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LNMO as a cathode material in Li-ion batteries: Reasons for capacity fade and measures taken to prevent it

KJ2900 - Bachelor's project

Bachelor's project in Chemistry
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May 2023

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ABSTRACT

Lithium nickel manganese oxide, LNMO, is a promising candidate as cathode material in Li-ion batteries (LIBs) due to its high energy density. Batteries with LNMO can experience capacity fade over time due to structural and chemical degradations that occur, as well as different interphases with the electrolyte. The degradation mechanisms of LNMO are studied intensively to be able to improve the performance and reliability of these batteries. Some of the strategies are protective coatings to mitigate structural degradation, modifications to the electrode composition to improve the stability of LNMO, and choosing suitable electrolytes for LNMO's high operating potential of 4.7 V. Optimization of the battery design to reduce the formation of a cathode-electrolyte interface (CEI) and solid-electrolyte interphase (SEI) layer on the surface of LNMO is being researched as a possible counter measure for the capacity fade. The use of additives such as glyceryl triacetate (GT) can form a stable CEI film on the surface of LNMO, reducing the electrolyte interphase parasitic reaction and protect LNMO. Al_2O_3-coating will act as an artificial SEI on the anode, stabilizing the SEI during cycling and suppress electrolyte decomposition.

SAMMENDRAG

Lithium nikkel manganoksid (LNMO) er en lovende kandidat som katodemateriale i Li-ion batterier (LIBs) på grunn av sin høye energitetthet. Batterier med LNMO som katodemateriale kan oppleve kapsitetstap over tid grunnet strukturelle og kjemiske nedbrytninger som oppstår, samt dannelse av ulike grenseflater med elektrolytten. Nedbrytningsmekanismene til LNMO studeres intensivt for å kunne forbedre ytelsen og påliteligheten til disse batteriene. Noen av strategiene er beskyttende belegg for å redusere strukturell nedbrytning, modifikasjoner av elektrodesammensetning for å forbedre stabiliteten til LNMO, og valg av egnet elektrolytt for LNMOs høye cellepotensial på 4,7 V. Optimalisering av batteridesignet for å redusere dannelse av katode-elektrolytt grenseflate (KEG) og faststoff- elektrolytt grenseflate (FEG) lag på overflaten av LNMO blir forsket på som et mottiltak for kapasitetstap. Ved bruk av tilsetningstoffer som glyceryl triacetate (GT) kan det dannes en stabil KEG-film på overflaten av LNMO, som reduserer elektrolyttsammensetningens parasittiske reaksjoner og beskytter LNMO. Et tynt belegg med Al_2O_3 vil kunne virke som en kunstig FEG, som stabiliserer FEG under sykling og undertrykker elektrolyttdekomponering.

CONTENTS

ABBREVIATIONS

List of all abbreviations in alphabetic order:

- **BE** Base Electrolyte
- **BVS** Bond Valence Sum
- **CEI** Cathode-Electrolyte Interphase
- **FEC** Fluoroethylene Carbonate
- **FEG** Faststoff-Elektrolytt Grenseflate
- **GT** Glyceryl Triacetate
- **IL** Ionic Liquid
- **ILE** Ionic Liquid Electrolyte
- **KEG** Katode-Elektrolytt Grenseflate
- **LIB** Lithium Ion Battery
- **LiPAA** Lithium Polyacrylate
- **LMO** $LiMn_2O_4$
- **LNMO** $LiNi_{0.5}Mn_{1.5}O_4$
- **PA** Proponic Anhydride
- **PFPPS** (PentaFluoroPhenylPropyl)trimethoxySilane
- **SEI** Solid-Electrolyte Interface
- **VC** Vinylene Carbonate

