithiation occur through a solid reaction. The GCD tests were performed with a Neware-CT-4008Tn-5V-20mA battery tester with 2.6 V and 4.1 V cut-off voltages.

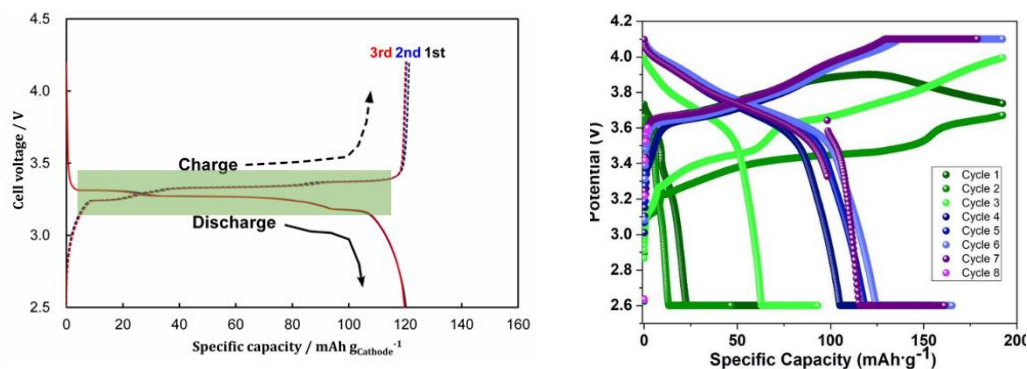


Figure 8: Difference between charge and discharge behavior of LFP and NMC based coin-cells. (Left) Charge and discharge curve of a coin-cell featuring LFP as cathode material, LiPF_6 as LE, and graphite as the anode material. (Right) Charge and discharge curve of a coin-cell featuring a NMC based cathode, LiPF_6 LE, and a Li^0 anode.

SEM/EDX. Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectroscopy (EDX) allows for analyzing materials at the microscale. SEM provides high-resolution images of surface structures, enabling detailed assessment of material features, distribution, and integrity. When combined with EDX, it facilitates elemental mapping and quantitative analysis, allowing for the identification of key elements in the sample. This approach is particularly useful for studying electrode materials, surface modifications, and detecting impurities. A FEI QUANTA 400 FEG ESEM was used to perform SEM analysis, with amplifications of 1000 $\times$, 5000 $\times$, and 20000 $\times$. Chemical composition analysis was performed with an EDAX Genesis X4M energy-dispersive X-ray spectrometer. In **Figure 9** an example is presented of a SEM observation of an NMC955 based composite cathode. The lighter grains correspond to the active material (point 2) and the grayish particles correspond to the LPSCI electrolyte (point 1) [121].

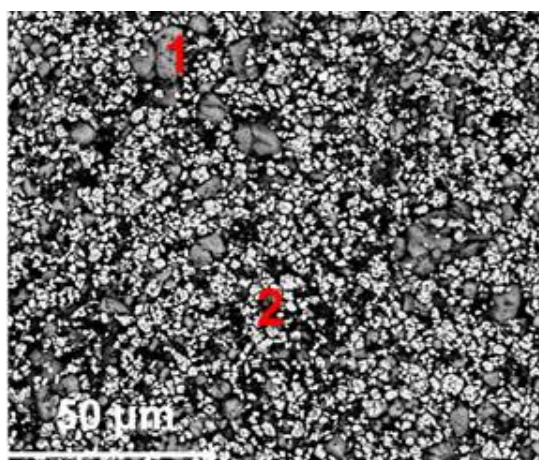


Figure 9: SEM observation with 2000 $\times$ amplification. The observed cathode as a composition of 57% NMC955 + 38% LPSCI + 3% C65 + 2% SBR. Reproduced from [121], under CCBY 4.0.

Hall effect and Sheet resistance measurements. Sheet resistance measurements are used to evaluate the electrical behavior of thin films and electrodes. This technique measures the resistance of a uniformly thick sheet, applying a four-point method and determining a value for sheet conductivity in a wide range of temperatures. This way it is possible to determine if the material is a conductor, insulator, or semiconductor [122]. The Hall effect occurs when a magnetic field is applied perpendicular to a current flowing through a material. This causes the moving charge carriers to be deflected to one side, creating a measurable voltage, known as the Hall voltage, across the material. From this, parameters such as charge carrier concentration, carrier's mobility, and charge carrier's type can be determined [123].

Together, Hall effect and sheet resistance measurements offer a complete picture of a material's electrical behavior. While sheet resistance analysis gives a general sense of conductivity, the Hall effect measurements help to explain it, characterizing charge carriers' nature and behavior. These tests were performed with a Linseis HCS 1 Hall effect measurement system. In **Figure 10** sheet conductivity, care carrier density, and charge mobility measurements experimental results are presented as an example, reproduce from [121].

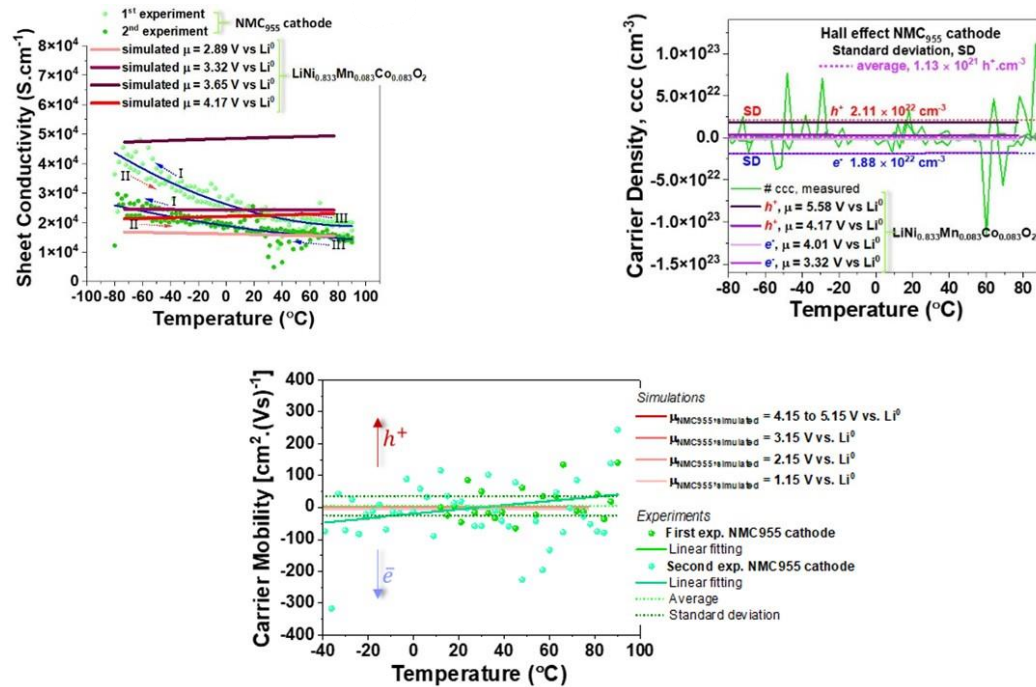


Figure 10: Experimental results from Hall effect and sheet resistance measurements. (Top left) Sheet conductivity as a function of temperature, (Top right) Charge carrier density as a function of temperature; (Bottom) Charge carriers' mobility as a function of temperature. These measurements were performed in an NMC955 composite cathode with composition 57% NMC955 + 38% LPSCI + 3% C65 + 2% SBR, and are reproduce from [121], under CCBY 4.0.

Galvanostatic Intermittent Titration Technique (GITT). This technique is used to study lithium-ion diffusion in battery materials. A constant current pulse is applied to the cell for a short period, causing a change in lithium-ion concentration, as positive Li^+ ions diffuse with the current. This is followed by a longer rest period, during which no external current is applied, Li^+ ions tend to their equilibrium state, and the voltage relaxes toward V_{ocv} . This cycle is repeated until the cell is fully charged, in the present case, until it reaches 4.1 V at rest. This procedure is followed by a symmetric one, where a negative current is applied until the cell is discharged. In this case, until it reaches 2.6 V at rest. By analyzing how the voltage responds during the pulse/rest cycles, GITT provides information about the diffusion coefficient of Li ion in the electrodes. A typical potential vs time curve is presented in **Figure 11** for illustrative reasons. The diffusion coefficient can be obtained using the following equation, if the applied currents are small, which is the typical case for single coin cells: $D = \frac{4}{\pi\tau} \cdot \left(\frac{nV_m}{S}\right)^2 \cdot \left(\frac{\Delta E_s}{\Delta E_t}\right)^2$, where τ is the pulse duration, n is the number of moles, V_m is the molar volume, S is the active surface area, and $\Delta E_s, \Delta E_t$ are voltage variations highlighted in **Figure 11**. GITT tests were performed with a Biologic VMP-300 potentiostat (Seyssinet-Pariset, France), using pulses of 100 seconds, with 1-hour rest periods.

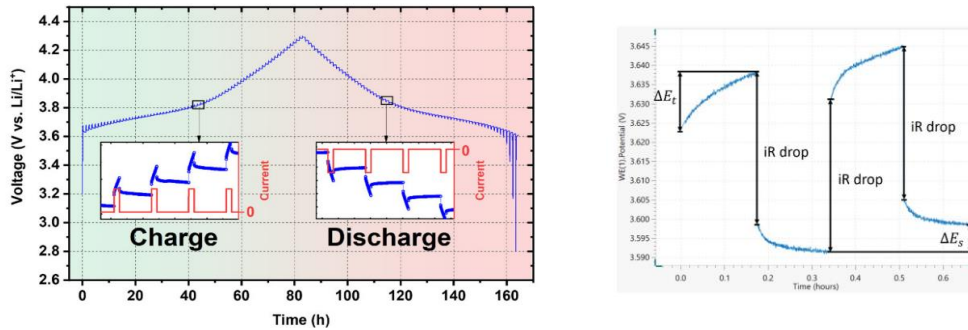


Figure 11: (Left) Typical experimental curve obtained after a full GITT procedure. In this case, the cell is charged with the application of current pulses and discharged at open circuit voltage. In some cases, the cell can be discharged and then charged with the same principles; reproduce under CC BY 4.0 from [124]. (Right) a close up on a pulse sequence to illustrate how the diffusion coefficient can be obtained using the equation for the diffusion coefficient.

4. Results and Discussion

4.1 Solubility tests

As explained in **Section 2.4**, a literature review identified two alternative binders to PVDF. The chosen binder and solvent should ideally be non-polar or have low polarity to prevent adverse reactions with the LPSCI. Toluene, chosen for its nonpolar nature, was employed in this study based on its prior successful application with LPSCI [107,125]. Replacing PVDF eliminates the need for NMP, addressing two issues at once. The two proposed binders for study are PIB and PVA. PIB is a non-polar, chemically inert polymer; its strong adhesion and flexibility are expected to help accommodate volume changes during cycling and enhance stability and lifespan [19,126]. PVA despite having higher polarity than PIB, was still studied as it is expected to be solvable with toluene, when temperature treatment is applied [125]. However, it is expected to provide good adhesion and improve film-forming ability. At room temperature, PIB is found in a rubbery and viscous fluid, while PVA is a dry, granulated powder.

PVA's solubility in toluene was tested at room temperature, 40 °C, and 60 °C to evaluate its suitability for electrode synthesis (**Figure 12**). In each test, 100 mg of PVA were mixed with 5 mL of toluene and stirred for 24 hours. At room temperature, after 24 hours, particles of the PVA powder were still visible in the flask, deposited at the bottom. However, once the temperature was raised to 40 °C, considerable improvements were observed, the final solution was homogeneous, and the polymer powder was completely dissolved (**Figure 12**). A final test was performed at 60 °C, with temperature as a synthesis variable. PVA was dissolved at the end of the stirring period, and the solution was considerably more viscous. This increased viscosity may indicate that PVA is near its glass transition temperature (~75 °C), suggesting potential thermal degradation or property changes. Due to both PIB and toluene being non-polar, no solubility test for PIB was necessary, and during cathode synthesis, PIB was confirmed to dissolve easily.



Figure 12: Results from solubility tests performed with PVA in toluene. (Left) After 24 hours stirring at room temperature, PVA particles are visible, deposited on the bottom of the flask; (Right) After 24 hours stirring at 40 °C a homogeneous solution is obtained.

To achieve the goal of designing cathodes with good electrochemical performance, long cycle life, and without PVDF, a composition inspired by the literature was adopted: 57% active material, 3% conductive agent, 40 – x% solid electrolyte, and x% binder, with x being equal to 2% and 4%. As discussed in **Section 2.2**, incorporating SE powder into the cathode composition is expected to enhance the interfacial compatibility between the cathode and the solid electrolyte. Solubility tests demonstrated that up to 0.2 g of PVA could be dissolved into toluene, corresponding to a 4% binder-to-solvent mass ratio. Since the binder's role was the focus of this study, its content was treated as a variable, with values of 2% and 4%. Although further solubility tests could be conducted to explore higher binder concentrations, maximizing the active material content is preferable to achieve the highest possible specific capacity. From these considerations, the first cathodes were synthesized at 40 °C, with varying binder percentage in their composition. NMC955 was selected as the active material. A summary of these cathodes is presented in **Table 2**. Even before assembling the coin cells, noticeable differences were observed between cathodes prepared with PIB and those with PVA. The PIB-based cathodes exhibited a honey-like, viscous texture during mixing and, after drying, were found to be mechanically robust. In contrast, PVA-based cathodes were more brittle and fragile, with visible cracks forming easily during handling. Nevertheless, two coin cells were fabricated from each batch for electrochemical testing.

Table 2: Summary of all synthesized cathodes.

Batch	Synthesis temperature	Binder %	Binder	Cathode composition
1	40 °C	2%	PIB	57% NMC 955 + 3% C65 + 38% LPSCI + 2% Binder
2			PVA	
3		4%	PIB	57% NMC 955 + 3% C65 + 36% LPSCI + 4% Binder
4			PVA	

4.2 Electrochemical characterization

Coin cells were fabricated using the methods outlined in **Section 3.2** and tested for performance. The initial sequence of PEIS, followed by CV and another PEIS, produced consistent results. There were no significant differences in cell behavior related to binder type, percentage, or mixing temperature. **Figure 13** shows the last cycle of the first PEIS, realized before CV for one cell of each batch. **Figure 14** shows the last PEIS cycle after CV tests for the same cells.

