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Challenges and Opportunities of Layered Cathodes of LiNixMnyCo(1-x-y)O2 for High-Performance Lithium-ion Batteries

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Challenges and Opportunities of Layered Cathodes of $LiNi_xMn_yCo_{(1-x-y)}O_2$ for High-Performance Lithium-ion Batteries

By Jason Frank

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Abstract

High energy density lithium-ion batteries (LIBs) are widely demanded for portable electronic devices and electrical vehicles. Layered-structure $LiCoO_2$ oxide (LCO) has been the most commonly used cathode material in commercial LIBs. Compared to LCO, $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) cathodes are particularly attractive due to their reduced cost and higher capacity. Among the NMC cathodes, nickel-containing $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$ (NMC532) is one of the most promising cathode materials undergoing intensive investigation, but suffers from a series of technical issues, such as structural instability, performance fading, and safety issues. In this report, material structure and synthetic methods of $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$, as well as current issues and progresses are introduced.

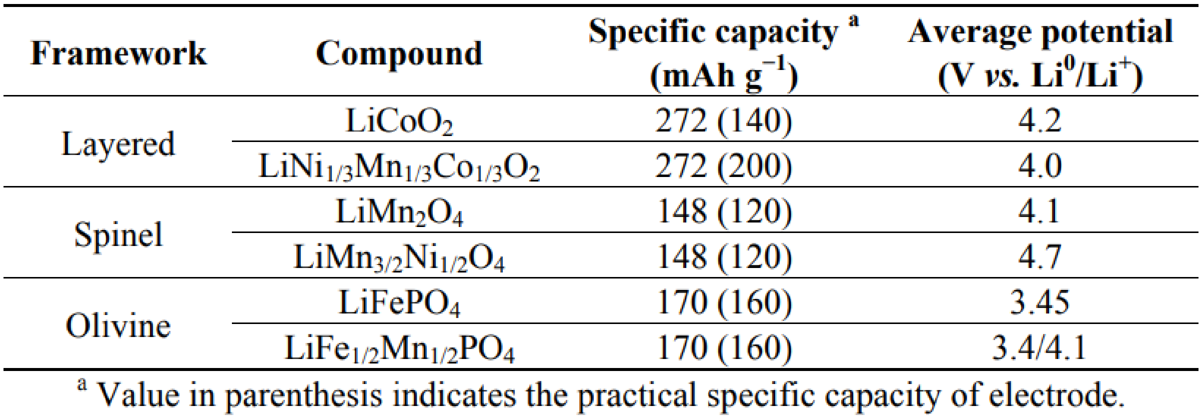
Keywords: $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$, material structure, synthetic methods, current issues, recent progresses

I. Intro

Lithium ion batteries have shown much promise as the premier battery technology for the future. There is still much work to be done to improve the capacity, life, and rate performance of these batteries. $LiNi_xMn_yCo_{(1-x-y)}$ (NMC) cathodes are being developed for improving the electrochemical performance of lithium-ion batteries. The US Department of Energy has set some goals for the performance of lithium-ion batteries in the future. The DOE wants the cost of batteries used in electric vehicles, for instance, to be reduced to \$80/kWh [1]. Other goals include increased range and a greatly reduced charge time for the batteries used in electric cars. This review will cover recent innovations and methods for improvement of the performance of NMC cathodes, as well as how safety concerns are being addressed.

$LiCoO_2$ is an older material used in lithium-ion batteries which has been supplanted by NMC and others due to the high cost of cobalt and the performance of newer options. $LiMn_2O_4$ was used as a cheaper, safer alternative but was hampered by a low specific capacity compared to $LiCoO_2$ [2]. Today, NMC is being used over other alternative materials due to its relative low cost, small volume change of only 2% during cycling [3], along with the natural abundance of the elements used. Cobalt is unfortunately very limited in its dispersion around the globe. Indeed, most cobalt comes from the Democratic Republic of Congo. The Congo has little political stability and few labor laws. The price of cobalt is therefore volatile compared to nickel and manganese. Nickel by comparison is more evenly distributed across the globe. Thus, NMC is being considered to help reduce dependence on cobalt.

NMC materials have been shown to have a higher specific capacity [4] compared to other candidates for cathode materials (figure 1).



Framework	**Compound**	**Specific capacity [a] (mAh g^{-1})**	**Average potential (V *vs.* Li^0/Li$^+$)**
Layered	$LiCoO_2$	272 (140)	4.2
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	272 (200)	4.0
Spinel	$LiMn_2O_4$	148 (120)	4.1
	$LiMn_{3/2}Ni_{1/2}O_4$	148 (120)	4.7
Olivine	$LiFePO_4$	170 (160)	3.45
	$LiFe_{1/2}Mn_{1/2}PO_4$	170 (160)	3.4/4.1

[a] Value in parenthesis indicates the practical specific capacity of electrode.

Figure 1: Characteristics of cathode compounds. [4] Julien et al. licensed under CC BY 3.0.

Note that NMC 111 has the highest practical capacity of any of the other compounds listed. Julien et al. also identified NMC as a good candidate for high power and high energy applications, but at the time did not name it as a good candidate for long cycle life.

II. Characteristics and Methods for NMC

$LiCoO_2$ has a structure similar to that of NMC, (Figure 2). It features distinct layers of cobalt oxide and lithium. $LiMn_2O_4$ keeps a spinel structure and lithium iron phosphate olivine structure is also shown. Lithium ions are free to flow from the cathode to the anode and vice versa.

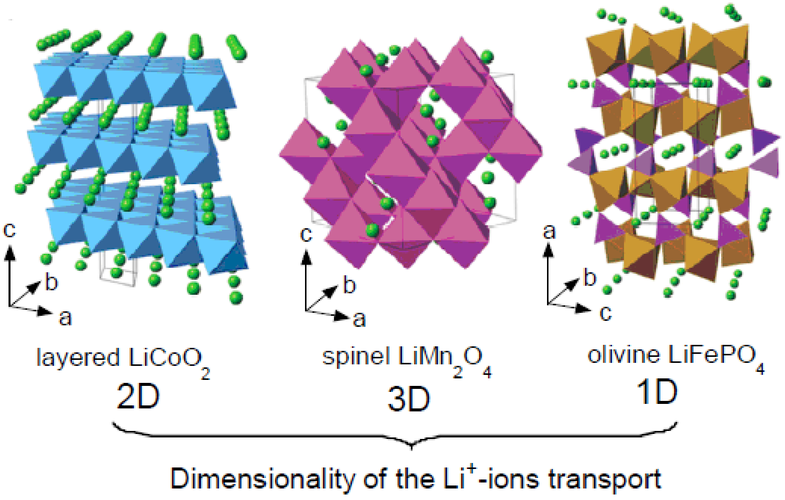


Figure 2: Structure of LIB cathode materials. [4] Julien et al. licensed under CC BY 3.0.

The structure of all NMC materials is similar, with a typical crystalline lattice structure as seen in figure 3 [4]. The difference between types of NMC is the ratios of the elements seen between Ni/Mn/Co. Note how the structure is highly layered like the $LiCoO_2$.

The performance of the cathode material in lithium batteries is "strongly affected by the properties of the particles, such as morphology, specific surface area, crystallinity and phase homogeneity." [6] Many papers demonstrate the differences between structure for NMC materials, as shown in figure 3. Figure 4 shows the ternary phase diagram for various types of NMC materials.

