Nickel-Rich and Lithium-Rich Layered Oxide Cathodes: Progress and Perspectives

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Ni-rich layered oxides and Li-rich layered oxides are topics of much research interest as cathodes for Li-ion batteries due to their low cost and higher discharge capacities compared to those of LiCoO$_2$ and LiMn$_2$O$_4$. However, Ni-rich layered oxides have several pitfalls, including difficulty in synthesizing a well-ordered material with all Ni$^{3+}$ ions, poor cyclability, moisture sensitivity, a thermal runaway reaction, and formation of a harmful surface layer caused by side reactions with the electrolyte. Recent efforts towards Ni-rich layered oxides have centered on optimizing the composition and processing conditions to obtain controlled bulk and surface compositions to overcome the capacity fade. Li-rich layered oxides also have negative aspects, including oxygen loss from the lattice during first charge, a large first cycle irreversible capacity loss, poor rate capability, side reactions with the electrolyte, low tap density, and voltage decay during extended cycling. Recent work on Li-rich layered oxides has focused on understanding the surface and bulk structures and eliminating the undesirable properties. Followed by a brief introduction, an account of recent developments on the understanding and performance gains of Ni-rich and Li-rich layered oxide cathodes is provided, along with future research directions.

1. Introduction

Li-ion batteries (LIBs) have become prevalent in modern day society, as they power cell phones, laptops, and electric vehicles (EV), among other items. Significant research attention is focused on them in order to expand their use in the EV market and for possible deployment in grid storage applications for renewable power sources, such as wind, solar, and geothermal. One of the most explored areas of research in LIBs is designing cathode materials that have improved capacity, stability, rate capability, cycle life, and safety, while keeping the cost low. Ni-rich layered oxides (NLOs) and Li-rich layered oxides (LLOs) are two families of cathodes that have received lots of attention as potential next-generation cathodes for LIBs. The prime advantage of these materials is their high discharge capacities (200 – 220 mAh g$^{-1}$ for NLOs and 250 – 300 mAh g$^{-1}$ for LLOs) and energy densities, as they represent a significant improvement over the most common commercial LIB cathodes: LiCoO$_2$ (140 mAh g$^{-1}$), LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (160 mAh g$^{-1}$), and LiMn$_2$O$_4$ (120 mAh g$^{-1}$). The other beneficial trait of these layered oxides is their lower cost due to a reduction in Co content. Although both NLOs and LLOs are similar in their basic composition and structure, they differ significantly in their electrochemical behavior/properties and crystal chemistry. NLOs suffer from the challenge of maintaining all Ni in the 3$^+$ oxidation state during synthesis, capacity fade, detrimental side reactions with the electrolyte caused by the high cycling voltage, and safety issues resulting from thermal runaway reactions. The structure of LLOs is described by researchers as either a solid solution or a nanocomposite of Li$_2$MnO$_3$ and LiMO$_2$, where M is a collection of metals, most often Mn, Ni, and Co. The high discharge capacity of LLOs is derived from its unique first charge-discharge cycle that consists of transition-metal (TM) oxidation followed by the oxidation and loss of oxide ions from the lattice during charge, which leads to a compensatory Mn reduction during discharge. Unfortunately, a myriad of challenges are also associated with LLOs. The LLOs suffer from oxygen loss from the lattice during first charge, high first cycle irreversible capacity loss (IRC), poor rate capability, low volumetric energy density due to a low tap density, and a substantial voltage decay over extended cycling due to a transformation to a spinel-like phase. These issues will be discussed in further detail here.

2. Ni-Rich Layered Oxides

2.1. LiNiO$_2$

LiNiO$_2$ has the $\alpha$-NaFeO$_2$ structure with the oxide ions forming a cubic close-packed arrangement (Figure 1a). LiNiO$_2$ was first
introduced by Dyer et al. in 1954. After the successful launch of the Li-ion battery in 1991, which used LiCoO₂ as the cathode material, LiNiO₂ has sparked a great deal of interest due to its cost effectiveness and structural similarity to LiCoO₂. However, it is rather difficult to synthesize the stoichiometric LiNiO₂ with a Li:Ni ratio of 1:1. The synthesis often results in the formation of a lithium-deficient LiₓNi₁₋ₓO₂ with part of the Ni present as Ni²⁺ and cation mixing between Ni and Li, as it is difficult to maintain all Ni as Ni³⁺ at the high synthesis temperatures of >700 °C. The presence of Ni in the Li layer can impede Li⁺ diffusion and lower rate capability. Nonetheless, Dahn et al. demonstrated the feasibility of coupling Li₀.₉₆Ni₁₀.₀₄O₂ with coke as the anode, which could operate for 300 cycles (Figure 1b). Öhazku et al. evaluated the relationship between the crystal structure and electrochemical performance, i.e., the integrated intensity of I(003)/I(104) is a key parameter that represents the degree of mixing of Ni and Li ions. Minimization of such disorder resulted in a high capacity and good reversibility (Figure 1c). Carrying out the synthesis in a flowing oxygen atmosphere or using excess Li precursor in the initial reaction mixture is helpful to decrease the amount of Ni²⁺, although not completely successful to keep all Ni as Ni³⁺, and obtaining over 200 mAh g⁻¹ with good cyclability.

2.2. LiNiₓMₓO₂ (M = metal)

The above-mentioned results indicate the difficulty of synthesizing stoichiometric LiNiO₂. These drawbacks could be greatly mitigated by substituting other ions such as Co,[5c,6] Fe,[7] Mn,[5c,7b,8] Ti,[5c,9] Mg,[9c,10] and Al[9d,10g,11] for Ni. Substitutions impact the layeredness of the structure, its stability upon lithium deintercalation, the capacity, and more importantly, the thermal properties at highly delithiated states.

2.2.1. Co Substitution

The LiNiₓCoₓO₂ solid solution is interesting in terms of structure and electrochemical performance due to its ease of synthesis and the similar redox potentials of Ni⁴⁺/⁴⁻ and Co⁴⁺/⁴⁻, which enables high voltage operation. Indeed, flowing oxygen was necessary to prepare LiNiO₂ to minimize the formation of Ni²⁺ and cation disorder. For the synthesis of the LiNiₓCoₓO₂ solid solution, however, oxygen is not necessarily required to produce a well-defined rhombohedral layered structure. Zhecheva et al. and Delmas et al. showed that Co substitution was highly effective in lowering the cation mixing between the Li and TM layers.[5b,c] Although a multistep phase transition occurs in LiNiO₂ during charge-discharge, improvement in the initial structural integrity simultaneously stabilizes the structure during cycling, leading to a single-phase reaction for LiNi₀.₅Co₀.₅O₂ during repetitive Li⁺ de-/intercalation.[5b,d] As a result, the capacity loss was not significant for Co-doped LiNiO₂ (Figure 1d).