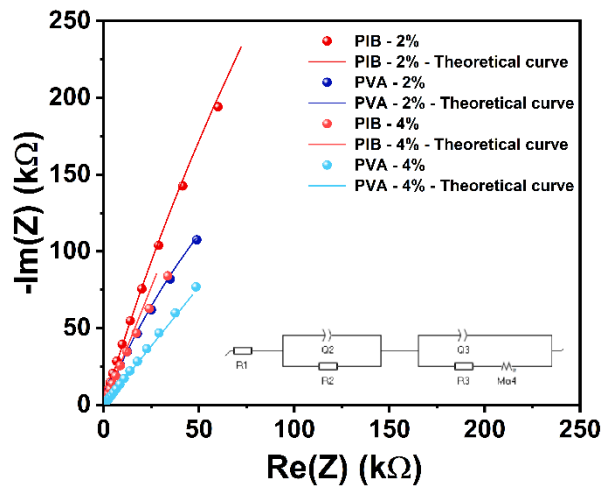


Figure 13: Last cycle of PEIS obtained before CV for one cell of each batch. The theoretical fits were obtained using the same equivalent circuit, which is shown on the bottom right corner of the graphic.

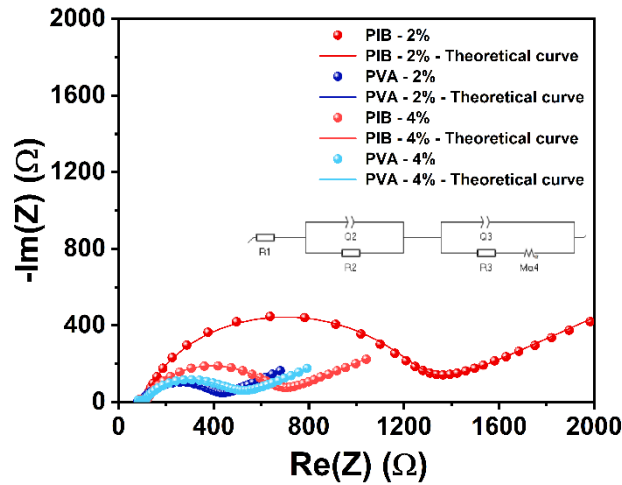


Figure 14: Last PEIS obtained after CV testing for the same cells from each batch. The same equivalent circuit was able to model the experimental data.

It is worth mentioning that the equivalent circuit used to model cell behavior was the same before and after the CV test for every cell, as shown in **Figure 13** and **Figure 14**. This consistency indicates that the fundamental mechanisms behind cell functioning are unchanged. Additionally, the impedances decreased significantly post CV test, which aligns with expectations, as interfaces are expected to develop and stabilize over time and cycling, reflecting cell conditioning. The following interpretation was applied: R_1 , an ohmic resistance, corresponds to the conduction of the most mobile ionic species at high frequencies and is associated with interfacial contact resistance; ideally, it should approach zero. R_2 , representing the diameter of the first semicircle in the Nyquist plot, models bulk ionic transport through the electrolyte via ion hopping. This process is effectively represented by a resistor (R_2) in parallel with a capacitor, capturing the dielectric behavior of the SE in an “ideal” capacitor. It does not account for the movement of the ions at the interfaces. In inorganic SSEs, Li^+ migration in one direction is accompanied by the movement of negatively charged vacancies in the opposite direction, influencing both electrodes simultaneously, and therefore the corresponding resistance is associated in parallel with the “ideal” capacitor. Interfacial processes, particularly those related to electrical double layer formation, are reflected in the elements Q_3 , R_3 , and R_{d4} . These elements represent non-ideal Li^+ diffusion within the double-layer structure, mainly occurring at the positive electrode and limited to a narrow region with unknown thickness, usually of the order of angstrom. In every case, R_1 and R_2 exhibit low and comparable values, indicating similar bulk conductivity (**Table 7**). A second semicircle is clearly visible in the PEIS curves after CV, signifying the formation of a double layer at the electrode, electrolyte interface. Notably, R_3 is higher in the PIB

cells, suggesting increased resistance to interfacial charge transfer or Li^+ accumulation (**Table 7**). Additionally, PEIS spectra exhibit a linear low-frequency tail, characteristic of diffusion-controlled processes, confirming the presence of diffusion behavior.

The CVs show a reduction peak at approximately 3.5 V while discharging (**Figure 15**). The current response rises above 4.1 V, suggesting a shift in charge carrier origin from e^- to h^+ (with possible loss of O_2^-), showcasing the importance of not charging beyond this cut-off voltage. The used voltage window was verified in already published theoretical simulations [121]. All CV curves are directly comparable since the active area is the same for all cells ($\approx 0.5 \text{ cm}^2$) and the mass of active material is in the same order of magnitude (see **Figure 15**). For both cathode formulations, the maximum current is approximately 1.8 mA, showing very similar behavior.

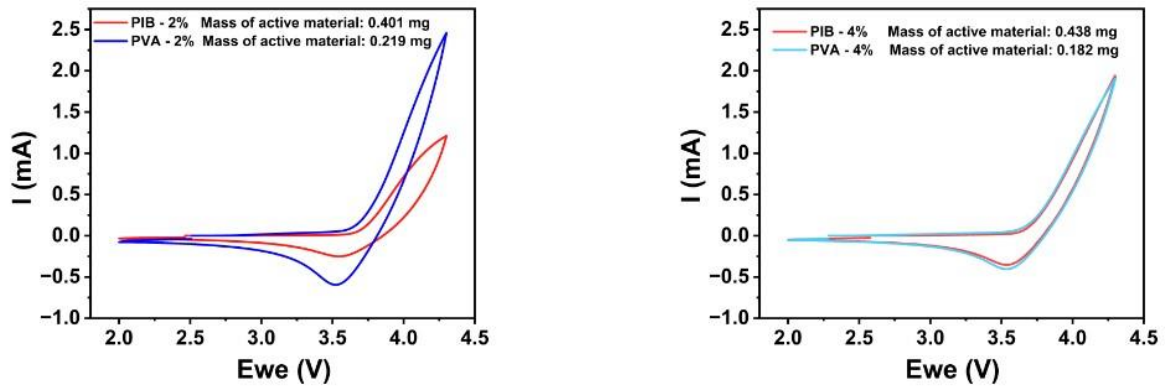


Figure 15: CV curves for the same cells from each batch. These are directly comparable since the active area is the same in every cell due to fabrication methods.

Following these initial tests, all cells were subjected to GCD. This test is the first that assesses the stability and lifecycle of the produced coin cells, and it was the first to showcase significant differences between cell's electrochemical performance. Cycling was conducted between 2.6 and 4.1 V at various C-rates (C/40, C/20, C/10, C/5, C/3, C/2, and C), at room temperature, and without any external pressure. To prevent structural degradation of the NMC955 due to complete lithium extraction, only approximately 70% of the lithium ions were targeted for de-lithiation. This limitation reduces the theoretical specific capacity of the NMC955 cathode to an estimated $192 \text{ mAh} \cdot \text{g}^{-1}$. Batches 1 and 2, containing 2% of binder in the cathode composition, could not keep performance with cycling, achieving low capacities in the first cycles and collapsing once the cycling protocol reached the more demanding and higher power C-rates. GCD curves obtained for these cells are presented in **Figure 16**. Cells containing 2% of PIB in their cathode reached a maximum of only $36 \text{ mAh} \cdot \text{g}^{-1}$ with a C/40 discharge

rate, and $21 \text{ mAh}\cdot\text{g}^{-1}$ in the more demanding 1C rate. Cells with 2% PVA reached higher values of $64 \text{ mAh}\cdot\text{g}^{-1}$ and $40 \text{ mAh}\cdot\text{g}^{-1}$, respectively, at the same rates.

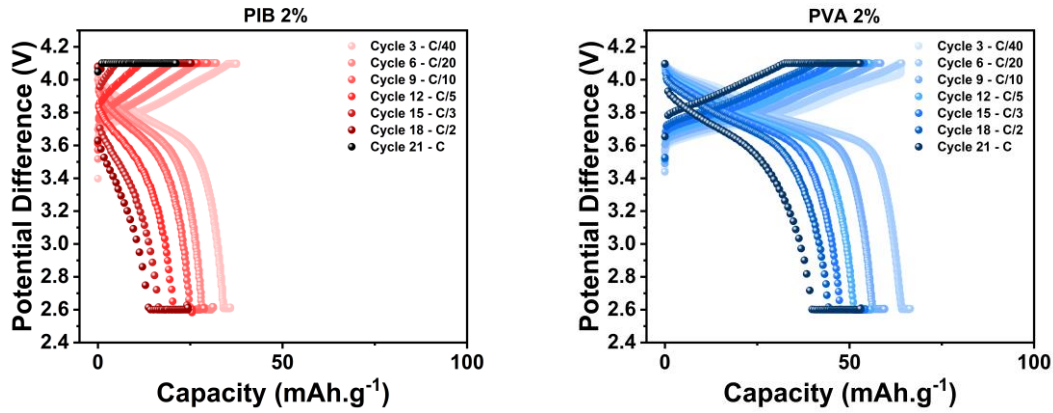


Figure 16: Experimental results of GCD testing for one cell of batch 1 and 2, the third and last cycle for each C-rate is plotted. Note that the scale goes only up to 100 mAh g^{-1} for visualization reasons, while scales in Figure 14 go up to 200 mAh g^{-1} .

On the other hand, batches 3 and 4 performed as expected. Fabricated cells were numbered 1 to 4 to simplify the analysis: cells 1 and 2 are the best performing cells with PIB and PVA, respectively; cells 3 and 4 are the cells with poorer performance. Cathodes with 4% binder in their composition were able to achieve satisfactory discharge capacities across diverse C rates (see **Figure 17**). From each of the batches, the cell with worse performance was selected to be dismantled and taken to postmortem analysis (**Section 4.4**). The best performing cells were left running, achieving a higher number of cycles.

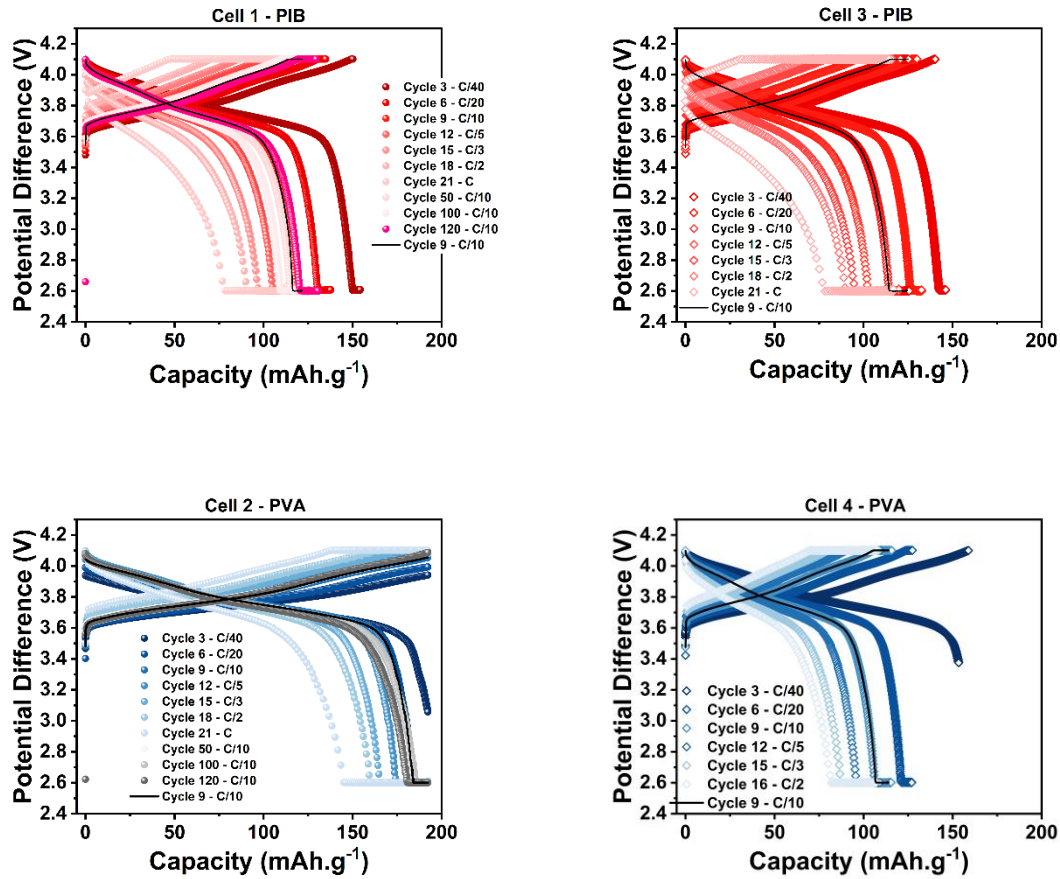


Figure 17: Experimental results of GCD testing for cells of batch 3 and 4, the third and last cycle for each C-rate is plotted.

For the PIB-based Cell 1, a maximum capacity of approximately $145 \text{ mAh}\cdot\text{g}^{-1}$ was achieved at C/40, with capacity decreasing as the C-rate increased (**Figure 17**). The theoretical capacity was not reached at any point during cycling. In contrast, the PVA-based Cell 2 reached the theoretical capacity multiple times, even without requiring a constant voltage step, for lower C-rates. For C/40, the theoretical capacity was achieved before reaching the upper cut-off voltage of 4.1 V. Although the capacity decreased with increasing C-rate, the cell maintained a minimum capacity of $150 \text{ mAh}\cdot\text{g}^{-1}$ at 1C, and with the addition of a CV step, it was able to reach the theoretical capacity (**Figure 17**). Furthermore, upon repeating the C/10 rate, the PVA-based binder cell demonstrated a higher capacity than at the beginning of cycling, suggesting ongoing improvement in electrochemical behavior (**Figure 18**). The electrochemical performance achieved shows that both cathodes can be used to fabricate stable, long-lasting cells with promising discharge capacities.

