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Satu Kristiina Heiskanen

Nina Laszczynski

Brett L. Lucht

University of Rhode Island, blucht@uri.edu

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Perspective—Surface Reactions of Electrolyte with $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ Cathodes for Lithium Ion Batteries

Satu Kristiina Heiskanen,^{*}  Nina Laszczynski, and Brett L. Lucht^{**z} 

University of Rhode Island, Department of Chemistry, Kingston, Rhode Island 02881, United States of America

Layered metal oxides with high nickel content are commonly used cathode materials in commercial lithium ion batteries due to high capacity and lower cost resulting from higher nickel content and lower cobalt content. Cathodes with increased nickel content suffer from rapid capacity fade due to a combination of thickening of the anode solid electrolyte interphase (SEI) and impedance growth on the cathode after extended cycling. While transition metal catalyzed degradation of the anode SEI has been widely proposed as a primary source of capacity loss, we propose that a related acid induced degradation of the anode SEI also occurs. © 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab981c]



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The most widely utilized cathode materials for lithium ion batteries are layered transition metal oxides. LiCoO_2 was the most frequently utilized cathode material in the first generation of lithium ion batteries. However, there is a significant interest in the use of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) cathodes with high nickel content for advanced lithium ion batteries. The increased Ni content is desirable since it results in improved capacity and reduced cost due to reduction of cobalt content within the cathode material. Conversely, NMC cathodes with higher nickel content have reduced cycling stability.¹ Additionally, there is an interest in increasing the energy density of NMC cathodes by increasing the voltage window from 4.2 V to 4.4 or 4.5 V vs Li/Li^+ . However, cycling NMC cathodes to higher potential also results in a decrease in cycling stability. There have been a significant number of investigations as to the underlying causes of the cycling instabilities of nickel rich NMC or NMC cathodes cycled to high potential. In this perspective, we will review recent reports on the reactions of the surface of the cathode with electrolyte and provide new insight and directions. We wish to acknowledge that there are other aspects of the cathode material which contribute to performance fade which will not be covered in this perspective; these include problems with lithium-nickel cation mixing in NMC materials with high nickel content and increased particle cracking and related increased surface area of cathode particles upon prolonged cycling. These topics have been recently reviewed and we direct the readers to the following Refs. 2, 3.

Current Status

Current lithium ion batteries have excellent cycling stability under standard operating conditions. As the technology has developed, the desire for increased energy density and lower cost has driven interest in cathode materials with both higher capacity and higher cutoff potential. However, this has resulted in a decrease in cycle and calendar life. One of the contributing factors to this performance fade is the reaction of the electrolyte with the surface of NMC cathode materials. However, at this time a strong understanding of the role of electrolyte in performance fade of NMC cathode materials is unclear.^{4–6}

The most common cathode materials utilized in commercial lithium ion batteries are layered metal oxides. While the initial lithium metal oxide of interest was LiCoO_2 , the field has primarily shifted toward mixed metal oxides including Ni, Co, Mn and Al. While $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and related materials have also

been rigorously investigated, this perspective will focus on $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC). Variation in initial capacity of NMC cycled to 4.2 V shows a clear trend to higher capacity with higher nickel content. Upon increasing the nickel content from 33% to 80% capacity increases from 155 mAh g^{-1} to 210 mAh g^{-1} .^{7,8} However, this increase in capacity is coupled with both a slight increase in capacity fade and a larger increase in cell impedance upon cycling. Surprisingly, ex situ surface analysis of NMC cathodes extracted after cycling reveals only small differences in the composition and thickness of the surface films for the NMC cathodes with different nickel contents. The similarity in surface films suggests that the capacity fade and impedance growth is not related to the deposition of electrolyte decomposition products on the NMC cathode surface. Other possible degradation mechanisms include the evolution of oxygen gas and lithium-nickel cation mixing leading to a disordered phase in the cathode material, or surface reconstruction of the cathode material.^{3,9}