2.2.2. Fe Substitution

In terms of cost, Fe is one of the best candidates because of its abundance in the earth’s crust. However, there are always large amounts of Fe and Ni present in the Li layers and the real composition exists as Li₁₋ₓ[Ni₁₋ₓFeₓ]ₓO₂, as proved by the Rietveld refinement results obtained from X-ray diffraction (XRD) and magnetic studies, lowering the rate capability.[12] The material also exhibits a large irreversible capacity in the first cycle and its capacity retention is unacceptably low, which can be ascribed to the structural disorder with serious cation mixing in the Li layers.[17c]
2.2.3. *Mn Substitution*

As an alternative substituent, Mn is worthy because of its low cost and the similarity of the ionic radii of Mn$^{3+}$ (0.65 Å) and Ni$^{3+}$ (0.60 Å). The solid solution of Li$_2$Ni$_{1-x}$Mn$_x$O$_2$ is isostructural with LiNiO$_2$, but the diffraction profiles indicate merging of the (006)/(102) and (100)/(110) pairs, which is close to cubic symmetry.$^{[8d]}$ The Rietveld refinement analysis suggests cation mixing between Li and Ni due to the internal redox reaction Mn$^{3+}$ + Ni$^{3+}$ → Mn$^{4+}$ + Ni$^{2+}$ as the Mn$^{3+}$/4 energy lies above the Ni$^{2+}$/3 energy. The creation of Ni$^{2+}$ leads to increased Li/Ni interlayer mixing due to the smaller size difference between Ni$^{2+}$ (0.69 Å) and Li$^+$(0.76 Å). The cation mixing results in a degradation of the electrochemical properties, although the thermal stability is improved at the highly delithiated state.$^{[5c]}$

2.2.4. *Ti Substitution*

Earlier studies reported the failure of Ti substitution because cation mixing was more progressed in the Li layers. Because Ti exists as Ti$^{4+}$ in layered oxides, Ni$^{2+}$ ions are formed to maintain charge neutrality, leading to increased cation disorder.$^{[9a]}$ Kim and Amine suggested that the introduced tetravalent Ti renders the structure rigid.$^{[9b]}$ This is a reasonable assumption because the Gibbs energy for the formation of TiO$_2$ at 25 °C (−888.8 kJ mol$^{-1}$) is sufficiently low to stabilize the crystal structure. The Ti substitution leads to good electrochemical performance (Figure 1e) at low doping levels (≤5%), but above which the resulting crystal structure becomes seriously disordered with a low $c/a$ ratio and broadened full-width of half maximum values of the diffraction peaks. A few later studies also demonstrated the effects of Ti on the structural and electrochemical performance.$^{[9e,f]}$

2.2.5. *Mg Substitution*

Another approach to minimize the occupation of divalent Ni in Li layers is to replace the divalent Ni present in Li$_{1-x}$Ni$_{1+x}$O$_2$ by Mg. In addition, Mg is known to improve the electric conductivity in LiCo$_{1/2}$Mg$_{1/2}$O$_2$ as a result of the formation of holes in the $Co^{3+}/4+ t_2$ band.$^{[12]}$ Rietveld refinement of the XRD data shows that the lithium deficiency space is filled with Mg$^{2+}$ ions due to the similarity of the ionic radii of Li$^+$ (0.76 Å) and Mg$^{2+}$ (0.72 Å), which does not participate in the redox process.$^{[10c,d]}$ Hence, the crystal structure is less affected by severe shrinkage of the interlayer spacing upon lithium deintercalation. These structural aspects endorse the significant improvement of the cycling behavior (Figure 1f). The general characteristics of the substitution of divalent ions include i) improvement of the thermal stability, ii) durability during high voltage operation, and iii) good cyclability.$^{[10a,b]}$ In addition, it is expected that in the charged state, the Mg doping prevents the decomposition of the lithium deficiency space with a low $c/a$ ratio and broadened full-width of half maximum values of the diffraction peaks. A few later studies also demonstrated the effects of Ti on the structural and electrochemical performance.$^{[9e,f]}$
of Li$_{x}$Ni$_{1-x}$O$_2$ into a spinel-like phase or into LiNiO$_2$ and NiO with the release of oxygen. The effect of Mg can be summarized as follows: i) the presence of inert species on the TM site helps prevent overcharging during charge and ii) the doped Mg reinforces the interatomic bonding in the NiO$_2$ layers. As a result, the exothermic reaction could be reduced and the main reaction temperature shifts toward a higher temperature. These phenomena are associated with structural stabilization achieved by Mg substitution.

2.2.6. Al Substitution

Replacement of Ni with Al is advantageous because the atomic weight of Al is lighter than that of other TM ions, so LiNi$_{1-x}$Al$_x$O$_2$ has an increased theoretical gravimetric capacity for a given amount of Li extraction. It is generally known that Al replacement for the TM site is not easy because of the formation of undesired oxide phases such as β-LiAlO$_2$, Al$_2$O$_3$, and γ-LiAlO$_2$ when calcined above 600 °C. This is because the phase formation rate of Al progresses slower than those of Li and Ni when a conventional solid-state reaction method is employed. For this reason, coprecipitation, sol-gel, or solution-based synthesis methods are preferred to obtain phase-pure LiNi$_{1-x}$Al$_x$O$_2$. Since α-LiAlO$_2$ (a = 2.800 Å, c = 14.22 Å) has a smaller a-axis and larger c-axis than LiNiO$_2$ (a = 2.880 Å, c = 14.19 Å), an anisotropic change of the lattice parameters is natural, provided that a solid solution is formed. LiNi$_{1-x}$Al$_x$O$_2$ suppresses all of the phase transitions observed for the LiNiO$_2$ system, i.e., the unit cell volume change was only about 2.5% when Li$^+$ was extracted up to Li$_0$Ni$_0.75$Al$_0.25$O$_2$, maintaining the original rhombohedral structure throughout Li$^+$ extraction. This impressive structural stabilization is observed only for the LiNi$_{1-x}$Al$_x$O$_2$ system. In addition, the reduction in the amount of the electro-active species Ni$^{3+}$, made through direct replacement with Al$^{3+}$ in the TM site, negates the benefits of the weight reduction and results in a capacity decrease. The cycling performance, however, is significantly improved due to structural stabilization (Figure 1g).

Interestingly, an additional voltage plateau is observed in the range of 4.5 – 4.8 V for LiNi$_{0.75}$Al$_{0.25}$O$_2$. Manthiram and Goodenough showed the influence of the inductive effect in increasing the redox energy of the Fe$^{2+}/^{3+}$ couple when going from an oxide such as Fe$_2$O$_3$ to a polyanion cathode such as Fe$_2$(SO$_4$)$_3$. In that case, the stronger S–O bond weakens the Fe–O bond and thereby increases the operating voltage of the Fe$^{2+}/^{3+}$ couple in Fe$_2$(SO$_4$)$_3$ compared to that in Fe$_2$O$_3$. By applying similar considerations, the increase in the operating voltage with Al substitution in LiNi$_{0.75}$Al$_{0.25}$O$_2$ could be due to the weakening of the Ni–O bond by the stronger Al–O bond through the inductive effect. On Li$^+$ extraction from LiNiO$_2$, there is a formation of an unstable Ni$^{4+}$, made through direct replacement with Al$^{3+}$ in the TM site. Li$_{0.45}$Ni$_{0.75}$Al$_{0.25}$O$_2$ occurred in several steps, primarily due to oxygen evolution from the delithiated material (Figure 2c). The original rhombohedral structure transforms to a spinel-like at 265 °C and it further evolves to a rock salt type structure in the end (Figure 2d). The main exothermic reaction is deeply

2.3. LiNi$_{1-x-y}$M$_{x}$M'$^{+}$O$_2$ (M, M' = metal)

2.3.1. LiNi$_{1-x-y}$Mg$_x$M'$^{+}$O$_2$ (M' = Ti and Al)

The Ti and Al substituents do not seriously affect the crystal structure, in particular Ni occupation in the Li layer, because of the differences in the ionic radii, where the smaller Al$^{3+}$ (0.535 Å) and Ti$^{3+}$ (0.605 Å) preferentially locate in the TM layers rather than in the Li layers. As mentioned previously, Mg$^{2+}$ is effective in increasing the electrical conductivity. Ti$^{4+}$ compensates for the charge deficiency caused by the divalent Ni in the TM layers. These synergetic effects greatly improve the structural integrity. Apart from the structural aspect, the addition of these electroinactive moieties tends to lower the delivered capacity because of the reduced amount of the electrochemically active Ni$^{3+/4+}$ in the oxide matrix. The electrochemical results of the LiNi$_{0.75}$Mg$_{0.125}$Ti$_{0.125}$O$_2$ cathode include retention of 89% of its capacity over approximately 85 cycles in the voltage range of 3.0–4.5 V, although the initial capacity was reduced due to the presence of redox-inactive elements in the compound, as expected. The co-doped LiNi$_{0.95}$Al$_{0.05}$Mg$_{0.05}$O$_2$ exhibited good reversible capacity with excellent capacity retention (Figure 2a). This may result from the presence of the strong Al–O bond, which renders the oxide matrix more rigid. These systems were found to show significantly improved thermal behavior at the expense of capacity. The inert elements prevent the complete removal of all the lithium, which minimizes possible structural collapse and oxygen evolution from the highly delithiated host structure. This is achieved by the improved structural integrity originating from the effects of strong Al–O and Ti–O bonds on the crystal structure, which suppresses oxygen evolution.