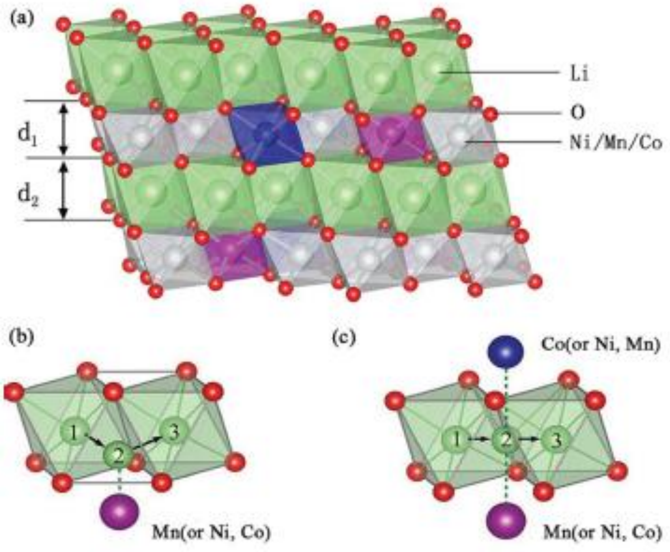


Figure 4. a) Lattice of NMC layered structure. Green atoms, Li; red atoms, O; silver/purple/blue atoms, Ni/Mn/Co transition metals. b) Tetrahedral site pathway and c) oxygen dumbbell pathway for Li-ion diffusion in NMC layered structure.

Figure 3: Lattice of NMC layered structure. [26] Cui et al. licensed under CC BY 3.0.

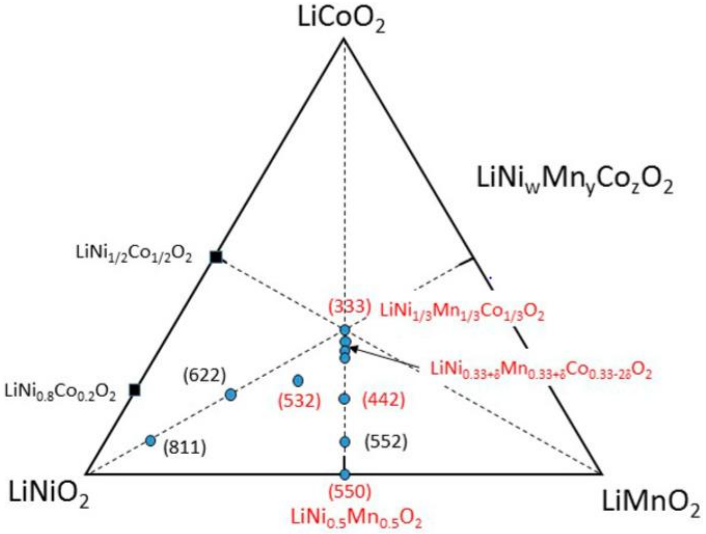


Figure 4: Ternary Phase Diagram of NMC cathode materials. [14] Julien et al. licensed under CC BY 4.0.

One major issue is the optimal ratio of Ni, Mn, and Co to use in a cathode. Amin et. al. analyzed the electronic and ionic transportation of NMC 111 and 532, concluding that “chemical diffusion is always limited by lithium-ion transport rather than electric conductivity.” [7] Many other researchers have analyzed the performance of the different types of NMC.

The methods to make NMC are similar for all types of NMC. Coprecipitation is the most common method for synthesizing NMC material for battery use. The metal compounds are mixed at high temperature and the precipitate is gathered.

There exist several experimental methods for synthesis of NMC cathodes, such as thermal destruction of organometallic compounds (TOMC), solid state (SS) [8], and single crystal synthesis [9] which all seek to reduce the particle size of NMC materials. It has been found that reducing the particle size of conventional NMC materials improves their performance, and these novel methods are meant to reduce particle size.

TOMC describes a process in which acetates containing the metals used in NMC are mixed with a high-pressure polyethylene (HPPE) matrix and hydrocarbon oil solution at temperature (230-250 C) in a reactor with argon gas to prevent unwanted reactions with air. After reactions within the solution cease, the sample is cooled and then remaining liquid is removed from the precipitate. The precipitate is then washed to remove remaining hydrocarbon oil. In the experiment discussed, the solution was later heat treated at 450-900 C for 12-18 hours again in argon gas.

Voronov’s solid state (SS) method starts with carbonate powders of the various metals involved which are then mixed and ground in a ball-mill for 30 minutes. The precursor is then heat treated in an alumina crucible for 14-18 hours at 450-900 C in air.

Li's single crystal synthesis method for NMC 532 begins with a typical coprecipitation method to obtain precursors. The precursors were mixed with Li_2CO_3 by hand with a mortar and pestle. The resulting mixtures were then sintered at high temperature (930-1020 C) for 12 hours. After cooling, the resulting solid material was ground again with a mortar and pestle and passed through a sieve.

In producing battery coin cells, the powdered or solid cathode material is combined with a liquid electrolyte (possibly an anode also for a full cell) and is pressed into a coin cell. The cell is typically heated for some time at a mild temperature (50-80 degrees C) to remove excess solvent.

NMC cathodes will need to be mass produced before they are truly viable for real-world application. Some work has been done to create and optimize high-throughput manufacturing methods. Currently, experimental battery cells are hand made in labs, and exhibit a degree of cell-to-cell variability. Liu et al. have detailed the mass production processes of MTI Corporation in California [10]. The general process is the same, but on a much larger scale. MTI's production line can process multiple samples and multiple different compositions at a time. Their planetary ball mill, for example, can process 16 different 2 ml samples at once.

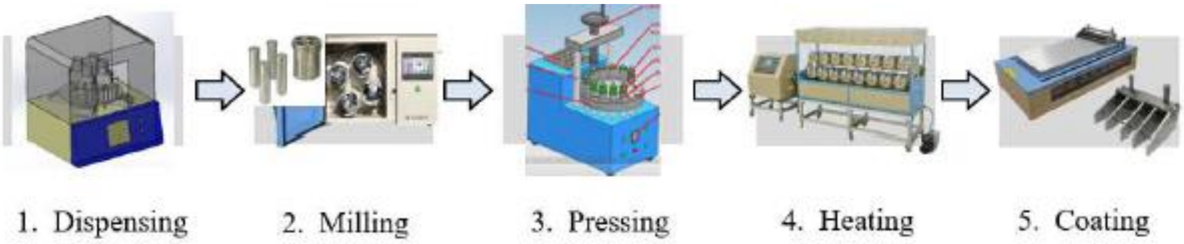


Figure 5: MTI Corporation's production line. [10] Liu et al. licensed under CC BY 4.0.

III. Issues and Challenges of NMC Cathodes

NMC cathodes suffer from several issues, including structural instability, formation of SEI, performance fading, and safety issues.

Solid Electrolyte Interface and Structural Issues

The formation of solid-electrolyte interface (SEI) represents a portion of the capacity loss during cycling. Zhang et al. performed post-mortem analyses of NMC 532/graphite cells and found that “minor cracks and some additional layers are formed on surfaces of both the cathode and anode” [11]. These layers are what is known as the SEI. As this layer forms, lithium ions become trapped in it and can no longer be used. This irreversibility has been observed to be linear (figure 6).