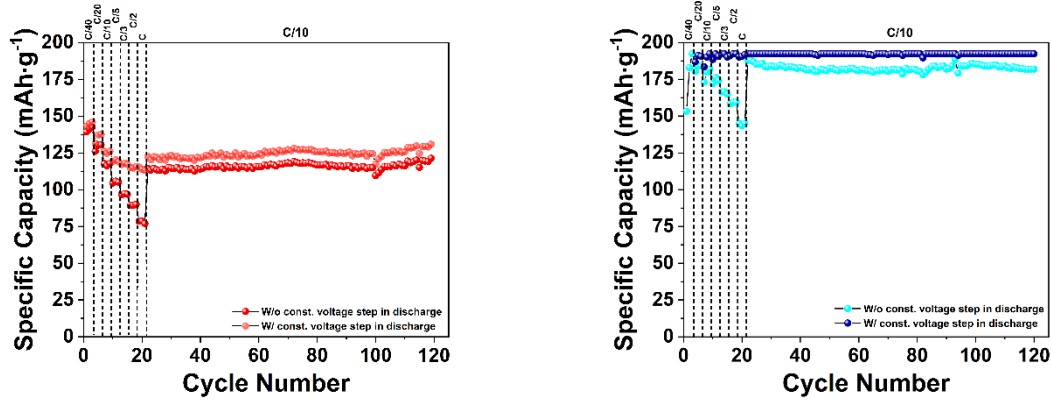


Figure 18: Specific discharge capacity as a function of number of cycles from Cell 1 (PIB binder), and specific discharge capacity as a function of number of cycles from Cell 2 (PVA binder).

To gain better understanding of cell behavior, an additional pair of cells was fabricated using the same procedure as before, with PIB- and PVA-based cathodes with a 4% binder content. These cells were labeled Cell 5 (PIB) and Cell 6 (PVA) and were used for GITT measurements, allowing for the best-performing cells to be cycled for longer.

During the GITT testing, Cell 6 failed prematurely, resulting in no meaningful data. Cell 5 successfully completed the test. Using the Python script (**Attachment B**), the Li ion diffusion coefficient was calculated. The GITT protocol ran for 18 current pulses, each lasting 100 seconds, followed by a 1 hour relaxation period. The corresponding voltage vs time profile is shown in **Figure 19**.

For Cell 5, the calculated diffusion coefficients ranged from 10^{-13} to $10^{-14} \text{ cm}^2\text{s}^{-1}$, which is consistent with values reported in the literature (10^{-10} to $10^{-14} \text{ cm}^2\text{s}^{-1}$). The average diffusion coefficient was determined to be $(1.1 \pm 0.6) \times 10^{-13} \text{ cm}^2\text{s}^{-1}$.

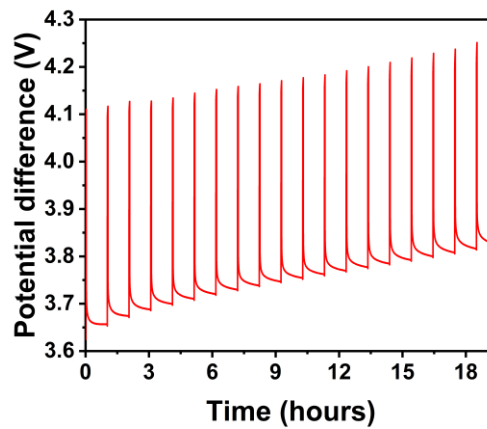


Figure 19: Voltage as a function of time for Cell 5.

4.3 Cathode characterization

This section is dedicated to the detailed characterization of the successfully synthesized cathodes. SEM/EDX, Hall effect and sheet resistance measurements were used to assess cathode's electric behavior and microstructure.

For SEM/EDX analysis, disk format samples were used. **Figure 20** shows the microstructure of the NMC955 (57%) + LPSCI (36%) + PIB (4%) + C65 (3%) composition. **Figure 20** illustrates the presence of an elastic matrix that effectively binds the cathode particles. PIB is a soft and elastic polymer with a glass transition temperature of approximately -70 °C. As a result, at room temperature, it behaves like a supercooled liquid and exhibits viscoelastic properties. This allows it to create the observed matrix that maintains the integrity of the cathode while absorbing mechanical stresses during cycling. The brighter regions, observed in **Figure 20** and confirmed by elemental analysis (**Table 3**), correspond to the NMC955 active material, while the surrounding matrix consists of a mixture of LPSCI, binder, and conductive carbon. **Figure 21** displays the microstructure of the NMC955 (57%) + LPSCI (36%) + PVA (4%) + C65 (3%) composition. In this case, no elastic matrix is observed; however, the cathode remains highly homogeneous. As with the previous composition, the brighter particles correspond to the NMC955 active material, while the darker, more diffuse areas are attributed to the lighter LPSCI and binder mixture. It is highlighted that the radiation used are backscattered electrons. Elemental analysis (**Table 3** and **Table 4**) confirms that all components are present in the expected stoichiometry. Both cathodes exhibit a uniform distribution of particles throughout the structure.

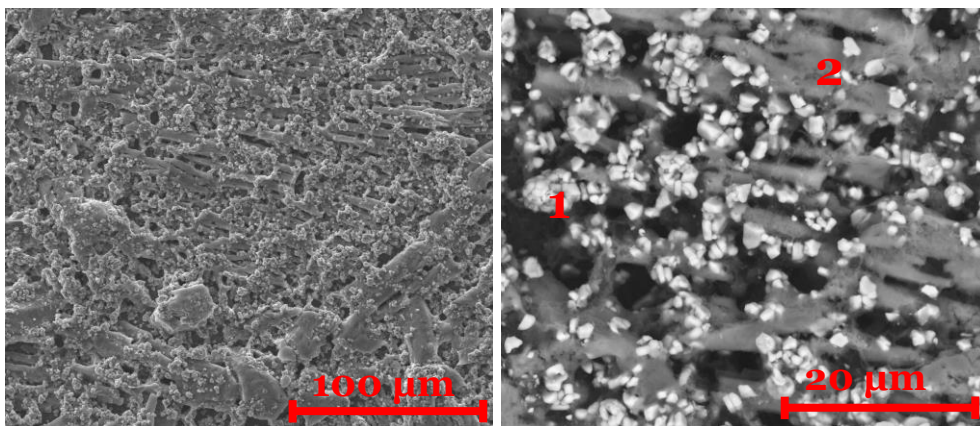


Figure 20: SEM/EDX acquired with backscattered electrons detector. (a), (b) Cathode with composition 57% NMC955 + 36% Li6PS5Cl + 3% C65 + 4% PIB observed with 1000× and 5000× magnification.

Table 3:Chemical composition obtained via EDX analysis of the PIB based cathode. The numbers 1 and 2 refer to Figure 15.

At %								
	C	O	Mn	Co	Ni	P	S	Cl
1	4.29	54.24	1.70	1.49	34.54	0.29	2.61	0.84
2	12.15	28.47	0.14	0.28	2.15	8.45	41.99	6.37

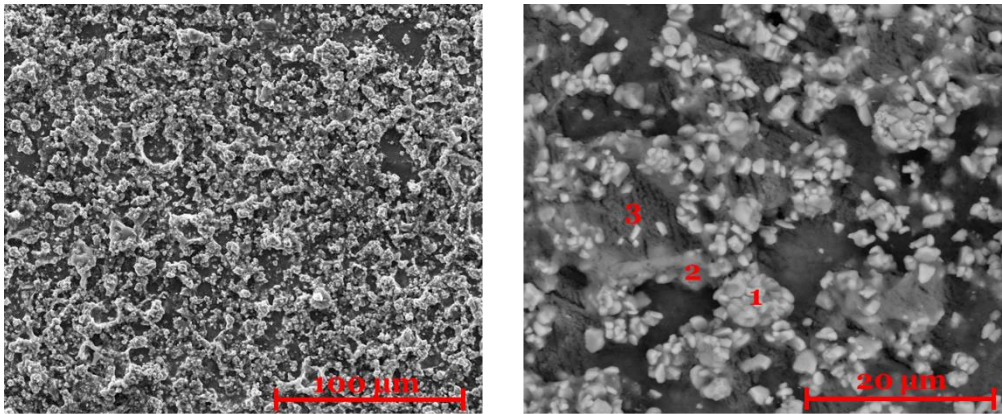


Figure 21: SEM/EDX acquired with backscattered electrons detector. (a), (b) Cathode with composition 57% NMC955 + 36% Li6PS5Cl + 3% C65 + 4% PVA observed with 1000× and 5000× magnification.

Table 4: Chemical composition obtained via EDX analysis of the PIB based cathode. Numbers 1, 2, and 3 refer to Figure 16.

At %								
	C	O	Mn	Co	Ni	P	S	Cl
1	5	44.67	1.93	2.01	64	0.90	6.22	0.75
2	8.78	3.00	1.51	2.67	80.85	2.61	13.23	1.42
3	13.19	19.15	0.44	0.50	2.65	7.66	47.40	9.01

In both composite cathodes, NMC955 and C65 are the only intrinsically conductive components, while LPSCI exhibits semiconductor–insulator behavior and the binders (PIB or PVA) are electronic insulators. For effective battery operation, the cathode must display conductive behavior. Sheet resistance measurements reveal that both cathode compositions display an increase in resistance (a decrease in conductivity) with increasing temperature (**Figure 22**), which is indicative of metallic or conductor behavior. This suggests that, despite the presence of semiconductor and insulator materials, the conductive network formed by NMC955 and C65 remains intact. Charge carrier concentration was determined using Hall effect measurements conducted under a magnetic field of up to ± 0.7 T, applied through two magnetic circuits. A Hall current of 3 mA was applied through the cathode sheets, and the Hall voltage (V_H) and Hall coefficient (R_H) were measured to calculate the charge carrier concentration (CCC), as detailed in **Section 3**. The polarity (positive or negative) of V_H depends on whether the charge carriers are positive or negative.

As shown in **Figure 22**, the PIB-based cathode exhibited an average carrier density of $8.79 \times 10^{20} \text{ cm}^{-3}$, associated with hole-type (h^+ , positive) carriers. In contrast, the PVA-based cathode showed an average carrier density of $-1.99 \times 10^{20} \text{ cm}^{-3}$, indicating electron-type (e^- , negative) carriers (**Figure 22**). The present number and polarity of average charge carriers indicate that the electrodes are degenerate semiconductors or heavily doped oxides, with partially metallic behavior. They are in the borderline between semiconductors and metallic conductors.

Mobility analysis (**Figure 22**) reveals a transition region for the PIB-based cathode between 60 and 80 °C, characterized by a sudden increase in negative charge mobility followed by alternating peaks of positive and negative carrier mobility. The average charge mobility between –40 and 60 °C is $10.26 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the PIB-based cathode and $-2.46 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the PVA-based cathode, showing once again that PIB and PVA binder-based cathodes are more prone to display positive and negative charge mobility, respectively, likely indicating that the PIB and PVA are, respectively, better cationic and electronic conductors. The change in charge mobility observed in the PIB-based cathode around 60–80 °C (**Figure 22**) is likely due to thermal softening, which can change its mechanical properties. As PIB transitions into a viscoelastic state, conductive pathways may be compromised by weakening contact between the active materials. Above –70 °C, PIB is a supercooled liquid. Above ≈ 200 °C, depending on the type of PIB (for example, from its molecular weight), it melts.

The results obtained for conductivity and CCC for PIB are consistent with those reported in [121] for SBR binder-based NMC955 cathode ($1.13 \times 10^{21} \text{ h}^+ \text{ cm}^{-3}$). The conductivity shows the same trend, decreasing with temperature, and the measured values are of the same order of magnitude. These findings reinforce the potential of NMC955 as a promising high-capacity material, particularly due to its compatibility with various alternative binders that are more sustainable than conventional options such as PVDF.

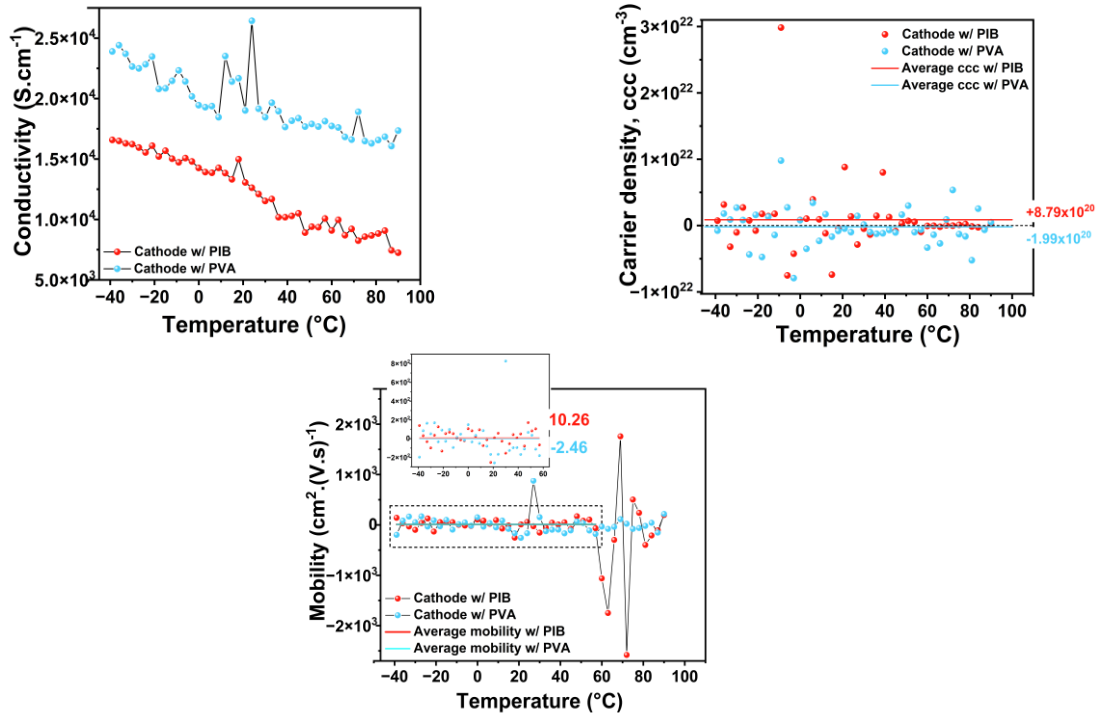


Figure 22: Experimental results from sheet resistance/Hall effect measurements: (Top left) Conductivity as a function of temperature: the obtained behavior is one of a typical metal; (Top Right) Charge carrier density as a function of temperature: positive in the cathode synthesized using PIB, and negative for the cathode containing PVA; (Bottom) Charge carrier mobility coefficient as a function of temperature.