CHAPTER

ONE

INTRODUCTION

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising cathode material to be used in lithium-ion batteries (LIBs). It is a high-capacity cathode material that offers a combination of high energy density and good power capability as discussed by Mathiram, Chemelewski and Lee [1]. In addition, LNMO is relatively cheap and environmentally friendly because it does not contain toxic heavy metals such as cobalt. LNMO is known to undergo different types of degradations over time, like the dissolution of manganese, discussed by N. Pieczonka *et al.* [2]. The degradations that occur decreases its performance, and the most common are structural degradation and surface degradations. Formation of unstable solid-electrolyte interphase (SEI) films on the anode and cathode-electrolyte interphase (CEI) film between cathode and electrolyte results in deteriation of the stability of LNMO and electrolyte [3]. To prevent degaradations and capacity fading, various electrolytes or surface treatments have been studied to further enhance the practical application. Zhou *et. al.* discusses the use of a 4d transition metal as a dopant into LNMO as an enhancement since 4d orbitals favors wider conduction bands than that of 3d orbitals [4]. Yan *et al.* studied the affects of Al_2O_3 coating to form a stable and artificial CEI on the cathode, scavenging both the acid from the electrolyte and may form a effective protective layer on the electrode [5].

In this project, reasons for capacity fade and measures taken to prevent this from happening with LNMO are going to be discussed. I aim to take a look at the cubic spinel structure of LNMO and present relevant theory about its structure and look at why the structure gives such good electrochemical properties. The various degradation mechanisms will be discussed, such as the chemical degradations and structural degradations that occur. Structural degradations are formation of various interphases between the electrolyte and anode/cathode. I will also discuss the various types of electrolytes used commercially today, as well as electrolytes used to improve the cycle life of LNMO. Lastly, I will discuss electrolyte decomposition, and how people have attempted to prevent degradations of the material.

CHAPTER

TWO

THEORY

2.1 Lithium-ion batteries and LNMO as a cathode material

Lithium-ion batteries (LIBs) are extensively employed as power sources in a wide range of applications because of their high energy densities, high coulombic efficiencies, low self-discharge features, and a range of chemical potentials accessible with diverse electrode designs. Commercial LIBs are mainly based on the Li^+ intercalation mechanism, but studies have shown that these batteries cannot offer the high-charge capacities of >200 $mAhg^{-1}$ required for particular applications [6]. Intercalation is the reversible insertion of an ion into the layers of a host material. Deintercalation on the other hand is the process of removing a guest ion from the layers of a host material through a reversal of the intercalation process. Because of this, researchers are showing a lot of interest in high energy density battery technologies, that are Li-rich and Ni-rich transition metal oxides. For example, these materials are high voltage spinels which benefit from high energy density, due to relatively high capacity and a high operating potential. But these materials are not commercialized yet because of some crucial issues. These issues are phase transitions, electrolyte decomposition, formation of an unstable solid-electrolyte interphase (SEI), volume expansion, surface reconstruction of active material particles, and electrode degradation during charge/discharge [6].

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has a high potential plateu of 4.7 V[1] and a theoretical specific capacity of 146.7 $mAhg^{-1}$. The specific capacity measures the electrochemical energy storage capacity of a battery or electrode, and measures the amount of charge that a battery or electrode can store per unit of mass or volume. The theoretical energy density of LNMO in LIB is 650 $Whkg^{-1}$, which is around 20-30% more than the cathode materials commercialized today [7, 8]. In a study by Kim *et al.* they found that at a low current density of 20 mAg^{-1}, a C-rate[2] of $\frac{1}{7}$C, LNMO showed a discharge capacity of 138 $mAhg^{-1}$ for 50 cycles. Turning up the rate to 3C, a gradual capacity loss could be observed, and the capacity retention

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[1] The operating voltage of $LiCoO_2$ which was primarily used is 3.7 V [4].

[2] C-rate is the rate at which a battery is charged or discharged relative to the battery's capacity in amperes. A C-rate of 1C means that a battery is charged or discharged in 1 hour.

was 84% after 50 cycles [9].