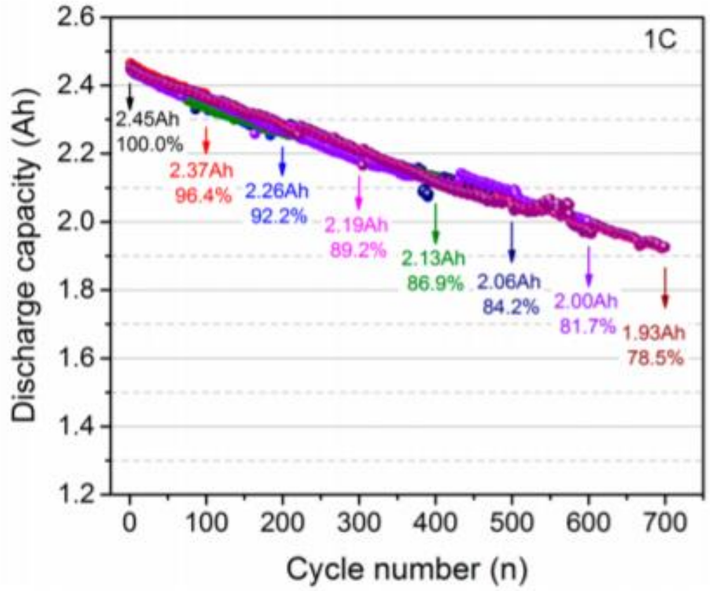


Figure 6: Long-term discharge capacity of LCO + NMC532/Gr fuel cells. [11] Zhang et al. licensed under CC BY 4.0.

Analysis of the cathodes in Zhang’s study showed that the NMC 532 material had significantly larger disruptions after 700 cycles compared to the small cracks in the lithium cobalt (LCO) material in the same cell. Such cracks are common.

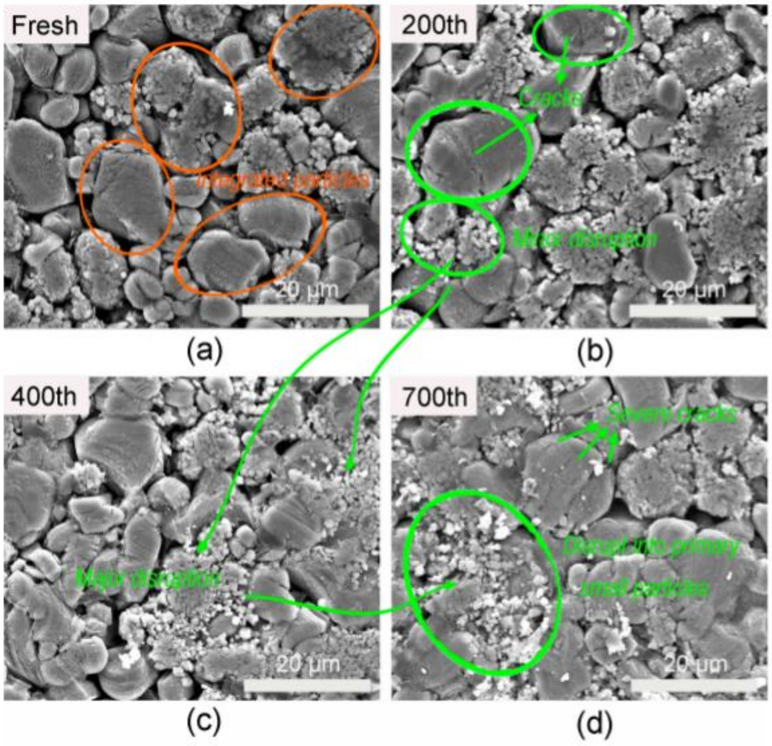


Figure 7: Crack growth in LCO + NMC 532 cathode. [11] Zhang et al. licensed under CC BY 4.0.

The formation of a surface layer on the cathode and anode was also observed. In figure 8, the formation of an SEI layer is observed over 700 cycles.

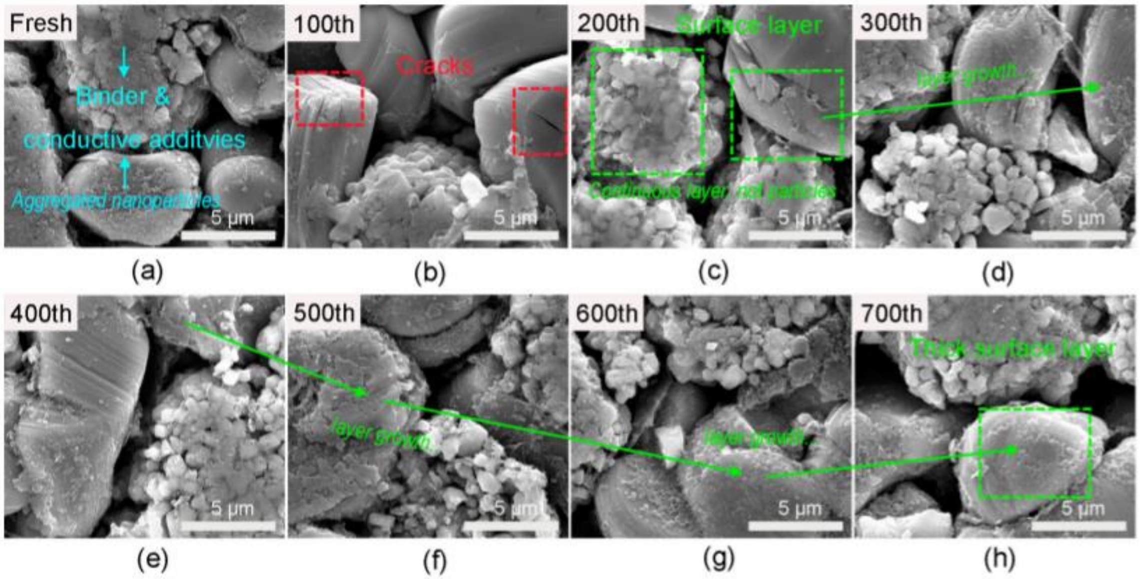


Figure 8: SEI layer formation on LCO + NMC 532 cathode. [11] Zhang et al. licensed under CC BY 4.0.

The formation of the SEI layer has been explained by Su et al. (Figure 9). NMC on the surface of the cathode dissolves into the electrolyte and can no longer transport lithium.

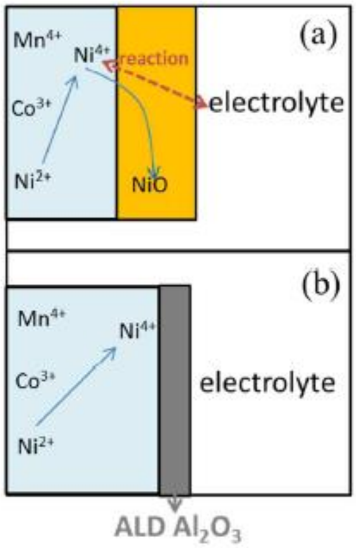


Figure 9: Schematic of (a) pristine and (b) ALD Al2O3 coated NCM532 electrodes after charged to high voltage conditions. [5] Reprinted with permission from reference 5. Copyright 2015 American Chemical Society.