4.4 Post-mortem characterization

As explained previously, the worst performing cells were dismantled and used to perform post-mortem characterization. These cells were opened inside a glovebox (the same where cathodes were synthesized and cell fabricated) and the cathode was carefully removed using plastic tweezers to avoid any contact between metals. These cathodes were then visualized using SEM and their chemical composition was estimated via EDX analysis.

In the PIB-based cathode, remnants of the elastic matrix were still visible, **Figure 23**. A decrease in sulfur content compared to the initial composition (**Table 3** and **Table 5**) was observed, consistent with the formation of sulfates as reported in [121]. NMC955

particles remained detectable, but a reduction in oxygen content was noted (**Table 3** and **Table 1**), likely due to oxygen release during charging. This observation is supported by the CV data, which showed increased current near 4.1 V, suggesting the occurrence of competing side reactions (**Figure 23**).

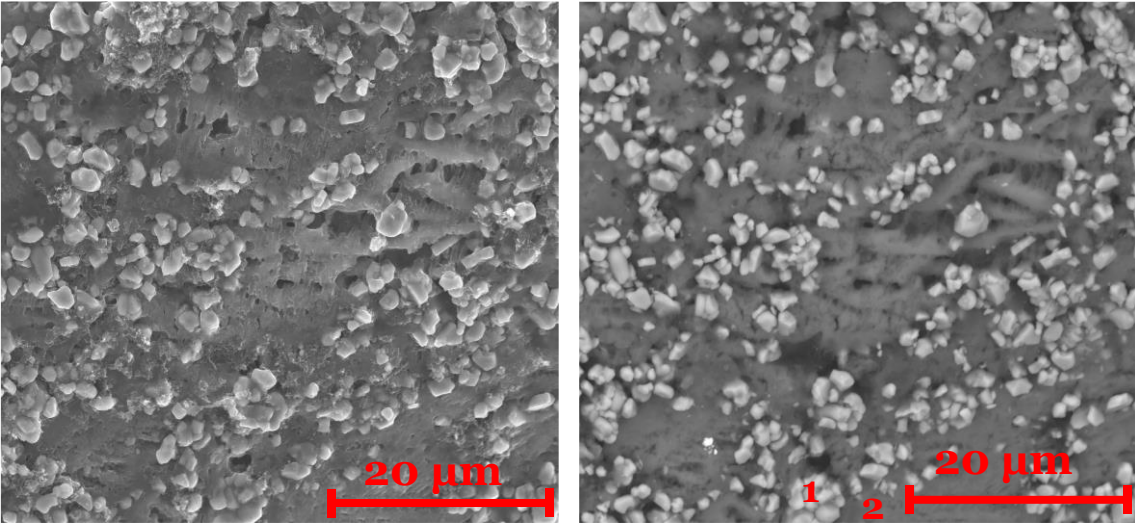


Figure 23: Post-mortem characterization of the cathode with composition 57% NMC955 + 36% Li₆PS₅Cl + 3% C65 + 4% PIB observed with 5000× magnification. Images were acquired with SEM/EDX and backscattered electrons detector.

Table 5: Post-mortem chemical composition obtained via EDX analysis of the PIB based cathode. Numbers 1 and 2 refer to Figure 18.

	At %							
	C	O	Mn	Co	Ni	P	S	Cl
1	9.01	47.69	1.69	1.87	37.68	0.33	1.40	0.33
2	24.28	25.87	0.51	0.65	1.12	8.10	33.82	9.51

For the PVA-based cathode (**Figure 24**), a similar reduction in oxygen content was observed (**Table 4** and **Table 6**). While **Figure 24** seems to show fewer deposited particles compared to **Figure 23**, this comparison should be interpreted with caution. The more difficult demolding process for the PVA sample may have damaged the surface, potentially affecting the observed microstructure and the quality of the analysis.

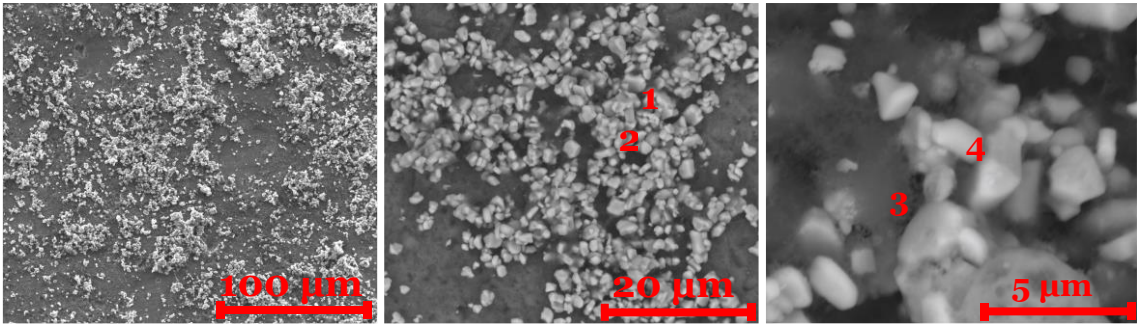


Figure 24: Post-mortem characterization of the cathode with composition 57% NMC955 + 36% Li₆PS₅Cl + 3% C65 + 4% PVA. Images were acquired with SEM/EDX and backscattered electrons using 1000×, 5000×, and 20,000× magnification, respectively.

Table 6: Post-mortem chemical composition obtained via EDX analysis of the PIB based cathode. Numbers 1-4 refer to Figure 19.

At %								
	C	O	Mn	Co	Ni	P	S	Cl
1	51.29	25.60	2.11	3.82	17.37	0.23	2.89	0.25
2	7.22	52.53	2.65	3.32	34.18	0.12	2.42	0.18
3	71.14	11.98	0.67	0.79	11.56	0.43	3	0.44
4	13.68	50.34	1.47	1.51	30.15	0.38	2.17	0.19

5. Conclusion

This thesis investigates the optimization of NMC955 based cathodes for solid-state batteries, focusing on replacing toxic binders and solvents with sustainable alternatives that are compatible with sulfide solid electrolytes. This study was divided in two main phases.

In the first phase, cathodes were synthesized using two alternative binders, PIB and PVA, using toluene as a solvent. LPSCI was incorporated into the cathode formulation to improve its compatibility with the electrolyte. Cathodes with different binder contents (2% and 4%) were made with the following composition: 57% NMC955 + 3% C65 + (40-x)% LPSCI + x% binder, with x being 2% or 4%. Cathodes were synthesized using a wet method, as these are more scalable and industrially viable.

In the second phase, the cathodes were integrated into coin cells with an NMC955/LPSCI/Li^o configuration and subjected to electrochemical characterization through PEIS, CV, and GCD. Additionally, microstructural and chemical composition analysis were conducted using SEM/EDX. Cathode's electric behavior was evaluated through sheet resistance and Hall effect measurements.

The results indicated that cathodes with 4% binder content outperformed those with 2%, irrespective of the type of binder used. Notably, the PVA formulation achieved the theoretical capacity of NMC955 ($192 \text{ mAh}\cdot\text{g}^{-1}$) at a rate of C/10, maintaining high capacities up to 1C for more than 100 cycles. In contrast, the PIB formulation reached a maximum capacity of $145 \text{ mAh}\cdot\text{g}^{-1}$ at C/40, demonstrating stable but lower performance for more than 100 cycles. SEM/EDX analysis revealed a homogeneous distribution of NMC955 particles and LPSCI in both formulations. In the case of the PIB cathode, an elastic matrix surrounding the active particles was observed, providing good mechanical cohesion. The cathode with PVA, on the other hand, had a more rigid and brittle structure, with well-defined interfaces between them. EDX confirmed the presence of the expected elements in proportions close to the theoretical ones, reflecting the correct incorporation of the components in the cathode composition.

These findings suggest that replacing PVDF and NMP with sustainable binders and solvents is a viable approach for producing cathodes compatible with sulfide electrolytes, and capable of achieving remarkable electrochemical performances. This work contributes to the development of safer, more eco-friendly, and high-performance solid-

state batteries. In particular, PVA emerged as a promising option, offering a high specific capacity, cycling stability, and compatibility with LPSCI.

The next phase of research should focus on optimizing the synthesis process, particularly the composition of the cathode, synthesis temperature, and mixing times. Investigating sustainable binders, such as natural polymers and hybrid composites, could enhance adhesion, flexibility, and conductivity. Additionally, studying thermal and mechanical treatments to improve interfaces may help reduce internal impedance and extend the longevity of the cells, although increasing synthesis complexity. Another important step is to assess the scalability of the synthesis process to adapt it for the industrial production of thin films and large-area electrodes. Initial scalability trials could start with fabricating pouch cells instead of coin cells, as this approach may better evaluate practical manufacturing feasibility by increasing the active area. These attempts are important to transition from laboratory scale advancements to commercially viable solid-state batteries that are safer, more efficient, and environmentally sustainable.

References

- [1] F. Mohammadi, M. Saif, A comprehensive overview of electric vehicle batteries market, *E-Prime - Advances in Electrical Engineering, Electronics and Energy* 3 (2023). <https://doi.org/10.1016/j.prime.2023.100127>.
- [2] I. Energy Agency, Global EV Outlook 2021 Accelerating ambitions despite the pandemic, 2021. www.iea.org/t&c/.
- [3] M. Niestadt, A. Bjørnåvold, BRIEFING EPRS | European Parliamentary Research Service, n.d.
- [4] I. Energy Agency, Global EV Outlook 2024 Moving towards increased affordability, 2024. www.iea.org.
- [5] W. Li, B. Song, A. Manthiram, High-voltage positive electrode materials for lithium-ion batteries, *Chem Soc Rev* 46 (2017) 3006–3059. <https://doi.org/10.1039/c6cs00875e>.
- [6] S. Huo, L. Sheng, W. Xue, L. Wang, H. Xu, H. Zhang, X. He, Challenges of polymer electrolyte with wide electrochemical window for high energy solid-state lithium batteries, *InfoMat* 5 (2023). <https://doi.org/10.1002/inf2.12394>.
- [7] B.M. Gomes, J.F. Ribeiro Moutinho, M.H. Braga, A perspective on the building blocks of a solid-state battery: from solid electrolytes to quantum power harvesting and storage, *J Mater Chem A Mater* 12 (2023) 690–722. <https://doi.org/10.1039/d3ta04228f>.
- [8] A. Celadon, H. Sun, S. Sun, G. Zhang, Batteries for electric vehicles: Technical advancements, environmental challenges, and market perspectives, *SusMat* (2024). <https://doi.org/10.1002/sus2.234>.
- [9] R.M. Salgado, F. Danzi, J.E. Oliveira, A. El-Azab, P.P. Camanho, M.H. Braga, The latest trends in electric vehicles batteries, *Molecules* 26 (2021). <https://doi.org/10.3390/molecules26113188>.
- [10] Y. Kim, W.M. Seong, A. Manthiram, Cobalt-free, high-nickel layered oxide cathodes for lithium-ion batteries: Progress, challenges, and perspectives, *Energy Storage Mater* 34 (2021) 250–259. <https://doi.org/10.1016/j.ensm.2020.09.020>.
- [11] A. Manthiram, A reflection on lithium-ion battery cathode chemistry, *Nat Commun* 11 (2020). <https://doi.org/10.1038/s41467-020-15355-0>.

- [12] A. Faber, B. Krause, B. Sánchez de la Sierra, UC Berkeley CEGA White Papers Title Artisanal Mining, Livelihoods, and Child Labor in the Cobalt Supply Chain of the Democratic Republic of Congo [Permalink https://escholarship.org/uc/item/17m9g4wm](https://escholarship.org/uc/item/17m9g4wm) Publication Date, n.d. <https://escholarship.org/uc/item/17m9g4wm>.
- [13] K. Schleich, Unveiling the Dark Side of Innovation: Sustainability, Cobalt Mining, and Modern-Day Slavery, *SMU Science and Technology Law Review* 27 (2024) 135. <https://doi.org/10.25172/smustlr.27.1.8>.
- [14] RECHARGE, PFAS restriction proposal - RECHARGE statement for 2nd Call for Evidence, Brussels, 2021. https://rechargebatteries.org/wp-content/uploads/2022/09/Call-for-Evidence_RECHARGE_-_PFAS-restriction-V1.pdf (accessed October 22, 2024).
- [15] C. Yang, J. Wang, P. Yang, Y. He, S. Wang, P. Zhao, H. Wang, Recovery of Valuable Metals from Spent $\text{LiNi}_0.8\text{Co}_0.1\text{Mn}_0.1\text{O}_2$ Cathode Materials Using Compound Leaching Agents of Sulfuric Acid and Oxalic Acid, *Sustainability (Switzerland)* 14 (2022). <https://doi.org/10.3390/su142114169>.
- [16] P.M. Tembo, C. Dyer, V. Subramanian, Lithium-ion battery recycling—a review of the material supply and policy infrastructure, *NPG Asia Mater* 16 (2024). <https://doi.org/10.1038/s41427-024-00562-8>.
- [17] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, Recycling lithium-ion batteries from electric vehicles, *Nature* 575 (2019) 75–86. <https://doi.org/10.1038/s41586-019-1682-5>.
- [18] P. Greb, Product Environmental Report iPhone 15 Pro and iPhone 15 Pro Max, 2023.
- [19] D. Das, S. Manna, S. Puravankara, Electrolytes, Additives and Binders for NMC Cathodes in Li-Ion Batteries—A Review, *Batteries* 9 (2023). <https://doi.org/10.3390/batteries9040193>.
- [20] Y. Lavoie, F. Danet, B. Lombard, Lithium-ion batteries for industrial applications, in: 2017 Petroleum and Chemical Industry Technical Conference (PCIC), IEEE, 2017: pp. 283–290. <https://doi.org/10.1109/PCICON.2017.8188747>.
- [21] A. Manthiram, An Outlook on Lithium Ion Battery Technology, *ACS Cent Sci* 3 (2017) 1063–1069. <https://doi.org/10.1021/acscentsci.7b00288>.