2.2 Structure of LNMO

To get a deeper understanding about the degradation of LNMO, its structural properties needs to be studied. LNMO can adapt two variants of the cubic spinel structure; an ordered structure with the $P4_332$ space group where Ni- and Mn-ions occupy $4b$ and $12d$ octahedral sites, respectively. The Li-ions occupy $8c$ sites and O-ions occupy the $8c$ and $24e$ sites. The second crystal structure is the disordered cubic spinel structure with the $Fd\overline{3}m$ space group. Here, Ni- and Mn-ions are randomly arranged on the $16d$ octahedral sites. The Li- and O-ions occupy the $8a$ and $32e$ sites, respectively [10]. The 3D Li-ion pathways present in the framework of the spinel structure allow for facile ion transport and can potentially enable high rate performance [8].

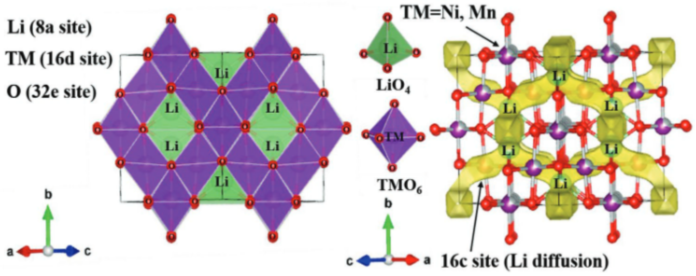

Figure 2.2.1: Illustration of the structure of LNMO. To the left is the disordered crystal structure of LNMO with $Fd\overline{3}m$ spacegroup. To the right is the 3D Li-atom diffusion pathway with the isosurface of ΔBVS[3] of 0.2 along $8a$-$16c$-$8a$-$16c$ zigzag path in the bulk structure of LNMO [11].

Figure 2.2.1 shows the 3D structure of LNMO with the $Fd\overline{3}m$ space group. The difference in cation ordering of Mn^{4+}- and Ni^{2+}-ions in the disordered $Fd\overline{3}m$ space group versus the ordered $P4_332$ space group leads to better electrochemical performance for the disordered phase than the ordered phase [12]. This is because of higher Li^+ diffusion coefficients. In addition, the ordered LNMO contains more of the redox couple of $Mn^{3+/4+}$. This leads to production of more Jahn-Teller ions, Mn^{3+}, compared to the disordered space group, which is considered to only contain Mn^{4+} in its oxide matrix [9]. As discussed by J. Yang *et al.*, it has been proven that the presence of Mn^{3+} affects the electrode performance. In theory, the larger ionic radius of Mn^{3+} compared to Mn^{4+} results in an expanded lattice, that benefit fast Li^+ diffusion. However, the drawback comes from the Jahn-Teller effect. The Jahn-Teller effect is a phenomenon that occurs making ions with degenerate electronic states distort their geometry to remove the degeneracy and lower their energy. The presence of degenerate orbitals in an ion leads to higher energy than it would have if the orbitals were not degenerate. The ion then lowers its energy by undergoing a geometric distortion and removes the degeneracy of the orbitals [13]. Mn^{3+} can induce structural distortion and dissolve into the electrolyte via

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[3] BVS relates the bond lengths around a metal center to its oxidation state. It is the sum of experimental bond valences incident at a given ion.

disproportionation reaction ($2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$), which in turn affects the capacity retention [10, 14].

2.3 Capacity fade

Capacity fade refers to the gradual loss of the ability of a battery, or other energy storage systems, to hold a charge and deliver energy over time. Reasons for capacity fade depend on different factors such as changes in temperature, chemical reactions during charging and discharging, and physical breakdown of the battery's components. The 3D diffusion channels present in the cubic spinel structure of LNMO allows fast lithiation[4] and delithiation[5] kinetics in the crystal structure, and contributes to excellent rate capability and render the material suitable for high power applications. But the oxidative decomposition of electrolyte at higher voltages, dissolution of transition metals during cycling and severe capacity fade at elevated temperatures are major challenges for commercialization of LNMO [15].