2.3.2. LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$

Co-doped LiNi$_{1-x-y}$Co$_x$O$_2$ was identified to possess improved electrochemical properties, which was supported by the formation of a better layered structure, as described in Section 2.2.1. Additionally, this system requires less severe synthesis conditions. However, Abraham et al. pointed out that the formation of an insulating Li$_{x}$Ni$_{1-x}$O$_y$-type layer on the particle surface is the main reason for the 43% power fade of the LiNi$_{0.9}$Co$_{0.1}$O$_2$ cell. Based on the studies of Al$^{3+}$ substitution, it is clear that Al$^{3+}$ substitution favors stabilization of the crystal structure, which significantly affects the electrode performance and thermal stability. Gulmard et al. reported that the occupation of Ni$^{2+}$ in the Li layer could be dramatically reduced below 1% in LiNi$_{0.7}$Co$_{0.3}$Al$_{0.1}$O$_2$. With the help of the additional Co$^{3+/4+}$ redox, the material can possess a high capacity and reversibility associated with a decrease in polarization, in which Al substitution occurs by forcing more electronic exchange between lithium and the oxygen network, as suggested by Cedergren's group. Thermal degradation of chemically delithiated Li$_{0.4}$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ occurred in several steps, primarily due to oxygen evolution from the delithiated material (Figure 2c). The original rhombohedral structure transforms to spinel-like at 265 °C and it further evolves to a rock salt type structure in the end (Figure 2d). The main exothermic reaction is deeply
related to the oxygen evolution during the phase transformation from the rhombohedral structure to spinel-like (Figure 2e).

In this temperature range, self-heating is also accelerated, resulting in thermal runaway of the cathode. \[19\]

2.4. \( \text{Li}[\text{Ni}_{1-x}\text{Mn}_x]\text{O}_2 \)

\( \text{Li}[\text{Ni}_{1-x}\text{Mn}_x]\text{O}_2 \) was first introduced by Dahn's group. \[8a\] It is a solid solution below \( x = 0.5 \), but its electrode performance deteriorates with increasing Mn content. Sphar et al. reported the formation of single-phase \( \text{Li}[\text{Ni}_{0.5}\text{Mn}_0.5]\text{O}_2 \) formed at 700 °C. \[20\]

The temperature was too low for optimized electrochemical performance and its capacity decreased from 150 mAh g\(^{-1}\) to 125 mAh g\(^{-1}\) after 25 cycles. Ohzuku et al. revisited the material and demonstrated a constant capacity of 150 mAh g\(^{-1}\) (Figure 3a). \[21\]

The formal charges of Ni and Mn are 2+ and 4+, respectively, in \( \text{Li}[\text{Ni}_{0.5}\text{Mn}_0.5]\text{O}_2 \). \[22\] Interestingly, only the Ni\(^{2+}/4+\) redox couples are electrochemically available (Figure 3b). \[22b\] Meanwhile, the tetravalent Mn is electrochemically inactive, but provides significant structural stability. Because Mn is tetravalent, there is no concern for the occurrence of the Jahn–Teller effect associated with Mn\(^{3+}\). Kang et al. replaced Mn with Ti to produce \( \text{Li}_{0.9}\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}_2 \), resulting in a rock salt structure. \[23\]

This demonstrates that tetravalent Mn plays a key role to stabilize the \( \alpha\)-NaFeO\(_2\) layer structure. This is further confirmed in the thermal stability results (Figure 3c). The onset exothermic temperature of charged \( \text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) with a smaller particle size (3 µm) was slightly lower (295 °C) than that of the sample with a larger particle size (10 µm, 302 °C). \[24\] This behavior proves that the electrochemically inactive Mn\(^{4+}\) portion provides significant structural stability at the delithiated state, even though the particle diameter is as small as 3 µm.

However, a large amount of Ni\(^{2+}\) (≈10%) present in the Li layers impedes Li\(^+\) diffusion in \( \text{Li}[\text{Ni}_{0.5}\text{Mn}_0.5]\text{O}_2 \). \[25\] Another aspect that should be resolved is the low electrical conductivity.
Figure 3. a) Charge–discharge curves of Li[Ni_{0.5}Mn_{0.5}]O_{2} in the voltage range of 2.5–4.3 V at a rate of 0.17 mA cm\(^{-2}\) at 30 °C. Reproduced with permission.[21b] Copyright 2003, Elsevier. b) Ni K-edge spectra of Li[Ni_{0.5}Mn_{0.5}]O_{2} charged to 4.9 V at a rate of C/50. Reproduced with permission.[22b] Copyright 2003, American Chemical Society. c) Comparison of DSC traces of Li_{2}[Ni_{x}Mn_{0.5}]O_{2} with different average particle sizes. Reproduced with permission.[24] Copyright 2003, Elsevier. d) Charge–discharge curves of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} in the voltage range of 2.5–4.6 V at a rate of 0.17 mA cm\(^{-2}\) at 30 °C. Reproduced with permission.[28b] Copyright 2003, Elsevier. e) Amount of Ni in the lithium layers of Li[Co_{x}Mn_{1-x}]O_{2} as Co content varies. Reproduced with permission.[26] Copyright 2002, The Electrochemical Society. f) Initial charge-discharge curves, g) cyclability, and h) rate capability of Li[Ni_{0.5}Co_{x}Mn_{0.5-x}]O_{2} (x = 0.1 – 0.4). Panels (f–h) reproduced with permission.[29] Copyright 2007, The Electrochemical Society.
Based on the experience of the familiar LiCoO$_2$, which has a high electric conductivity and almost no cation mixing, Li[Ni$_{1-x}$Co$_x$Mn$_x$]O$_2$ ($x = 0–0.5$) obtained by the addition of Co to Li[Ni$_{0.5}$Mn$_{0.5}$]O$_2$ could successfully stabilize the layered crystal structure.\cite{26} These compositions were first introduced by Liu et al. and Yoshio et al.\cite{27} The occupation of Ni$^{2+}$ in the Li layer could be reduced to 2.4% in Li[Ni$_{1-x}$Co$_x$Mn$_x$]O$_2$, delivering a reversible capacity of ~150 mAh g$^{-1}$ to 4.3 V. Soon after, Ohzuku et al. fabricated Li[Ni$_{1-x}$Co$_x$Mn$_{1/3}$]O$_2$, which delivers a reversible capacity of ~150 mAh g$^{-1}$ to 4.2 V and 220 mAh g$^{-1}$ to 5 V (Figure 3d).\cite{28} MacNeil et al. discovered a continuous solid solution of Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ ($x = 0–0.5$), which obeys Vegard’s law in that both the a- and c-axis parameters decreased linearly with increasing Co content (Figure 3e).\cite{29} Interestingly, the delivered capacities increased to 170 mAh g$^{-1}$ as the amount of Co is increased (Figure 3f,g) when charged to 4.3 V.\cite{29} This is due to the contribution of the additional redox reaction associated with Co$^{3+/4+}$. At high rates, there is an obvious variation of the delivered capacity (Figure 3h) where a higher content of Co is preferred to yield a better rate capability because of the high electrical conductivity characteristics of LiCoO$_2$. The oxidation states of the TM ions in Li[Ni$_{1-x}$Co$_x$Mn$_x$]O$_2$\cite{22a,b,30} and Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ ($x = 0–0.5$)\cite{31} are Ni$^{2+}$, Co$^{3+}$, and Mn$^{4+}$. By increasing the upper cut-off voltage to 4.6 V, the Co substitution for Ni and Mn gave rise to an increase in the initial discharge capacity. However, the replacement brought about severe capacity fading during extensive cycling. This data raises an issue regarding the capacity versus retention, where it is important to possess good capacity retention along with a high capacity. The highest capacity obtained was approximately 170 mAh g$^{-1}$ for Li[Ni$_{0.8}$Co$_{0.2}$Mn$_{0.0}$]O$_2$.