- [22] J. Wen, Y. Yu, C. Chen, A review on lithium-ion batteries safety issues: Existing problems and possible solutions, *Materials Express* 2 (2012) 197–212. <https://doi.org/10.1166/mex.2012.1075>.
- [23] A. Manthiram, A reflection on lithium-ion battery cathode chemistry, *Nat Commun* 11 (2020). <https://doi.org/10.1038/s41467-020-15355-0>.
- [24] C. Daniel, D. Mohanty, J. Li, D.L. Wood, Cathode materials review, in: *AIP Conf Proc*, American Institute of Physics Inc., 2014: pp. 26–43. <https://doi.org/10.1063/1.4878478>.
- [25] Y. Kim, W.M. Seong, A. Manthiram, Cobalt-free, high-nickel layered oxide cathodes for lithium-ion batteries: Progress, challenges, and perspectives, *Energy Storage Mater* 34 (2021) 250–259. <https://doi.org/10.1016/j.ensm.2020.09.020>.
- [26] T. Ohzuku, Y. Makimura, Layered Lithium Insertion Material of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for Lithium-Ion Batteries, *Chem Lett* 30 (2001) 642–643. <https://doi.org/10.1246/cl.2001.642>.
- [27] T. Ohzuku, Y. Makimura, Layered Lithium Insertion Material of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$: A Possible Alternative to LiCoO_2 for Advanced Lithium-Ion Batteries, *Chem Lett* 30 (2001) 744–745. <https://doi.org/10.1246/cl.2001.744>.
- [28] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Li_xCoO_2 ($0 < x \leq 1$): A NEW CATHODE MATERIAL FOR BATTERIES OF HIGH ENERGY DENSITY, 1980.
- [29] Y. Lyu, X. Wu, K. Wang, Z. Feng, T. Cheng, Y. Liu, M. Wang, R. Chen, L. Xu, J. Zhou, Y. Lu, B. Guo, An Overview on the Advances of LiCoO_2 Cathodes for Lithium-Ion Batteries, *Adv Energy Mater* 11 (2021). <https://doi.org/10.1002/aenm.202000982>.
- [30] I. Belharouak, Y.-K. Sun, J. Liu, K. Amine, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ as a suitable cathode for high power applications, *J Power Sources* 123 (2003) 247–252. [https://doi.org/10.1016/S0378-7753\(03\)00529-9](https://doi.org/10.1016/S0378-7753(03)00529-9).
- [31] M. Malik, K.H. Chan, G. Azimi, Review on the synthesis of $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) cathodes for lithium-ion batteries, *Mater Today Energy* 28 (2022). <https://doi.org/10.1016/j.mtener.2022.101066>.
- [32] MSE Supplies, MSE PRO Lithium Nickel Manganese Cobalt Oxide Cathode Powder 500g, NMC622, (2024).

- [33] A.L. Lipson, J.L. Durham, M. Leresche, I. Abu-Baker, M.J. Murphy, T.T. Fister, L. Wang, F. Zhou, L. Liu, K. Kim, D. Johnson, Improving the Thermal Stability of NMC 622 Li-Ion Battery Cathodes through Doping during Coprecipitation, *ACS Appl Mater Interfaces* 12 (2020) 18512–18518. <https://doi.org/10.1021/acsami.0c01448>.
- [34] R. Jung, P. Strobl, F. Maglia, C. Stinner, H.A. Gasteiger, Temperature Dependence of Oxygen Release from $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) Cathode Materials for Li-Ion Batteries, *J Electrochem Soc* 165 (2018) A2869–A2879. <https://doi.org/10.1149/2.1261811jes>.
- [35] J. Li, L.E. Downie, L. Ma, W. Qiu, J.R. Dahn, Study of the Failure Mechanisms of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ Cathode Material for Lithium Ion Batteries, *J Electrochem Soc* 162 (2015) A1401–A1408. <https://doi.org/10.1149/2.1011507jes>.
- [36] C.S. Yoon, M.H. Choi, B.-B. Lim, E.-J. Lee, Y.-K. Sun, Review—High-Capacity $\text{Li}[\text{Ni}_{1-x}\text{Co}_x/2\text{Mn}_x/2]\text{O}_2$ ($x = 0.1, 0.05, 0$) Cathodes for Next-Generation Li-Ion Battery, *J Electrochem Soc* 162 (2015) A2483–A2489. <https://doi.org/10.1149/2.0101514jes>.
- [37] X. Yu, A. Manthiram, Electrode–Electrolyte Interfaces in Lithium–Sulfur Batteries with Liquid or Inorganic Solid Electrolytes, *Acc Chem Res* 50 (2017) 2653–2660. <https://doi.org/10.1021/acs.accounts.7b00460>.
- [38] G. Bucci, B. Talamini, A. Renuka Balakrishna, Y.M. Chiang, W.C. Carter, Mechanical instability of electrode-electrolyte interfaces in solid-state batteries, *Phys Rev Mater* 2 (2018). <https://doi.org/10.1103/PhysRevMaterials.2.105407>.
- [39] R. Koerver, I. Aygün, T. Leichtweiß, C. Dietrich, W. Zhang, J.O. Binder, P. Hartmann, W.G. Zeier, J. Janek, Capacity Fade in Solid-State Batteries: Interphase Formation and Chemomechanical Processes in Nickel-Rich Layered Oxide Cathodes and Lithium Thiophosphate Solid Electrolytes, *Chemistry of Materials* 29 (2017) 5574–5582. <https://doi.org/10.1021/acs.chemmater.7b00931>.
- [40] K. Nie, Y. Hong, J. Qiu, Q. Li, X. Yu, H. Li, L. Chen, Interfaces between cathode and electrolyte in solid state lithium batteries: Challenges and perspectives, *Front Chem* 6 (2018). <https://doi.org/10.3389/fchem.2018.00616>.
- [41] B. Liu, S.D. Pu, C. Doerr, D. Spencer Jolly, R.A. House, D.L.R. Melvin, P. Adamson, P.S. Grant, X. Gao, P.G. Bruce, The effect of volume change and stack

- pressure on solid-state battery cathodes, *SusMat* 3 (2023) 721–728. <https://doi.org/10.1002/sus2.162>.
- [42] D. Wang, Q. Sun, J. Luo, J. Liang, Y. Sun, R. Li, K. Adair, L. Zhang, R. Yang, S. Lu, H. Huang, X. Sun, Mitigating the Interfacial Degradation in Cathodes for High-Performance Oxide-Based Solid-State Lithium Batteries, *ACS Appl Mater Interfaces* 11 (2019) 4954–4961. <https://doi.org/10.1021/acsami.8b17881>.
- [43] N.D. Phillip, A.S. Westover, C. Daniel, G.M. Veith, Structural Degradation of High Voltage Lithium Nickel Manganese Cobalt Oxide (NMC) Cathodes in Solid-State Batteries and Implications for Next Generation Energy Storage, *ACS Appl Energy Mater* 3 (2020) 1768–1774. <https://doi.org/10.1021/acsaem.9b02230>.
- [44] X. Bai, F. Xie, Z. Zhang, M. Cao, Q. Wang, S. Wang, C. Liu, X. Su, Z. Lin, G. Cui, Prospects and Strategies for Single-Crystal NCM Materials to Solve All-Solid-State Battery Cathode Interface Problems, *Adv Energy Mater* (2024). <https://doi.org/10.1002/aenm.202401336>.
- [45] P. Yao, H. Yu, Z. Ding, Y. Liu, J. Lu, M. Lavorgna, J. Wu, X. Liu, Review on Polymer-Based Composite Electrolytes for Lithium Batteries, *Front Chem* 7 (2019). <https://doi.org/10.3389/fchem.2019.00522>.
- [46] H. Kwak, S. Wang, J. Park, Y. Liu, K.T. Kim, Y. Choi, Y. Mo, Y.S. Jung, Emerging Halide Superionic Conductors for All-Solid-State Batteries: Design, Synthesis, and Practical Applications, *ACS Energy Lett* 7 (2022) 1776–1805. <https://doi.org/10.1021/acsenenergylett.2c00438>.
- [47] Z. Zhang, L. Zhang, Y. Liu, C. Yu, X. Yan, B. Xu, L. min Wang, Synthesis and characterization of argyrodite solid electrolytes for all-solid-state Li-ion batteries, *J Alloys Compd* 747 (2018) 227–235. <https://doi.org/10.1016/j.jallcom.2018.03.027>.
- [48] T. Brahmbhatt, G. Yang, E. Self, J. Nanda, Cathode–Sulfide Solid Electrolyte Interfacial Instability: Challenges and Solutions, *Front Energy Res* (2020). <https://doi.org/10.3389/fenrg.2020.570754>.
- [49] J. Haruyama, K. Sodeyama, L. Han, K. Takada, Y. Tateyama, Space-charge layer effect at interface between oxide cathode and sulfide electrolyte in all-solid-state lithium-ion battery, *Chemistry of Materials* 26 (2014) 4248–4255. <https://doi.org/10.1021/cm5016959>.

- [50] S.H. Jung, U. Kim, J. Kim, S. Jun, C.S. Yoon, Y.S. Jung, Y. Sun, Ni-Rich Layered Cathode Materials with Electrochemo-Mechanically Compliant Microstructures for All-Solid-State Li Batteries, *Adv Energy Mater* 10 (2020). <https://doi.org/10.1002/aenm.201903360>.
- [51] Y. Lee, J. Lee, K.Y. Lee, J. Mun, J.K. Lee, W. Choi, Facile formation of a Li₃PO₄ coating layer during the synthesis of a lithium-rich layered oxide for high-capacity lithium-ion batteries, *J Power Sources* 315 (2016) 284–293. <https://doi.org/10.1016/j.jpowsour.2016.03.024>.
- [52] B.J. Chae, T. Yim, Sulfonate-immobilized artificial cathode electrolyte interphases layer on Ni-rich cathode, *J Power Sources* 360 (2017) 480–487. <https://doi.org/10.1016/j.jpowsour.2017.06.037>.
- [53] F. Schipper, H. Bouzaglo, M. Dixit, E.M. Erickson, T. Weigel, M. Talianker, J. Grinblat, L. Burstein, M. Schmidt, J. Lampert, C. Erk, B. Markovsky, D.T. Major, D. Aurbach, From Surface ZrO₂ Coating to Bulk Zr Doping by High Temperature Annealing of Nickel-Rich Lithiated Oxides and Their Enhanced Electrochemical Performance in Lithium Ion Batteries, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201701682>.
- [54] A. Chahbaz, Y. Luo, G. Stahl, H. Dittler, T. Jaumann, M. Glinka, C. Lingen, D.U. Sauer, W. Li, Pressure-Induced Capacity Recovery and Performance Enhancements in LTO/NMC-LCO Batteries, *Adv Funct Mater* (2024). <https://doi.org/10.1002/adfm.202419229>.
- [55] C.S. Yoon, U.H. Kim, G.T. Park, S.J. Kim, K.H. Kim, J. Kim, Y.K. Sun, Self-Passivation of a LiNiO₂ Cathode for a Lithium-Ion Battery through Zr Doping, *ACS Energy Lett* 3 (2018) 1634–1639. <https://doi.org/10.1021/acsenergylett.8b00805>.
- [56] Y.H. Lee, D.H. Kim, J.M. Yoon, I.C. Choi, J.H. Choi, K.J. Jeon, Y.C. Ha, C.M. Park, Empowering all-solid-state Li-ion batteries with self-stabilizing Sn-based anodes, *Joule* 8 (2024) 2777–2793. <https://doi.org/10.1016/j.joule.2024.08.011>.
- [57] S.C. Han, M. Ali, Y.J. Kim, J. Park, Y.-J. Lee, J.-W. Park, H. Park, G. Park, E. Lee, B.G. Kim, Y.-C. Ha, Unraveling electrochemo-mechanical aspects of core-shell composite cathode for sulfide based all-solid-state batteries, *J Mater Chem A Mater* (2024). <https://doi.org/10.1039/d4ta04063e>.

- [58] X. Hu, W. Qiang, B. Huang, Surface layer design of cathode materials based on mechanical stability towards long cycle life for lithium secondary batteries, *Energy Storage Mater* 8 (2017) 141–146. <https://doi.org/10.1016/j.ensm.2017.05.011>.
- [59] Z. Chen, D. Chao, J. Lin, Z. Shen, Recent progress in surface coating of layered $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ for lithium-ion batteries, *Mater Res Bull* 96 (2017) 491–502. <https://doi.org/10.1016/j.materresbull.2017.05.021>.
- [60] L. Liang, G. Hu, F. Jiang, Y. Cao, Electrochemical behaviours of SiO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials by a novel modification method, *J Alloys Compd* 657 (2016) 570–581. <https://doi.org/10.1016/j.jallcom.2015.10.177>.
- [61] Y. Xia, J. Zheng, C. Wang, M. Gu, Designing principle for Ni-rich cathode materials with high energy density for practical applications, 2018.
- [62] E. Zhao, M. Chen, Z. Hu, D. Chen, L. Yang, X. Xiao, Improved cycle stability of high-capacity Ni-rich $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ at high cut-off voltage by Li_2SiO_3 coating, *J Power Sources* 343 (2017) 345–353. <https://doi.org/10.1016/j.jpowsour.2017.01.066>.
- [63] J. Hu, H. Wang, B. Xiao, P. Liu, T. Huang, Y. Li, X. Ren, Q. Zhang, J. Liu, X. Ouyang, X. Sun, Challenges and approaches of single-crystal Ni-rich layered cathodes in lithium batteries, *Natl Sci Rev* 10 (2023). <https://doi.org/10.1093/nsr/nwad252>.
- [64] S. Yun, J. Yu, W. Lee, H. Lee, W.-S. Yoon, Achieving structural stability and enhanced electrochemical performance through Nb-doping into Li- and Mn-rich layered cathode for lithium-ion batteries, *Mater Horiz* 10 (2023) 829–841. <https://doi.org/10.1039/D2MH01254E>.
- [65] Y. Li, X. Liu, L. Wang, X. Feng, D. Ren, Y. Wu, G. Xu, L. Lu, J. Hou, W. Zhang, Y. Wang, W. Xu, Y. Ren, Z. Wang, J. Huang, X. Meng, X. Han, H. Wang, X. He, Z. Chen, K. Amine, M. Ouyang, Thermal runaway mechanism of lithium-ion battery with $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode materials, *Nano Energy* 85 (2021) 105878. <https://doi.org/10.1016/j.nanoen.2021.105878>.
- [66] F. Guo, Y. Hu, L. Qiu, Y. Jiang, Y. Deng, J. Zhou, Z. Zheng, Y. Liu, Y. Sun, Z. Wu, Y. Song, X. Guo, Surface energy alteration-derived grain size regulation countering capacity deterioration in high-voltage single-crystal Ni-rich cathodes, *J Mater Chem A Mater* 11 (2023) 11819–11830. <https://doi.org/10.1039/D2TA08703K>.

