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# $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes for lithium-ion batteries

*Exploring strategies for a stable electrode-electrolyte  
interphase*

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### Abstract

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Climate change, a pressing global issue, can be partially addressed by using electric vehicles to reduce  $\text{CO}_2$  emissions. In this context, high-energy and high-power density batteries are vital. The  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO)-based cell is in this regard appealing as it fulfils several requirements, but is unfortunately constrained by capacity fading, especially at elevated temperatures. LNMO operates at  $\sim 4.7$  V (vs.  $\text{Li}^+/\text{Li}$ ) at which conventional Li-ion battery (LIB) electrolytes are not thermodynamically stable.

This thesis investigates the degradation mechanisms in LNMO cells and various practical strategies to tackle these problems. In the first part, a technique named synthetic charge-discharge profile voltammetry (SCPV) is developed to better understand the oxidative stability of some of the common electrolytes. The second part focuses on the use of binders that could potentially enable the formation of an artificial cathode-electrolyte interphase in LNMO cells. Polyacrylonitrile (PAN), which is often considered to be oxidatively stable, is however shown to degrade under the operating voltages of LNMO. A second polymer, polyacrylic acid (PAA), was studied for higher electrode mass loadings, but a high internal resistance resulted in poor initial discharge capacity as compared to the carboxymethyl cellulose (CMC) benchmark.

In order to effectively mitigate capacity fading, three different electrolytes were explored in LNMO cells in the third section. First, an ionic liquid-based electrolyte, 1.2 M lithium bis(fluorosulfonyl)imide (LiFSI) in N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ( $\text{PYR}_{13}\text{FSI}$ ), was used. X-ray photoelectron spectroscopy (XPS) analysis revealed that this electrolyte stabilized the electrode by forming robust and predominantly inorganic surface layers which stabilized the electrode. Second, the study of an electrolyte containing sulfolane showed that, despite initial cycles displaying a higher degradation, the passivation layers created on the electrodes enable stable cycling. In a third study, tris(trimethylsilyl)phosphite (TMSPi) and lithium difluoro(oxalato)borate (LiDFOB) were investigated as electrolyte additives in a conventional electrolyte, and 1 wt.% and 2 wt.% of the additives, respectively, showed improved electrochemical performance in LNMO-graphite full cells, highlighting the role of these additives in enabling interphase layers at both the positive and negative electrodes. Collectively, these studies offer insights on how crucial the interfacial chemistry is for stable operation of LNMO cells, and pinpoint strategies to tailor this further.

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*To my parents  
Ambily & Mathew*



# List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

- I. **Mathew, A.**, Lacey, M., Brandell, D., Investigating oxidative stability of lithium-ion battery electrolytes using synthetic charge-discharge profile voltammetry. *Journal of Power Sources Advances*, 11 (2021) 100071
- II. **Mathew, A.**, Misiewicz, C., Lacey, M., Heiskanen, S., Mindemark, J., Berg, E., Younesi, R., Brandell, D., Understanding the capacity fade in polyacrylonitrile binder-based  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cells. *Batteries & Supercaps*, 5 (2022) e20220027
- III. **Mathew, A.**, van Ekeren, W., Lacey, M., Heiskanen, S., Younesi, R., Brandell, D., Limitations of polyacrylic acid binders when employed in thick LNMO Li-ion battery electrodes. *In manuscript*
- IV. Østli, E.,<sup>‡</sup> **Mathew, A.**,<sup>‡</sup> Tolchard, J., Lacey, M., Brandell, D., Svensson, A., Selbach, S., Wagner, N., Stabilizing the cathode interphase of LNMO using an ionic-liquid based electrolyte. *Submitted manuscript*
- V. Salian, G., **Mathew, A.**, Gond, R., van Ekeren, W., Højberg, J., Elkjær, C., Lacey, M., Heiskanen, S., Brandell, D., Younesi, R., Understanding the electrochemical and interfacial behaviour of sulfolane based electrolyte in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -graphite full-cells. *Batteries & Supercaps*, (2023) e202200565
- VI. Jamal, A., Salian, G., **Mathew, A.**, Wahyudi, W., Carvalho, R., Gond, R., Brandell, D., Heiskanen, S., Younesi, R., Tris(trimethylsilyl) phosphite and lithium difluoro(oxalato)borate as dual electrolyte additives towards long-cycling for high-voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite lithium-ion batteries. *In manuscript*

<sup>‡</sup> These authors contributed equally to the work.

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**Disclaimer:** Parts of this thesis are based on my licentiate thesis titled *Understanding degradation phenomena in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes for lithium ion batteries* (Uppsala University, 2021)

## Paper not included in the thesis

- Hernández, G., Johansson, I., **Mathew, A.**, Sångeland, C., Brandell, D., Mindemark, J, Going beyond sweep voltammetry: Alternative approaches in search of the elusive electrochemical stability of polymer electrolytes. *Journal of the Electrochemical Society*, 168 (2021) 100523

## My contributions to the papers:

- I. Contributed to the planning of the project. Performed all experiments, took part in the scientific discussions and wrote the manuscript with input from co-authors.
- II. Contributed to the planning of the project. Performed all experiments except the OEMS characterization, was involved in all the scientific discussions, performed the data analysis and wrote the manuscript with input from co-authors.
- III. Contributed to the planning of the project. Performed all experiments except the pressure evolution studies and rheology measurements, was part of all scientific discussions, performed data analysis and wrote the manuscript with input from co-authors.
- IV. Planned the SCPV and XPS parts of the project together with co-authors. I was involved in all scientific discussions, wrote the corresponding parts of the manuscript and provided feedback on the manuscript.
- V. Planned the SCPV part of the project together with co-authors. I was involved in all scientific discussions, wrote the corresponding part of the manuscript and provided feedback on the manuscript.
- VI. Contributed to the planning of the project. I was involved in carrying out the sample preparations and the galvanostatic cycling measurements. I was part of all scientific discussions, reviewed and provided feedback on the manuscript.



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# Abbreviations

CE	Coulombic efficiency
CEI	Cathode-electrolyte interphase
CMC	Carboxy methyl cellulose
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EMC	Ethyl methyl carbonate
ESW	Electrochemical stability window
FEC	Fluoroethylene carbonate
GBL	$\gamma$ -butyro-lactone
GC	Glassy carbon
HF	Hydrogen fluoride
HFP	Hexafluoropropylene
HOMO	Highest occupied molecular orbital
ICI	Intermittent current interruption
ILE	Ionic liquid electrolyte
LCO	Lithium cobalt oxide
LiBOB	Lithium bis(oxalato)borate
LiDFOB	Lithium difluoro(oxalato)borate
LiDFP	Lithium difluorophosphate
LiFSI	Lithium bis(fluorosulfonyl)imide
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LMO	Lithium manganese oxide
LNMO	Lithium nickel manganese oxide
LSV	Linear sweep voltammetry
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LTO	Lithium titanate oxide
LUMO	Lowest occupied molecular orbital
NCA	Lithium nickel cobalt aluminium oxide
NMC	Lithium nickel manganese oxide
NMP	N-methyl-2-pyrrolidone
OCV	Open circuit voltage

OEMS	Online electrochemical mass spectrometry
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PMP	N-propyl-N-methylpyrrolidinium
PPI	Potential-profile importation
PVdF	Poly(vinylidene difluoride)
PVdF-HFP	Poly(vinylidene difluoride-co-hexafluoropropylene)
PYR <sub>13</sub> FSI	N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide
SBR	Styrene butadiene rubber
SCPV	Synthetic charge-discharge profile voltammetry
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SPE	Solid polymer electrolyte
TEGDME	Tetraethylene glycol dimethyl ether
TFSI	Bis(trifluoromethanesulfonyl)imide
TMSPa	Tris(trimethylsilyl) phosphate
TMSPi	Tris(trimethylsilyl) phosphite
VC	Vinylene carbonate
VdF	Vinylidene difluoride
VMP	Versatile multichannel potentiostat
XPS	X-ray photoelectron spectroscopy



# 1. Introduction

Today, we are in a race against time to limit the global warming to 1.5 °C. Nations across the world are trying and implementing different strategies to achieve this goal. However, we are far from meeting this goal set at the 2015 Paris Agreement. The Earth has warmed between 1.1 and 1.3 °C since the industrial revolution and according to the climate scientist Dr. Joeri Rogelj<sup>1</sup> of Imperial College London, there is a 25% possibility that we will reach a 3 °C rise in global temperature by the end of this century with the current policies that are in place. This rise in global temperature is a great concern, and the CO<sub>2</sub> emissions - the leading source of climate change - from automobiles, electricity generation and industrial processes that use traditional fossil fuels are among the primary culprits. Excessive usage of these non-renewable energy sources not only depletes them but also pollutes the environment substantially. Renewable energy sources such as solar, wind, and tidal power are, however, inconvenient to employ as a source of continuous energy production due to their intermittent nature.

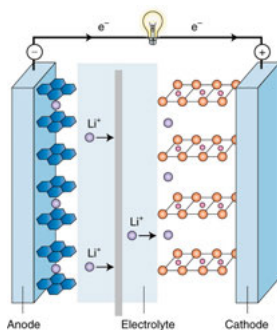
Electrochemical energy storage is attractive among the various energy storage techniques available, including thermal, thermochemical, magnetic, chemical, hydrogen, and so on considering its energy efficiency, lifetime and cost.<sup>2,3</sup> Fuel cells are currently not regarded as a key alternative for energy storage in most commercial applications, including electric vehicles, due to the lack of technology to transport and store hydrogen. Moreover, although supercapacitors can supply energy faster than batteries, they lack the high energy density needed for many of these applications. This makes batteries a better choice of energy storage device than others, and there is a high demand for batteries to be used, especially in vehicles.

In parallel to this demand, there exists a substantial effort to improve the factors mentioned above, such as energy efficiency, life-time and cost, for batteries. This generally needs to be combined with other attractive battery properties such as high energy density, power density and low toxicity. Owing to their high energy storage capacity, lithium-ion batteries (LIBs) are currently gaining rapidly increasing popularity, especially in the automobile sector.<sup>4,5</sup>

## 1.1 Lithium-ion batteries

LIBs are ubiquitous in today's society; from powering wrist-watches to mobile phones to laptops to electric vehicles – a world without LIBs would bring us back decades in technological development. Three LIB pioneers, John B Goodenough, Akira Yoshino, and M Stanley Whittingham, were awarded the 2019 Nobel Prize in Chemistry for their outstanding discovery and development of LIBs that have shaped the contemporary world.

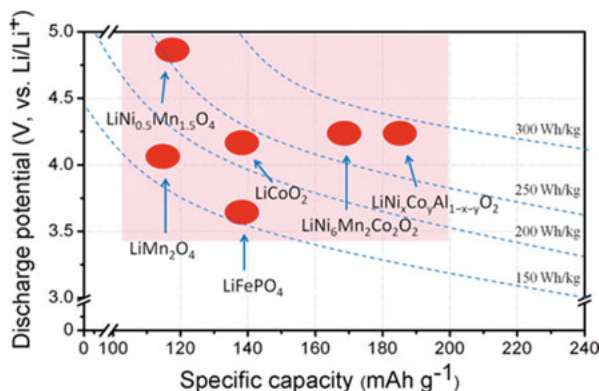
Typically, a LIB contains two electrodes, a positive and a negative electrode, separated internally in the battery by a so-called separator, generally a porous material which allows infiltration of electrolyte and thereby transportation of  $\text{Li}^+$  ions. During charge,  $\text{Li}^+$  ions shuttle between the positive and negative electrode and vice versa during the discharge step while energy is converted at these electrodes. Figure 1 shows a schematic representation of a LIB and its major components.



**Figure 1.** Schematic of lithium-ion battery components.<sup>6</sup> Reprinted with permission from reference.<sup>6</sup> Copyright (2018) Springer Nature.

Currently, substantial efforts are being made to develop cathodes with higher operating voltages and/or specific capacities, as the product of these two parameters determines the energy density of a cell. Sony commercialized the first LIB in 1991, which used a  $\text{LiCoO}_2$  (LCO) cathode. Although belonging to the class of 4 V cathodes, LCO has poor thermal stability which can result in destructive failure due to runaway reactions. Moreover, it is also questionable from a cost and sustainability perspective.<sup>7</sup> Goodenough's group began working on  $\text{LiFePO}_4$  (LFP) as an alternative, which has an excellent thermal stability and is widely used today, but has a lower operating voltage of 3.5 V vs  $\text{Li}^+/\text{Li}$ .<sup>8</sup> Further development of the LCO cathode has paved way to advances into the family of  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$  (NMC) cathode materials.<sup>9</sup> NMC cathodes contains comparatively less cobalt than LCO and have capacities of  $\sim 160\text{--}200\text{ Ah kg}^{-1}$ , which lead to the widespread use of NMC cells in electric vehicles, but it also faces challenges such as structural instability and capacity fading over time.<sup>10,11</sup> Different cathode materials offer different advantages,

which is why they are used in slightly different applications. For example, LCO has remained dominant in portable electronic applications due to its high volumetric energy, but its higher cost and poor thermal stability make it an unsuitable material for electric vehicles, where NMC is superior. Another interesting cathode material which operates at about 4.2 V vs  $\text{Li}^+/\text{Li}$  is the spinel compound  $\text{LiMn}_2\text{O}_4$ , which uses the low-cost element Mn instead of Co, but faces significant challenges such as electrolyte oxidation at high potentials and substantial transition metal dissolution.<sup>7</sup> The other promising next-generation spinel cathode material  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO), in the class of 5 V, is discussed in the next section. Figure 2 shows a schematic representation of the comparison of energy densities, specific capacities and operating voltages of some of the intercalation type of cathode materials exploited in LIBs.