However, this reaction between the electrolyte and electrode can be slowed with atomic layer deposition. This strategy will be discussed in detail in section IV.

Performance Fading and Longevity

Most papers featured in this review are focused on the improvement of battery life and capacity. NMC cathodes face a significant decrease in capacity after many cycles, similar to that seen in silicon anodes [12]. This is one of the most challenging issues facing NMC materials, and many different methods are being tested to mitigate the problem. Managing or preventing the growth of the SEI is one goal of researchers trying to improve battery performance.

A major limiting factor in Li-ion cathodes is their poor conductivity. [13] A typical approach to improve the conductivity is carbon additives, which will be discussed later. NMC has inherently poor rate performance “due to low intrinsic electronic and ionic conductivity [14]”. This poor performance is attributed to “low electron transport of the material and slow Li-ion kinetics within the grains.”

Increasing the particle size of the active material was identified as an obstacle to improving the rate capability. [15] Manufacturing techniques such as ball milling and other synthesis methods often have the goal of reducing particle size.

Safety Issues

NMC materials have been shown to have a low reaction in temperature due to state of overcharge [16]. However, NMC materials still have a risk of exploding due to oxygen release at certain temperatures [17].

Bak et al. performed an analysis of various types of NMC for oxygen released at different temperatures (Figure 10).

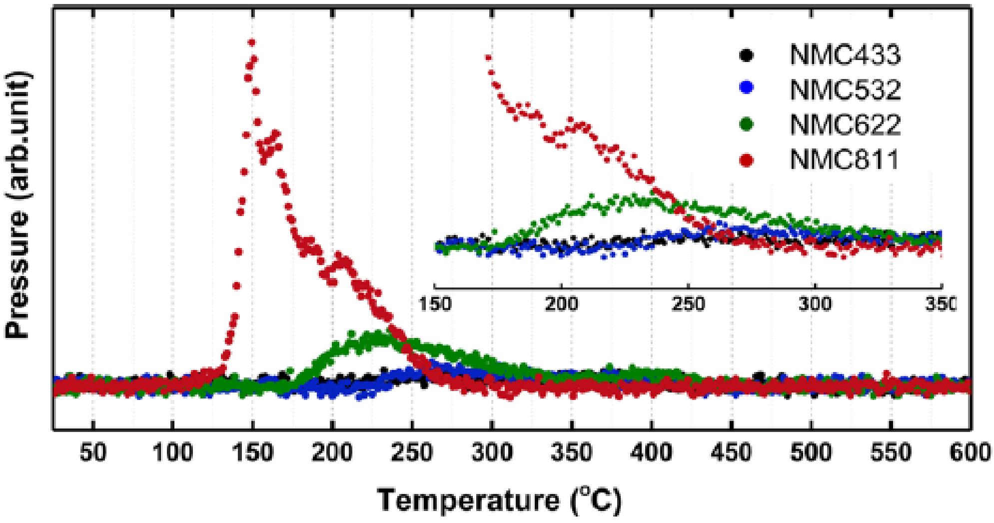


Figure 10: Mass spectroscopy profiles for the oxygen (O2, m/z = 32) collected simultaneously during measurement of TR-XRD [17] Reprinted with permission from reference 17. Copyright 2014 American Chemical Society.

Note the near zero pressure rise from NMC 433 and 532. The phase changes of the NMC materials were also recorded with temperature in figure 11:

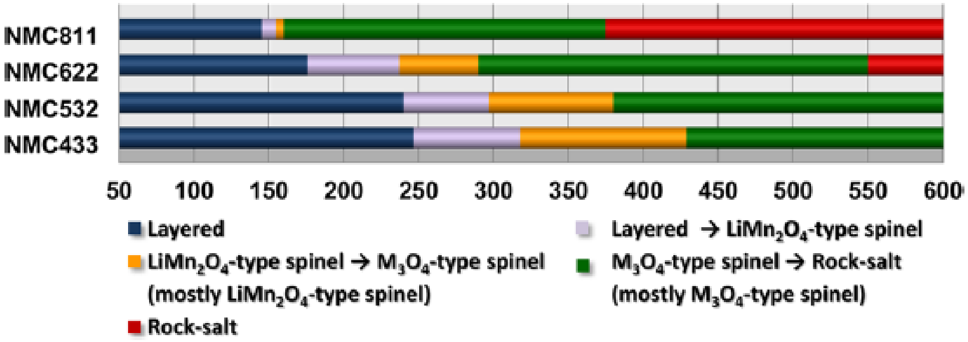


Figure 11: Temperature Region of phase transitions for NMC samples. [17] Reprinted with permission from reference 17. Copyright 2014 American Chemical Society.

From this diagram it can be concluded that oxygen release in NMC cathodes correlates with a rapid phase change in the cathode material. In order to reduce this oxygen release and the potential for combustion, the phase change needs to be slowed.

Manufacturing Issues

No manufacturing process is perfect, but for an NMC cathode, a defect can mean greatly reduced performance and life of the cell [18]. Several different types of common defects have already been identified as well as their causes. Figure 12 shows how for an NMC 532 cathode various defects affected the performance of a cell. Mohanty et. Al. suggest that agglomerates are created when the coating of the NMC material is not mixed well enough, pinholes are created because of bubbles in the slurry, and defective coating areas are a result of tool malfunctions or inaccurate mixing protocols. Note how agglomerates and several small defective areas reduced capacity retention significantly more than the other defects tested and should be avoided.

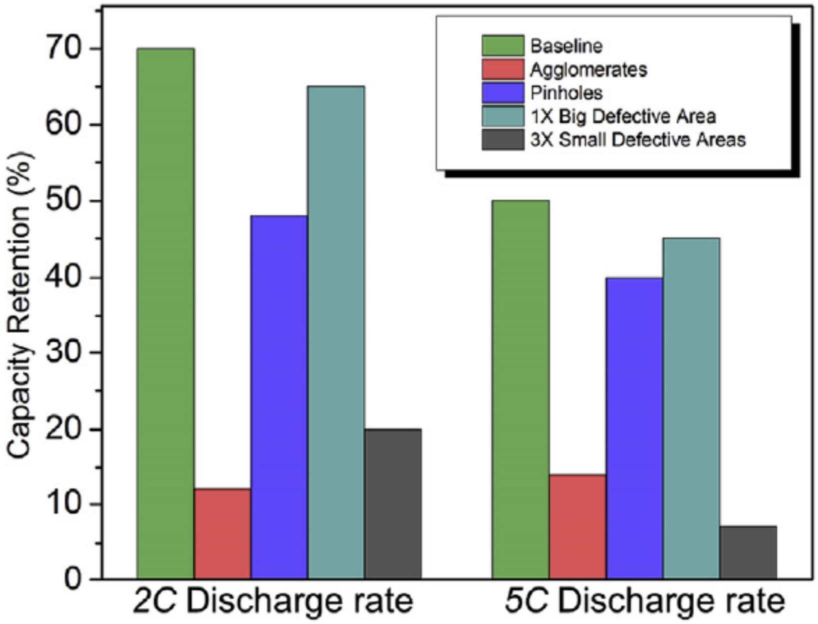


Figure 12: The capacity retention values after 200 cycles for baseline and defective electrodes at the 2C discharge rate and at the 5C discharged rate. [18] Reprinted with permission from reference 18. Copyright 2016 Journal of Power Sources.