- [67] X. Ou, T. Liu, W. Zhong, X. Fan, X. Guo, X. Huang, L. Cao, J. Hu, B. Zhang, Y.S. Chu, G. Hu, Z. Lin, M. Dahbi, J. Alami, K. Amine, C. Yang, J. Lu, Enabling high energy lithium metal batteries via single-crystal Ni-rich cathode material co-doping strategy, *Nat Commun* 13 (2022). <https://doi.org/10.1038/s41467-022-30020-4>.
- [68] H.H. Ryu, B. Namkoong, J.H. Kim, I. Belharouak, C.S. Yoon, Y.K. Sun, Capacity Fading Mechanisms in Ni-Rich Single-Crystal NCM Cathodes, *ACS Energy Lett* 6 (2021) 2726–2734. <https://doi.org/10.1021/acseenergylett.1c01089>.
- [69] L. Mu, R. Zhang, W.H. Kan, Y. Zhang, L. Li, C. Kuai, B. Zydlewski, M.M. Rahman, C.J. Sun, S. Sainio, M. Avdeev, D. Nordlund, H.L. Xin, F. Lin, Dopant Distribution in Co-Free High-Energy Layered Cathode Materials, *Chemistry of Materials* 31 (2019) 9769–9776. <https://doi.org/10.1021/acs.chemmater.9b03603>.
- [70] A. Beutl, A. Orue, P. López-Aranguren, A. Itziar Pitillas Martinez, M.H. Braga, V. Kekkonen, A. Tron, Round-robin test of all-solid-state battery with sulfide electrolyte assembly in coin-type cell configuration, *Electrochemical Science Advances* (2024). <https://doi.org/10.1002/elsa.202400004>.
- [71] H. Laufen, S. Berg, J. Engeser, M. Strautmann, A. Koprivc, C. Rahe, E. Figgemeier, D.U. Sauer, Correlation between Voltage, Strain, and Impedance as a Function of Pressure of a Nickel-Rich NMC Lithium-Ion Pouch Cell, *Adv Mater Technol* 9 (2024). <https://doi.org/10.1002/admt.202301965>.
- [72] J.-H. Shim, C.-Y. Kim, S.-W. Cho, A. Missiul, J.-K. Kim, Y.J. Ahn, S. Lee, Effects of heat-treatment atmosphere on electrochemical performances of Ni-rich mixed-metal oxide ($\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$) as a cathode material for lithium ion battery, *Electrochim Acta* 138 (2014) 15–21. <https://doi.org/10.1016/j.electacta.2014.06.079>.
- [73] G. Sun, X. Yin, W. Yang, A. Song, C. Jia, W. Yang, Q. Du, Z. Ma, G. Shao, The effect of cation mixing controlled by thermal treatment duration on the electrochemical stability of lithium transition-metal oxides, *Physical Chemistry Chemical Physics* 19 (2017) 29886–29894. <https://doi.org/10.1039/c7cp05530g>.
- [74] J.L. White, F.S. Gittleston, M. Homer, F. El Gabaly, Nickel and Cobalt Oxidation State Evolution at Ni-Rich NMC Cathode Surfaces during Treatment, *Journal of Physical Chemistry C* 124 (2020) 16508–16514. <https://doi.org/10.1021/acs.jpcc.0c04794>.

- [75] C. Doerrer, I. Capone, S. Narayanan, J. Liu, C.R.M. Grovenor, M. Pasta, P.S. Grant, High Energy Density Single-Crystal NMC/Li6PS5Cl Cathodes for All-Solid-State Lithium-Metal Batteries, *ACS Appl Mater Interfaces* 13 (2021) 37809–37815. <https://doi.org/10.1021/acsami.1c07952>.
- [76] W. James, Effect of Fabrication Pressure and NMC Cathode Composition on Effect of Fabrication Pressure and NMC Cathode Composition on LPSCl Electrolyte for Solid-State Battery Performance LPSCl Electrolyte for Solid-State Battery Performance Improvement Improvement Recommended Citation Recommended Citation James, Winervil, "Effect of Fabrication Pressure and NMC Cathode Composition on LPSCl Electrolyte for, n.d. <https://repository.rit.edu/theses>.
- [77] C.M. Julien, A. Mauger, NCA, NCM811, and the route to Ni-Richer lithium-Ion batteries, *Energies (Basel)* 13 (2020). <https://doi.org/10.3390/en13236363>.
- [78] F. Zhang, Y. Guo, L. Zhang, P. Jia, X. Liu, P. Qiu, H. Zhang, J. Huang, A review of the effect of external pressure on all-solid-state batteries, *ETransportation* 15 (2023). <https://doi.org/10.1016/j.etrans.2022.100220>.
- [79] M.H. Lee, Y.J. Kang, S.T. Myung, Y.K. Sun, Synthetic optimization of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ via co-precipitation, *Electrochim Acta* 50 (2004) 939–948. <https://doi.org/10.1016/j.electacta.2004.07.038>.
- [80] C.-C. Wang, K.A. Jarvis, P.J. Ferreira, A. Manthiram, Effect of Synthesis Conditions on the First Charge and Reversible Capacities of Lithium-Rich Layered Oxide Cathodes, *Chemistry of Materials* 25 (2013) 3267–3275. <https://doi.org/10.1021/cm402181f>.
- [81] S. Zhao, W. Jiang, X. Zhu, M. Ling, C. Liang, Understanding the synthesis of inorganic solid-state electrolytes for Li ion batteries: Features and progress, *Sustainable Materials and Technologies* 33 (2022). <https://doi.org/10.1016/j.susmat.2022.e00491>.
- [82] T. Ohzuku, Y. Makimura, Layered Lithium Insertion Material of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ for Lithium-Ion Batteries, *Chem Lett* 30 (2001) 642–643. <https://doi.org/10.1246/cl.2001.642>.
- [83] H. Liu, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, Cathode materials for lithium ion batteries prepared by sol-gel methods, *Journal of Solid State Electrochemistry* 8 (2004) 450–466. <https://doi.org/10.1007/s10008-004-0521-1>.

- [84] S. Mallick, A. Patel, X.G. Sun, M.P. Paranthaman, M. Mou, J.H. Mugumya, M. Jiang, M.L. Rasche, H. Lopez, R.B. Gupta, Low-cobalt active cathode materials for high-performance lithium-ion batteries: synthesis and performance enhancement methods, *J Mater Chem A Mater* 11 (2023) 3789–3821. <https://doi.org/10.1039/d2ta08251a>.
- [85] C.X. Ding, Q.S. Meng, L. Wang, C.H. Chen, Synthesis, structure, and electrochemical characteristics of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ prepared by thermal polymerization, *Mater Res Bull* 44 (2009) 492–498. <https://doi.org/10.1016/j.materresbull.2008.08.012>.
- [86] M.H. Lee, Y.J. Kang, S.T. Myung, Y.K. Sun, Synthetic optimization of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ via co-precipitation, *Electrochim Acta* 50 (2004) 939–948. <https://doi.org/10.1016/j.electacta.2004.07.038>.
- [87] J. Cho, $\text{LiNi}_{0.74}\text{Co}_{(0.26-x)}\text{Mg}_x\text{O}_2$ cathode material for a Li-ion cell, *Chemistry of Materials* 12 (2000) 3089–3094. <https://doi.org/10.1021/cm000153l>.
- [88] H. Li, Q. Xu, X.X. Shi, D.W. Song, L.Q. Zhang, Electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with different synthesis methods, *Rare Metals* 34 (2015) 580–585. <https://doi.org/10.1007/s12598-013-0088-z>.
- [89] C.C. Pan, C.E. Banks, W.X. Song, C.W. Wang, Q.Y. Chen, X.B. Ji, Recent development of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$: Impact of micro/nano structures for imparting improvements in lithium batteries, *Transactions of Nonferrous Metals Society of China (English Edition)* 23 (2013) 108–119. [https://doi.org/10.1016/S1003-6326\(13\)62436-X](https://doi.org/10.1016/S1003-6326(13)62436-X).
- [90] L. Liang, K. Du, Z. Peng, Y. Cao, J. Duan, J. Jiang, G. Hu, Co-precipitation synthesis of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor and characterization of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material for secondary lithium batteries, *Electrochim Acta* 130 (2014) 82–89. <https://doi.org/10.1016/j.electacta.2014.02.100>.
- [91] D. Wang, I. Belharouak, G. Zhou, K. Amine, Synthesis of Lithium and Manganese-Rich Cathode Materials via an Oxalate Co-Precipitation Method, *J Electrochem Soc* 160 (2013) A3108–A3112. <https://doi.org/10.1149/2.016305jes>.
- [92] H. Liu, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, Cathode materials for lithium ion batteries prepared by sol-gel methods, *Journal of Solid State Electrochemistry* 8 (2004) 450–466. <https://doi.org/10.1007/s10008-004-0521-1>.

- [93] G. Singh, A. Sil, S. Ghosh, A. Panwar, Effect of citric acid content on synthesis of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and its electrochemical characteristics, *Ceram Int* 36 (2010) 1831–1836. <https://doi.org/10.1016/j.ceramint.2010.03.028>.
- [94] Z.-D. Huang, X.-M. Liu, S.-W. Oh, B. Zhang, P.-C. Ma, J.-K. Kim, Microscopically porous, interconnected single crystal $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material for Lithium ion batteries, *J Mater Chem* 21 (2011) 10777. <https://doi.org/10.1039/c1jm00059d>.
- [95] Z.W. Xiao, Y.J. Zhang, Y.F. Wang, Synthesis of high-capacity $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode by transition metal acetates, *Transactions of Nonferrous Metals Society of China (English Edition)* 25 (2015) 1568–1574. [https://doi.org/10.1016/S1003-6326\(15\)63759-1](https://doi.org/10.1016/S1003-6326(15)63759-1).
- [96] K.M. Shaju, P.G. Bruce, Macroporous $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$: A High-Power and High-Energy Cathode for Rechargeable Lithium Batteries, *Advanced Materials* 18 (2006) 2330–2334. <https://doi.org/10.1002/adma.200600958>.
- [97] P. Vahdatkhah, O. Voznyy, S.K. Sadrnezhad, Engineering of surface oxygen vacancies in Co-free concentration-gradient Li-rich cathodes for high-capacity batteries, *Materials Today Sustainability* 21 (2023). <https://doi.org/10.1016/j.mtsust.2022.100309>.
- [98] W. Liang, Y. Zhao, L. Shi, Z. Wang, Y. Wang, M. Zhang, S. Yuan, Advances of high-performance $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ cathode materials and their precursor particles via co-precipitation process, *Particuology* 86 (2024) 67–85. <https://doi.org/10.1016/j.partic.2023.05.001>.
- [99] M. Jiang, Q. Zhang, X. Wu, Z. Chen, D.L. Danilov, R.A. Eichel, P.H.L. Notten, Synthesis of Ni-Rich Layered-Oxide Nanomaterials with Enhanced Li-Ion Diffusion Pathways as High-Rate Cathodes for Li-Ion Batteries, *ACS Appl Energy Mater* 3 (2020) 6583–6590. <https://doi.org/10.1021/acsaem.0c00765>.
- [100] S.T. Myung, M.H. Lee, S. Komaba, N. Kumagai, Y.K. Sun, Hydrothermal synthesis of layered $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ as positive electrode material for lithium secondary battery, *Electrochim Acta* 50 (2005) 4800–4806. <https://doi.org/10.1016/j.electacta.2005.02.034>.
- [101] P.S. Grant, D. Greenwood, K. Pardikar, R. Smith, T. Entwistle, L.A. Middlemiss, G. Murray, S.A. Cussen, M.J. Lain, M.J. Capener, M. Copley, C.D. Reynolds, S.D. Hare, M.J.H. Simmons, E. Kendrick, S.P. Zankowski, S. Wheeler, P. Zhu, P.R.

- Slater, Y.S. Zhang, A.R.T. Morrison, W. Dawson, J. Li, P.R. Shearing, D.J.L. Brett, G. Matthews, R. Ge, R. Drummond, E.C. Tredenick, C. Cheng, S.R. Duncan, A.M. Boyce, M. Faraji-Niri, J. Marco, L.A. Roman-Ramirez, C. Harper, P. Blackmore, T. Shelley, A. Mohsseni, D.J. Cumming, Roadmap on Li-ion battery manufacturing research, *JPhys Energy* 4 (2022). <https://doi.org/10.1088/2515-7655/ac8e30>.
- [102] I. Skvortsova, A.A. Savina, E.D. Orlova, V.S. Gorshkov, A.M. Abakumov, Microwave-Assisted Hydrothermal Synthesis of Space Fillers to Enhance Volumetric Energy Density of NMC811 Cathode Material for Li-Ion Batteries, *Batteries* 8 (2022). <https://doi.org/10.3390/batteries8070067>.
- [103] K. Wu, Q. Li, R. Dang, X. Deng, M. Chen, Y.L. Lee, X. Xiao, Z. Hu, A novel synthesis strategy to improve cycle stability of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ at high cut-off voltages through core-shell structuring, *Nano Res* 12 (2019) 2460–2467. <https://doi.org/10.1007/s12274-019-2469-6>.
- [104] A.C. Rolandi, I. de Meatza, N. Casado, M. Forsyth, D. Mecerreyes, C. Pozo-Gonzalo, Unlocking sustainable power: advances in aqueous processing and water-soluble binders for NMC cathodes in high-voltage Li-ion batteries, *RSC Sustainability* 2 (2024) 2125–2149. <https://doi.org/10.1039/d4su00098f>.
- [105] A. Rensmo, E.K. Savvidou, I.T. Cousins, X. Hu, S. Schellenberger, J.P. Benskin, Lithium-ion battery recycling: a source of per- and polyfluoroalkyl substances (PFAS) to the environment?, *Environ Sci Process Impacts* 25 (2023) 1015–1030. <https://doi.org/10.1039/d2em00511e>.
- [106] C. Singer, S. Schmalzbauer, R. Daub, Influence of the slurry composition on thin-film components for the wet coating process of sulfide-based all-solid-state batteries, *J Energy Storage* 68 (2023) 107703. <https://doi.org/10.1016/j.est.2023.107703>.
- [107] Y. Nikodimos, C.J. Huang, B.W. Taklu, W.N. Su, B.J. Hwang, Chemical stability of sulfide solid-state electrolytes: stability toward humid air and compatibility with solvents and binders, *Energy Environ Sci* 15 (2022) 991–1033. <https://doi.org/10.1039/d1ee03032a>.
- [108] D. Bresser, D. Buchholz, A. Moretti, A. Varzi, S. Passerini, Alternative binders for sustainable electrochemical energy storage-the transition to aqueous electrode processing and bio-derived polymers, *Energy Environ Sci* 11 (2018) 3096–3127. <https://doi.org/10.1039/c8ee00640g>.