2.3.1 Chemical degradation

Chemical degradation (thermal decomposition), is a process of extensive chemical species change due to heat [17]. Carbonate electrolyes with additives are the electrolytes most frequently used today. These carbonate electrolytes are for example ethylene carbonate (EC) and diethyl carbonate (DMC). Additives used with the carbonate electrolytes are fluoroethylene carbonate (FEC) and vinylene carbonate (VC). FEC and VC has high flammability and volatility [18]. Deng *et al.* discusses that at a temperature close to 55°C, the electrolyte oxidation becomes severe. During the charge-discharge cyclic process, the cathode electrolyte interphase (CEI) film is constantly thickening and the spinel LNMO undergoes severe capacity fade [19]. By thermally treating LNMO above 700°C results in oxygen deficiency ($LiNi_{0.5}Mn_{1.5}O_{4-\mu}$) or a nickel deficiency ($LiNi_{0.5-x}Mn_{1.5+x}O_{4-\delta}$). Both results induce partial reduction of Mn^{4+} to Mn^{3+}, compensating for the charge balance due to the nickel and oxygen deficiencies [20]. This phenomena can be summarized by looking at the disproportionation reaction, indicating that the more Mn^{3+} present, the more Mn dissolution will happen [21].

2.3.2 Structural and surface degradation

In electrochemistry, degradation refers to the gradual loss of performance or functionality of an electrochemical system over time due to various processes that occurs during its operation. Cui *et al.* discuss how capacity fade occurs due to redox reactions taking place. They demonstrate that for LNMO, the capacity fade is mainly due to the plateau where Ni redox reactions take place. Manganese dissolution is one of the main factors underlying the deterioration of spinel structure. When the cells are charged at high potentials over 4.7 V, two plateaus appear.

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[4] Lithiation is the process where Li-ions diffuse to and react with the cathode [16].

[5] Delithiation is the process where Li-ions leave the cathode under an external field [16].

One plateau correlates to the oxidation of manganese (4 V) and the second to $Ni^{4+} \rightarrow Ni^{3+} \rightarrow Ni^{2+}$ (4.7 V) [22]. Due to this phenomena, Cui *et al.* concludes that the contribution of manganese to the capacity loss is negligible. This is also backed up by Pieczonka *et al.*, who researched the effect of manganese reduced at Li-metal anodes, leading to severe capacity fade due to manganese and lithium dissolution [2].

The typical configuration of the LIB is electron migration and Li-ion diffusion that inevitably takes place on the surface of active material particles and various interfaces between each component. The 3D Li-ion diffusion network in the crystal structure of LNMO makes the kinetics for Li-ion intercalation/deintercalation sensitive to the crystal orientation of the structure. The formation of SEI films on the anode surface, as well as a CEI layer between cathode and electrolyte, seriously deteriorate the stability of LNMO and the electrolyte, leading to poor cycling stability of the LNMO electrode at high work potential (5 V) [3]. The SEI-layer is formed instantaneously upon contact between the metal and the solution. It consists of insoluble and partially soluble reduction products of electrolyte components. The thickness of the SEI layer is determined by the electron- tunneling range, and the layer acts as an interphase between the solution and metal. The properties of SEI is that of a solid electrolyte, having high electronic resistivity [23].

Interfaces between the electrode-electrolyte solution in all kinds of LIBs are intrinsically unstable and therefore require formation of passivating layers to optimalize stable operations. The cathode potential in LIBs commercialized today, like $LiMn_2O_4$ (LMO), operates at a potential of 4.0-4.2 V, making the surface of LMO stable because the electrolyte is thermodynamically stable at this potential. Graphite anodes used in LIBs operates at lower potentials than the cathode, which in turn makes the surface not thermodynamic stable [3, 18]. The graphite anode gets kinetically stabilized from the formation of a SEI. The SEI formation mitigates further reduction reactions of the electrolyte solutions on the graphite anode, making the formation of SEI on graphite a positive phenomena. While the SEI helps the graphite anode, the oxidizing environment of high- voltage cathodes prevents formation of a stable CEI. This leads to inevitable continuous solution oxidation [24].