IV. Strategies for Improving NMC Performance

As discussed earlier, much of the current research regarding NMC materials in batteries is concerned with improving performance of the batteries.

Additives

A common approach to improving performance is adding various materials to the NMC slurry. Carbon nanotubes, nanoribbons, graphene, and carbon black [19] have been tested. Layer thickness of these additives is typically 40 micrometers thick. Researchers have tested the effects of each such material individually and in conjunction with others. For instance, carbon black alone was found to leave many holes in the coating on the electrode, but when carbon nanotubes were added, the number of holes largely decreased [17]. Combining various carbon additives improved the capacity, life, and rate performance of the 532 cathodes.

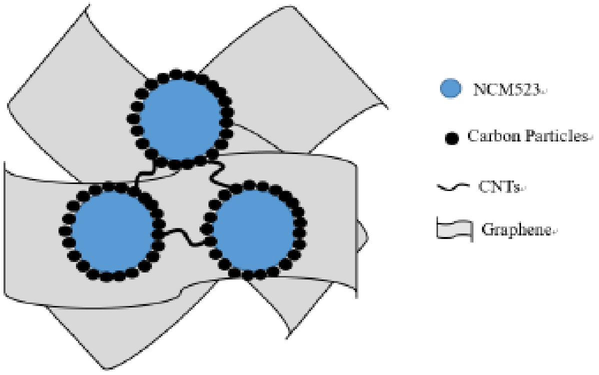


Figure 13: Diagram of carbon additives. [19] Chen et al. licensed under CC BY 4.0.

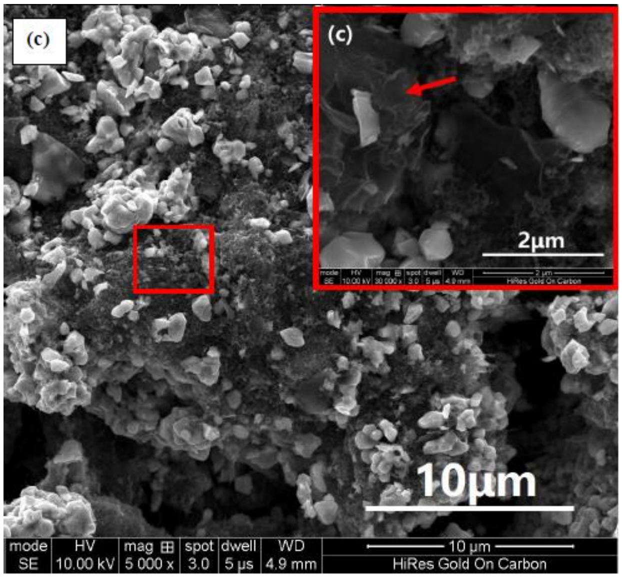


Figure 14: SEM image of electrode with carbon black, CNT's, and graphene. [19] Chen et al. licensed under CC BY 4.0.

The performance improvement for Chen et al. is as follows:

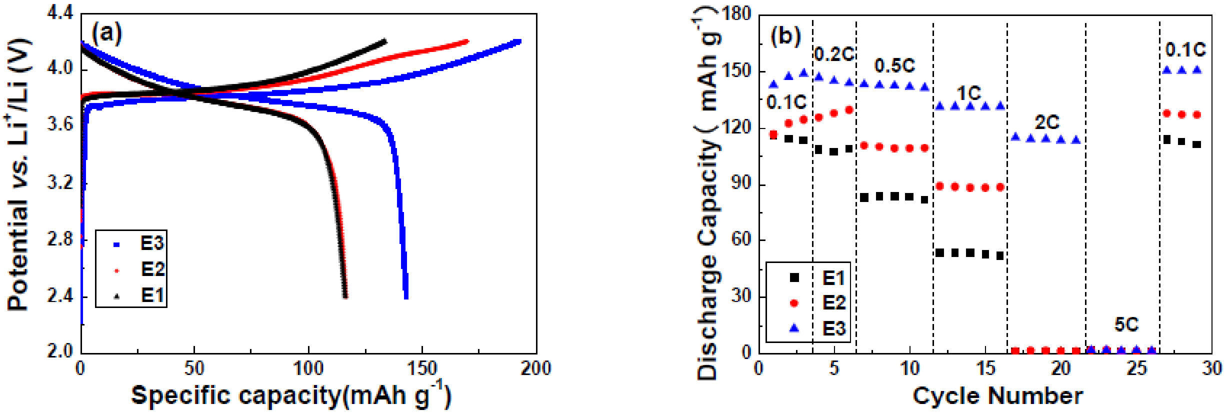


Figure 15: Electrochemical performances of three types of electrode: (a) the initial charge/discharge profile at 0.1C; (b) rate capabilities. [19] Chen et al. licensed under CC BY 4.0.

The carbon additives themselves can also be modified, as discovered by Su et al. [13] in which a commercially available carbon black was compared to a novel carbon black from Cabot (CBC).

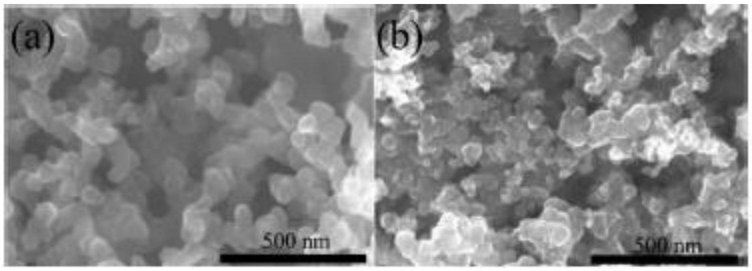


Figure 16: Commercial vs novel carbon black. [13] Su et al. licensed under CC BY 4.0.

The rate performance of the CBC was better compared to the existing commercially available carbon black, even when just 1% wt was used (figure 17).

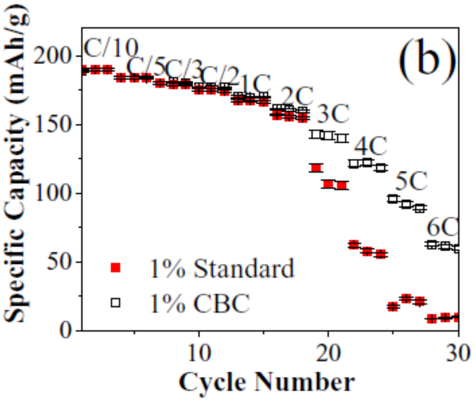


Figure 17: Rate performance of commercial vs. novel carbon black. [13] Su et al. licensed under CC BY 4.0.

Su et al. measured little difference when using 5% of either compound. However, there was a marked difference in the rate performance when just 1% of the CBC nanoparticle and standard carbon black was used. The mechanism for why this novel particle works better was described because of lower electric resistance of the particle. The CBC has a smaller particle size compared to the commercial carbon black.

Doping

Doping involves adding yet another element to the cathode with the goal of slowing or stopping phase changes as a function of temperature. Guo et al. added both aluminum and fluorine to combine the advantages of both types of doping [20]. This method mitigated the layered-to-spinel transition and inhibited capacity fade (Figure 18). This meant that both the safety aspect and a performance aspect were addressed with one method.