- [109] J. Xu, S.L. Chou, Q.F. Gu, H.K. Liu, S.X. Dou, The effect of different binders on electrochemical properties of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode material in lithium ion batteries, *J Power Sources* 225 (2013) 172–178. <https://doi.org/10.1016/j.jpowsour.2012.10.033>.
- [110] Z. Chen, G.T. Kim, D. Chao, N. Loeffler, M. Copley, J. Lin, Z. Shen, S. Passerini, Toward greener lithium-ion batteries: Aqueous binder-based $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ cathode material with superior electrochemical performance, *J Power Sources* 372 (2017) 180–187. <https://doi.org/10.1016/j.jpowsour.2017.10.074>.
- [111] J.-H. Kuo, C.-C. Li, Water-Based Process to the Preparation of Nickel-Rich $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ Cathode, *J Electrochem Soc* 167 (2020) 100504. <https://doi.org/10.1149/1945-7111/ab95c5>.
- [112] S. Vauthier, M. Alvarez-Tirado, G. Guzmán-González, L.C. Tomé, S. Cotte, L. Castro, A. Guéguen, D. Mecerreyes, N. Casado, High-performance pyrrolidinium-based poly(ionic liquid) binders for Li-ion and Li-air batteries, *Mater Today Chem* 27 (2023). <https://doi.org/10.1016/j.mtchem.2022.101293>.
- [113] X. Zhao, L. Shen, N. Zhang, J. Yang, G. Liu, J. Wu, X. Yao, Stable Binder Boosting Sulfide Solid Electrolyte Thin Membrane for All-Solid-State Lithium Batteries, *Energy Material Advances* 5 (2024). <https://doi.org/10.34133/energymatadv.0074>.
- [114] H. Chen, M. Ling, L. Hencz, H.Y. Ling, G. Li, Z. Lin, G. Liu, S. Zhang, Exploring Chemical, Mechanical, and Electrical Functionalities of Binders for Advanced Energy-Storage Devices, *Chem Rev* 118 (2018) 8936–8982. <https://doi.org/10.1021/acs.chemrev.8b00241>.
- [115] S. Wang, X. Zhang, S. Liu, C. Xin, C. Xue, F. Richter, L. Li, L. Fan, Y. Lin, Y. Shen, J. Janek, C.W. Nan, High-conductivity free-standing $\text{Li}_6\text{PS}_5\text{Cl}$ /poly(vinylidene difluoride) composite solid electrolyte membranes for lithium-ion batteries, *Journal of Materiomics* 6 (2020) 70–76. <https://doi.org/10.1016/j.jmat.2019.12.010>.
- [116] R. Li, N. Chen, S. Liu, Y. Mao, Z. Liao, K. Qiu, P. Wang, T. Zhang, S. Hao, G. Zhu, C. Guo, X. Liu, D. Ren, L. Lu, M. Ouyang, Finely-Tuned Polar-Nonpolar Synergistic Binder Enables Ultra-Thin Sulfide Solid Electrolyte Membrane for All-Solid-State Batteries, *Adv Funct Mater* 34 (2024). <https://doi.org/10.1002/adfm.202409403>.

- [117] Y. Li, C. Kim, E. Williams, Y.F. Su, J. Nanda, G. Yang, Tailoring Binder Molecular Weight to Enhance Slurry-Cast NMC Cathodes for Sulfide Solid-State Batteries, *Energy and Environmental Materials* (2024). <https://doi.org/10.1002/eem2.12858>.
- [118] M. Yamamoto, Y. Terauchi, A. Sakuda, M. Takahashi, Binder-free sheet-type all-solid-state batteries with enhanced rate capabilities and high energy densities, *Sci Rep* 8 (2018) 1212. <https://doi.org/10.1038/s41598-018-19398-8>.
- [119] S. Ha, G. Pozzato, S. Onori, Electrochemical characterization tools for lithium-ion batteries, *Journal of Solid State Electrochemistry* 28 (2024) 1131–1157. <https://doi.org/10.1007/s10008-023-05717-1>.
- [120] T. Kim, W. Choi, H.C. Shin, J.Y. Choi, J.M. Kim, M.S. Park, W.S. Yoon, Applications of voltammetry in lithium ion battery research, *Journal of Electrochemical Science and Technology* 11 (2020) 14–25. <https://doi.org/10.33961/jecst.2019.00619>.
- [121] B.M. Gomes, M.C. Baptista, A. Orue, B. Dhrubajyoti, S. Terlicka, P. Sjövall, N. Zamperlin, C. Fonseca, J. Smajic, V. Kekkonen, W. Vonk, A. Tron, A. Schena, A. Ahniyaz, M.H. Braga, All-solid-state lithium batteries with NMC₉₅₅ cathodes: PVDF-free formulation with SBR and capacity recovery insights, *Energy Materials* 5 (2025). <https://doi.org/10.20517/energymater.2024.297>.
- [122] M. Naftaly, S. Das, J. Gallop, K. Pan, F. Alkhalil, D. Kariyapperuma, S. Constant, C. Ramsdale, L. Hao, Sheet Resistance Measurements of Conductive Thin Films: A Comparison of Techniques, *Electronics (Basel)* 10 (2021) 960. <https://doi.org/10.3390/electronics10080960>.
- [123] A. Fujisawa, T. Nishino, Y. Hamakawa, Hall-Effect Measurement on Polycrystalline SnO₂ Thin Films, *Jpn J Appl Phys* 27 (1988) 552. <https://doi.org/10.1143/JJAP.27.552>.
- [124] J. Kim, S. Park, S. Hwang, W.-S. Yoon, Principles and Applications of Galvanostatic Intermittent Titration Technique for Lithium-ion Batteries, *Journal of Electrochemical Science and Technology* 13 (2022) 19–31. <https://doi.org/10.33961/jecst.2021.00836>.
- [125] S. Sau, S. Pandit, S. Kundu, Crosslinked poly (vinyl alcohol): Structural, optical and mechanical properties, *Surfaces and Interfaces* 25 (2021) 101198. <https://doi.org/10.1016/j.surfin.2021.101198>.

- [126] M. Srivastava, A.K. M. R., K. Zaghib, Binders for Li-Ion Battery Technologies and Beyond: A Comprehensive Review, Batteries 10 (2024) 268. <https://doi.org/10.3390/batteries10080268>.

Attachment A

IRF2025

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8th International Conference INTEGRITY-RELIABILITY-FAILURE

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A Perspective on Cathode Materials for Electrical Vehicle industry

MatER
Materials Energy Research

José M. Pinheiro¹, Beatriz M. Gomes^{1,2}, M. Helena Braga^{1,2}

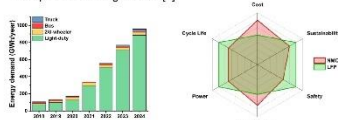
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1- INTRODUCTION

As conventional lithium-ion batteries approach their performance limits, all-solid-state batteries (SSBs) emerge as a promising alternative, achieving higher energy densities, improved safety, and longer lifespans. These advancements are crucial for the growing and electric vehicle (EV) industry [1].

The cathode plays a vital role in the performance and economic viability of all battery systems, as it limits specific capacity and constitutes a significant portion of the overall cost. Currently, EVs typically utilize cathodes based on LFP or NMC [2]. The shift to SSBs implies a reassessment of cathode materials to ensure compatibility with solid electrolytes, without compromising scalability or affordability [3,4].

This poster presents a comprehensive analysis of cathode material development for solid-state batteries, highlighting innovations that align with industry requirements for high performance and cost-effectiveness. Emphasis is also placed on sustainability, since new technologies need to consider environmental impacts and to be consistent with evolving European Union regulations [5].



2- OBJECTIVES

Reports and forecasts from multiple sources



Assess industry trends and innovation at R&D level

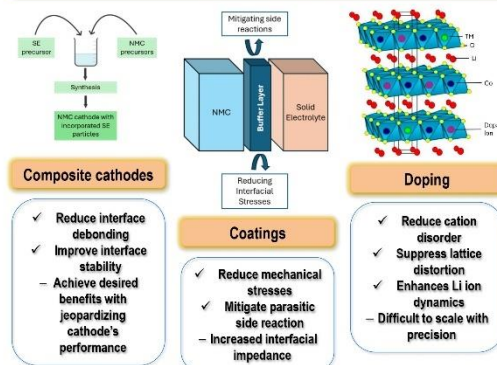
ACKNOWLEDGMENT

I am thankful to the Department of Chemical and Biological Engineering for supporting my work. I would also like to thank my colleagues at MatER Lab for helping me in my learning and research.

3- RESULTS



Cathodes Optimization



Battery system engineering

Dual power architectures

- Combining multiple chemistries allows to surpass materials intrinsic limitation
- Energy allocation is dynamically adjusted based on driving patterns and needs

Self-generating anodes

- Enables an increase in gravimetric energy density
- Reduces the volume of the battery pack
- Compatible with LFP and NMC

CONCLUSIONS

- China dominates the battery supply chain, with a strong presence from raw material extraction to state-of-the-art innovation;
- Companies are investing heavily in SSBs to achieve higher performances;
- The development of advanced cathodes via doping, coatings, and optimized synthesis is crucial;
- Dual chemistry systems will combine the best characteristics of each material to go beyond material intrinsic performance limitations.

REFERENCES

- [1] Mohammadi, F.; Sali, M. A Comprehensive Overview of Electric Vehicle Batteries Market: e-Prime - Advances in Electrical Engineering, Electronics and Energy 2023, 3.
- [2] I. Energy Agency, Global EV Outlook 2024 Moving towards increased affordability, 2024. www.iea.org.
- [3] A. Tiori, R. Hamid, N. Zhang, A. Beutl Rational Optimization of Cathode Composites for Sulfide-Based All-Solid-State Batteries. Nanomaterials 2023, 13, 327.
- [4] Kim, Y.; Seong, W.M.; Manthiram, A. Cobalt-Free, High-Nickel Layered Oxide Cathodes for Lithium-Ion Batteries: Progress, Challenges, and Perspectives. Energy Storage Mater. 2021, 34, 250–269.
- [5] FPAS Restitutor Proposal RECHARGE Statement for 2nd Rd Call for Evidence October 2021.

Advanced Cathode Materials for the Next Generation of Electric Vehicles

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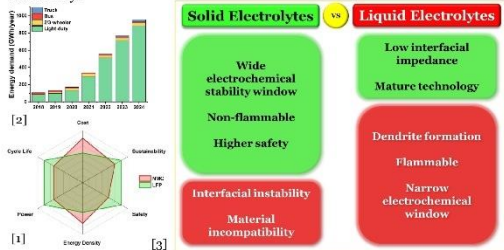
² LAETA, University of Porto, Engineering Faculty, 4200-465, Porto, Portugal

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INTRODUCTION | OBJECTIVES

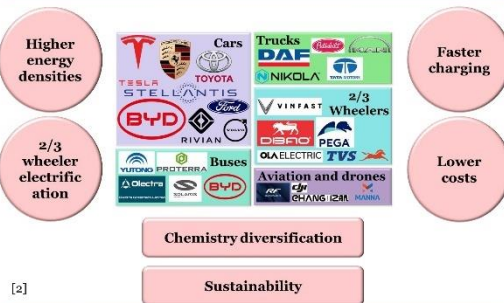
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The cathode plays a vital role in the performance and economic viability of all battery systems, as it limits specific capacity and constitutes a significant portion of the overall cost. Currently, EVs typically utilize cathodes based on LFP or NMC [2]. The shift to SSBs implies a reevaluation of cathode materials to ensure they are compatible with solid electrolytes while being high-performing and affordable [3,4]. This poster outlines the strategies developed to enhance and produce high-performance cathode materials for SSBs, focusing on sustainability and scalability.



MATERIALS & METHODS

Industry trends



REFERENCES

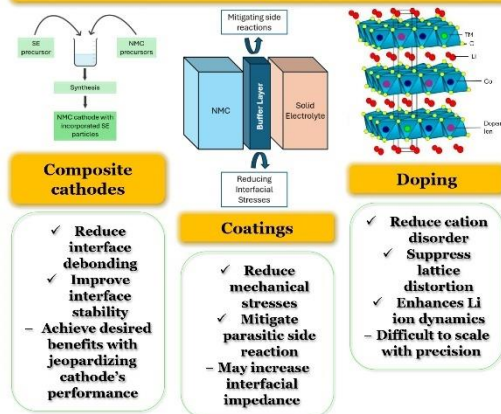
- [1] W. Li et al (2017), Royal Society of Chemistry
- [2] I. Energy Agency (2024). [Online]. Available: www.iea.org
- [3] F. Zheng et al (2018) J Power Sources, 389, 198–213
- [4] A. Manthiram (2020) Nature Research

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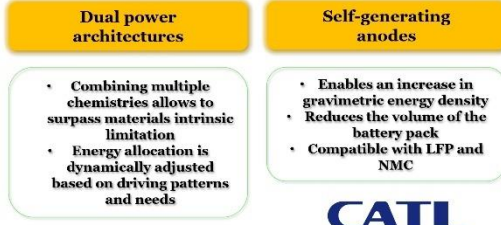
I am thankful to the Department of Chemical and Biological Engineering for supporting my work. I would also like to thank my colleagues at MATER Lab for helping me in my learning and research.