A higher level of Ni incorporation leads to a higher reversible capacity in Li[Ni$_{1-2x}$Co$_x$Mn$_x$]O$_2$ because Ni$^{2+}$ can be fully oxidized to Ni$^{4+}$, while it is hard to oxidize Co beyond Co$^{3+/4+}$ without oxidizing O$^{2-}$ ions and Mn$^{4+}$ remains inactive.\cite{29,31,32} As can be seen in Figure 4a, when $x = 0.3$ in Li[Ni$_{1-2x}$Co$_x$Mn$_x$]O$_2$, the photon energy shift is close to that of NiO. The pre-edge spectrum of Li[Ni$_{0.8}$Co$_{0.2}$Mn$_{0.0}$]O$_2$ is also nearly identical to that of
NiO, as shown in the inset of Figure 4a. For \( x = 0.2 \) and 0.25 in \( \text{LiNi}_{1-x/3}\text{Co}_{x/3}\text{Mn}_{x/3}\text{O}_2 \), the inflection is slightly lower compared to that in \( \text{LiNiO}_2 \). However, it is still higher than that in NiO. The main inflection (8330–8365 eV) of Ni for \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) is almost identical to \( \text{LiNiO}_2 \), indicating that the oxidation state of Ni is close to 3+. This means that reduction of the Co and Mn contents brings about partial formation of \( \text{Ni}^{3+} \) from \( \text{Ni}^{2+} \). This confirms that almost all of the \( \text{Ni}^{2+} \) in \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) changed to \( \text{Ni}^{3+} \) in \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \). The initial discharge capacity increases with increasing Ni content due to the increasing redox-active species of \( \text{Ni}^{3+/4+}, \text{Co}^{3+/4+}, \) and \( \text{Mn}^{3+/4+} \) with 165 mAh g\(^{-1}\) for \( x = 0.3 \), 173 mAh g\(^{-1}\) for \( x = 0.25 \), 177 mAh g\(^{-1}\) for \( x = 0.2 \), and 200 mAh g\(^{-1}\) for \( x = 0.1 \) (Figure 4b). The operating voltage in the initial charging stage decreases as the Mn content in the total amount of TM ions decreases. However, the discharge voltages are similar for all of the compositions. This indicates that the capacities of \( \text{LiNi}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) and \( \text{LiNi}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) are strongly dependent on the Ni content, reaching approximately 200 mAh g\(^{-1}\) for \( \text{LiNi}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.6}\text{O}_2 \), which is comparable to conventional \( \text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2 \) (190 mAh g\(^{-1}\) at 4.3 V charge cut-off).\(^{[33]}\)

The Ni-rich materials always evolve from oxygen evolution from the oxide lattice in the temperature range of 150–300 °C when deeply delithiated.\(^{[31c,38a,3,19,29,31,34]}\) The exothermic decomposition temperature gradually shifts to lower temperatures accompanied with higher heat generation as the Ni content increases. As summarized in Figure 4d, the \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) cathode exhibits the best capacity retention and thermal stability among the \( \text{LiNi}_{1-x/3}\text{Co}_{x/3}\text{Mn}_{x/3}\text{O}_2 \) samples. By contrast, its discharge capacity is limited due to the lower amount of Ni. The \( \text{LiNi}_{1-x/3}\text{Co}_{x/3}\text{Mn}_{x/3}\text{O}_2 \) (\( x = 0.075 \)) cathode that contains the highest Ni content experiences severe capacity fading. The capacity fading mechanism is believed to be due to the overall volume expansion of the electrode during cycling and surface structural degradation (transformation to the rock salt structure). Hence, the composition and microstructure of \( \text{LiNi}_{1-x/3}\text{Co}_{x/3}\text{Mn}_{x/3}\text{O}_2 \) needs to be further optimized or modified by heteroelements, in particular the surface, to attain an ideal cathode material with high capacity and thermal stability.

To date, several coating approaches have been introduced to improve the cycle retention, rate capability, and thermal stability of cathode materials. The coating materials include carbon, metal oxides, metal carbonates, metal aluminates, metal phosphates, metal fluorides, metal oxyfluorides, and metal hydroxides.\(^{[35]}\) Surface coating of these materials results in improvements of the cathode materials, which can be attributed to the following: i) protection of the cathode surface from undesired chemical reactions with the organic electrolyte and the consequent suppression of solid-electrolyte interphase (SEI) layer formation, and ii) scavenging by the coating materials of trace amounts of HF present in the electrolyte.

### 2.5. From Core–Shell to Full Concentration-Gradient Samples

Even though a surface coating can effectively improve the structural and thermal stabilities of cathode materials, it is not easy to completely encapsulate the active particles with thin coating layers, which sometimes causes the formation of an island-like coating. Therefore, a new concept was introduced to satisfy the requirements for Ni-rich materials to provide high capacity and good thermal properties. Sun's group proposed the concept of core-shell cathode materials with a Ni-rich core and a Mn-rich shell (Figure 5a,b).\(^{[36]}\) The Ni-rich \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) core has a high capacity but poor structural stability due to unwanted surface reactions with the electrolyte. On the other hand, the shell part of \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) has good structural and thermal stabilities, but a low specific capacity and poor rate capability. These properties can be hybridized in a particle, namely, a core–shell structure with a composition of \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) (0.8)\( \text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \) (0.2). The core–shell electrode demonstrated superior cyclability in full-cell tests, which is ascribed to the stabilized structure derived from the presence of tetravalent Mn in the \( \text{LiNi}_{0.8}\text{Mn}_{0.5}\text{O}_2 \) shell. If the core material, \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \), is present in the shell part, such extraordinary electrode performance would not be achieved due to the structural instability of the core material.

These core–shell structures, however, also have a fatal limitation of boundary cracks between the core and shell due to the different volume expansions during cycling. To overcome this challenge, a new core–shell material with a concentration-gradient shell was introduced.\(^{[37]}\) The end part of the Ni-rich core is directly connected with the concentration-gradient shell to produce a continuous compositional change from the core composition of \( \text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2 \) to the outer composition of \( \text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2 \) (Figure 5b). This approach was very effective to enhance the cycle retention of core–shell gradient (CSG)-type materials due to the minimized formation of microcracks. The CSG material showed good discharge capacity and excellent cycle retention of 96.5% with a graphite anode over 500 cycles at room temperature.\(^{[37]}\)