Ma *et al.* found in their research that the Fermi energy of the two redox couples of Ni^{3+}/Ni^{2+} and Ni^{4+}/Ni^{3+} is beyond the thermodynamic stability area of the commercially available electrolytes, mainly liquid carbonate electrolytes. The surface chemical reactivity of LNMO with the electrolyte could lead to electrolyte oxidation and generate various organic and inorganic products, that could cover the surface of LNMO as a CEI [3]. Stabilizing the CEI to passivate the cathode surface is therefore of increasing importance. LNMO cathodes may develop passivating films in standard electrolyte solutions based on the solvents. In correlation to this, LNMO cathodes and graphite anodes always exhibit stability problems during prolonged cycling, especially during elevated temperatures. This affects the materials capacity fade by the side reactions happening at the cathode, which in turn badly influences the passivation of the graphite anode, resulting in a loss of active Li-ions in the cells [24]. J.-H. Kim *et al.* also researched the capacity loss during cycling because of CEI formation. The Li^+ can be consumed in continuous CEI formation, reducing the amount of active lithium in the cell. LNMO contains a limited amount of lithium, so this mechanism can result in ongoing capacity loss during cycling. A product of this, the LNMO in the full-cell will only be lithiated enough to operate in the high-voltage plateau region (∼4.75 V) without accessing lower voltage plateaus after 110 cycles at ∼4 and 4.68 V [25].

2.3.3 Electrolyte degradation

The most critical barrier for successful commercialization of LNMO in LIBs is the electrolyte decomposition and concurrent degradation reactions at the cathode or electrolyte interfaces at high voltages [26]. Research on different electrolytes is therefore being performed to decrease the formation of CEI film that impede the Li-ion diffusion. $LiPF_6$-based carbonate electrolyte that is commercially used today is very unstable and continuously oxidated at cathode interphase once the voltage is over 4.3 V. Deposition and HF derived from decomposition of the electrolyte leads to resistance of ion transport. HF also increases the electrode-electrolyte interphase layer, as well as promoting transition-metal dissolution in the electrolyte [27]. Another possibility is the use of Silicon (Si) as anode instead of graphite due to its high specific capacity of 3579 $mAhg^{-1}$ vs. 372 $mAhg^{-1}$ of graphite. The Si-anode also shows low delithiation potential with lithium. The problem with Si-electrode is its poor electrode stability caused by volume change (∼280% for Si versus 13.2% for C) during lithiation or delithiation, which limits the amount Si used [18]. Therefore, electrolytes that make a flexible SEI is being researched.

2.4 Various attempts to decrease capacity fade

The conventional carbonate electrolytes used with additives shows stability of Si-anodes through a more stable SEI. To substitute the carbonate electrolytes, ionic liquids (ILs) have been studied as a replacement due to their high thermal and electrochemical stability, high lithium salt solubility, and low flammability as well as low volatility because of very low vapor pressure. Putting these ILs as ioniq liquid electrolytes (ILEs) in LIBs, have shown more and less promising capacities and cycling stability with electrodes consisting of a silicon thick film [18].

Chae *et al.* propose that to reduce electrolyte oxidation, a passiviation film needs to be formed. For the passivation film two conditions should be met for it to successfully operate as a protective layer. The passivating film must be stable against the oxidative decompostion under the LNMO working potential. The film should also be protective against the electrochemical oxidation of electrolytes by fully covering the surface of the electrode. Perfluorinated benzenes contains fluorine atoms, and this meets the first criteria because the fluorine atoms lower the highest occupied molecular orbital level of carbonaceous molecules, resulting in an increased oxidation stability [28]. Other organic molecules with F-atoms within their structure show a high stability against the electrochemical oxidation that occurs. A direct result of the second criteria could suppress electrolyte oxidation.

Then the molecules containing fluorine atoms need to fully cover the electrode surface so that the electrodes are impermeable [28].