RESULTS & DISCUSSION

Cathodes Optimization



Battery system engineering



CONCLUSION

- China dominates the battery supply chain, with a strong presence from raw material extraction to state-of-the-art innovation;
- Companies are investing heavily in SSBs to achieve higher performances;
- The development of advanced cathodes via doping, coatings, and optimized synthesis is crucial;
- Dual chemistry systems will combine the best characteristics of each material to go beyond material intrinsic performance limitations.

Attachment B

```
In [ ]: in_pulse = False
start_vol = None
index = 0

for i in range(len(time)):
    estado = matrix[i, 0]
    vol_value = matrix[i, 2]
    if estado == "pulse":
        if not in_pulse:
            start_vol = vol_value
            in_pulse = True
        end_vol = vol_value
    elif estado == "rest" and in_pulse:
        d_Et = end_vol - start_vol
        deltas[index, 1] = d_Et
        in_pulse = False
        index += 1

valores_finais_rest = []
for i in range(1, len(matrix)):
    estado_atual = matrix[i, 0]
    estado_anterior = matrix[i - 1, 0]
    if estado_anterior == "rest" and estado_atual == "pulse":
        valor = matrix[i - 1, 2]
        valores_finais_rest.append(valor)
if matrix[-1, 0] == "rest":
    valores_finais_rest.append(matrix[-1, 2])

for i in range(len(valores_finais_rest)-1):
    d_Es = valores_finais_rest[i+1] - valores_finais_rest[i]
    deltas[i, 2] = d_Es

D = np.zeros(len(deltas))
for i in range(1, len(D)-1):
    D[i] = pre_coef * (deltas[i, 2]/deltas[i, 1])**2

D = D[1:-1]
```

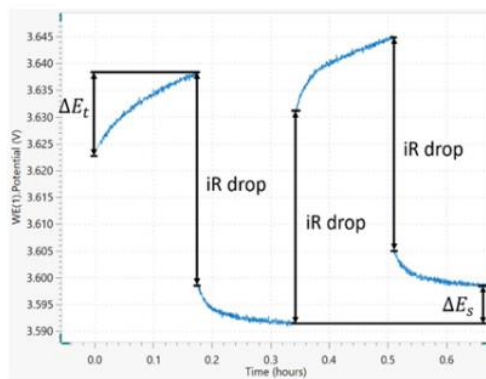
```
In [ ]: with plt.style.context('seaborn-v0.8-darkgrid'):
fig, ax = plt.subplots(figsize=(8, 6), constrained_layout=True)

scatter = ax.scatter(np.arange(1, len(D)+1), D, c='royalblue', s=50, alpha=0.7, label='Diffusion coefficient')

ax.set_title('Diffusion Coefficient', fontsize=20, fontweight='bold', pad=20)
ax.set_xlabel('Pulse Number', fontsize=14, fontweight='bold', labelpad=12)
ax.set_ylabel('Diff. Coefficient', fontsize=14, fontweight='bold', labelpad=12)
ax.set_xlim(0, pulses + 1)
ax.tick_params(axis='both', which='major', labelsize=14)
ax.xaxis.set_major_locator(MultipleLocator(1))
ax.legend()
plt.savefig('diffusion_coefficient_plot.png', dpi=300, bbox_inches='tight')

plt.show()
```

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



```
In [ ]: #Set parameters

mative = 0.328*10**-3 # mass of active material in grams
molar mass = 97.456 # molar mass in g/mol
r = 0.4 # limiting radius in cm
Vm = 20.7 # molar volume in cm^3/mol
t = 100 # pulse duration in seconds

n = mative/molar mass
S = np.pi*r**2 # electrode-electrolyte contact area

pre_coef = 4/(np.pi*t)*(n*Vm/S)**2

pulse_bool = matrix[:, 0] == 'pulse'
pulse_start = (pulse_bool[1:] & ~pulse_bool[:-1])
pulses = np.sum(pulse_start)

print("Number of pulses:", pulses)

deltas = np.zeros([pulses, 3])
deltas[:,0] = np.arange(pulses)

In [ ]: import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
from matplotlib.ticker import MultipleLocator
from matplotlib.colors import LinearSegmentedColormap

In [ ]: #Open and read data
data = pd.read_csv('teste_gitt.txt', delimiter=' ', header=None)
time = data.iloc[:,0].to_numpy()
vol = data.iloc[:,1].to_numpy()
cur = data.iloc[:,2].to_numpy()

plt.style.use('seaborn-v0_8-pastel')
fig, ax = plt.subplots(figsize=(8, 6), constrained_layout=True)

volt, = ax.plot(time, vol, label='Voltage', color='royalblue', linewidth=2.5, linestyle='-')

ax.set_title('Voltage vs Time', fontsize=18, fontweight='bold', pad=20)
ax.set_xlabel('Time(s)', fontsize=14, fontweight='bold', labelpad=10)
ax.set_ylabel('Voltage (V)', fontsize=14, fontweight='bold', labelpad=10)

ax.tick_params(axis='both', which='major', labelsize=12)
ax.xaxis.set_major_locator(MultipleLocator(10000))
ax.yaxis.set_major_locator(MultipleLocator(0.1))
ax.yaxis.set_minor_locator(MultipleLocator(0.05))

legend = ax.legend(loc='upper right', fontsize=10, framealpha=1, shadow=True, fancybox=True)
legend.get_frame().set_facecolor('white')

ax.set_xlim(0, time[-1])
ax.set_ylim(min(vol)-0.1, max(vol)+0.1)
plt.show()

matrix = np.column_stack((np.zeros_like(time), time, vol, cur))
matrix = matrix.astype(object)

for i in range(matrix.shape[0]):
    if matrix[i, 3] == 0:
        matrix[i, 0] = "rest"
    else:
        matrix[i, 0] = "pulse"
```

Attachment C

```
In [ ]: import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
from matplotlib.ticker import MultipleLocator
```

Read and organize data

```
In [ ]: data = pd.read_csv('jp44.txt', delimiter=' ', header=None)

state = data.iloc[:,0].to_numpy()
cur = data.iloc[:,1].to_numpy()
vol = data.iloc[:,2].to_numpy()
capacity = data.iloc[:,3].to_numpy()

m_active = 0.438*10**-3

cur = cur[state != 'Rest']
vol = vol[state != 'Rest']
capacity = capacity[state != 'Rest']
state = state[state != 'Rest']

prev = state[0]
cycle = np.zeros_like(state, dtype=int)
cycle[0] = 1
n = 1

for i in range(1, len(state)): #considering 1st state as CCCV_Chg
    if state[i] == prev:
        # Same state as previous - same cycle
        cycle[i] = n
    elif (prev == 'CCCV_Chg' and state[i] == 'CCCV_DChg'):
        # Charge → Discharge transition - same cycle
        cycle[i] = n
        prev = state[i]
    elif (prev == 'CCCV_DChg' and state[i] == 'CCCV_Chg'):
        # Discharge → Charge transition - new cycle
        n += 1
        cycle[i] = n
        prev = state[i]

matrix = np.column_stack((cycle, state, cur, vol, capacity))
```

Charge

```
In [ ]: def Chg(M, v_plateau=4.1, tol=0.01):
df = pd.DataFrame(M, columns=["Cycle", "Tipo", "I", "V", "Cap"])

    resultados = []
    # -----Visualize organized data frame-----
    # for Cycle, grupo in df[df["Tipo"] == "CCCV_Chg"].groupby("Cycle"):
    #     print(f"\n=== Cycle {Cycle} ===")
    #     print(grupo)
    #     print(f"Rows: {len(grupo)}")
    # -----
    for Cycle, grupo in df[df["Tipo"] == "CCCV_Chg"].groupby("Cycle"):

        volt = grupo["V"].to_numpy()
        cap = grupo["Cap"].to_numpy()

        cap_final = cap[-1]

        dV = volt - v_plateau
        mask_plateau = np.abs(dV) <= tol
        idx_plateau = np.where(mask_plateau == True)[0]

        if len(idx_plateau) > 0: # plateau achieved
            cap_plateau_ini = cap[idx_plateau[0]]
            resultados.append([Cycle, cap_plateau_ini, Cycle, cap_final])
        else: #plateau not achieved
            resultados.append([Cycle, cap_final, Cycle, np.nan])

    return np.array(resultados)

result_Chg = Chg(matrix)
result_Chg[:,1] /= m_active
result_Chg[:,1] /= m_active
# Chg_capacity_vs_cycle_<NAME OF THE CELL>.txt
np.savetxt('Chg_capacity_vs_cycle_jp44.txt', result_Chg)
```

Charge - Plot

```
In [ ]: plt.style.use('seaborn-v0_8-pastel')

fig, ax = plt.subplots(figsize=(10, 6), constrained_layout=True)

WoCV, = ax.plot(result_Chg[:,0], result_Chg[:,1], label='W/o constant voltage step',
                color='royalblue', linewidth=2.5, linestyle='dotted')
WCV, = ax.plot(result_Chg[:,0], result_Chg[:,1], label='W/ constant voltage step',
               color='red', linewidth=2.5, linestyle='dotted')

ax.fill_between(result_Chg[:,0], result_Chg[:,1], result_Chg[:,1],
               where=(result_Chg[:,1] >= result_Chg[:,1]), color='skyblue', alpha=0.2)

ax.set_title('Discharge specific capacity as a function of cycle number', fontsize=20, fontweight='bold', pad=20)
ax.set_xlabel('Cycle number', fontsize=14, fontweight='bold', labelpad=10)
ax.set_ylabel('Capacity (mAh\cdotg$^{-1}$)', fontsize=14, fontweight='bold', labelpad=10)

ax.tick_params(axis='both', which='major', labelsize=10)
ax.xaxis.set_major_locator(MultipleLocator(10))
ax.yaxis.set_major_locator(MultipleLocator(20))

legend = ax.legend(loc='lower right', fontsize=10, framealpha=1, shadow=True, fancybox=True)
legend.get_frame().set_facecolor('white')

ax.set_xlim(0, len(result_Chg)+5)
ax.set_ylim(0, 200)
plt.show()
```

Discharge

```
In [ ]: def DChg(M, v_plateau=2.6, tol=0.01):
        df = pd.DataFrame(M, columns=["Cycle", "Tipo", "I", "V", "Cap"])

        resultados = []
        # -----Visualize organized data frame-----
        for Cycle, grupo in df[df["Tipo"] == "CCCV_DChg"].groupby("Cycle"):
            print(f"\n== Cycle {Cycle} ==")
            print(grupo)
            print(f"Rows: {len(grupo)}")
        # -----
        for Cycle, grupo in df[df["Tipo"] == "CCCV_DChg"].groupby("Cycle"):

            volt = grupo["V"].to_numpy()
            cap = grupo["Cap"].to_numpy()

            cap_final = cap[-1]

            dV = volt - v_plateau
            mask_plateau = np.abs(dV) <= tol
            idx_plateau = np.where(mask_plateau == True)[0]

            if len(idx_plateau) > 0: # plateau achieved
                cap_plateau_ini = cap[idx_plateau[0]]
                resultados.append([Cycle, cap_plateau_ini, Cycle, cap_final])
            else: #plateau not achieved
                resultados.append([Cycle, cap_final, Cycle, np.nan])

        return np.array(resultados)

result_DChg = DChg(matrix)
result_DChg[:,1] /= m_active
result_DChg[:,1] /= m_active
# DChg_capacity_vs_cycle <NAME OF THE CELL>.txt
np.savetxt('DChg_capacity_vs_cycle_ip44.txt', result_DChg)
```

Discharge - Plot

```
In [ ]: plt.style.use('seaborn-v0_8-pastel')

fig, ax = plt.subplots(figsize=(10, 6), constrained_layout=True)

WoCV, = ax.plot(result_DChg[:,0], result_DChg[:,1], label='W/o constant voltage step',
                color='royalblue', linewidth=2.5, linestyle='dotted')
WCV, = ax.plot(result_DChg[:,0], result_DChg[:,1], label='W/ constant voltage step',
               color='red', linewidth=2.5, linestyle='dotted')

ax.fill_between(result_DChg[:,0], result_DChg[:,1], result_DChg[:,1],
               where=(result_DChg[:,1] >= result_DChg[:,1]), color='skyblue', alpha=0.2)

ax.set_title('Discharge specific capacity as a function of cycle number', fontsize=20, fontweight='bold', pad=20)
ax.set_xlabel('Cycle number', fontsize=14, fontweight='bold', labelpad=10)
ax.set_ylabel('Capacity (mAh\cdotg$^{-1}$)', fontsize=14, fontweight='bold', labelpad=10)

ax.tick_params(axis='both', which='major', labelsize=10)
ax.xaxis.set_major_locator(MultipleLocator(10))
ax.yaxis.set_major_locator(MultipleLocator(20))

legend = ax.legend(loc='lower right', fontsize=10, framealpha=1, shadow=True, fancybox=True)
legend.get_frame().set_facecolor('white')

ax.set_xlim(0, len(result_DChg)+5)
ax.set_ylim(0, 200)
plt.show()
```

Attachment D

Table 7: Equivalent circuit parameters used to fit experimental data presented in Figure 13 and Figure 14.

Before CV (Figure 13)	2 %	PIB	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (M Ω)	R_{d4} ($\mu\Omega$)	t_4 (μs)	a_4
			81	2	30	12	0.8	1.4	18	0	0.2
		PVA	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 (nF $\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} ($\mu\Omega$)	t_4 (ps)	a_4
			90	32	50	2	1	15	14	0.3	0.8
	4 %	PIB	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 (nF $\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} ($\mu\Omega$)	t_4 (ps)	a_4
			91	32	50	2	1	15	14	0.3	0.8
		PVA	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} (k Ω)	t_4 (s)	a_4
			78	0.4	42	16	0.6	2941	0	0	1
After CV (Figure 14)	2 %	PIB	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} (Ω)	t_4 (μs)	a_4
			77	0.8	26	0.9	0.8	1114	5	0.2	0.3
		PVA	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} (Ω)	t_4 (ms)	a_4
			79	0.8	38	3	0.8	485	59	2	0.3
	4 %	PIB	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} (Ω)	t_4 (μs)	a_4
			79	0.8	38	3	0.8	485	59	2	0.3
		PVA	R_1 (Ω)	C_2 (nF)	R_2 (Ω)	Q_3 ($\mu\text{F}\cdot\text{s}^{a-1}$)	a_3	R_3 (Ω)	R_{d4} (Ω)	t_4 (s)	a_4
			76	1	32	5	0.7	324	785	22	0.5