The effect of cutoff voltage on NMC materials with different Ni contents has also been studied. Investigation of the cycling performance of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cycled to either a moderate (4.2 V) or high cutoff potential (4.5 V), surprisingly revealed similar capacity fade for the cathodes cycled to the different potentials. However, the impedance growth for cathodes cycled to higher potential is much greater than that for cathodes cycled to lower potential.¹⁰ Electrochemical analysis of cathode-cathode and anode-anode symmetric cells, extracted from cycled full cells, clearly reveals that the impedance growth upon cycling is dominated by the cathode and that the impedance growth is significantly worse for cells cycled to high voltage. In order to develop a better understanding of the source of impedance growth, ex situ surface analysis was conducted. X-ray photo electron spectroscopy (XPS) analysis of the NMC surface reveals that surface metal oxide concentration is lower for cells cycled to 4.5 V than for cells cycled to 4.2 V. This is consistent with the deposition of electrolyte decomposition to generate a thicker surface film for the cathode cycled to 4.5 V. The surfaces of anodes were also analyzed by XPS which suggested that the surface films were very similar for cells cycled to either potential. It was also determined that anodes cycled to either potential contain low concentrations of transition metals but there was no clear trend in transition metal content as a function of cycling potential. Further analysis of the electrodes by infra-red with attenuated total reflectance (IR-ATR) provided supporting results. The surface of cathode cycled to 4.2 V contained only low concentrations of Li_2CO_3 and lithium alkyl carbonates, while cells cycled to 4.5 V contained stronger absorptions characteristic of lithium carbonates along with an additional peak consistent with polycarbonate at 1740 cm^{-1} . The IR spectra of the anodes are very similar for cells cycled to either voltage, consistent with the XPS results. Similar investigations were conducted on $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathodes. Initial capacities were found to be

*Electrochemical Society Student Member.

**Electrochemical Society Member.

^zE-mail: blucht@uri.edu

higher for the cells cycled to higher potential (4.6 V vs 4.3 V).¹¹ Unlike the observations for $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, significantly more capacity fading was observed for cells containing $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cycled to higher potential after 100 cycles. However, similar to observations for $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cells, a significantly larger impedance increase was observed for cells cycled to the higher potential than for cells cycled to the lower potential.

Related investigations have been conducted on cells containing cathodes with higher nickel content. $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cells were cycled to moderate and high potential, 4.2 and 4.6 V respectively (Fig. 1). Cells cycled to higher potential have significantly higher initial capacity, but the capacity fade is more severe than observed for $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ or $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cells.¹² Similar to observations with $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cells cycled to higher potentials have significant increases in cell impedance after cycling. In addition, there are large changes to the dQ/dV plots for the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cells cycled to higher potential. The increased impedance and changes to the dQ/dV plots are likely related to the generation of micro-cracks in the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ particles, as previously reported.³ Ex situ surface analysis of the cathodes extracted from $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cells cycled to moderate and high potential was also conducted via a combination of XPS and IR-ATR, but the surface films were very similar for both cycling profiles suggesting that cathode surface film formation did not correlate with cutoff potential. In an effort to better understand the performance differences, the changes to the electrolyte were investigated. Online Electrochemical Mass Spectroscopy (OEMS) analysis of graphite- $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cells suggests similar quantities of alkyl carbonate transesterification reactions, the conversion of ethyl methyl carbonate to dimethyl carbonate and diethyl carbonate, at both potentials (4.2 V and 4.6 V). However, for cells cycled to 4.6 V, more CO_2 evolution is observed and oxygen evolution is initiated.¹² No oxygen evolution is observed at 4.2 V by OEMS suggesting that cycling to higher potential results in irreversible changes to the bulk cathode materials, as described above. Gas chromatography with mass selective detection (GCMS) analysis of the extracted electrolytes confirms a large increase in transesterification products on first cycle with minimal increases in transesterification after the first cycle. However, the concentration of transesterification products is similar for cells cycled to both 4.2 and 4.6 V, consistent with the OEMS results. Ex situ surface analysis of the anodes reveals a thicker anode SEI with cells cycled to higher voltage, consistent with transition metal dissolution and damage to the anode SEI resulting in subsequent SEI thickening. In addition, an increase in the LiF concentration and a

change in the phosphorus XPS spectrum were noted, consistent with additional deposition of LiPF_6 based decomposition products.