The core–shell and concentration-gradient structures mitigate the disadvantages of Ni-rich layered cathode materials. However, these materials still have insufficient stability properties, especially during cycling testing at elevated temperatures. The CSG material has a thin outer surface layer, which may affect the thermal stability. Provided that the shell is thickened, good thermal stability and long term cycling properties can be obtained, whereas the resulting total energy density of the cathode material would decrease. This motivated the introduction of full concentration gradient (FCG)-type layered cathode materials (Figure 5c).\(^{[38]}\) Among these FCG-type materials, FCG-Li\( \text{Ni}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}\text{O}_2 \) has a high specific capacity of 215 mAh g\(^{-1}\) at a 0.2 C-rate in the voltage range of 2.7–4.5 V. This result is greater than that of the Ni-rich inner core (a higher amount of Ni than the average FCG composition). In addition, FCG-Li\( \text{Ni}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}\text{O}_2 \) also demonstrated excellent capacity retention over 1000 cycles at both 25 °C and 55 °C (Figure 5d). The most important feature of FCG-type materials is the compositional variation of the TM ions from the inner core to the outer shell. To provide structural and thermal stabilities, the Mn content also gradually increases from the inner core to the outer shell. FCG-type materials have been further improved by modifying the primary particle morphology to nanorods, which can be radially aligned toward the outer shell within the secondary micro-sphere particle (Figure 5c,e). The above mentioned
Figure 5. a) Schematic drawings of core–shell Li\([(Ni_{0.8}Co_{0.1}Mn_{0.1})_{1-x}(Ni_{0.5}Mn_{0.5})_{x}]O_2\) particle and the resulting SEM image of fractured core–shell Li\([(Ni_{0.8}Co_{0.1}Mn_{0.1})_{0.8}(Ni_{0.5}Mn_{0.5})_{0.2}]O_2\) particle. Reproduced with permission.\(^{36}\) Copyright 2005, American Chemical Society. b) Ni-rich core surrounded by concentration-gradient outer layer and the resulting SEM image of the final Li\[Ni_{0.64}Co_{0.18}Mn_{0.18}\]O_2. Reproduced and adapted with permission.\(^{37a}\) Copyright 2009, Macmillan Publishers Limited. c) Full concentration gradient lithium transition-metal oxide particle with the nickel concentration decreasing from the center towards the outer layer and the concentration of manganese increasing accordingly (center). Reproduced and adapted with permission.\(^{38a}\) Copyright 2012, Macmillan Publishers Limited. Cross-sectional TEM image of a full concentration gradient particle composed of long nanowires (left), and discharge capacity of mesocarbon microbead graphite/full concentration gradient cathode full-cells at room and high temperatures in the voltage range of 3–4.4 V (right). Reproduced and adapted with permission.\(^{38b}\) Copyright 2013, American Chemical Society.
core–shell cathode materials were composed of micrometer-scale spherical particles with a polygonal primary particle shape. Electrolyte tends to penetrate into the small voids among the primary particles, which allow diffusion of Li ions along the grain boundary of each primary particle. Also, the exposed surface area of the FCG-type materials to the electrolyte is large, which in turn results in increased reactivity at the interface and can cause deterioration of the electrode performance and inferior safety of the cell. It is interesting that the nanorods point from the center towards the surface. These nanorod primary particles are radially aligned for the full concentration-gradient particle. This configuration of nanorods reduces voids present in spherical particles so that the contact area with the electrolyte is minimized, which enables diminution of side reactions, in particular when the cathode material is highly oxidized. It is evident that FCG particles with a nominal composition of Li[Li\(_{1/3}\)Mn\(_{2/3}\)]O\(_2\) exhibited extraordinary cycling performance over 1000 cycles in full cell tests with a carbon anode (Figure 5e). The capacity retention was approximately 95% at 25 °C and 71% at 55 °C for the short nanorod FCG particles. Even after increasing the upper cut-off voltage to 4.4 V vs. carbon, the long nanorod FCG particles showed a high capacity retention of about 72% over 1000 cycles. It is believed that this behavior is related to the radial distribution of the long nanorods, which minimizes the presence of voids among primary nanorod particles.

Ni-rich compounds usually exhibit a large exothermic peak in the temperature range of 190–220 °C, whereas the presence of the shell or concentration gradient shell delays the main exothermic reaction to a temperature as high as 300 °C, where the differential scanning calorimetry profiles were similar to those of the outer shell composition.\(^{(38)}\) This result clearly indicates that the stability of the outer shell composition is responsible for the significant improvement of the thermal properties of the concentration gradient shell compound. The gradual concentration change of the stable tetravalent Mn in the concentration gradient shell resulted in this enhanced thermal stability, which accentuates the importance of the chemical composition of the outer shell.

3. Li-Rich Layered Oxides

3.1. Introduction

The roots of LLO research go back to 1991, when Thackeray et al., inspired by Hunter’s work, produced Li\(_{1.09}\)Mn\(_{0.91}\)O\(_2\) by acid treatment followed by relithiation of Li\(_2\)MnO\(_3\), and introduced the idea of xLi\(_{2}\)MnO\(_3\)(1 – x)LiMO\(_2\).\(^{(39)}\) Years later, Kalyani et al. discovered that Li\(_x\)Mn\(_{3-x}\)O\(_4\) could be electrochemically cycled.\(^{(40)}\) Lu et al. put these ideas together and studied the Li\(_x\)[Li\(_{1/3}\)Mn\(_{2/3}\)]O\(_2\) series in detail.\(^{(41)}\) Research interest in this topic expanded in the following years, with a lot of the initial work focusing on improving the electrochemical behavior by incorporating other metal ions into the structure or by surface coating, understanding the unique mechanism of the first charge-discharge reaction, and clarifying the structure of the materials. The compositions of LLOs are often written in one of three different notations. The first two notations are $x$Li\([Li_{1/3}Mn_{2/3}]O_2(1-x)LiMO_2$ and $x$Li\(_2\)MnO\(_3\)(1 – $x$)LiMO\(_2\), while the third notation is $Li_{1+x}M_{1-x}O_2$, where M = Mn, Co, Ni, etc. One can easily convert among the three notations. For example, 0.6Li\([Li_{1/3}Mn_{2/3}]O_2\)-0.4LiMnO\(_2\) is the same as 0.5Li\(_2\)MnO\(_3\)-0.5LiMnO\(_2\), which is equivalent to $Li_{1.2}MnO_{2.6}NiO_{0.2}$ if M = $M_{[Ni_{1/3}N_{1.2}]}. This is a common, often investigated, LLO composition.

3.2. Structure

As with all LIB cathode materials, the structure of LLOs can dramatically affect the electrochemical performance, so it is essential that the structure of LLOs be clarified. LLOs can be thought of as a combination of LiMnO\(_2\) and Li\(_2\)MnO\(_3\). LiMnO\(_2\) has a rhombohedral $R3m$ structure, while Li\(_2\)MnO\(_3\) adopts a $C2/m$ monoclinic structure. The two structures, which can be seen in Figure 6a, are very similar, as Li\(_2\)MnO\(_3\) can be written in the normal layered stoichiometry as Li\([Li_{1/3}Mn_{2/3}]O_2\). The different space group of Li\(_2\)MnO\(_3\) arises from the ordering between the Li\(^+\) and Mn\(^{4+}\) ions in the TM layer of the structure. Both LiMnO\(_2\) and Li\(_2\)MnO\(_3\) have a cubic close packed oxygen array in which all the resulting octahedral sites are filled by alternating layers of Li and TM or Li/TM. The peaks in a typical LLO XRD pattern can be indexed to the $R3m$ space group, with the exception of some weak reflections in the 20°–25° range, as shown in Figure 6c. These superstructure reflections are due to Li\(^+\)/Mn\(^{4+}\) ordering in the TM layer, and they, along with the major peaks, can be indexed to the $C2/m$ space group. Reitveld refinement of powder and synchrotron XRD data provide excellent fits when using both space groups in their models, but XRD data can only reveal the average crystal structure.\(^{(42)}\) More advanced characterization techniques must be applied in order to study the local structure of LLO.

Due to the similarity of the LiMnO\(_2\) and Li\(_2\)MnO\(_3\) phases, the local structure of LLOs is very complex, difficult to elucidate, and essential to understanding these materials and their performance. To study the local structure, high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and electron energy-loss spectroscopy (EELS) analysis are required. Significant research efforts have been made to discern the local LLO structure, but there is still no clear consensus among researchers. Several researchers have found evidence of solid solution behavior. For instance, numerous studies have found that LLOs obey Vegard’s law in that their structural parameters vary linearly with composition.\(^{(43)}\) Researchers have also used advanced TEM analysis to directly show the formation of a single structure at the atomic level, although some studies have found $R3m$ symmetry, while others have found $C2/m$ symmetry.\(^{(44,45)}\) An HAADF-STEM image of a particle exhibiting $C2/m$ symmetry can be seen in Figure 6b. Other studies discovered two-phase behavior by showing distinct regions of monoclinic and rhombohedral symmetry within the same particle or Mn-rich domains.\(^{(46)}\) Perhaps the most widely accepted model is the nanocomposite model put forth by Thackeray et al.\(^{(47)}\) They posit that because there are not enough Li ions in the TM layer in most LLO compositions to maintain the 1 Li to 2 TM ratio found in Li\(_2\)MnO\(_3\), there are Li\(_2\)MnO\(_3\)-like and...
LiMO₂-like nanodomains that result in short-range order but not a full solid solution, which has been supported by several studies. Consensus on the local structure of LLO will most likely continue to be elusive because the structure has been found to be sensitive to multiple factors, including Li content, cooling rate, composition, synthesis temperature, etc.