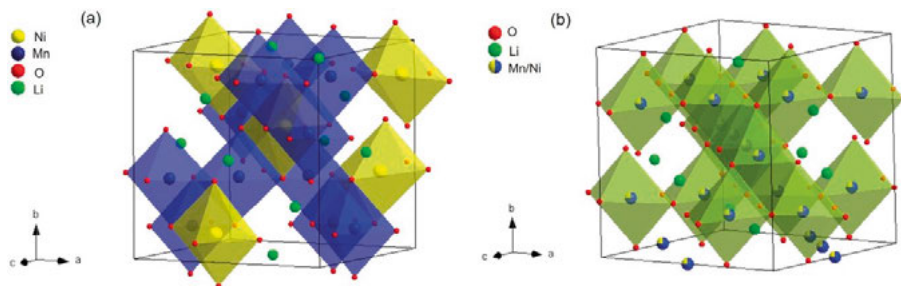
**Figure 2.** For the common intercalation-type cathodes materials, the practical discharge potentials, specific capacities, and approximate cell-level energy densities are shown when used together with graphite anodes. Reprinted with permission from reference.<sup>12</sup> Copyright (2019) American Chemical Society.

## 1.2 The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material

The LNMO material is a nickel substituted form of the prototype  $\text{LiMn}_2\text{O}_4$  (LMO). Both these materials are of the spinel structural type, meaning that they have a general formulation of  $\text{AB}_2\text{X}_4$ . The spinel structure provides three-dimensional channels in the atomic-level structure, which allows for fast lithium ion diffusion during the electrochemical processes. This makes these cathodes promising material for high power applications, such as electric vehicles.<sup>12</sup> Moreover, the LNMO voltage plateau at  $\sim 4.7$  V vs.  $\text{Li}^+/\text{Li}$  arising from the  $\text{Ni}^{2+}/\text{Ni}^{4+}$  redox couple and its specific capacity of  $147 \text{ mAh g}^{-1}$  gives this material a high theoretical energy density, roughly on par with NMC.<sup>13</sup> The absence of cobalt in the structure – an element with high cost and associated with ethical concerns – and the alternative utilisation of manganese, which is

cheap, adds to the benefits of this cathode. The possibility of water-based processing of the LNMO electrode and reduced cost in terms of abundance of the elements used in LNMO is quite beneficial.<sup>14</sup>

Depending on the Mn/Ni ordering in LNMO that results from its synthesis conditions, two distinct crystal structures exist for this compound. In the disordered structure with  $Fd\bar{3}m$  symmetry, the Mn and Ni ions are randomly distributed in the 16d octahedral sites which is often synthesized at 900 °C and followed by a fast cooling process.<sup>15</sup> In the ordered LNMO structure with  $P4_332$  symmetry, Mn and Ni ions are located in separate octahedral sites, 12d and 4a, respectively.<sup>16</sup> The ordered LNMO is usually annealed at 750 °C followed by cooling at a lower rate. Figure 3 shows a schematic illustration of ordered and disordered crystal structure of LNMO. Practically, it is difficult to obtain completely ordered or disordered phases of LNMO powder, since it is possible to have Mn/Ni ordered local structures in a fully disordered sample.<sup>16</sup> Although some of the papers contend that ordered structures have improved electrochemical performance, the majority of them agree that the disordered LNMO phase has superior electrochemical performance. This has led to some disagreement on the subject.<sup>17</sup>



**Figure 3.** Schematic illustration of a) ordered and b) disordered crystal structure of LNMO. Reprinted with permission from reference.<sup>18</sup> Copyright (2022) Wiley-VCH GmbH.

Unfortunately, LNMO cathodes suffer from a number of problems during battery operation, which eventually leads to fast capacity fading which limits the cycle-life of the cell. These issues are discussed below.

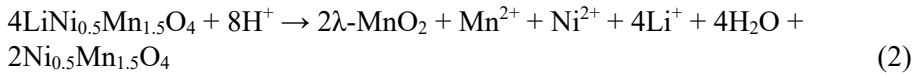
The most common and traditional LIB electrolyte combination consists of  $\text{LiPF}_6$  salt dissolved in organic carbonate-based solvents, which generally are stable to oxidation below  $\sim 4.5$  V vs.  $\text{Li}^+/\text{Li}$ . Operating beyond this limit results in oxidative decomposition of the electrolyte, and, as a result, significant capacity fading.<sup>19</sup> This high operating potential in combination with common LIB electrolytes is a crucial challenge for the LNMO systems. In addition to the decomposition of electrolyte solvent, the dissolved salts also tend to decompose at these higher potentials, and the electrolytes are reported to form side-products such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{POF}_3$ ,  $\text{C}_2\text{H}_5\text{OCOOPF}_4$  etc.<sup>20</sup>



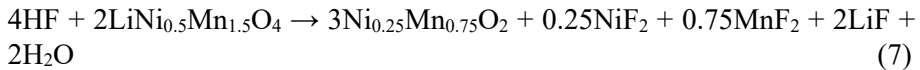
Apart from electrolyte oxidation, transition metal dissolution is a common problem with spinel electrodes such as LMO and LNMO. This process is understood to originate from the disproportionation reaction of manganese that occurs on the LMO or LNMO electrode surface:<sup>21</sup>



Under ideal conditions, all manganese in fully lithiated LNMO is expected to be in the +4 oxidation state, however, synthesis conditions may result in oxygen deficiencies and other impurity phases resulting in the presence of  $\text{Mn}^{3+}$  ions in the structure as well. This is believed to be one of the main reasons for transition metal dissolution. Moreover, Aurbach et al. have shown that at a higher temperature of 60 °C, LNMO transforms to  $\lambda$ - $\text{MnO}_2$  following the Reaction (2).<sup>22</sup>



The presence of trace amounts of water in the cell components reacts with the  $\text{LiPF}_6$  salt and generates hydrogen fluoride (HF). The following chemical reactions arising from the reaction of water with the salt also leads to structural changes in LNMO and enhanced transition metal dissolution.<sup>23–25</sup>



Reaction products such as  $\text{MnF}_2$ ,  $\text{NiF}_2$ ,  $\text{LiF}$  have been reported to be found on the LNMO surface as a result of dissolution of manganese and nickel from the structure, resulting in a higher impedance in the cell.<sup>21</sup> The decomposition of the organic electrolyte solvents and/or the binders may also produce polymeric decomposition products. The rate of the decomposition reactions evolving at the electrode-electrolyte interphase is high at elevated temperatures. Conventional electrolyte components such as carbonate solvents and  $\text{LiPF}_6$  salts are also subject to thermal instabilities, which results in an accelerated decomposition and evolution of decomposition products, including volatile species.<sup>26</sup> These also intensify the dissolution of  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions into the electrolyte.

Furthermore, the degradation products and the dissolved transition metals move from the cathode to the anode during battery operation and are incorporated into the solid electrolyte interphase (SEI) formed on the surface of the anode.<sup>27</sup> This movement of side-products from one electrode to the other is often called ‘cross-talk’, and this process creates additional impedance on the anode surface and triggers more side reactions. A study by Aktekin et al. showed that in LTO||LNMO full cells, the major reason for cell failure was a loss of lithium inventory caused by high amounts of side reactions at the LTO electrode, rather than side-reactions at the cathode side.<sup>28</sup>

### 1.3 LNMO research – the state-of-the-art

Researchers have used various methods to tackle these challenges, such as developing new electrolyte compositions that incorporate tailored solvents, salts, and additives; implementing surface modifications on the electrode through organic and inorganic coatings; customizing the binders utilized; modifying the bulk material by altering synthesis conditions and examining the role of cation (Mn and Ni) ordering; doping the cations with elements such as Fe, Cr, Ga; and adjusting the particle size and morphology, among others.<sup>13</sup> One main challenge with LNMO cells is the lack of a suitable electrolyte that is either stable at the high potentials at which LNMO cells operate or allows for the formation of a stable passivation layer on the positive electrode. The use of a high-voltage compatible electrolyte formulation is the most straightforward and practical answer to this problem. Sulfolane, for example, is regarded as a solvent with an oxidative stability over 5 V vs.  $\text{Li}^+/\text{Li}$  from both experimental and computational studies,<sup>29</sup> and several research studies have suggested that sulfolane-based electrolytes exhibit better electrochemical and interfacial characteristics in LNMO systems when compared to carbonate based electrolytes.<sup>30,31</sup> However, one shortcoming of electrolytes adopted for high-voltage cathodes is that they are typically prone to reductive decomposition at low potentials at anodes such as graphite.<sup>32</sup> Nitriles are also well-known for their high oxidative stability, but, like sulfolane, suffer from severe reductive decomposition at low potentials. For example, nitrile-based solvents such as adiponitrile have been explored together with  $\gamma$ -butyrolactone (GBL) as co-solvent and fluoroethylene carbonate (FEC) additive with  $\text{LiBF}_4$  salt as an electrolyte for LNMO cathodes.<sup>33</sup> According to the findings of this study, the surface layers on LNMO are likely to be comprised of decomposition products such as  $\text{Li}_x\text{PF}_y$  and  $\text{LiF}$ , which are generated at higher potentials. These products then play a role in preventing the breakdown of electrolyte solvents with low reduction potential.

The salt used in the electrolyte, as well as its concentration, play an important role for the overall cell performance.  $\text{LiPF}_6$ , the most commonly used LIB salt, degrades in the presence of trace water in the cell, forming corrosive

HF. HF promotes the transition metal dissolution, as discussed in Section 1.2, leading to increased side reactions, including cross-talk.<sup>34</sup> However, the use of  $\text{LiPF}_6$  in the electrolytes helps in the formation of a protective passivation layer on the Al current collectors, made up of  $\text{Al}_2\text{O}_3$  and  $\text{AlF}_3$  compounds, which prevents Al corrosion at high voltages.<sup>35</sup> Due to their improved electrochemical and thermal stability, imide anion-based salts like lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiTFSI}$ ) and lithium bis(fluorosulfonyl)imide ( $\text{LiFSI}$ ) have been investigated as alternatives to the commonly used  $\text{LiPF}_6$  salt.<sup>31</sup> However, these salts are unable to provide adequate passivation of the Al substrate. This results in ongoing anodic dissolution of the Al current collector and eventual failure of the cell. Feng et al. conducted a study that investigated the impact of the concentration of  $\text{LiBF}_4$  salt on the stability and electrochemical characteristics of LNMO.<sup>36</sup> The study found that adding an optimal amount of this salt had a positive impact on both the passivation layer and the rate performance of the system.

Ionic liquids have emerged as promising electrolyte solvents for LNMO-based LIBs, owing to their favourable characteristics such as high thermal stability, wide electrochemical windows, nonflammability, and low volatility.<sup>25</sup> Several types of ionic liquid-based electrolytes have demonstrated enhanced performance in LNMO cells. These include pyrrolidinium (1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, ester-modified methyl methylcarboxymethyl pyrrolidinium bis(trifluoromethanesulfonyl)imide,<sup>37</sup> N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide<sup>38</sup> among others. Nonetheless, ionic liquid electrolytes possess certain inherent drawbacks, including expensive production and high viscosities at room temperature, which lead to low ionic conductivities, inadequate electrode and separator wettability, and suboptimal compatibility with anodes.<sup>39</sup>

Alternatively, different electrolyte additives have also been studied for LNMO systems, such as lithium bis(oxalato)borate ( $\text{LiBOB}$ ),  $\text{LiDFOB}$ , lithium aryl trimethyl borates, phosphite derivatives, and so on, to enable the formation of a stable passivation layer.<sup>40</sup>

A further alternative class is the solid polymer electrolytes (SPEs). In a review article by Cui's group, the development and challenges of solid polymer electrolytes utilized in LNMO cells are gathered.<sup>12</sup> They classified the SPEs for LNMO into six types such as oxyethylene containing polymers, polycarbonate-based, polysiloxane-based, vinylidene difluoride-based, methyl methacrylate containing polymers and cyano-functional group containing polymers. From this summary, it can be concluded that issues such as poor compatibility with the lithium anode, limited ionic conductivity, and, most significantly, the interfacial stability at the cathode electrolyte interphase are challenges which need to be addressed further, also for this category of electrolytes.