Future Needs and Prospects

Different research groups have reported different reactions of the electrolyte with NMC cathodes. However, the generally observed reactions are similar for all NMC cathodes cycled to high potential and are generally worse with higher Ni content. Some of these differences can be attributed to different materials suppliers or storage conditions of the NMC cathodes.¹³ NMC cathodes react slowly with dry air to generate surface films of Li_2CO_3 and different quantities of Li_2CO_3 and other surface differences could partially explain different trends for different research groups. We will attempt to summarize the various trends and propose areas for future investigation. It is important to note that there have been reports on improved performance of NMC cathodes with pre-generated surface films such as Al_2O_3 .¹⁴ This suggests that the surface of the cathode materials is very important for long term performance. Alternatively, reports have suggested that the presence of electrolyte additives can significantly improve performance, suggesting that the electrolyte is also important.⁶

The results discussed above suggest that while the reactions of electrolyte with the surface of NMC cathodes are important, the build-up of electrolyte decomposition products on the surface of the cathode does not likely have a large impact on performance losses. The presence and thicknesses of surface films composed of electrolyte decomposition products poorly correlate with capacity loss and impedance growth. The impedance growth on the cathode more clearly correlates with the formation of a rock salt phase on the surface and related NMC particle cracking.^{2,3,15}

While most of the impedance increases for NMC cells with high Ni content or cycled to high potential are observed on the cathode, capacity losses are typically attributed to the anode. As discussed above, SEI thickening on the anode upon cycling is dependent upon both the cut-off potential and Ni content of the cathode. The SEI thickening has typically been attributed to transition metal dissolution from the cathode and deposition on the anode. Several investigations reveal a correlation between capacity loss and transition metal content in the anode SEI.^{4,5,12} Alternatively, other research has reported poor correlation between transitional metal content and capacity loss when cells are cycled with electrolytes which contain additives.⁶ Interestingly, nearly stoichiometric dissolution of the different transition metals (Ni, Mn, and Co) from

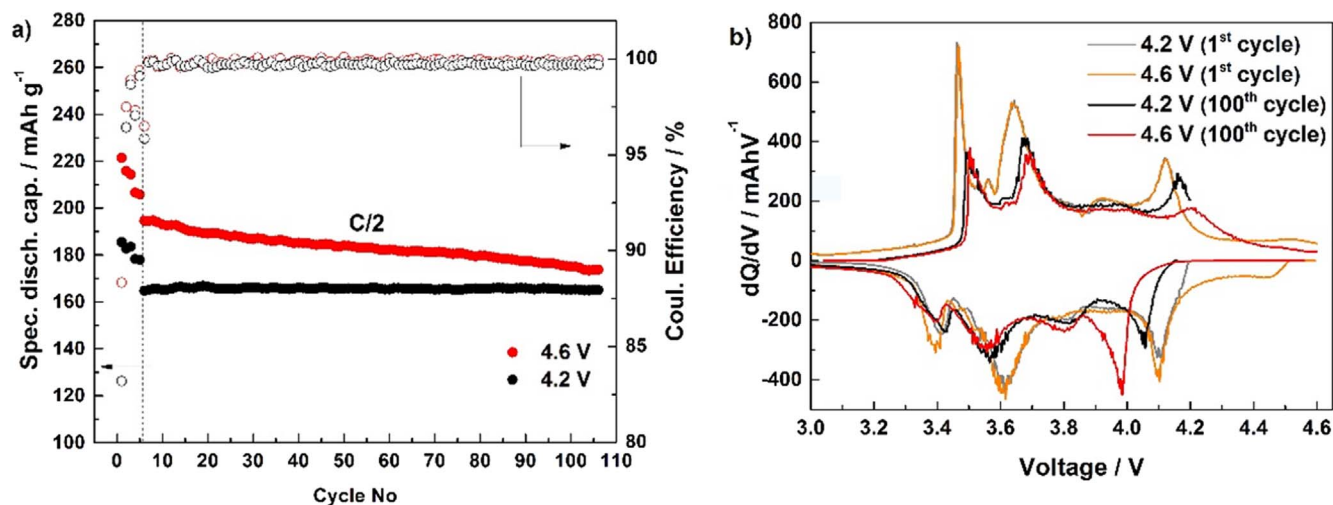


Figure 1. Electrochemical performance of Graphite/NMC811 cells cycled at different cut-off voltages of 4.2 and 4.6 V, respectively. (a) Galvanostatic cycling at a C-rate of C/2 after formation cycles at C/20 (1), C/10 (2–3) and C/5 (4–5), (b) differential capacity plots of the 1st and 100th cycle.¹² figure reproduced with permission of J. Electrochem. Soc.