3.3. First Charge–Discharge Cycle Mechanism

One of the defining features of LLOs is their unique first charge-discharge cycle mechanism, which is still not fully understood. The initial charge cycle consists of two regions. During the first part, Li is extracted due to the oxidation of the TM ions to the \( +4 \) oxidation state. This process occurs up to \( \approx 4.4 \) V and consists of Li being removed concomitantly with oxygen; oxide ions are oxidized and lost as \( \text{O}_2 \) gas, but LLOs can be thought of as losing \( \text{Li}_2\text{O} \). In this article, these regions will be referred to as the “sloping region” and the “oxygen-loss plateau”. The initial discharge cycle is also complex due to the complicated nature of the first charge cycle. During the first discharge, the TM ions that were oxidized during the sloping region are reduced back to their initial states. Then, because of the lost oxygen ions during charge, another ion must be reduced, so some Mn\(^{4+}\) ions are reduced to Mn\(^{3+}\). While this mechanism can explain the high capacities seen with LLOs (up to 300 mAh g\(^{-1}\)), it would require nearly every Mn\(^{4+}\) ion to be reduced to Mn\(^{3+}\). Other mechanisms, such as reversible oxygen reduction, side reactions with the electrolyte, and/or proton exchange, are also believed to provide additional capacity. These mechanisms will be further discussed in later sections.

Numerous studies have focused on the substitution of different metal ions into a base LLO composition, often \( \text{Li}_1.2\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2 \), in order to alter the length of the sloping region and oxygen-loss plateau. When substituting an additional metal ion into the composition, Ni and Mn should be kept in their \( +2 \) and \( +4 \) oxidation states, respectively, so the new compositions must be chosen carefully. This means that a \( +2 \) ion, such as Mg\(^{2+}\), should replace Ni\(^{2+}\), while a \( +4 \) ion, such as Ti\(^{4+}\), should...
replace Mn$^{4+}$. A 3$^+$ ion, such as Al$^{3+}$, should replace Mn$^{4+}$ and Ni$^{2+}$ equally. Any dopant ion that can be oxidized above 4$^+$ will significantly increase the length of the sloping region. Examples of this include Ru and Cr, as they can be oxidized to 5$^+$ and 6$^+$, respectively. Conversely, substitution of electroinactive ions, such as Mg$^{2+}$, Al$^{3+}$, and Ga$^{3+}$, markedly decrease the length of the sloping region. Ions that maintain the same level of electroactivity, such as Co$^{3+}$ and Fe$^{3+}$, cause slight changes in the length of the sloping region due to changes in conductivity and whether or not they can be fully oxidized to the 4$^+$ state. The effect of substituted ions on the length of the plateau region is not as straightforward, however, as it varies with the covalency of the metal-oxygen bond. The covalence of this bond is determined by the position of the metal 3d band relative to the oxygen-$2p$ band. The overlap of the Co$^{3+}$/4$^+$ t$_{2g}$ band with the top of the O$^{2-}$ 2p band leads to Co as the only dopant found to significantly increase the oxygen-loss plateau length.

Other metal ions, such as Ti$^{4+}$, reduce the length of the oxygen-loss plateau upon substitution due to their less covalent metal–oxygen bonds. This is usually an intrinsic property of the ion, but sometimes can be caused by other factors, such as the formation of Ru–Ru dimers. Figure 7a illustrates the effect of Co$^{3+}$ and Ti$^{4+}$ doping on the sloping region and the oxygen-loss plateau, while Figure 7b depicts a qualitative energy band diagram of those materials.

A lot of recent work in this area has focused on better elucidating the oxygen-loss plateau mechanism. Because the oxygen-loss behavior is derived from the Li$_2$MnO$_3$ character of the LLO system, one might think that studying the cycling mechanism of Li$_2$MnO$_3$ would provide insight into the mechanism of LLO. To that end, Li$_2$MnO$_3$ has also been investigated extensively, where it was found that H$^+$/Li$^+$ ion exchange accounts for some of the electrochemical activity in the plateau region. However, Dogan et al. and Croy et al. used nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS) measurements to show that not only ion exchange does not occur in LLOs during the oxygen-loss plateau, but also the Li$_2$MnO$_3$ component of LLOs does not behave structurally or electrochemically like pure Li$_2$MnO$_3$. They did, however, find the progressive build-up of proton-containing species, presumably on the cathode surface during extended cycling. This leaves oxide ion oxidation and subsequent loss of Li$_2$O as the accepted cause of the oxygen-loss plateau. It has been confirmed using differential electrochemical mass spectrometry (DEMS), synchrotron XRD, EELS, and Rietveld refinement that oxide ions are oxidized and oxygen gas is evolved during the oxygen-loss plateau. Recently, however, Delmas et al. have proposed a more complicated mechanism of irreversible oxide-ion oxidation and subsequent oxygen loss at the surface of the particles coupled with reversible oxide-ion oxidation in the bulk. They used electrochemical measurements, neutron diffraction, chemical analysis, Raman spectroscopy, and HAADF-STEM to reach this conclusion by showing that oxygen gas is evolved at the surface. TM ions migrate from the surface to the bulk in a densification process, but that the bulk structure does not undergo any significant structural change.

Several studies by Tarascon et al. have focused on Li$_2$RuO$_3$-based materials that are similar in structure to Li$_2$MnO$_3$ in order to study the electrochemical mechanism of LLO. They were able to demonstrate that oxide ions can be reversibly oxidized to peroxide/superoxide-like species and that the propensity to do so, as opposed to being irreversibly lost as oxygen gas, can be altered by cation substitution, such as Sn, which affects the d-sp hybridization of the metal-oxygen bond. Other work has been done on first cycle mechanism, but it will be discussed in the sections on IRC and voltage decay.
3.4. Obstacles to Commercialization

While researchers have made great strides in understanding the structure and properties of LLOs, as well as improving their performance and mitigating some of their deficiencies, significant progress is still required in order for LLOs to become commercially viable. The major challenges associated with LLOs include voltage decay during cycling, large 1st cycle IRC, poor rate capability, and low volumetric energy density. A brief overview of these issues and some recent progress in overcoming these challenges is presented in the next sections.