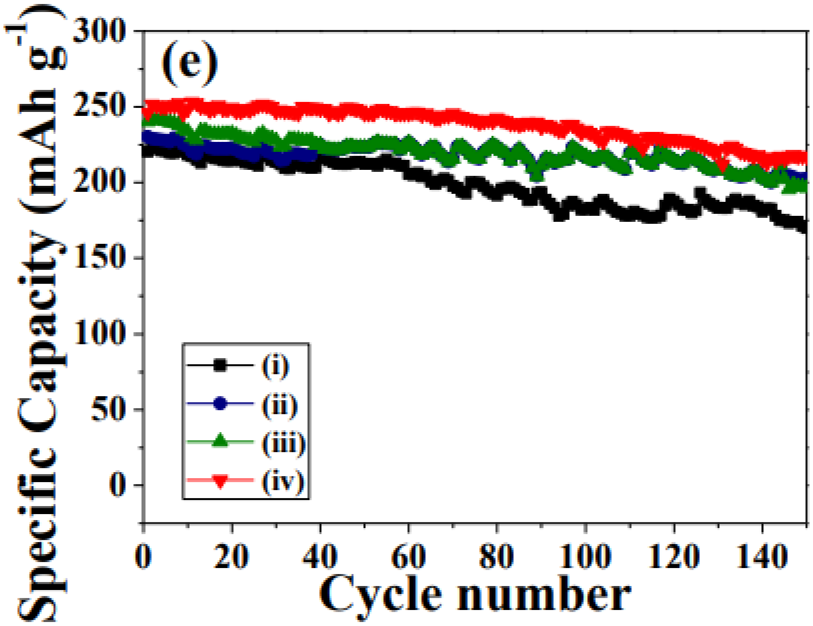


Figure 18: Capacity was greatest and had the best capacity retention when concentration of Al and F were highest in this study (iv). [20] Reprinted with permission from reference 20. Copyright 2017 Electrochimica Acta.

Surface Coatings

Atomic layer deposition (ALD) and molecular layer deposition (MLD) are used to add a thin layer of aluminum oxide (AL_2O_3), zinc oxide (ZnO), or titanium dioxide (TiO_2) to the surface of the NMC structure. This layer is typically on the scale of a few nanometers thick [21]. ALD allows for precise control of layer thickness, composition, and a high degree of homogeneity. Surface coatings are applied with the goal of improving cathode conductivity and life by preventing hindering electrode/electrolyte reactions (Figure 19). Su et al. showed that 5 coatings of Al2O3 on NMC 532 cathodes were optimal in improving performance of the material. [5]

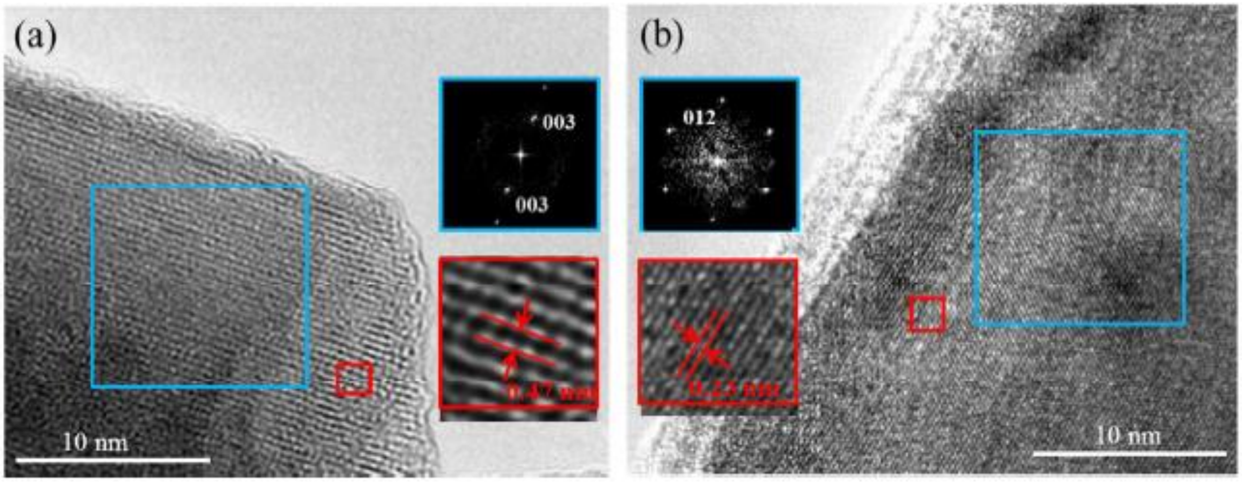


Figure 19: TEM Images of an uncoated electrode (a) and a 10-ALD electrode (b). [5] Reprinted with permission from reference 5. Copyright 2015 American Chemical Society.

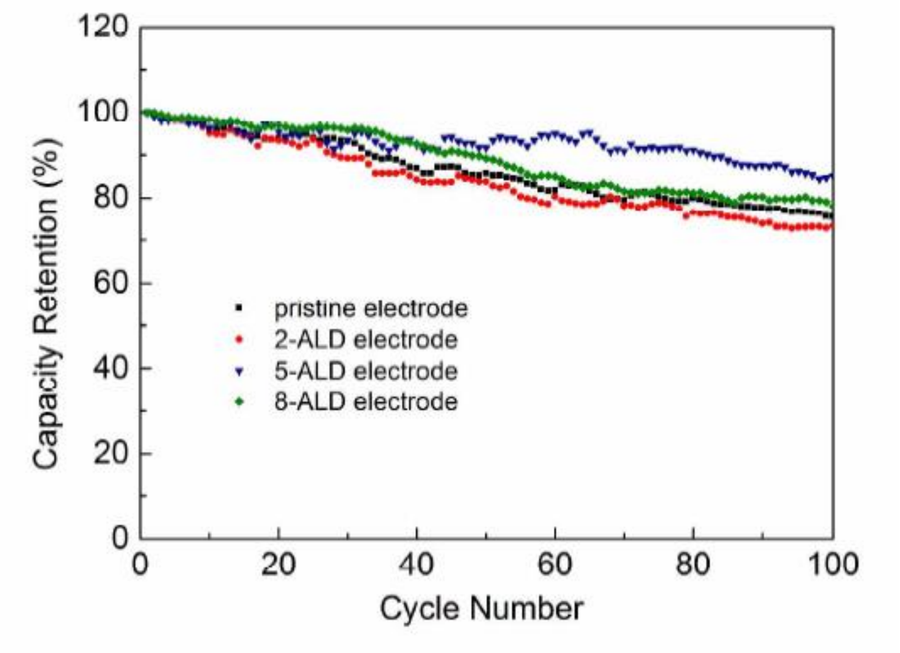


Figure 20: Capacity retention of ALD coated electrodes after 100 cycles. [5] Reprinted with permission from reference 5. Copyright 2015 American Chemical Society.

Laskar et al. found that just 2 coatings of Al2O3-Ga2O3 was optimal for NMC 532 and improved capacity 270% over the uncoated cathodes at a high rate of 10C [22] (Figure 21).