Inorganic surface coating agents such as  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlPO}_4$ ,  $\text{Bi}_2\text{O}_3$ , graphene oxide, etc., have been applied on the LNMO surface to enable a stable

electrode-electrolyte interface and reduce the direct electrolyte contact with the electrode.<sup>40</sup> Similarly, attempts have also been made with organic polymers such as polyimide,<sup>41</sup> polypyrrole,<sup>42</sup> cyclized-polyacrylonitrile,<sup>43</sup> coatings with self-assembled monolayers of fluoroalkylsilane and octadecylsilane,<sup>44</sup> and many more. Furthermore, efforts to improve the surface chemistry of the LNMO electrode by modifying the employed binder system have been reported. The effect of water-soluble, environment-friendly sodium carboxymethyl cellulose (CMC),<sup>45</sup> CMC crosslinked with guar gum,<sup>46</sup> sodium alginate,<sup>47</sup> etc., have been studied. Although extensive research to extend the cycle life of LNMO cells is being conducted by various research groups, and some progress in terms of capacity retention has been reported, more development is required for practical applications, particularly for full cells at elevated temperatures. Moreover, there is a lack of knowledge regarding the failure mechanisms of LNMO in these different systems. This remains a major obstacle for progress in the area.

## 1.4 Tailoring electrode-electrolyte interphases

The main aim of this thesis was to investigate innovative methods for improving the cathode-electrolyte interphase (CEI). This goal was pursued using two different strategies: the first involved experimenting with alternative binders, whereas the second concentrated on exploring alternative electrolytes. These strategies are discussed in detail in the following sections.

### 1.4.1 Functional binders

A binder, typically made of a polymer, is a minor yet vital component of a battery electrode that is used to bind the active particles together within the electrode during battery operation. The binder helps in creating a conductive network between the current collector and the active particles in addition to ensuring the electrode's mechanical integrity. A binder which plays a role also for other properties, such as aiding in the formation of an interphase layer, in addition to its basic function of binding particles together and maintaining surface integrity, is referred in this thesis as a *functional* binder. Ideally, binders should be chemically stable when in contact with the electrolyte, as well as electrochemically stable in the cell environment, to prevent any undesired side reactions. Should any side reactions occur, they ought to assist in developing a passivation layer that is stable and conductive to lithium ions, thus inhibiting subsequent side reactions. Binders should also have other properties so as not to be a limiting factor for a cell's performance. One of these properties is enhancing the ionic conductivity in the electrode, ensuring the mobility of lithium ions. Additionally, a binder in an electrode should have an optimum swellability when in contact with the electrolyte. Excessive swelling can lead

to poor mechanical properties and electrode cracking, while a low degree of swelling may limit the contact between the electrode components, increase the charge-transfer resistance and potentially reduce the performance of the cell.<sup>48</sup>

Traditional binder materials for battery electrodes include poly(vinylidene difluoride) (PVdF) and copolymers of vinylidene difluoride (VdF) and hexafluoropropylene (HFP).<sup>49</sup> The PVdF-based electrodes are normally processed in N-methyl-2-pyrrolidone (NMP), which is a toxic solvent both to humans and the environment, has a low vapour pressure, and requires significant drying energy and a solvent recovery system in production, which adds significant cost and factory space, making it less ideal.<sup>50</sup> Alternative binders for electrodes that are environmentally compatible and cost-effective for electrode processability are currently being investigated. One promising type is water-based binders. Among the water-based binders, the combination of styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC) is well-studied and well-recognized as an effective way to produce high-performance graphite electrodes.<sup>46</sup> Several researchers have also investigated the use of water-soluble CMC as a binder in LNMO electrodes.<sup>45,51</sup> Several of these research studies have shown that CMC and its derivatives yield comparable capacity retention in LNMO cells when compared to PVdF-based electrodes. Some of the other water-based binders that have been studied previously for LNMO electrodes include derivatives of alginates, polyacrylates, polyvinyl acetate, chitosan and so on.<sup>47,52,53</sup> A significant drawback of water-based processed electrodes is the occurrence of cracks during the drying process, particularly for thick electrodes. Recent studies show that the undesirable effects of using water in cathode processing, such as current collector corrosion, leaching of lithium ions and poor adhesion of electrode coatings to the current collector at higher electrode loadings, can be reduced by incorporating suitable processing additives like phosphoric acid and citric acid, or by modifying the current collector itself.<sup>51,54,55</sup>

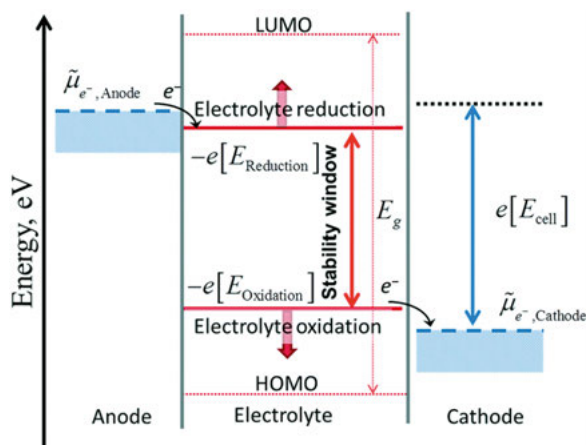
The choice of binder, as well as the binder content, can have a strong influence on the battery's performance, including the discharge capacity, rate capability, cycle life, and so on. In principle, the functionality of a binder can be tailored using synthetic polymer chemistry. For example, binders have been observed to positively influence the formation of electrode-electrolyte interphases on both the cathode and anode surfaces, if they are designed or selected correctly.<sup>49,51,56–59</sup>

## 1.4.2 Electrolytes

The LIB electrolyte serves as a medium that transports  $\text{Li}^+$  ions between the positive and negative electrodes. All LIB electrolytes contain a lithium salt, most commonly  $\text{LiPF}_6$ , to allow  $\text{Li}^+$  ion movement during cell operation, as mentioned in Section 1.2. The conduction of these ions depends on the Li salt being able to dissolve and dissociate in a solvent, often a solvent combination.

The most common combination of electrolyte solvents is alkyl carbonate-based solvents such as ethylene carbonate (EC) for adequate negative electrode passivation and either diethyl carbonate (DEC), dimethyl carbonate (DMC), or ethyl methyl carbonate (EMC) as a co-solvent to reduce the viscosity of the electrolyte to facilitate higher conduction of  $\text{Li}^+$  ions and the anion. The stability of the electrolytes throughout the operating range of the cell is a crucial factor when selecting an electrolyte for a certain cell chemistry. But LNMO operates at a higher voltage, i.e.,  $\sim 4.7$  V (vs.  $\text{Li}^+/\text{Li}$ ), which is above the thermodynamic stability window of the conventional electrolyte, and electrolyte development is therefore necessary.

The span between the potentials at which an electrolyte reduces at a negative electrode and oxidises at a positive electrode is known as the electrolyte's electrochemical stability window (ESW). Figure 4 shows the common notation of the electrochemical potential window, indicating the HOMO and LUMO energy levels and also the correct notation for the positive and negative potential limits for the electrochemical stability. It is, however, a common misconception to describe the ESW of an electrolyte in the simple terms of energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the electrolyte solvent molecules, since the overall reaction thermodynamics of both reactants and products including solvent molecules, salt and electrode surfaces are then not taken into account.<sup>60</sup>



**Figure 4.** Electrochemical stability window. Reprinted with permission from reference.<sup>60</sup> Copyright (2018) Royal Society of Chemistry.

It is crucial to have a stable interphase layer, known as the CEI, formed due to the decomposition of electrolyte during initial cycles at the cathode surface to prevent additional electrolyte degradation. This interphase layer must, ide-

ally, be electronically insulating and  $\text{Li}^+$  conducting to ensure good electrochemical performance.<sup>61</sup> Homogeneity as well as the chemical, electrochemical, and mechanical stability of the CEI layer are also vital for a superior and long cycle life of the battery.<sup>62</sup> The CEI layer is composed of different by-products, organic and inorganic species such as  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{ROLi}$ ,  $\text{ROCO}_2\text{Li}$ , and so on, where R represents an alkyl group.<sup>63</sup> It is crucial for the stable operation of a battery that the CEI layer is not soluble in the electrolyte, as this might give severe capacity fading.

Multiple efforts have focused on the use of additives in the electrolyte to tune the CEI to build a stable and robust CEI layer.<sup>64–66</sup> Various electrolyte additives, including FEC, vinylene carbonate (VC), tris(trimethylsilyl) phosphite (TMSPi), tris(trimethylsilyl) phosphate (TMSPa), and others, have been studied and tested in different battery chemistries.<sup>62</sup> To facilitate the formation of a cathode interphase, electrolyte additives are chosen such that they have a lower oxidation potential than the other components of the electrolyte, allowing for sacrificial oxidation of the additives.<sup>61</sup> The choice of an appropriate additive is determined by its intended application, and certain additives such as TMSPi and TMSPa are recognized for their capacity to scavenge HF, which is often a by-product that can damage the cell's performance by causing corrosion.<sup>67,68</sup>

## 2. Scope of the thesis

The research carried out in this thesis work can be categorised into three different sections, with the overriding goal being understanding degradation phenomena and addressing interfacial problems in LNMO cells by different mitigation strategies.

The first section, summarized in **Paper I**, discusses the limitations of the linear sweep voltammetry (LSV) technique – the state-of-the-art approach to investigate the electrochemical stability of electrolytes – to determine the oxidative stability of an electrolyte, and describe the development of a new method termed ‘synthetic charge-discharge profile voltammetry’ (SCPV). This method can lead to a better quantitative understanding of the amount of charge generated from any degradation that occurs during anodic and cathodic sweeps in a cell, in a way that is more representative.

In the second section, in **Paper II** and **III**, different binders have been investigated for LNMO electrodes. In **Paper II**, PAN, well-known for its oxidative stability, has been explored as a potential binder. However, for a range of different concentrations of PAN employed, a rapid capacity loss was observed, and degradation of PAN was identified as the main cause. In **Paper III**, the practical use of polyacrylic acid (PAA), a water-based binder, is examined in thick LNMO electrodes and compared to those that use sodium carboxy methylcellulose (CMC) as a binder, in terms of electrochemical performance in full-cells with graphite. This work also discusses the limitations of PAA from a practical point of view.

In the third section, three different electrolyte formulations were tested and analysed in LNMO-graphite full cells. In **Paper IV**, an ionic liquid-based electrolyte, LiFSI in PYR<sub>13</sub>FSI, was studied in terms of oxidative stability and electrochemical performance, and the results were compared with a standard electrolyte. The interphase layers formed on both LNMO and graphite electrodes were characterized using XPS. **Paper V** evaluates the performance of a sulfolane based electrolyte compared to a standard electrolyte in LNMO cells. An emphasis on the oxidative stability investigations was made in this paper, and correlated to differences in electrochemical performance between the different electrolytes. **Paper VI** examines the impact of two distinct electrolyte additives — tris(trimethylsilyl)phosphite (TMSPi) and lithium difluoro(oxalato)borate (LiDFOB) — in a standard electrolyte to understand



their role in the interphase stability on both cathode and anode surfaces. The results are then compared to a standard electrolyte without any additives.

Collectively, the papers included in this thesis work contribute to improve our understanding of the degradation processes that occur in LNMO cells and to develop improved passivation layers that could limit electrolyte decomposition and capacity decay. By developing new methodology and studying possible failure mechanisms, this thesis also tries to offer insights on the interfacial chemistry of the LNMO electrodes. This serves as a basis for further development of this promising LIB electrode material.

### 3. Methodology

In this chapter, the main emphasis is placed on two distinct electroanalytical methodologies that have been employed in the majority of the work carried out for this thesis, and that can be considered non-standard: synthetic charge-discharge profile voltammetry and intermittent current interruption. However, several other common complementary techniques have been utilized in this thesis but are not specifically addressed within this chapter.

#### 3.1 Synthetic charge-discharge profile voltammetry

To better understand how electrolytes decompose, electrochemical cells were cycled by following the voltage profile of an active material (LNMO in this case), instead of at a constant scan rate as in LSV measurements. This technique has been termed as SCPV. From the obtained amount of charge passed during both anodic and cathodic sweeps using this technique, different parasitic faradaic reactions at each potential region can be isolated and analysed. This technique thus allows for more directly comparable data with the corresponding half-cell.

First, the LNMO voltage profile was obtained using a LNMO|LP40|Li cell. The potential-time profile of the charge step of the half-cell was then interpolated to obtain 1000 data points spaced equally in terms of potential. The following SCPV measurements were carried out using a BioLogic instrument and the potential profile table was imported into the software using the “Potential-profile importation” (PPI) technique in the EC-Lab software. The same procedure was performed for the discharge step of the half-cell and was similarly imported. Multiple SCPV cycles were obtained using both charge and discharge profiles, which were looped for the desired number of cycles.

#### 3.2 Intermittent current interruption

The intermittent current interruption (ICI) method involves cycling electrochemical cells galvanostatically, but with regular pauses of 1 second every 5 minutes, in the works carried out in this thesis, to keep track of resistance changes in the cell from the potential responses. This analysis technique, as

employed in this work, is implemented according to the protocol developed by M.J. Lacey.<sup>69–71</sup>

The ICI technique has in recent years shown to be exceptionally useful in battery research. It can produce equivalent information as electrochemical impedance spectroscopy (EIS) measurements – the ICI analysis approach quantifies resistance as time- and current-independent parameters in a way that the exact parameters can be derived from EIS – tracking the resistive and diffusive behaviours throughout the lifetime of the cell, but using the same cell setup and test equipment as for galvanostatic cycling, more specifically, DC methods like ICI do not require a frequency response analyser. In ICI measurements, the change in potential ( $\Delta E$ ) can be described as a function of step time ( $t$ ), the time recorded after the current interruption, according to prior derivations done. The response to the current interruption is modelled as an ohmic resistance in series with a diffusion process, and the relationship is:

$$\Delta E(t) = \Delta I (R + k\sqrt{t}) \quad (8)$$

where  $I$  is the current before interruption,  $R$  is the internal resistance and  $k$  is the diffusion resistance coefficient.