3.4.1. Voltage Decay

Voltage decay, which may also be denoted as voltage fade, is perhaps the greatest obstacle to LLO commercialization, and it refers to the fact that during extended cycling, LLOs suffer from a significant decrease in operating voltage. This in turn causes a reduced energy density and difficulty in determining the state of charge of battery cells. It is understood that there is a gradual structural change to a new phase during extended cycling, that TM ions migrate into Li sites in both the TM and Li layers, and a TM-rich and Li-poor surface phase is formed, where TM ions are reduced and react with the electrolyte.\[57\] Though the exact structure of the defect phase is not fully understood, it is commonly referred to as a spinel-type phase, which is the term used in this progress report. Numerous published reports have shown evidence of the increasing spinel-like phase growth during extended cycling through dQ/dV analysis, XAS, and HRTEM, some of which are shown in Figure 8a.\[58\]

![Figure 8](image)

**Figure 8.** a) High-resolution HAADF-STEM images of Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) after (from left to right) 0, 5, 45, and 100 cycles showing the gradual growth of the spinel-like surface layer. Reproduced with permission.\[57a\] Copyright 2014, American Chemical Society. b) Voltage profiles of Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) synthesized using a (from left to right) co-precipitation, sol–gel, and hydrothermal assisted method showing voltage decay during extended cycling. Reproduced with permission.\[62\] Copyright 2014, American Chemical Society. c) The 1st (left) and 50th (right) cycle normalized discharge profiles of Li\(_{1.2-x}\)Mn\(_{0.54}\)Ni\(_{0.13}\)Co\(_{0.13-x}\)O\(_2\) (x = 0, 0.05, 0.075, and 0.1) showing the reduced voltage decay at higher x values. Reproduced with permission.\[66b\] Copyright 2014, The Royal Society of Chemistry.
the migration of TM ions from the octahedral sites of the metal layer through tetrahedral sites to empty octahedral sites in the Li layer and the formation of Li dumbbell structures, which are two Li ions trapped in tetrahedral sites above and below a Li site vacancy in the metal layer.\textsuperscript{66b} Sathiya et al., however, found that TM ions migrating to the Li layer was not a major cause of concern, but instead problems arise when TM ions are trapped in tetrahedral sites, which can be reduced by using larger TM ions.\textsuperscript{56b}

Extensive work has recently been done at Argonne National Laboratory to elucidate the voltage decay mechanism.\textsuperscript{53b,59,61} Among many other findings, they propose a mechanism that leads to voltage decay.\textsuperscript{61b} Upon charging, some TM ions migrate to tetrahedral sites, and then once discharged to \( \approx 3.3 \) V, they may follow one of three paths. They may migrate back to octahedral sites in the TM layer, which leads to an energy difference that manifests as hysteresis during cycling. They may become trapped in the tetrahedral sites, which leads to decreased Li diffusion, increased impedance, and reduced capacity, or they may migrate to octahedral sites in the Li layer, which alters the local structure to one with a lower operating voltage, causing voltage decay. Synthesis technique and conditions can also affect voltage decay, as researchers have reduced voltage decay by utilizing a hydrothermal assisted synthesis method instead of the standard co-precipitation and sol-gel methods to produce greater Ni-homogeneity throughout the particles.\textsuperscript{62} This led to a uniform \( C2/m \) phase particle as opposed to a mixture of \( \text{R}3\text{m} \) and \( C2/m \) phases, minimized the number of Ni\textsuperscript{4+} ions at the particle surface, which are highly reactive with the electrolyte, and enhanced the Ni–Mn interactions that have been shown to stabilize the LLO structure.\textsuperscript{57a,63}

Figure 8b shows the vast differences in voltage decay produced by various synthesis techniques. Specific surface facets can greatly affect the mechanism, as Yan et al. concluded that surfaces terminating in purely cations or purely anions were resistant to structural changes, whereas surfaces terminating in a mix of cations and anions produced a surface layer that was Mn-rich on the outside but Ni-rich on the inside.\textsuperscript{57a} They proposed that Ni migrated from the bulk to the surface, where it reacted with the electrolyte at a faster rate than Mn, which led to voltage decay due to decreased redox capability and a reduction in stabilizing Mn–Ni interactions.

Other mechanistic studies have found that two competing rate laws determine the kinetics of voltage decay and that proton insertion does not play a role in the process.\textsuperscript{53b,64} While it was originally thought that voltage decay arose due to the high voltage required to activate the Li\textsubscript{2}MnO\textsubscript{3} component of LLOs, Li et al. have shown that the process occurs even when LLOs are cycled well below this activation threshold.\textsuperscript{85} A simple analysis to visualize the voltage decay is to just compare the shapes of voltage profiles of an early cycle to one after extended cycling; however this method is not always accurate due to differences in specific capacities and the fact that electrode impedance also affects voltage decay. Normalizing voltage profiles eliminates the first issue, while Bettge et al. suggests a testing protocol focused on the iR-corrected average voltage of materials to overcome the second.\textsuperscript{86}

Researchers are attacking this problem from several different directions. One of which is intelligently altering the composition of LLOs through doping. Lee and Manthiram showed that while the octahedral site stabilization energy (OSSE) of the TM ions is a significant factor in the phase transformation of layered oxides, it does not play as large a role in LLOs due to the differences in their dumbbell formations.\textsuperscript{66b} On the other hand, they found that decreasing the length of the oxygen-loss plateau by increasing the Ni content at the expense of the Li and Co content is an effective means of reducing voltage decay, which agrees with another study that shows increasing Li\textsubscript{2}MnO\textsubscript{3} content increases voltage decay.\textsuperscript{61b,66b} This inhibits voltage decay by reducing the amount of Li ions in the TM layers, so fewer dumbbells are formed and by creating fewer oxygen vacancies, which in turn hinders TM ion migration. The voltage decay reduction produced by their novel LLO series is depicted in Figure 8c.

Song et al. extended this idea by increasing the sloping region at the expense of the oxygen-loss plateau even further by doping with Cr and saw reduced voltage decay.\textsuperscript{67} Ates et al. and Li et al. recently used the addition of Na\textsuperscript{+} and K\textsuperscript{+} ions, respectively, to show that monovalent dopants can provide structural stability to LLOs and block the layered-to-spinel transformation.\textsuperscript{68} Ates et al. published another report that used Ni\textsuperscript{3+} doping to improve voltage decay by decreasing the amount of Mn\textsuperscript{2+} created during the first discharge, which increases the average discharge voltage and inhibits the growth of the spinel-like phase.\textsuperscript{68} Zheng et al. coated LLO with AlF\textsubscript{3} and found that it reduces voltage decay by providing structural stability and protecting the electrode from side reactions with the electrolyte; however, a previous study did not see any improvement by various other coatings.\textsuperscript{70} Recent attempts at forming composite materials by combining LLOs with high-voltage spinel materials have had success, as the spinel additive stabilizes the layered structure and inhibits the additional growth of the spinel-like phase.\textsuperscript{63a,71} Composites can be created by using less Li than is stoichiometrically required during calcining or by growing a spinel outer layer on LLO seed particles using a modified sol-gel process.

### 3.4.2. Rate Capability

Another significant issue with LLOs is their low rate capability. This is caused by several factors, including the insulating nature of Mn\textsuperscript{4+} ions in the Li\textsubscript{2}MnO\textsubscript{3} component, a large charge-transfer resistance at the interface between the particle and the electrolyte, a thick SEI layer that forms during cycling, poor delithiation kinetics (particularly in the Li\textsubscript{2}MnO\textsubscript{3} component), and the often large particles of LLOs synthesized by researchers.\textsuperscript{72}