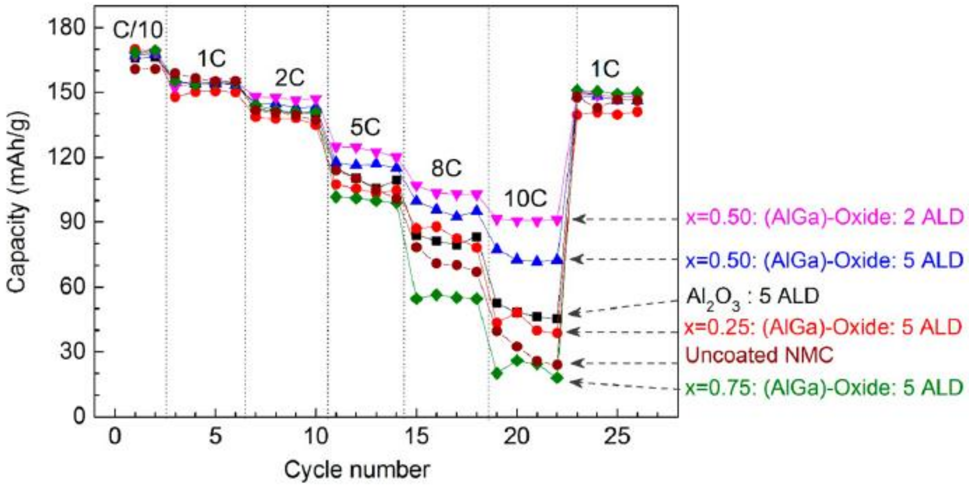


Figure 21: Rate performance of different ALD layer thicknesses [22]. Reprinted with permission from reference 22. Copyright 2016 American Chemical Society.

Elemental mapping of ALD from Laskar showed an even distribution of elements on the surface of the cathode. This would suggest an even coating over the entire cathode which is desirable to prevent SEI formation.

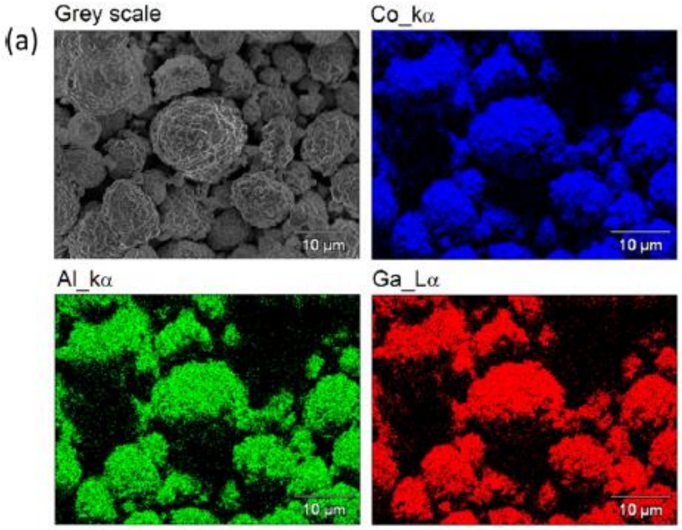


Figure 22: EDXS elemental mapping of NMC coated with Al2O3− Ga2O3 alloy film obtained from copulsing ALD method. The similarity in Ga and Alintensity profiles indicate uniform mixing, and uniform coverage, at spatial resolution of ∼0.25 μm. (b) [22] Reprinted with permission from reference 22. Copyright 2016 American Chemical Society.

The layer thickness and difference in structure between the NMC and the ALD layer can be seen in figure 23. Note the layered, crystalline structure of the NMC versus the disordered structure of the AlGa-oxide layer.

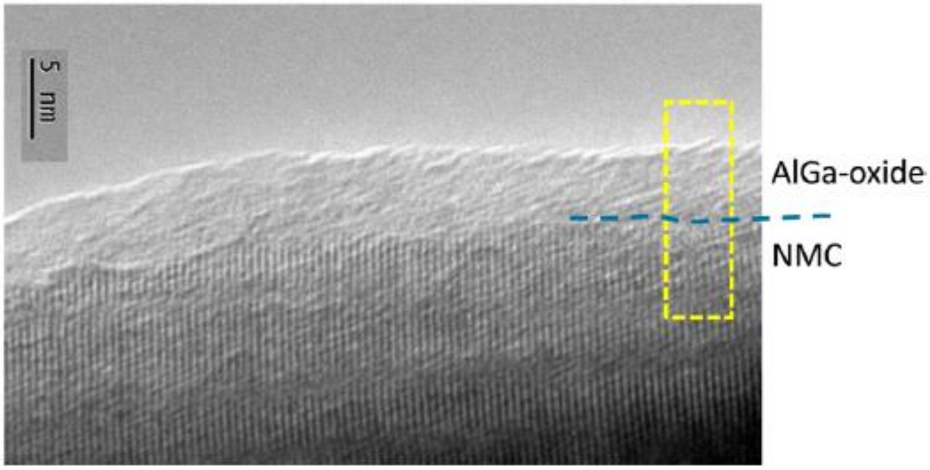


Figure 23: TEM image reveals the amorphous nature of the AlGa-oxide coating on crystalline NMC particle. [22] Reprinted with permission from reference 22. Copyright 2016 American Chemical Society.

Electrolyte Modification

The electrolyte used in a lithium-ion battery can also have a large impact on its performance. Both the composition of the electrolyte and the amount of electrolyte was analyzed. An et al. tested the performance of NMC 532 cathodes with different electrolyte volumes to pore volume factors in pouch cells, and Long et al. tested that of coin cells. An found an ideal ratio of 1.9 [23] while Long found an ideal factor of 2.7 [24]. The ratio is defined as the ratio of electrolyte volume to pore volume on the cathode and anode. The discrepancy between the ideal ratio for coin and pouch cells is explained by An: “Coin cells have large dead volume at spring zone and around spacers in the cans while pouch cells are tightly sealed in flexible pouches without spacers and springs under vacuum.”

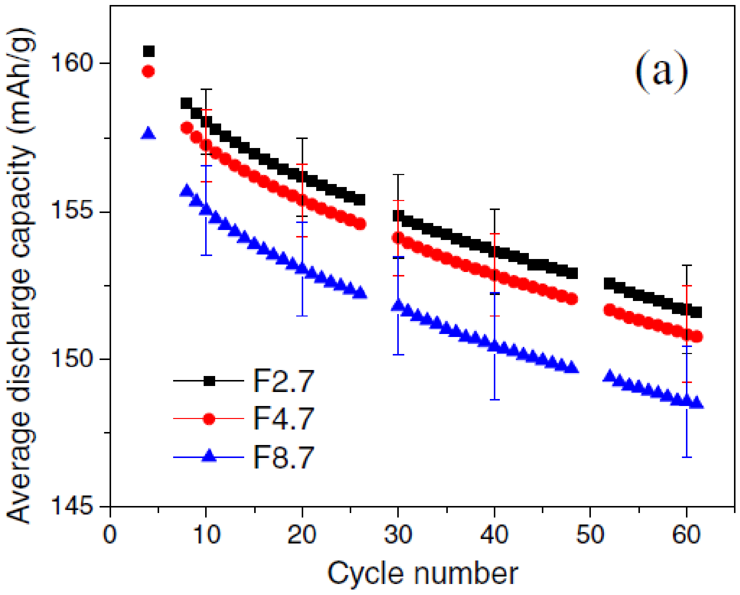


Figure 24: Discharge capacity comparison for different electrolyte volumes. [24] Reprinted with permission from reference 24. Copyright 2016 Journal of the Electrochemical Society.