A linear regression of the potential against square root of the step time is performed during the ICI analysis. The internal resistance  $R$  for each current interruption in the analysis is then obtained by dividing the intercept of the time-independent part of the potential change ( $\Delta E(0)$ ) by current, as shown below:

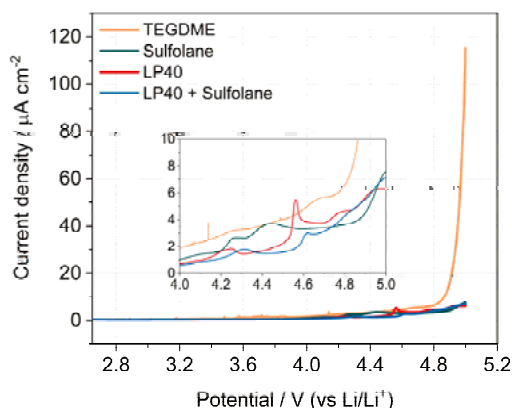
$$R = -\frac{\Delta E(0)}{\Delta I} \quad (9)$$

## 4. Key results and discussion

### 4.1 Determining the electrochemical stability of electrolytes

A cell that operates within the ESW of an electrolyte or employs one that forms a stable passivation layer on the electrodes from decomposition products is a fundamental requirement when selecting a battery electrolyte.<sup>72,73</sup> The LSV technique, which is frequently employed to measure the anodic stability of an electrolyte, can however lead to inaccuracies and cause the ESW values to be overestimated.<sup>74</sup> In **Paper I**, the LSV technique is critically evaluated using some of the most commonly used liquid electrolytes in LIBs. By addressing the limitations and challenges inherent in this technique, the development of the alternative SCPV method is explored and validated in **Paper I**.

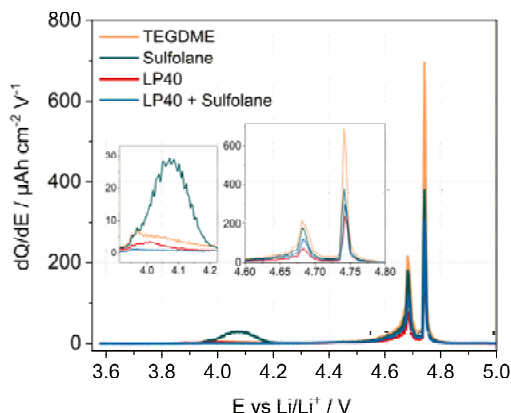
Figure 5 shows the LSV results of four different electrolytes: tetraethylene glycol dimethyl ether (TEGDME), sulfolane, LP40 and LP40:sulfolane (1:1 v/v), all with 1 M LiPF<sub>6</sub> salt, measured using a carbon coated aluminum foil as the working electrode vs. Li metal at 0.1 mV/s scan rate. As often discussed in literature, defining the stability limit using an onset current density such as 1 mA cm<sup>-2</sup> has no theoretical significance and is fully arbitrary. Figure 5 demonstrates how difficult it is to determine the exact voltage point at which the breakdown process begins, and hence that it is difficult to deduce the oxidative stability from these curves.



**Figure 5.** Linear sweep voltammograms of Li | electrolyte | C-coated Al foil cells from the OCV up to 5 V vs.  $\text{Li}^+/\text{Li}$  using a scan rate of 0.1 mV/s. The inset shows a magnification of the data obtained between 4 and 5 V vs.  $\text{Li}^+/\text{Li}$ . From **Paper I**.

The SCPV technique introduced in **Paper I** applies a voltage profile of an active material of interest, in this case LNMO, to a system with an "inert" working electrode and measures the amount of charge or current that flows during this process. This technique is designed for more direct relevance to practical application compared to LSV in that it does not use a constant sweep rate, but rather mimics the voltage profile of the active material, allowing researchers to investigate battery electrolytes under more realistic and relevant cycling conditions. The amount of charge obtained in a cell without an active material, i.e. a cell with carbon coated aluminum against lithium, is here estimated utilizing both the charge and discharge profiles of LNMO. The inert electrode aids in providing a qualitative understanding of the parasitic reactions occurring in the cell, whereas the ideal cell format would be with the "real" electrode, as that used in the corresponding battery, but it would then be very difficult to separate the faradaic reactions arising from electrolyte decomposition and from the active material.

The differential capacity plot in Figure 6 exhibits peaks representing faradaic reactions occurring during the first SCPV potential sweep in the four different electrolyte systems. These peaks suggest degradation reactions, with higher peak intensities indicating a higher magnitude of degradation. The charge passed during the potential sweep displays peaks at specific potentials, which correspond to the potential plateaus in the LNMO potential profile itself. Specifically, the minor plateau at 4.0-4.1 V corresponds to the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couple, while the longer plateau at 4.67 V and 4.74 V corresponds to the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Ni}^{3+}/\text{Ni}^{4+}$  redox couples, respectively, in an LNMO half-cell. Therefore, the total charge passed during each sweep is not continuous but instead relies on the time spent at each voltage level.



**Figure 6.** Amount of charge passed in the first charge cycle obtained using the SCPV technique plotted as change of  $dQ/dE$  as function of  $E$ . Insets show magnifications in the ranges 3.9–4.2 V and 4.5–4.8 V, respectively. The coin cells were cycled with a carbon coated aluminium electrode against lithium. From **Paper I**.

This study revealed that, despite being recognized for its relatively high oxidative stability, the sulfolane-based electrolyte passed a greater amount of charge than other electrolytes in the lower plateau region, which was unexpected. On the other hand, the TEGDME-based electrolyte was observed to pass a higher charge in the higher plateau region. Furthermore, the LSV results in Figure 5 suggest that LP40 would pass more charge than sulfolane, but in the SCPV experiments, it was found that the amount of charge passed by sulfolane was more than double that of LP40, with  $15.68 \mu\text{Ah cm}^{-2}$  for sulfolane compared to  $7.02 \mu\text{Ah cm}^{-2}$  for LP40. The asymmetrical peak shape in the lower plateau region, which rises early and falls gradually, except for sulfolane, could indicate the formation and presence of a passivation layer.

CE is frequently used as a predictor of parasitic reactions in battery cells, with a lower CE indicating more side-reactions. The CE of LNMO cells (see Figure 4 in **Paper I**) using the electrolytes studied in this work shows that the first cycle CE of sulfolane, LP40 and LP40:sulfolane electrolytes reflects the trends in the SCPV results and are in good agreement. Previous research has shown that electrolyte oxidation is the primary cause of cell failure in LNMO systems, with active material loss accounting for merely a minor portion of it.<sup>28</sup> Thereby, the correlation between a lower CE and the large degree of electrolyte oxidation seen in the SCPV results, indicates the applicability of the technique.

Although the SCPV method can provide information on the parasitic reactions in certain voltage ranges, it remains difficult to determine the precise limit of oxidative stability. The effect of the working electrode used was found to be a contributing factor to the notable differences observed in the galvanostatic cycling and multiple SCPV analyses, such as the failure of the LNMO half-cell with TEGDME and the more stable passivation behavior in the

LP40:sulfolane electrolyte. These differences may be due to catalytic effects from the active material and distinct Li electrode behavior resulting from the varied currents passed in SCPV and galvanostatic experiments, which cannot be accounted for using SCPV alone.

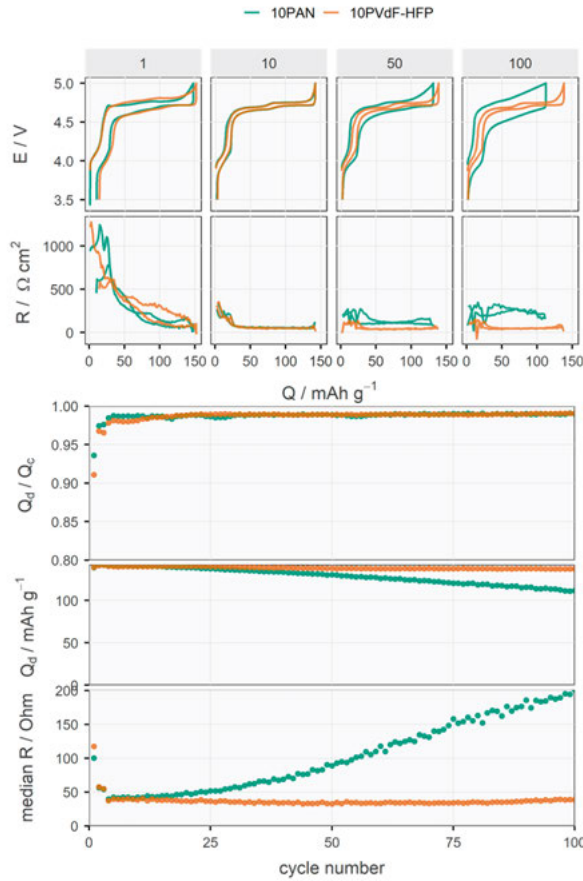
## 4.2 Functional binders

### 4.2.1 Limitations of polyacrylonitrile as a binder for LNMO electrodes

One of the efficient ways to suppress or reduce the effect of electrolyte oxidation is to enable a stable interphase between the cathode and the electrolyte.<sup>75</sup> Tailoring the binder provides an opportunity to implement this without adding additional inactive components in the cell, since the binder generally distributes homogeneously over the surfaces of all electrode components.<sup>76,77</sup> Polyacrylonitrile (PAN) is generally understood to have a comparatively high oxidative stability – at least if compared to other ion-coordinating polymers – owing to the nitrile functional groups present in its structure.<sup>78–80</sup> The polar and strong electron withdrawing nature of the polynitriles have been speculated to form strong bonds with the active material and current collector, rendering it a potentially advantageous binder.<sup>81</sup> In **Paper II**, PAN was evaluated as a binder for LNMO electrode. Together with surface characterization, different electrochemical analyses were performed in order to better understand its role in this highly reactive electrochemical environment.

LNMO electrodes with different PAN binder concentrations were studied and compared to the corresponding concentrations of conventionally used PVdF-HFP binder-based electrodes. The surface morphology of PAN-based electrodes indicated that LNMO spherical particles are mostly covered with carbon black conductive additive and the binder (see Figure 1 in **Paper II**), but in contrast, electrodes with PVdF-HFP show an uneven distribution of carbon black and PVdF-HFP. The homogenous surface coverage in the PAN based electrode could be attributed to the adhesive and cohesive interactions of the polymer arising from the strong polarity of the nitrile functional groups. Galvanostatic cycling studies in half-cells indicated however that the electrodes with the highest concentration of binder, i.e., 20PAN, exhibited rapid capacity fade with only 64 mAh g<sup>-1</sup> remaining after 95 cycles. The results clearly show a trend that higher concentrations of PAN binder generates more rapid capacity fading, see Figure 2a in **Paper II**. The observation of more extensive capacity fade and lower CE (see figures 2a and 2b, respectively, in **Paper II**) indicates that higher binder loadings cause more side-reactions in the PAN system. However, PVdF-HFP does not follow the same pattern as PAN (see Figure 2c in **Paper II**) in the sense that it is the lowest binder loading that displays the most rapid capacity fade and the lowest CE.

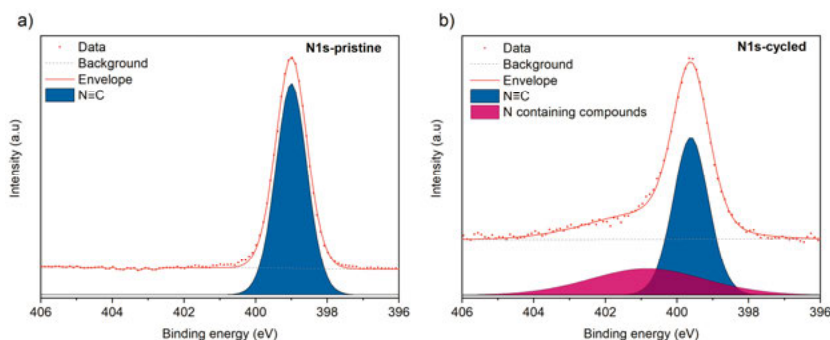
From the ICI analysis of 10PAN and 10PVdF-HFP cells, as shown in Figure 7, there is no significant difference between the two binders in the total internal resistance,  $R$ , during the first few cycles. The large hysteresis observed in the 100<sup>th</sup> cycle in the charge-discharge curve of 10PAN compared to 10PVdF-HFP indicates a higher resistance in this cell. The rapid decrease in discharge capacity is correlated with the increase in median resistance in the PAN-based cell, which suggests PAN degradation and resistance build-up in the cell. In contrast to other processes like decomposition in the bulk electrolyte, EIS measurements (see Figure 4 in **Paper II**) demonstrate that a single process dominates the growth in resistance, which is most likely caused by surface effects in the electrode and originates from PAN degradation given that no similar resistance increase is observed in PVdF-HFP-based cells.