Yang *et al.* discusses the possible use of microsized particles to mitigate the side reactions with the electrolyte by lowering the specific surface area of LNMO. Reducing the size of LNMO particles to increase the specific surface area of LNMO decreases the rate capability because the increase of Li^+ diffusion length, L, lengthens the diffusion time from the following equation: $t = L^2/2D_{Li}$[6], allowing Mn dissolution to happen for an extended duration of time, and thus leading to poorer cycling stability [10]. Coating of both the cathode and anode side with Al_2O_3 has been attempted by Yan *et al.*. On the cathode side, the Al_2O_3 coating could modify the interfacial reaction between the cathode and electrolyte and possibly lead to less dissolution of transition metal ions from LNMO. A coating with the right thickness of Al_2O_3 will act as an artificial CEI to suppress electrolyte decomposition and stabilize the CEI when cycling. This reduces the consumption of active Li^+-ions. As an added bonus, the coating can take HF from the electrolyte, forming a stable and effective protective layer on the electrode surface. Al_2O_3 is amphoteric, acting as an acid and a base. The coating scavenges both HF and H_2O from the electrolyte to form hydrated aluminum fluoride structures (e.g. $H_2AlF_5(H_2O)_5$) [5, 29].

Doping of LNMO is also a possible method of improving the stability and cycle life of LNMO. By chosing a 4d transition metal as a dopant could give better stability, cycle life and electrochemical performance. Comparing the 3d and 4d orbital shows that the 4d orbitals favors wider conduction bands with the 2p orbital of oxygen than that of the 3d orbitals due to larger radius of the second-row transition metal ions. Such 4d transition metal could be ruthenium (Ru) as discussed by Zhou *et al.* [4]. Ruthenium (Ru/Ru^{4+}), has an ionic radius of 0.62 Å, so when doped into LNMO, Ru can form stable structures. This is because Ni^{2+} has an ionic radius of 0.69 Å, and Mn-ions have ionic radius of 0.53 Å (Mn^{4+}) and 0.64 Å (Mn^{3+}). Thus when Ru replaces the Ni- ion and Mn-ions it will not modify the crystal structure [4].

Another approach to create a stable electrode-electrolyte interphase for LNMO cathodes is to use polymeric coatings (e.g. lithium polyacrylate, LiPAA). LiPAA acts as a binder and passivation layer during the the electrode fabrication process and donates Li^+- ion to counter the Li^+-ion lost during cycling. On the other hand, the use of aqueous polymeric binders brings unwanted side reactions such as dissolution of Ni and Mn (transition metals) and Li-ion leaching in the aqueous solution [11].

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[6] D_{Li} is the diffusion coefficient of Li^+.

CHAPTER

THREE

DISCUSSION

3.1 Chemical degradation

The performance of a LIB is affected by the cycling temperature. This is because the manganese induce a partial reduction of Mn^{4+} to Mn^{3+} to compensate the oxygen and nickel deficiencies that occur. The Mn^{3+} then dissolves into the electrolyte due to the disproportionation reaction, leading to Jahn-Teller distortion, affecting the capacity retention and decreasing the cycling performance of LNMO [10, 20, 21]. To counter this, Liang *et al.* studied the effect of the particle size of LNMO single crystals, calcinating the LNMO at 850°C, 900°C and 950°C (LNMO-850, LNMO-900, LNMO-950) after a two-step method consisting of an alcohol gel solvent method and a segment sintering reaction. The LNMO-900 material provided a stable structural and chemical stability at elevated temperatures due to a moderate specific surface area. LNMO- 900 had a capacity retention of 87.3% at 1C and 25°C after 500 cycles, and showed unexpected stability at elevated temperatures. After 200 cycles at 55°C and 1C, LNMO-900 showed a capacity retention of 76.65% [21]. The LNMO-850 and LNMO-950 materials has caused side reactions during the initial charge process, resulting in a thicker CEI film. This means that Li^+ are consumed in the film, leading to low couloumb efficiency in the initial cycle and low average capacity during cycles [21].