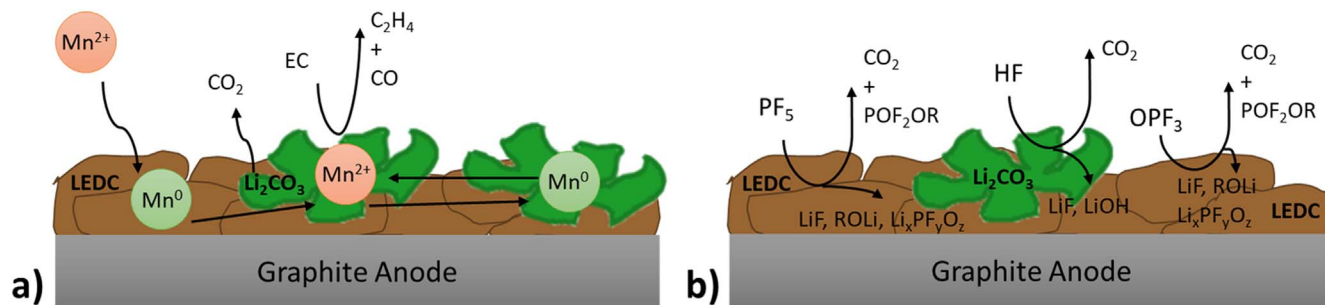


Figure 2. A schematic representation of the (a) manganese catalyzed degradation of the anode SEI adapted from Solchenbach et al.,¹⁶ and (b) acidic species induced decomposition of anode SEI components.

NMC cathodes has also been reported. In addition, Mn deposition has been reported to result in greater damage to the anode SEI than Ni deposition (Fig. 2a).¹⁶ However, these results are inconsistent with observations of greater capacity loss for high Ni NMC since Mn dissolution, the more damaging transition metal, would be lowered since there is less Mn in the NMC. Thus, while transition metal dissolution and deposition, may contribute to damaging of the SEI and consequent capacity losses, it is not likely the primary source.

Alternatively, researchers have commented that transition metal dissolution at the NMC cathode coincides with the generation of acidic species (PF₅, OPF₃, and HF) which result from electrolyte oxidation at the cathode at high potential.^{17,18} The same acidic species have been reported from the thermal decomposition of LiPF₆/carbonate electrolytes.¹⁹ These acidic species have been reported to rapidly accelerate the thermal decomposition of lithium alkyl carbonates, the primary components of the anode SEI.^{20,21} Thus, the oxidative generation of the acidic species at the cathode interface followed by crossover to the anode and catalytic decomposition of the anode SEI is likely a significant contributor to capacity loss on the graphitic anode in graphite/NMC cells as shown in Fig. 2b, especially at high potential or high Ni content where electrolyte oxidation is more problematic.²² This is consistent with the reported changes in the F1s and P2p XPS spectra of anodes cycled to high potential.¹²

The addition of electrolyte additives which either stabilize the anode SEI, such as vinylene carbonate (VC) or fluoroethylene carbonate (FEC), or scavenge acidic species such as TMSP²³ would slow damage to the SEI and improve capacity, as reported.⁶ In addition, the presence of basic surface films such as Al₂O₃ would also remove acidic species from solution and thus consistent with reported improvements. Thus, our suggestion related to the development of superior electrolyte formulations for NMC cathodes cycled to high potential or containing high Ni content is the development of both superior acid scavenging and SEI stabilizing electrolyte additives.

Summary

In summary, while the transition metal content in the anode SEI correlates with capacity loss for some NMC cathodes cycled to high potential and NMC cathodes containing high nickel content, it is unclear if the presence of the transition metal is the primary source of capacity loss, or a coincidence. NMC particle cracking or NMC phase transitions appear to be the primary source of cathode impedance increases as opposed to the formation of the cathode electrolyte interphase. Researchers have reported that native surface impurities such as Li₂CO₃ or surface modifications such as alumina coated NMC can inhibit transition metal dissolution or particle cracking. However, the mechanism of these modifications remains elusive. Finally, many investigations have focused on the effect of electrolyte additives on the performance of NMC cathodes at high potential, high Ni content, or both. While, some clear performance enhancements have been observed, the mechanisms of performance

enhancement such as the formation of a stable cathode passivation layer, inhibition of transition metal dissolution, or inhibition of the side reactions of the electrolyte, is unclear. However, electrolyte oxidation on the surface of NMC cathodes generates electrolyte soluble acidic species which can crossover to the anode resulting in acid induced damage of the anode SEI and subsequent capacity fade.

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ORCID

Satu Kristiina Heiskanen <https://orcid.org/0000-0001-9812-0147>
Brett L. Lucht <https://orcid.org/0000-0002-4660-0840>

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