**Figure 7.** ICI data for LNMO half-cells with 10PAN and 10PVdF-HFP cells. In the 1st and 2nd rows, the voltage profiles and corresponding internal resistance changes against specific capacity for cycles 1, 10, 50, and 100 are displayed. Coulombic efficiency, discharge capacity and median resistance changes over 100 cycles are shown in the 3rd, 4th and 5th rows of the figure, respectively. From **Paper II**.



OEMS characterization indicated no formation of any nitrogen-containing volatile products from the degradation of PAN. The OEMS results also showed that the total amount of gas evolved in the LNMO systems, both using PAN and PVdF-HFP binders, was far less than what would be predicted for layered oxides operating in the same voltage range.<sup>82</sup> Contrary to the single N1s environment at 399 eV (see Figure 8), which corresponds to the C≡N bond originating from PAN, XPS measurements on electrodes cycled with 20PAN interestingly revealed more than one N1s environment. These findings demonstrated that PAN had indeed been degraded, and the broad peak at 399.8 eV suggested the presence of C=N or other nitrogen-containing compounds. A potential decomposition reaction would be the result of a cyclization of PAN in the highly oxidizing environment (see Figure 8 in **Paper II**). The XPS results, together with the OEMS data, also indicated that the degradation products were mostly solid and not volatile. The solubility of PAN in EC, the electrolyte component, could also partly explain the poor cell performance in PAN-containing cells.



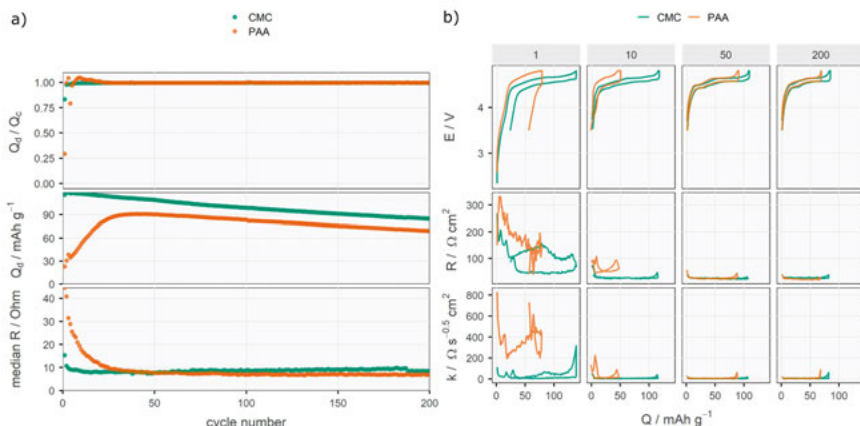
**Figure 8.** Deconvolution spectra of 20 PAN electrode a) pristine N1s and b) cycled N1s. From **Paper II**.

In summary, the findings in **Paper II** demonstrate that PAN performs poorly as a binder in LNMO cells and that its stability can be questioned. It is observed that PAN definitely undergoes side-reactions under the operating conditions associated with LNMO; if not because of the high voltage, then because of other processes that cause side reactions, such as catalysis by the LNMO active material itself. Another intriguing finding is that binders with substantially poorer theoretical oxidative stability than PAN, such as CMC, have been demonstrated to perform just as well as PVdF-HFP for a number of battery cathode chemistries, including LNMO.<sup>83–85</sup> It is likely that any decomposition products created during cell cycling create a solid passivating layer on the cathode, allowing for stable cycling, which accounts for the good performance of binders like CMC. This suggests that kinetic stability, rather than thermodynamic stability, is what determines a practical high-voltage cell.

#### 4.2.2 Problems with using PAA as a binder in thick LNMO electrodes

In Section 4.2.1, it was mentioned that modifying the binder system in the LNMO electrode can allow for the formation of an interphase layer that may limit the direct interaction between the active particles and electrolyte, leading to reduced degradation of the electrolyte and dissolution of transition metals from the cathode. In **Paper III**, a similar approach was adopted using polyacrylic acid (PAA) due to the higher hydrogen bonding strength and polarity of  $\text{-COOH}$  groups in PAA with the oxygen atoms in the active component, LNMO.<sup>86,87</sup> The hypothesis was that this approach would limit the detrimental direct contact with the electrolyte. Earlier research has suggested that the use of PAA and its derivatives can improve the electrochemical performance in different battery chemistries.<sup>58,88–90</sup> The aim of the study in **Paper III** was to gain a more in-depth understanding of the performance of PAA as a binder in relatively thick LNMO electrodes used in full-cells with graphite, with the objective of investigating the effects when approaching industrial standards. The results were compared with those obtained using CMC binder in LNMO electrodes.

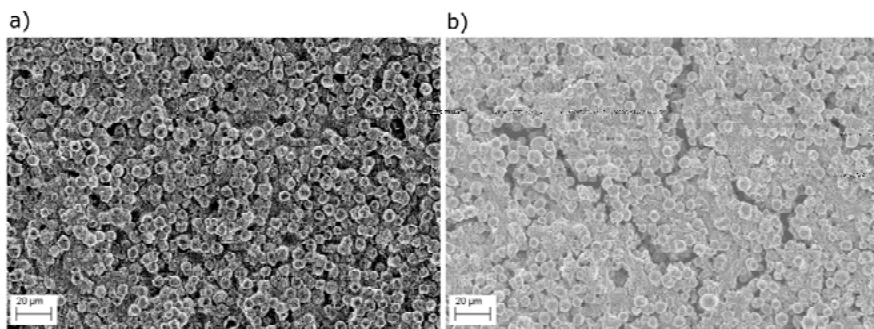
Figure 9 illustrates the ICI results of LNMO-graphite cells employing PAA or CMC binders, with an active mass loading of approximately  $10 \text{ mg cm}^{-2}$ . Figure 9a shows CE, discharge capacity, and median resistance with increasing cycle number, from top-to-bottom. The cell with PAA shows poor CE and a lower discharge capacity in the first cycle, which could be correlated to the high internal resistance in the cell. A gradual reduction in the internal resistance of the PAA cell is accompanied by an increase in discharge capacity, indicating that high resistance is a key factor limiting the discharge capacity of the cell. The sloping voltage profiles in Figure 9b of cycles 1 and 10, lacking a clear endpoint, suggest that there is a considerable iR drop within the electrode, limiting the charge process. The insufficient electrolyte wetting and low electrolyte permeability become apparent at high mass loadings, and this may explain the increase in capacity seen over the first  $\sim 25$  cycles.



**Figure 9.** ICI data for LNMO-Graphite full cells using either CMC or PAA as binder. From top to down, a shows CE, discharge capacity and median resistance. From top to down, b indicates the voltage profile, resistance curves and the diffusion coefficients of cycle 1, 10, 50 and 200. From **Paper III**.

On the other hand, the cell that contains CMC binder has an initial capacity of approximately 83% and initial discharge capacity of  $116 \text{ mAh g}^{-1}$ . After 200 cycles, it retains around 73% of its initial capacity. Moreover, the initial internal resistance of the CMC-based cell is relatively lower, and it remains relatively constant with increasing cycle number, in comparison to the PAA-based cell.

Morphology analysis of the electrode surface, shown in Figure 10a, demonstrates that the electrode using CMC binder, relatively cause a uniformity in distribution, whereas in Figure 10b, cracks are evident in the electrode that employs PAA. The cracks found in the electrode hinder the ability of active particles to transfer electrons, leading to a decrease in overall electrode conductivity. As a result, the electrochemically active area decreases, which limits the active particles accessing the  $\text{Li}^+$  ions resulting in a reduced electrochemical performance in the cell.



**Figure 10.** SEM images of LNMO electrode using a) CMC and b) PAA binder. From **Paper III**.

Based on the results presented, it can be concluded that PAA is not an effective binder for high mass loading LNMO electrodes, which renders it largely unsuitable. According to literature, the PAA polymer tends to agglomerate in water because of hydrogen bonds between its carboxylic groups, while the Li salts of PAA have stretched polymer chains due to electrostatic repulsion between their carboxylate groups.<sup>91</sup> However, our research using Na-PAA as a binder for a thick LNMO slurry coating (see Figure S4 in **Paper III**) revealed that the resulting electrodes had many cracks after vacuum drying, which made further analysis less worthy to pursue. Despite these negative results, however, it is still possible that these materials can be optimized to enhance their performance for use in advanced batteries, such as including additional functionalities to tune the binder properties and/or mixing or copolymerising with other polymers to improve the binder properties.

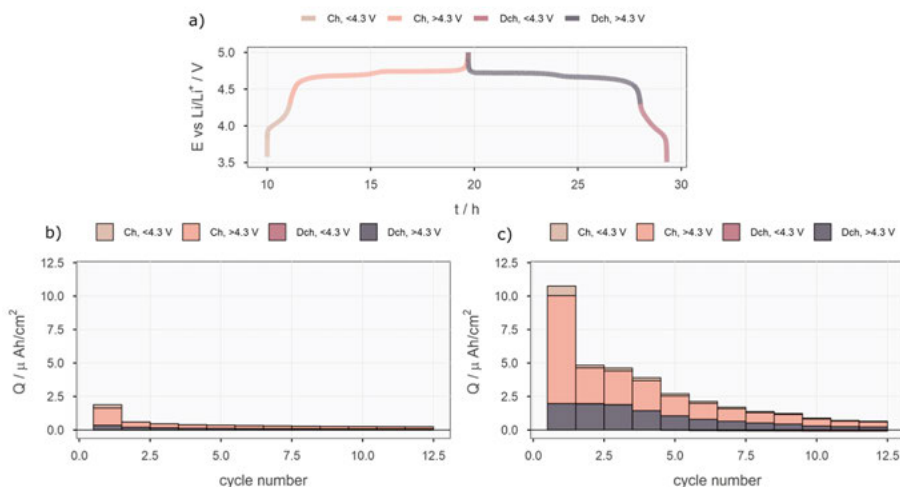
## 4.3 Alternative electrolytes

### 4.3.1 Interphase stability of LNMO cells using an ionic liquid

Ionic liquids are attractive substitutes for traditional organic carbonate-based electrolytes because of their wide ESW, high thermal stability, minimal flammability and low volatility.<sup>92,93</sup> In **Paper IV**, an ionic liquid-based electrolyte (ILE) for LNMO-graphite cells was evaluated using 1.2 M lithium bis(fluorosulfonyl)imide (LiFSI) in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR<sub>13</sub>FSI). Several studies on ionic liquids, including PYR<sub>13</sub>FSI-LiFSI, have targeted high-voltage cell chemistry, including that of LNMO, taking into account its potential benefits at high voltage.<sup>94–97</sup> Implementation of 1 M LiFSI in PYR<sub>13</sub>FSI was previously demonstrated in LNMO half-cells by Lee et al. who were able to achieve stable cycling and improved rate capability even at an elevated temperature.<sup>98</sup> In **Paper IV**, a

comprehensive understanding of the oxidative stability of this ILE and its degradation at the electrode-electrolyte interphase, together with its electrochemical performance in LNMO-graphite full cells, are assessed. The SCPV technique, studied in **Paper I**, was employed in this work to evaluate the oxidative stability of the ILE in comparison with the traditionally used LP40, as well as its ability to form a passivation layer on the LNMO electrode.

In both the charge and discharge voltage profiles, Figure 11a depicts the LNMO voltage profile that is employed in this technique, which is separated into two regions: the lower plateau region, < 4.3 V, and the higher plateau region, > 4.3 V. The amount of electrolyte degradation is demonstrated by the increased amount of charge passed in both regions in LP40 (see Figure 11c) compared to ILE (see Figure 11b). The higher amount of charge in the upper plateau region in the first cycle indicates that LP40 has oxidized more compared to ILE. It also appears that in the succeeding cycles, the amount of charge passed in the ILE-based cell is considerably smaller than in the LP40-based cell. The consistently low amount of charge in the first few cycles indicates that a stable passivation layer has developed in the ILE-based cell early on.