3.2 Structural and surface degradation

The need for stabilizing CEI and passivating the cathodes in LIBs is of great importance due to the development of high-voltage cathodes (>4.5 V vs. Li) [24]. Tan *et al.* pruposes the use of additives to the electrolyte-solution. In their research, they tested glyceryl triacetate (GT) and propionic anhydride (PA) as additives in a base electrolyte (BE, consisting of 1 mol L^{-1} $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate). The result of testing these different electrolyte samples demonstrated that the capacity retention of the LNMO/Li cell with GT was 84.9% at 1C after 500 cycles, higher than PA (17.6% after 500 cycles) and BE (8.6% after 500 cycles). This indicates that GT was prioritized to oxidate, forming a stable CEI film on the surface of LNMO, and effectively reduce the electrolyte interphase parasitic reaction, protecting the LNMO structure stability, enhancing the cycle performance of LNMO/Li cell [27]. In addition to the impact of Mn-ion dissolution into the electrolyte, the redox couple of Ni^{4+}/Ni^{2+} can oxidize the electrolyte, forming a CEI film on the surface of cathode particles. This impedes the Li-ion diffusion across the LNMO/electrolyte interface [3]. Ma *et al.* found in their research that Cr^{3+} substitution for Ni^{2+} and Mn^{4+} segregated the Ni-ion from the surface bulk and improved the cycling performance of LNMO at 55°C, concluding with Ni-deficiency is beneficial for the stabilization of the electrode/electrolyte interface and decrease of surface resistance [3].

Coating and doping of LNMO has shown a lot of promising results. Coating the cathode side with Al_2O_3 acts on both the cathode side and anode side. Yan *et al.* researched the use of Al_2O_3 coating on LNMO. The Al_2O_3 coated LNMO showed a capacity retention rate of 95.51% after 200 cycles at 1C rate, and a specific discharge capacity of 117.7 $mAhg^{-1}$, much higher than that of pristine LNMO (78.48% and 104.8 $mAhg^{-1}$). This can be explained by at the anode side, the Al_2O_3 coating on the anode, with an optimal thickness, acts as an artificial SEI to suppress electrolyte decomposition, stabilizing SEI during cycling, and in turn reducing the consumption of active Li^+-ions. The coating also reacts with HF from the electrolyte, forming a stable and effective protective layer on the electrode surface. They found in their research that LNMO and mesocarbon microbeans coated Al_2O_3 electrodes showed the best cycling stability with a cycling retention rate of 91.34% after 100 cycles at 0.5C rate during charge and 1C during discharge [5].

Doping could prevent capacity fade. Since the crystal structure remains stable when LNMO is Ru doped, the 4d orbital of Ru could enhance the electrochemical properties of LNMO more than that of the 3d orbitals from Mn. Zhou *et al.* found that the 4% Ru-doped sample showed the best electrochemical properties, in regard to discharge capacity, cycle stability, and rate performance. The sample had an initial discharge capacity of 125 $mAhg^{-1}$ at 0.25C rate, a capacity retention of 92% after 50 discharge/charge cycles. At high current density of 1C, the Ru-doped sample showed a discharge capacity of 103 $mAhg^{-1}$, while un- doped LNMO had only 86 $mAhg^{-1}$. Ru increases the conduction band with the 2p orbital of oxygen, making the doped sample exhibit better electrochemical properties, interlayer spacing and reduces the charge-transfer impedance for the Li- ion exchange [4]. In a research done by Liang *et al.* found similar beneficial results by doping LNMO. They used antimon (Sb), and chemically engineered it into the 16*c* and 16*d* sites at the same time, which suppress the loss of Mn from the material. In their results, they found a theoretical specific capacity of 99% at 1C, maintaining 87.6% (127.4 $mAhg^{-1}$) and 72.4% (105.4 $mAhg^{-1}$) of the initial capacity after 1500 and 3000 cycles. The Sb doped sample also showed a energy density higher than that of LNMO, reaching 668.9 $Whkg^{-1}$[30].

Yang *et al.* discusses the possible use of microsized particles to mitigate the side reactions with the electrolyte by lowering the specific surface area of LNMO. In addition, the formation of the passivating SEI layer on the surface of the electrode prevent electrolyte decomposition, but the SEI layer usually gets broken up by particle dissolution and volume change during cycling [10]. In their research they found that the microsized LNMO in the disordered phase delivered at 5C discharge capacities near 130 mAhg^{-1} and the capacity retention exceeding 90% after 300 cycles. Which is supported by the theory of a decrease in Li$^+$ diffusion length shortens diffusion time, effectively mitigating side reactions with the electrolyte due to lower specific surface area [10].