Note the decreasing performance as the electrolyte volume reaches F4.7 and F8.7. Long et al. speculated that this is due to “increased SEI formation in early cycles. The components of the SEI likely have a finite solubility, which may result in greater dissolution of the SEI requiring additional consumption of cyclable lithium. In addition, excessive electrolyte can act as a lubricant and make electrode alignment difficult by causing the electrodes to slip.” [24]

Miscellaneous

Aqueous electrode processing [25] is also being applied to batteries to improve their life and capacity. This method has the potential to “reduce the processing cost, by avoiding the need for the recovery of the processing solvent, facilitate the recyclability, and decrease the environmental impact of such potentially fluorine-free cathodes.”

Layer distance between lithium and NMC layers (Figure 25) and therefore temperature affects the rate of lithium-ion diffusion in a cell. Cui et. al. found that NMC 622 had the best lithium diffusion coefficient and the least change depending on temperature. [26]

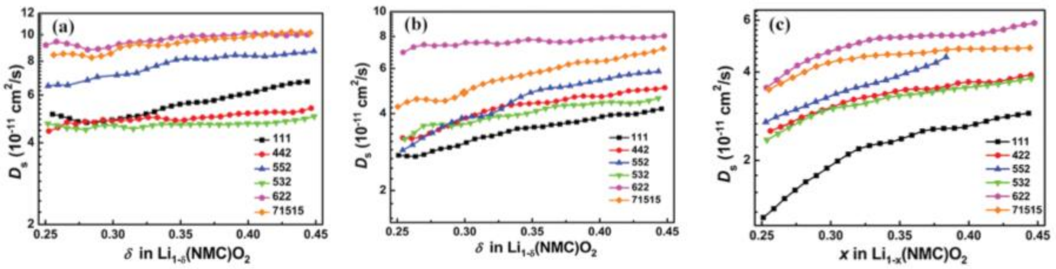


Figure 25: Diffusion coefficient of different materials versus state of charge in a) 50° C (323 K), b) 25° C (298 K), and 0° C (273 K). [26] Reprinted with permission from reference 26. Copyright 2015 Advanced Energy Materials.

Wu et al. came up with a unique "pre-lithiation" process which aims to reduce the first-cycle capacity loss by charging the cell to a low potential before cycling. Bringing the NMC 532 cathode to a 1.2V led to an interphase normally found only on anode surfaces (Figure 26). The layer formed was roughly 40 nm thick and minimized the loss of manganese ions and side reactions in later cycling. This layer can easily be formed and incorporated in future designs. [27]

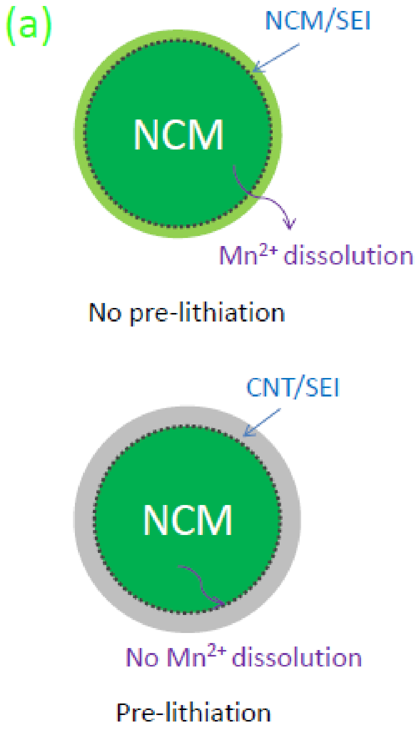


Figure 26: Illustration of the layer formed by pre-lithiation. [27] Reprinted with permission from reference 27. Copyright 2015 American Chemical Society.

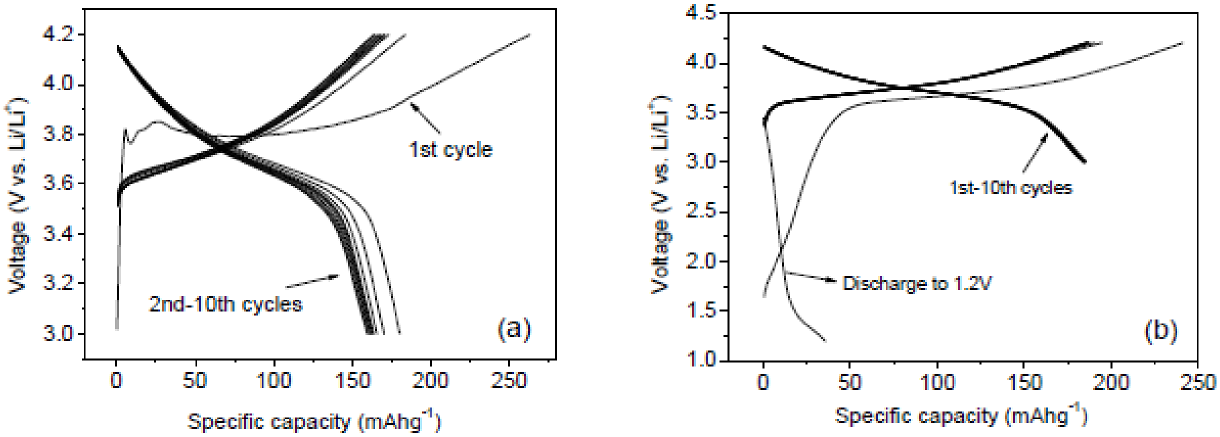


Figure 27: Charge/Discharge cycles of pristine cathode (a) and pre-lithiated cathode (b). Reprinted with permission from reference 27. Copyright 2015 American Chemical Society.

Conclusions and Outlooks

Layered lithium Ni-containing compounds $LiNi_{1-x-y}Co_xMn_yO_2$ are technologically important cathode materials for Li-ion batteries. Each of the three transition metals can contribute to the whole properties of the cathode materials. Within the NMC system, the inexpensive $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$ cathode material which exhibits good electrochemical performance and high thermal stability, is widely used in commercial LIBs. As we know, NCA cathode materials have already been used in Tesla for electric vehicle application. However, because of their limited rate capability and drastic degradation in capacity and cycle-life at elevated temperatures and high operation voltages, some efforts are still needed to optimize the electrochemical performance of $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$ cathodes. Recently, researchers are mainly focusing on doping and surfacing coating to minimize the issues faced by $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$, such as cation mixing and surface side reactions. In particular, ALD coating becomes more and more popular, because it can utilize sequential and self-limiting surface reactions that enable tailored conformal coatings with Å-level thickness control. Additionally, ALD can be employed for powders and directly on fully fabricated electrodes.

In the interest of the environment, considerations and future studies need to be made regarding the sustainability of LIBs, particularly regarding waste. Recycling methods should be utilized when practical. Further studies should be done to explore the effect of nanomaterials when they are released into the environment. These particles could be destructive on the cellular level. The effect of elements like nickel, cobalt, and manganese being released should also be evaluated. Although they occur naturally, they may pose a threat at high concentrations.

In summary, the relationship between structure and performance of $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$ cathode materials have been better understood and improved greatly these years. Certainly, these oxides still have many remaining challenges related to structural instability, surface side reactions, and safety concerns. Even so, through continuous scientific efforts, the energy density and reliability of $LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$ cathode material can reach a level comparable to that of NCA, which are suitable for electronic vehicles in the future.

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