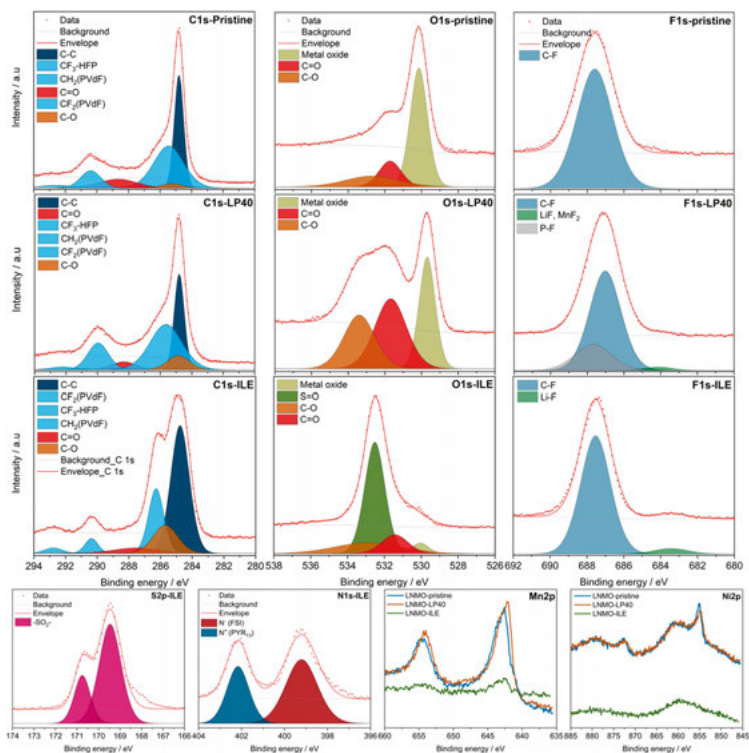


**Figure 11.** a) Voltage profile of the LNMO half-cell and (b and c) multiple SCPV cycles with cells containing b) ILE (See Figure S1 in **Paper IV** for zoomed in data) and c) LP40 as electrolyte. The cells contain carbon-coated aluminum as the working electrode and Li as both counter and reference electrode. From **Paper IV**.

The discharge capacities and coulombic efficiencies of LNMO-graphite cells cycled with ILE and LP40 at two different temperatures, i.e., 25 °C and 45 °C, are presented in Figure 4 in **Paper IV**. Higher discharge capacities and coulombic efficiencies at both temperatures are demonstrated by cells cycled with ILE, indicating improved electrochemical performance. The higher coulombic efficiency

values for the cells cycled with ILE are also in good agreement with the SCPV results.

In-house XPS measurements were carried out to determine the composition of the pristine electrodes and the surface layer composition of the cycled LNMO electrodes with both ILE and LP40. The organic portions of the CEI layer on the electrode cycled with LP40 and ILE did not show any significant changes in composition compared to the pristine electrode, as observed in the C1s spectra (see Figure 12). The O1s spectra of the electrode that were cycled with ILE show a considerably lower intensity of metal oxide species, which suggests that a thicker CEI layer has formed on the LNMO surface compared to that of the LNMO electrode cycled with LP40. Furthermore, the F1s spectrum of the electrode cycled with ILE pointed out the presence of LiF inorganic species, which is often critical for the stable formation of a CEI and decreases the possibility of any additional electrolyte side-reactions.<sup>99,100</sup> The presence of SO<sub>2</sub> and S=O species, N-containing species derived from the breakdown of FSI anions, and the cationic portion of the ionic liquid also provide support to the idea that the CEI layer is primarily dominated by inorganic species.<sup>98</sup> Overall, the XPS findings showed that the CEI with ILE was more stable than the CEI with LP40, which is consistent with the increased capacity retention of LNMO-graphite cells with ILE.



**Figure 12.** Deconvoluted XPS spectra of C1s, O1s, F1s, S2p, N1s, Mn2p and Ni2p of LNMO electrodes – pristine, and cycled with either LP40 or ILE for 40 cycles. From **Paper IV**.

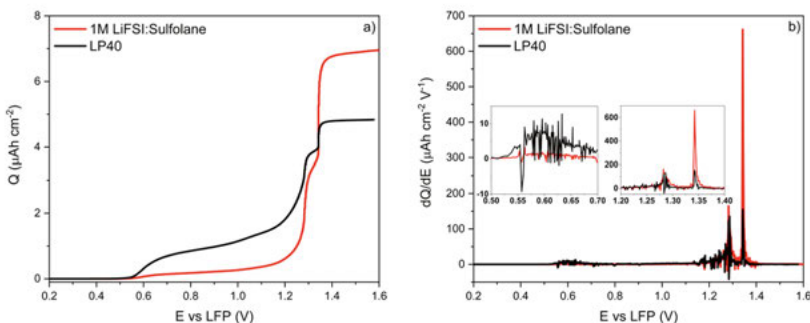
Ionic liquid-based electrolytes such as  $\text{PYR}_{13}\text{FSI-LiFSI}$  show promise as a substitute for conventional electrolytes in LNMO systems, particularly at elevated temperatures, according to the findings of **Paper IV**. However, it needs further optimization to not limit its performance at room or lower temperatures. The use of a co-solvent to make ionic liquids less viscous is one approach under study to overcome this limitation.<sup>101</sup>

#### 4.3.2 The role of sulfolane-based electrolyte in LNMO-graphite cells

Due to their well-known electrochemical stability, sulfolane-based electrolytes have attracted great attention and have been previously investigated for use in high-voltage systems like LNMO.<sup>29,102,103</sup> A stable and robust interfacial layer, particularly the CEI layer on LNMO electrodes, is essential to inhibit additional electrolyte oxidation. Thereby, a solid understanding of electrolyte degradation and the formation of interphases is necessary.<sup>104</sup> In **Paper V**, sulfolane is investigated together with LiFSI salt as an electrolyte, and the electrochemical performance in LNMO-graphite full cells is assessed in terms

of the anodic stability of the electrolyte as well as the interfacial processes taking place at both the LNMO and graphite interphases.

As opposed to the general understanding of sulfolane, the observation of electrolyte degradation was validated in LNMO operating voltages in both **Paper I** and **Paper V** using SCPV. The main difference in the experiments was the different salt and salt concentration used, as well as the cell set-up with a delithiated LFP counter-electrode being used in a 3-electrode set-up in **Paper V**. The amount of charge passed during the initial anodic scan in Figure 13a indicates the extent of electrolyte degradation, with sulfolane showing a higher quantity of charge than LP40. The electrolytes degrade more rapidly in the upper plateau region ( $>0.9$  V vs. LFP), i.e., plateaus corresponding to the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Ni}^{3+}/\text{Ni}^{4+}$  redox couples in LNMO half-cell, and sulfolane-based electrolytes degrade more quickly than LP40-based ones. Multiple SCPV scans were run for both cells, and consistently lower evolution of charges over ten cycles suggests that stable passivation layers were likely formed in both instances. However, the sulfolane-based cell consistently showed a higher quantity of charge compared to the LP40-based cell, which may explain the lower coulombic efficiency observed for the former in the galvanostatic cycling experiments. Nevertheless, it is important to remember that the effect of the cell components, including the working electrode, counter electrode, and whether the cell is configured with two or three electrodes, is crucial when analyzing the SCPV data. Therefore, the actual suitability of an electrolyte can only be determined by assessing its performance in the specific application it is intended for, as opposed to simplified experimental set-ups (such as SCPV) where the active material electrode is not present.



**Figure 13.** a) The amount of charge passed for sulfolane and LP40 based cells in the first anodic sweep of the SCPV method ( $Q$  vs.  $E$ ) and b) the corresponding differential plot ( $dQ/dE$  vs.  $E$ ). From **Paper V**.

The galvanostatic cycling results (see Figure 5c in **Paper V**) showed that LNMO-graphite cells using the sulfolane-based electrolyte had a higher initial discharge capacity and better capacity retention over 500 cycles than those



using the LP40 electrolyte. However, sulfolane-based cells exhibited an initial low CE, which suggests higher degradation of the electrolyte during the initial cycles. ICI experiments were conducted in 3-electrode cells to comprehensively understand how resistance changes over cycling. The results (see Figure 6 in **Paper V**) indicated that the major resistances were developing from the LNMO cathode, while the graphite anode had very little impact on resistance in both types of electrolytes.

XPS analysis conducted on the cycled LNMO and graphite electrodes revealed the formation of various decomposition products on the electrodes. When cycled with the sulfolane-based electrolyte, the LNMO and graphite electrode interphases were found to be more hydrocarbon-rich and contain FSI based species whereas they were richer in ether and deprived of LiF when cycled using LP40 (see Figure 7 in **Paper V**). The cycled LNMO electrodes appeared to form a thick CEI when cycled in LP40, leading to a diminished O 1s peak from the transition metal oxides in the LNMO electrode. In summary, the XPS results indicate that the interphase layers formed when cycled in LP40 are polymeric in nature and lack lithium fluoride (LiF), while the SEI in the sulfolane-based electrolyte is more inorganic and hydrocarbon-rich, containing LiF that helps to form a stable interphase layer, resulting in better cell cycle stability.

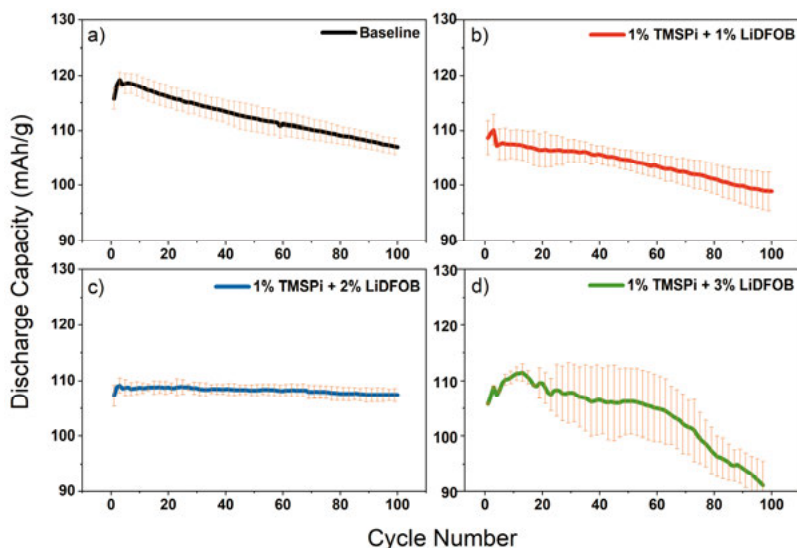
Overall, the LNMO-graphite full cells cycled using sulfolane-based electrolytes exhibited better cycling performance compared to LP40. Even though the sulfolane electrolyte exhibited higher degradation in the initial cycles, it is observed that stable passivation layers formed at the interphases help to maintain better cycling stability compared to the conventional LP40 electrolyte. These findings, coupled with the low pressure evolution observed in the sulfolane-based cells during its initial cycles, indicate that this system is promising for further advancement.

#### 4.3.3 TMSPi and LiDFOB as dual electrolyte additives in LNMO-graphite cells

Apart from exchanging the electrolyte solvent system, several studies have indicated the positive role of electrolyte additives for preventing electrolyte degradation, especially at high voltages, in order to improve electrochemical performance and extend battery lifetime.<sup>66,105–107</sup> The use of various electrolyte additives, including VC, FEC, LiBOB, lithium difluorophosphate (LiDFP), and others, for film formation has been demonstrated to improve the cycling stability for a range of LIB chemistries.<sup>107,108</sup> In **Paper VI**, tris(trimethylsilyl)phosphite (TMSPi) and lithium difluoro(oxalato)borate (LiDFOB) were studied as dual electrolyte additives in LP40, serving as an electrolyte for LNMO-graphite full-cells. It is recognized that when TMSPi is oxidized, it can create a beneficial CEI and also remove hydrogen fluoride (HF) produced

during cycling.<sup>109</sup> Conversely, LiDFOB has been previously investigated for its beneficial impact on SEI formation through its reduction at the graphite, and research also suggests its involvement in the creation of CEI at the positive electrode, particularly in NMC-based batteries, thereby serving a dual purpose.<sup>110</sup>

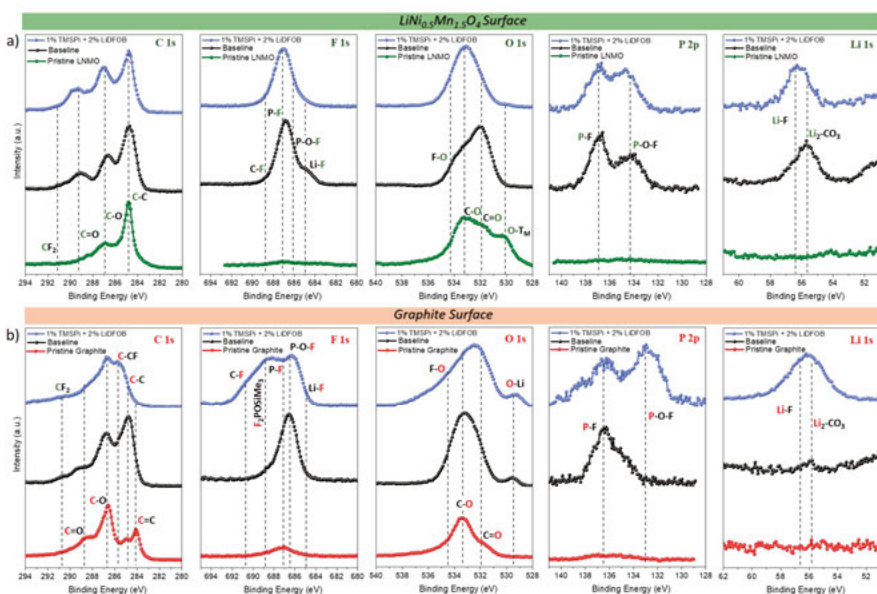
Again, LP40 served as the baseline electrolyte. Figure 14 illustrates the discharge capacities of LNMO-graphite cells with different electrolyte combinations that were tested for 100 cycles. The cell that utilized LP40, 1 wt.% TMSPI, and 2 wt.% LiDFOB demonstrated the best capacity retention and the highest CE out of all the electrolyte combinations tested. Additionally, long-term cycling (see Figure 6 in **Paper VI**) at the C/3 rate, further confirmed that the cells cycled with electrolytes containing these additives at both room temperature and at an elevated temperature of 55 °C demonstrated a higher overall discharge capacity and CE. This suggests that the incorporation of these additives in the electrolyte can enhance the performance and lifespan of the cells over extended cycling periods.