3.3 Electrolytes

Formation of SEI films happens immediately as the material is put in contact with the solution. The highly reducing conditions from of the anode leads to electrochemical decomposition of the electrolyte, and the passivating SEI layer is formed. Lithium can become trapped within the SEI, making it not able to diffuse. Replacing the graphite anode with another material with higher specific capacity, such as silicon, could mitigate the destructive formation of unstable SEI films that causes electrochemical decomposition of the electrolyte at the anode side. But poor electrode stability caused by the volume changes in silicon upon (de)lithiation, causes challenges to occur [18]. Rogstad *et al.* researched the possible use of ILEs as electrolytes for LIBs with a silicon anode. The studied ILEs were pyrrolidinium, imidazolium and phosphonium cations with bis(fluorosulfonyl)imide (FSI) anion, and pyrrolidinium with bis(trifluoromethanesulfonyl)imide (TFSI) on silicon. They found that at 60°C, cells cycled with the FSI electrolyte performed best at all C rates, even delivering discharge capacities of around 1000 mAhg^{-1} at 2C rate when using the phosphonium based ILE. This could be explained through lower polarization of the cell and lower loss of active material from the more stable and ion conductive SEI that forms. The fact that both the coulombic efficiency and discharge capacity are higher for the FSI electrolyte than the others researched, indicates a better passivating SEI. The Li$^+$ transport properties is highest for this electrolyte at elevated temperatures as well, resulting in high rate performance at elevated temperatures [18].

As previously discussed, the use of fluorine atoms lowers the highest occupied molecular orbital of carbonaceous molecules, increasing the oxidation stability. By covering the entire surface of LNMO it could be possible to suppress the failure modes at the 5 V positive electrode, electrolyte oxidation and film deposition, acid generation and Ni/Mn dissolution [28]. In a study done by Chae *et al.*, they grafted (pentafluorophenylpropyl)trimethoxysilane (PFPPS) onto LNMO. In their work, they found that the PFPPS layer do in fact suppress the electrolyte oxidation in the high-voltage region, leading to higer coulombic efficiency. It also mitigates acid generation, and the metal dissolution decreases. The features allow improved capacity retention and better efficiency all together. At elevated temperatures (up to 60°C), the PFPPS-LNMO retains almost all of its initial capacity after 100 cycles, whilst pristine LNMO loses about 88% of its initial lithiation capacity after 100 cycles [28].

CHAPTER FOUR

CONCLUSIONS

In conclusion, the use of LNMO as a cathode material in LIBs is limited by capacity fade, which can be attributed to chemical, structural, and surface degradation. Chemical degradation occurs due to the dissolution of active material ions into the electrolyte, leading to capacity loss and low cycling performance. Structural and surface degradation are mainly caused by the electrolyte interphase parasitic reaction, which can be addressed by stabilizing the CEI on the surface of the cathode particles. Coating and doping of LNMO cathodes have shown promising results in reducing the degradation of LIBs. The use of additives such as glyceryl triacetate (GT) has been proposed to form a stable CEI film on the surface of LNMO, reducing the electrolyte interphase parasitic reaction and protecting the structure of LNMO. In addition, the use of fluorine atoms and PFPPS coating on LNMO has also shown improvements to the passivating layer's stability. This leads to better coulombic efficiency, better capacity retention, and an overall improved efficiency. Moreover, Al_2O_3 coating acts as an artificial SEI on the anode and suppresses the electrolyte decomposition, stabilizing the SEI during cycling, as well as reducing the consumption of active Li^+-ions. Thermal treatment which causes Ni-deficiency and Ru^{4+} substitution for Ni^{2+} and Mn^{4+} has also been found to be beneficial in stabilizing the electrode/electrolyte interface and decreasing surface resistance, improving the cycling performance of LNMO cathodes. The use of ILEs with FSI and TFSI anions have shown promising results in terms of lower polarization and the formation of a more stable and ion conductive SEI. The findings from various researchers sheds light on the importance of understanding SEI and CEI formation mechanisms to further mitigate capacity fade and improving the cycle life of the high-voltage spinel cathode LNMO.

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