**Figure 14.** The discharge capacity as a function of the cycle number for cells containing different concentrations of additives. The results for the baseline electrolytes are depicted along with an error bar representing a standard deviation based on the results from five cells. From **Paper VI**.

The dQ/dV plots (see Figure 5 in **Paper VI**) obtained during the initial charge of the formation cycle were used to observe the decomposition voltages of the electrolyte additives. The 2.1 V (vs. Li<sup>+</sup>/Li) peak likely represents the breakdown of LiDFOB, while the 4.4 V (vs. Li<sup>+</sup>/Li) peak suggests the decomposition of TMSPI.

The XPS analysis (see Figure 15) revealed that the LNMO cathode surface of the cell cycled with electrolyte containing additives had a thicker surface layer compared to the one cycled without additives. This finding aligns with the ICI results, which indicate that the cell with additives had a higher internal resistance than the one without. According to earlier studies, TMSPi tends to react with  $\text{LiPF}_6$  to produce  $\text{LiPF}_x\text{O}_y$  while LiDFOB creates F-B species that reinforce the surface layers that are formed.<sup>68,111</sup> The XPS results for the graphite anode suggest the presence of an SEI layer thicker than 10 nm. The SEI formed by the standard electrolyte was enriched with carbon, while the SEI formed by the electrolyte with additives had a more significant presence of fluorine. The detection of Mn 2p and Ni 2p on the graphite surface indicates that transition metal dissolution had occurred. The intensity of these signals was relatively higher for the graphite electrode cycled with the standard electrolyte, while the degree of Mn dissolution was lower in the case when the cell was cycled with the electrolyte containing additives. These findings suggest that the surface layers formed on the LNMO surface have a beneficial effect.



**Figure 15.** (a) C 1s, F 1s, O 1s, P 2p and Li 1s XPS spectra of the pristine and cycled LNMO cathode in the electrolytes with and without additives. (b) C 1s, F 1s, O 1s, P 2p and Li 1s spectra of the pristine and cycled graphite anode in the electrolytes with or without additives. From **Paper VI**.

These findings highlight the positive role of the dual electrolyte additives, TMSPi and LiDFOB in LP40 electrolyte for application in LNMO-graphite cells. However, TMSPi was found to degrade over time when stored in elec-

trolytes containing  $\text{LiPF}_6$ , a phenomenon that has been observed by other researchers in the past.<sup>109</sup> This degradation must be taken into account to not reduce the beneficial effect of improving cycling stability with aging.

## 5. Conclusions

In conclusion, the research presented in this thesis can be categorized into three distinct sections, with the main objective being to comprehend the degradation phenomena and address the interfacial problems in LNMO cells using diverse mitigation strategies.

In the first section, a novel method, SCPV, is presented that was developed and validated to better understand electrochemical stability of electrolytes in a more realistic and representative manner compared to the traditionally used LSV. Multiple SCPV cycles enable a deeper comprehension of the passivation behavior. The SCPV method has made it apparent that prolonged exposure to higher voltages, such as 4.7 V, results in a greater amount of degradation in the cell. The results also suggest that although SCPV offers an advantage over LSV by not using a fixed voltage scan rate, determining the accurate electrochemical stability range of an electrolyte system is still difficult. One remaining significant challenge with this method, similar to LSV, is that the chosen working electrode fails to effectively replicate the LNMO electrode, thereby disregarding any impacts arising from for example the surface area and catalytic properties. Additionally, this technique does not separate any reductive electrolyte decomposition or any charges that may arise from binder decomposition. Nevertheless, this method was found to be practically more useful than LSV in quantifying the electrochemical stability of battery electrolytes.

The second section of the thesis involves the analysis of two different binders and a comparison of their electrochemical performances with that of the more conventional binder systems. Following the successful approach of using PAN as a binder in negative electrodes and taking into account its widely acknowledged oxidative stability, the role of PAN as a binder in LNMO electrodes was investigated. The performance of LNMO cells was, however, negatively impacted by the degradation of PAN, which was more pronounced in cells with a higher concentration of binders. Secondly, PAA, a water-based binder, widely studied in many negative and positive electrode chemistries, was evaluated. This investigation focused on studying PAA in relatively thick LNMO electrodes. The subpar cell performance observed was mainly attributed to the inhomogeneous distribution of the binder and higher internal resistance of PAA-based cells, which resulted in poor initial discharge capacities compared to CMC-based cells. The results from this part of the thesis highlight that using functional binders to improve cell performance remains a

challenging strategy, which requires a careful selection of materials that do not cause additional problems within the cell. For example, the nitrile group in PAN appears to react electrochemically, while the carboxyl group in PAA may form hydrogen bonds within the polymer matrix, leading to poor distribution and/or agglomerations. Thereby, the surface chemistry of the LNMO electrodes did not improve, and seems to instead be dominated by N- or O-rich species, generating more rapid capacity fading of the corresponding cells.

The primary focus of the third section of this thesis is to explore and examine potential electrolyte components and compositions for application in LNMO-graphite full cells. The overall goal of all three electrolyte studies was to determine whether it is possible to improve the stability of the interphases at both the cathode and anode and thereby improve the overall performance of the cell. Compared to LP40, the ionic liquid-based electrolyte, the sulfolane-based electrolyte, and the electrolyte containing dual additives (TMSPi and LiDFOB) exhibited enhanced cycling stability.

The ILE demonstrated lower degradation and greater oxidative stability than LP40, as evidenced by SCPV. XPS analysis revealed that the ILE also formed robust, predominantly inorganic surface layers on the LNMO cathode, which helped to stabilize the electrode. The findings of the sulfolane study indicate that the sulfolane electrolyte experiences more degradation at higher potential, which contradicts previous reports that suggested it had higher oxidative stability. Nonetheless, it was found that the CEI was hydrocarbon-rich and contained TFSI based species, while the SEI was LiF-rich, and these properties helped to reduce any further electrolyte degradation. Whereas in the additives study, the combination of the two additives was observed to produce interphase layers predominantly consisting of inorganic species, resulting in a significant suppression of electrolyte degradation. While these systems have shown progress, further research is needed to overcome the limitations such as the gradual capacity fade in all of these systems, the roll-over failure observed using the ILE, and the lifetime limit of TMSPi that currently prevent their practical application.

Literature describes various methods to address the capacity fading issue seen for LNMO cells. However, as shown in this thesis, there still exist a gap in our knowledge regarding the understanding of the overall cell chemistry. Although several factors simultaneously impact the cell performance, the ineffective outcomes of the binder studies raise doubts regarding the usefulness of experimenting with organic species like binders, especially considering the favorable outcomes from electrolyte studies that indicate CEI layers formed on the LNMO electrode consist mostly of inorganic materials. These seem to aid in the formation of a more robust nature of the CEI than the organic species, which appear to be more poorly passivating. Interestingly, the concept of applying inorganic coatings using materials like  $\text{Al}_2\text{O}_3$  onto LNMO through techniques such as atomic layer deposition has been explored, revealing that other types of drawbacks are associated with such approaches.<sup>112</sup> Coating the

LNMO powder or the LNMO electrode with more fluorine-containing species, rendering LiF, have on the other hand been shown to enhance the passivation behavior of the LNMO cell. While this is a possible next step for the stabilization of LNMO, this approach nonetheless raises sustainability concerns.

In the context of LIBs, LNMO is a promising candidate for next-generation batteries, especially for EVs. Tailoring the chemistry of the CEI layer for its robustness and inertness should therefore be an even stronger focus in the future, since this is key for making this material reach its commercial stage. The observations made in this thesis can hopefully serve as references for future development of the LNMO interphase chemistry, and the methodologies developed can be vital tools for electrolyte characterization. There are tremendous gains to make when progressing towards the realization of LNMO.

## 6. Sammanfattning på svenska

Enligt 2020 års årliga klimtrapport från 'National Oceanic and Atmospheric Administration' i USA var årtiondet 2011-2020 det varmaste uppmätta någonsin. År 2017 var uppvärmningen som orsakats av mänsklig aktivitet  $1\text{ }^{\circ}\text{C}$  högre än de förindustriella nivåerna, och ökade samtidigt med en hastighet av  $0,2\text{ }^{\circ}\text{C}$  varje årtionde. Till följd av den alarmerande takten av global uppvärmning och klimatförändringar antogs Parisavtalet som presenterar ansträngningar för att begränsa den globala uppvärmningens temperatur till under  $1,5\text{ }^{\circ}\text{C}$ .

Koldioxid som produceras från förbränning av fossila bränslen, så som kol, naturgas och olja är en av de främsta växthusgaserna som bidrar till den globala uppvärmningen. Genom att använda batterier för elektrokemisk energilagring kan förnybara energikällor bli ett mer pålitligt alternativ, vilket är en lösning som blivit populär de senaste decennierna i och med den ökande efterfrågan på energi. De är särskilt användbara för portabel energilagring i elektriska fordon, som ett alternativ till fossila bränslen, som bensin och diesel.

Ett batteri är baserat på elektrokemiska reaktioner, dvs. en reduktion där en jon eller molekyl tar upp en elektron, och en oxidation där jonen eller molekylen istället lämnar ifrån sig en elektron. Batterier består av en positiv elektrod, en negativ elektrod, en elektrolyt och en separator som fysiskt separerar elektroderna. I detta sammanhang är det uppladdningsbara litiumjonbatteriet (LIB) välkänt för sin höga energi- och effekttäthet, jämfört med andra batterityper. Detta gör att dessa batterier håller längre och levererar energin snabbare, något som är attraktivt för användning inom elfordonsindustrin. Det gör material som  $\text{LiNi}_{0,5}\text{Mn}_{1,5}\text{O}_4$  (LNMO) attraktiva, eftersom de verkar vid en hög spänning ( $4,7\text{ V}$  mot  $\text{Li}^+/\text{Li}$ ) vilket gör att batteriet får en relativt hög energitäthet.

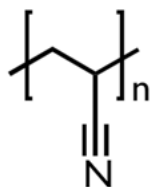
Utöver energitätheten finns det ett flertal faktorer som gör LNMO till ett attraktivt material för batterier. Genom de 3D-litiumjondiffusionskanaler som finns i strukturen hos LNMO möjliggörs höga urladdningshastigheter och därmed snabbbladning. Samtidigt innehåller materialet ingen kobolt, en dyr råvara som är giftig för människor och är förknippat med etiska problem kring dess utvinning. LNMO innehåller även en relativt låg mängd nickel, vilket är ytterligare en dyr råvara. Det finns dock nackdelar med materialet som gör det svårt att använda kommersiellt. De elektrolyter som används i LIBs oxideras vid höga spänningar, och övergångsmetallerna i katoden, mangan och nickel,



tenderar att lösas upp i elektrolyten. Detta gör att kapaciteten avtar med tiden, särskilt vid höga temperaturer.

Potentialen vid vilken elektrolyten oxiderar vid den positiva elektroden kallas den oxidativa stabiliteten och uppmäts ofta experimentellt med hjälp av linjär svepvoltammetri (LSV). Dock har metoden sina begränsningar och leder ofta till en överskattning av elektrolyternas oxidativa stabilitet. I **Papper I** utvecklas och valideras en ny teknik kallad syntetisk laddnings-urladdnings-voltammetri ('synthetic charge-discharge profile voltammetry', SCPV) genom mätningar på ett antal elektrolyter. Metoden är baserad på att efterlikna spänningen hos det aktiva materialet, i detta fall LMNO, vid laddning och urladdning. Detta gör det möjligt att utvärdera den oxidativa stabiliteten mer noggrant för att kunna redogöra för potentiella förändringar vid gränssytan av elektroden och elektrolyten.

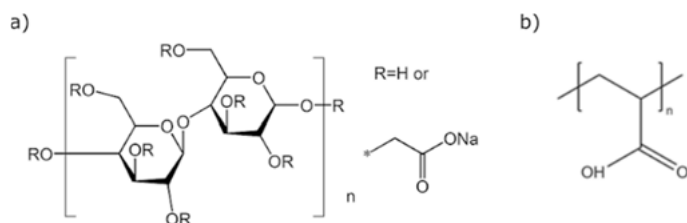
För att motverka svårigheterna hos LNMO-celler är det viktigt att ha ett stabilt ytlager på elektroderna. Bindemedel i elektroden påverkar denna gränssyta, som för katoden kallas katod-elektrolyt-gränssyta ('cathode electrolyte interphase' CEI). Bindemedel är polymera material som binder ihop det aktiva materialet i elektroden. Eftersom polyakrylnitril (PAN) (Figur 16 visar den kemiska strukturen av PAN) har en välkänd oxidativ stabilitet användes PAN som bindemedel i LNMO-elektroder i **Papper II**. Celler med olika koncentrationer av PAN i elektroderna undersöktes, där en ökad koncentration av PAN visade sig leda till en snabbare avtagande kapacitet. Det har visats att PAN försämrar och skapar resistiva skikt i katoden. Den avtagande kapaciteten i celler med PAN-baserat bindemedel analyserades med ett antal karakteriseringstekniker, så som Intermittent Current Interruption (ICI) som används för att kontrollera resistansförändringar i cellen under användning. Även fotoelektronspektroskopi (XPS) användes för att undersöka förändringar i den kemiska kompositionen i elektroden. Överraskande nog indikerade resultaten från XPS mätningarna att det bildats fasta ytlagersprodukter från PAN på ytan av LNMO-elektroden, vilket motsade den initiala hypotesen.



**Figur 16.** Kemiska strukturer av PAN

**Papper III** baserades på en liknande hypotes som i **Papper II**, men baserat på ett annat vattenlösligt bindemedel, polyakrylsyra (PAA). Karboxylgrup-

perna i PAA förväntades bilda starka bindningar på ytan av LNMO-elektroden, vilken då undviker skadlig kontakt med elektrolyten, som i sin tur minimerar oxidationen av elektrolyten och andra oönskade sidoreaktioner. De elektrokemiska resultaten i denna studie jämfördes med ett annat väl studerat vattenbaserat bindemedel, natriumkarboxymetyl-cellulosa (CMC). Figur 17 visar de kemiska strukturerna för PAA och CMC. De PAA-baserade cellerna med tjocka LNMO-elektroder visade på svaga elektrokemiska resultat, framförallt i de första cyklerna, vilket korrelerades med en ojämn fördelning av bindemedlet i elektroden och hög intern resistans. Detta betonar vikten av materialens kompatibilitet vid användning av tjockare elektroder och kravet att fokusera på industriella krav.



**Figur 17.** Kemiska strukturer av a) CMC b) PAA

**Papper IV, V och VI** i denna avhandling undersöker olika elektrolyter i LNMO-grafit celler. **Papper VI** prövar användningen av en jonvätska kallad N-Propyl-N-metylpyrrolidinium-bis(fluorsulfonyl)imid (PYR<sub>13</sub>FSI) tillsammans med ett 1,2 M litumbis(fluorsulfonyl)imid (LiFSI) salt som elektrolyt för LNMO. Joniska vätskor är föreningar som endast innehåller joner, med en smältpunkt under 100 °C. Trots att den höga viskositeten hos den joniska flytande elektrolyten ('ionic liquid electrolyte', ILE) kan begränsa dess förmåga att fungera vid högre cyklingshastigheter under normala temperaturer, så upptäcktes det att LNMO-grafit celler visade förbättrad cyklingsprestanda vid både 20 °C och 45 °C med ILE än med LP40 (1 M litiumhexafluorofosfat (LiPF<sub>6</sub>) i 1:1 etylenkarbonat och dietylenkarbonat (EC:DEC))-baserad elektrolyt. ILE observerades ha lägre nedbrytning än LP40 och även stabilisera katten med framförallt oorganiska komponenter.

I **Papper V** testades ett etylenkarbonat (EC)-fritt lösningsmedel, sulfolan, med LiFSI-salt. Under den första cykeln visade sulfolanelektrolyten mer degradering än för den konventionella karbonatbaserade elektrolyten. Trots det visade resultaten bättre cyklingsprestanda. Den bättre elektrokemiska prestandan förklarades med stabilare ytlagerskikt som bildats på både anod och katod.

Eftersom de konventionella karbonatbaserade elektrolyterna inte är stabila vid den elektrokemiska potentialen av LNMO, tillsätts ytterligare elektrolytkomponenter som kallas additiv för att degradera före elektrolyten och således bidra till bildning av mer stabila ytlagerskikt på elektrodytan, vilket i sin tur

förhindrar ytterligare elektrolytdegradering. **Papper VI** undersöker effekterna av att tillsätta två olika elektrolytadditiv, tris(trimetylsilyl)fosfit (TMSPi) och litiumdifluor(oxalato)borat (LiDFOB), till den konventionella karbonatbase-rade elektrolyten. Studien undersöker effekten av dessa tillsatser på elektrokemisk cyklingsstabilitet samt stabiliteten av ytlagret. Bland de olika koncentrationerna av tillsatser som testades visade 1 wt.% TMSPi och 2 wt.% LiDFOB i LP40 bättre elektrokemisk prestanda i LNMO-grafitceller vid både rumstemperatur och vid en högre temperatur. TMSPi bidrog till att bilda ett fördelaktigt gränsskikt i LNMO, medan LiDFOB spelade en fördelaktig roll i bildandet av gränsskiktet i grafitelektroden.

Sammanfattningsvis har denna avhandling visat på försök att förklara några av nedbrytningsmekanismerna hos LNMO katoder och har utforskat olika strategier för att dämpa dem. Olyckligtvis har studierna kring bindemedlen visat verkningslösa resultat vilket har indikerat att användning av sådana organiska föreningar för att förbättra gränsskikten har varit mindre givande. Samtidigt har studien på elektrolyter visat något positiva resultat, och föreslår att de ledande oorganiska sorterna bidrar till bildandet av gränsskikt som kan bidra med förbättrade elektrokemiska resultat.

## Summary in English

According to the 2020 Annual Climate Report by the National Oceanic and Atmospheric Administration in the U.S, the 2011-2020 was the warmest decade on record. In 2017, the global average increase in total surface air and marine surface temperatures caused by human activity surpassed pre-industrial levels by approximately 1 °C, with a growth rate of 0.2 °C per decade. Given the alarming rate of global warming and climate change, the Paris Agreement on climate change proposed efforts to limit global warming temperature to below 1.5 °C.

Carbon dioxide produced from the burning of non-renewable energy sources such as fossil fuels, including coal, natural gas, and oil, is one of the main culprits for greenhouse gases causing global warming. The use of batteries for electrochemical energy storage has gained popularity in recent decades in response to the growing demand for energy. They are extensively utilized for portable energy storage, such as in electric vehicles, as an alternative to traditional fossil fuels like gasoline and diesel.

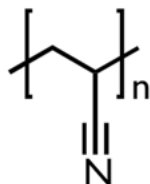
A battery operates through electrochemical reactions, i.e., reduction, where an ion or molecule gains an electron, and oxidation, where an ion or molecule loses an electron. It consists of a positive electrode, negative electrode, electrolyte, and a separator physically separating the electrodes. In this context, the rechargeable lithium-ion battery (LIB) is known for its high energy density and power density compared to other battery chemistries. Batteries with high energy and power densities are attractive for use in electric vehicle applications because they last longer and deliver energy more quickly. This is why  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) positive electrode batteries are intriguing, because they operate at a high voltage (4.7 V vs.  $\text{Li}^+/\text{Li}$ ) meaning that they have a reasonably good energy density.

LNMO cells are an attractive battery option due to their fast charging and high discharge rates, which are enabled by the 3D-lithium ion diffusion channels in their structure. Additionally, they do not require cobalt, which is costly, toxic to humans and ethically problematic. Moreover, these batteries have a relatively low amount of nickel content, which is another expensive metal. However, the decomposition of standard LIB electrolytes at high voltages, as well as the dissolution of transition metals like manganese and nickel from the cathode, cause rapid capacity fade, particularly in full cells and at high temperatures. These drawbacks make the commercial implementation of these cells challenging.

The potential at which the electrolyte oxidises at a positive electrode, called the oxidative stability of a battery electrolyte, is often experimentally estimated using a technique called linear sweep voltammetry (LSV). LSV is not without limitations and often leads to an overestimation of the oxidative stability of electrolytes. In **Paper I**, a novel technique called synthetic charge-discharge profile voltammetry (SCPV) is developed and validated using a few

liquid electrolytes. SCPV is based on mimicking the charge-discharge voltage profile of an active material, in this case LNMO, in order to evaluate the oxidative stability by more accurately accounting for potential changes at the electrode-electrolyte interphase.

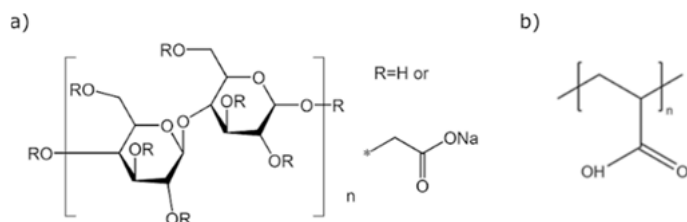
One way to alleviate challenges with LNMO cells is to have a stable electrode-electrolyte interphase. The surface chemistry of the electrode, and thus the electrode-electrolyte interphase, or cathode electrolyte interphase (CEI) in the case of positive electrodes like LNMO, can be greatly influenced by the binders used in the electrode. Binders are polymeric materials generally used to bind the active materials together in an electrode. Considering its generally well-known oxidative stability, polyacrylonitrile (PAN) (Figure 18 shows the chemical structure of PAN) was utilised as a binder in LNMO electrodes in **Paper II**. Cells with various PAN concentrations in the electrode were investigated. However, it was observed that cells with higher PAN concentrations exhibited faster capacity fading. It has been demonstrated that PAN deteriorates and creates resistive layers within the cathode. The capacity fade in cells based on PAN binder was studied using several characterization techniques, including intermittent current interruption (ICI) to monitor resistance changes in the cell while the cell is operating and X-ray photoelectron spectroscopy (XPS) to detect chemical composition changes in the electrode. Surprisingly, XPS results showed the presence of solid PAN decomposition products on the surface of the LNMO electrode, which contradicted the initial hypothesis.



**Figure 18.** Chemical structure of PAN

**Paper III** investigated a similar hypothesis as **Paper II** but with a different water-soluble binder, polyacrylic acid (PAA), to evaluate its effect on the performance of the electrode. The carboxyl functional groups present in PAA were hypothesized to form strong bonds with the LNMO surface and avoid detrimental contact with the electrolyte, minimizing electrolyte oxidation and other undesirable side-reactions. The electrochemical results in this study were compared with another well-studied water-based binder: sodium carboxymethyl cellulose (CMC). Figure 19 shows the chemical structures of both PAA and CMC. Poor electrochemical performance with PAA based cells, especially in the initial cycles, observed in thick LNMO electrodes was corre-

lated with inadequate binder distribution in the electrode and high internal resistance, emphasizing the necessity of material compatibility at higher electrode loadings and underscores the need to focus on industrial requirements.



**Figure 19.** Chemical structures of a) CMC b) PAA

**Papers IV, V, and VI** in this thesis explore different liquid electrolytes tested in LNMO-graphite full cells. **Paper IV** examines the potential use of an ionic liquid called N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR<sub>13</sub>FSI) with 1.2 M lithium bis(fluorosulfonyl)imide (LiFSI) salt as an electrolyte for LNMO system. Ionic liquids are compounds comprising only ionic species, with a melting point below 100 °C. Although the high viscosity of the ionic liquid electrolyte (ILE) may restrict its ability to function at faster cycling rates under normal temperatures, it was discovered that LNMO-graphite cells exhibited improved cycling performance at both 20 °C and 45 °C when using the ILE as compared to using a LP40 (1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in 1:1 ethylene carbonate and diethylene carbonate (EC:DEC)) electrolyte. The ILE was observed to have less degradation than LP40 and it was found to stabilize the cathode with mainly inorganic components.

In **Paper V**, an ethylene carbonate (EC)-free solvent, sulfolane, with LiFSI salt was tested. During the first cycle, the sulfolane electrolyte showed more degradation than the conventional carbonate-based electrolyte. However, the sulfolane electrolyte-based LNMO-graphite cells exhibited better cycling performance. The better electrochemical performance was correlated with more stable interphase layers formed on both the anode and cathode interphase layers.

Since the conventional carbonate-based electrolytes are not stable at the operating voltages of LNMO, additional electrolyte components called additives are added to decompose before the electrolyte and help form better and more stable interphase layers on the electrode surface, preventing further electrolyte degradation. **Paper VI** investigates the effects of adding two different electrolyte additives, tris(trimethylsilyl)phosphite (TMSPi) and lithium difluoro(oxalato)borate (LiDFOB), to the conventional carbonate-based electrolyte. The study examines the impact of these additives on electrochemical cycling stability and interphase stability. Among the various concentrations of

additives tested, 1 wt.% TMSPi and 2 wt.% LiDFOB in LP40 showed better electrochemical performance in LNMO-graphite cells at both room temperature and at a higher temperature. TMSPi helped in the formation of a beneficial interphase layer in LNMO, while LiDFOB played a beneficial role in the formation of the interphase layer in the graphite electrode.

In conclusion, this thesis has made efforts to explain some of the degradation phenomena in LNMO cathodes and has explored various strategies to mitigate them. The studies on binders have, unfortunately, shown largely ineffective outcomes, indicating that experimenting with such organic species to improve the interphase layers is less fruitful. On the other hand, the studies on electrolytes have shown fairly positive results, and suggest that the predominant inorganic species contribute to the formation of interphases that can provide improved electrochemical results.

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