There are several strategies that researchers have used in order to increase the rate capability of LLOs. The first and most prevalent method to enhance rate capability is through surface modification, which can refer to either coating the particle surface with a compound or treating the surface to enact a structural change. Surface modification increases rate capability by decreasing the charge-transfer resistance, increasing particle conductivity, and/or altering the SEI layer thickness and composition. Electrically conductive coatings, which are often made of polymers, carbon-based materials, or carbon composites, enhance the rate capability by increasing the conductivity of
LLOs. Examples of these coatings include carbon, graphene-like carbon, carbon nanotubes, polyaniline, a polystyrene/polysulfone-based polymer (PEDOT:PSS), an Li$_3$PO$_4$/C composite, and reduced graphene oxide (rGO)/AlPO$_4$ composites. A TEM image of an rGO/AlPO$_4$ composite coated particle and the rate capability improvement can be seen in Figure 9 b,c, respectively. The remaining coatings can be summarized as metal oxides and metal phosphates, and their rate capability improvement is derived from lowering the charge-transfer resistance by creating a different interface with the electrolyte. Therefore, the coatings also change the nature of the SEI layer formation, often resulting in thinner coatings that are less insulating than those on the uncoated materials. Cu$_2$O, Sm$_2$O$_3$/CeO$_2$, Pr$_6$O$_{11}$, V$_2$O$_5$, MnO, and Al$_2$O$_3$ are examples of successful metal oxide coatings. Some examples of metal phosphate coatings include AlPO$_4$, CoPO$_4$, CePO$_4$, Li$_3$V$_2$(PO$_4$)$_3$, LiNiPO$_4$, and Co$_3$(PO$_4$)$_2$. One additional coating that has been found to markedly improve rate capability, along with other electrochemical properties, is AlF$_3$. When dealing with surface coatings, special care must be taken to ensure that the particles are coated uniformly and that the coating thickness is optimized. With many coatings, there is a thickness “sweet spot”, where they are thick enough to impart structural stability but not too thick as to impede electronic and ionic conductivity. Surface treatment is an additional method of improving the rate capability of LLOs, which often consists of exposing the active material to a treatment solution followed by an annealing step. LLOs treated with Super P carbon, NH$_4$SO$_4$, and persulfates have been found to increase the rate capability by removing Li$^+$ ions from the particle surfaces, inducing a structural change to a spinel phase on the surface. This improves conductivity and enhances rate capability. Furthermore, there are several additional methods utilized to increase the rate capability: altering the synthesis method in order to make particles with shorter Li ion diffusion paths, elemental substitution, and forming composites with other materials. In order to shrink the Li-ion diffusion paths, various nanostructures are employed. For instance, researchers have
synthesized micrometer-sized secondary particles made up of 80–200 nm sized primary particles, 30 nm diameter nanowires made by ion exchange that possess a very impressive 5C discharge capacity of 275 mAh g\(^{-1}\), and nanoparticles that preferentially expose the (010) surface plane in order to increase Li-ion diffusion.\(^{[79]}\) The downside to nanoparticles is that they have a drastically increased surface area, which leads to greater SEI layer formation, side reactions with the electrolyte, and safety concerns due to increased oxygen loss.

Elemental substitution is a simple approach to boost rate capability. Certain dopants are able to reduce the impedance of the bulk material and may increase lattice parameters if they have a larger ionic radius, which reduces the energy barrier and promotes Li-ion diffusion. These dopants include Mg, Al, Co, Cr, Fe, Ru, Na, and F, although F doping may actually form an LiF coating instead of going into the lattice.\(^{[42b,68a,79]}\)

A final method to strengthen the rate capability of LLOs is to physically blend it with another material to form a composite. Blending LLOs with high-voltage spinel (LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\)) is the most studied composite, as spinels have excellent rate capability due to their 3D Li-ion transport, and they also possess the same cubic close packed oxygen lattice as LLOs.\(^{[63a,71b]}\) Moreover, Gallagher et al. found that mixing LLOs with LiFePO\(_4\) enhanced the rate capability and pulse power due to the lower impedance provided by the olivine structure at low states of charge.\(^{[80]}\)

### 3.4.3. First Cycle Irreversible Capacity Loss

A large first cycle IRC, often 60–100 mAh g\(^{-1}\), is a third crucial issue for LLOs. In the literature, some researchers instead refer to this issue as a low first cycle Coulombic efficiency, where values are usually less than 80%, but both phrasings refer to the same topic. As with most other electrochemical properties of LLOs, the large IRC is linked to the unique first charge-discharge cycle.\(^{[41c,83]}\) During the oxygen-loss plateau, Li\(_2\)O is removed from the structure, leaving oxygen vacancies and Li vacancies in both the TM and Li layers behind. At the end of the first charge cycle, some of these vacancies are eliminated through structural densification caused by TM migration.\(^{[82]}\) Cations in the TM layer migrate through tetrahedral sites to empty Li sites in the TM layer and in the Li layer, and a corresponding amount of oxygen vacancies are also eliminated. For every oxygen vacancy eliminated, one Li vacancy is also eliminated. Because of this process, not all of the Li ions extracted during the first charge can be inserted back into the structure, causing the high IRC. These excess Li ions are then free to react with products of the electrolyte decomposition to form a thicker SEI layer. Researchers have found that most but not all of the oxygen vacancies are eliminated during the first cycle.\(^{[82]}\) The remaining vacancies could be removed during subsequent cycles, which could manifest as fading capacity.

Researchers have used several different solutions to combat the IRC problem. Composite materials can be made by blending LLOs together with a Li-insertion host in order to recapture the Li ions that cannot be reintegrated to the LLO structure. Manthiram's group pioneered this method, initially using V\(_2\)O\(_5\) before later investigating LiV\(_2\)PO\(_4\), Li\(_2\)Mn\(_2\)O\(_4\), and VO\(_2\)(B).\(^{[81]}\) The effect of VO\(_2\)(B) addition on the first cycle IRC can be seen in Figure 9a. They were able to completely eliminate the first cycle IRC using this method, but the addition of the other hosts decreases the gravimetric capacity. Gallagher et al. also reported a decreased IRC when they incorporated LiFePO\(_4\) into an LLO composite.\(^{[80]}\) The use of Li-insertion hosts only manages the effects of the IRC mechanism, instead of trying to solve the underlying causes of oxygen loss and TM migration. Various methods have been used to attack the root causes of the large IRC. Surface treatment is again a prevalent and successful method for reducing the IRC. As mentioned in the rate capability section, coatings provide structural stability to LLOs,\(^{[82]}\) which also helps maintain more of the vacancies that are formed, so they reduce IRC via two different processes.\(^{[82]}\) Nearly all of the coatings mentioned in the rate capability section reduce the IRC, so they will not be listed in detail here again.\(^{[73a,g,74b,c,f,g,75b,84]}\) One interesting example, however, is LiV\(_2\)O\(_4\), because it serves as a coating and a Li-insertion host.\(^{[74e]}\) Some of the surface treatments previously mentioned, such as Na\(_2\)S\(_2\)O\(_5\) and HNO\(_3\), can also reduce the IRC as they chemically remove Li\(_2\)O, causing a surface structural transformation which essentially serves as a coating layer.\(^{[76c,85]}\)

Altering the material composition can also have beneficial effects in reducing the IRC. Substituting Ru for Mn has been found to markedly reduce the IRC, presumably due to the reduced Li\(_2\)MnO\(_3\) character of the material.\(^{[86]}\) Tarascon et al. also significantly reduced the IRC by developing another family of LLO materials, Sn-doped Li\(_2\)RuO\(_3\).\(^{[86]}\) The low IRC is due to the large Sn\(^{4+}\) ions that resist TM migration and the ability of Ru\(^{4+}\) to promote reversible oxide-ion oxidation, which reduces oxygen loss and vacancy formation. The IRC can also be reduced by altering the cycling protocol. Van Bommel et al. used stepwise charging to reduce the IRC by maintaining more oxygen vacancies after the oxygen-loss plateau.\(^{[87]}\) Multiple groups have also found that cycling at higher temperatures decreases the IRC significantly, but this may be due to increased side reactions with the electrolyte instead of increased Li reinsertion.\(^{[88]}\) A recent study by Shunmugasundaram et al. used the novel idea of synthesizing LLO materials with metal site vacancies to considerably reduce the IRC.\(^{[89]}\) By inducing metal site vacancies, they created a material that is Li-rich by having a Li:TM ratio greater than 1 and exhibiting an oxygen-loss plateau, but it is structurally analogous to traditional layered oxides due to the lack of Li\(^{+}\) ions in the TM layer. These built-in metal vacancies still allow for near complete Li reinsertion even after some structural densification occurs.

### 3.4.4. Volumetric Energy Density

The final hurdle to LLO commercialization is their low volumetric energy density, which is caused by a combination of voltage decay, capacity fade, and often small particle size. Voltage decay refers to the gradual structural transformation of the LLO material to a spinel-like phase, which results in reduced operating voltage. Readers can refer to Section 3.4.1 for a thorough discussion on this topic. The capacity fade of LLOs proceeds through multiple mechanisms: Li\(^{+}\) ions react and become trapped in the SEI layer, HF molecules created by trace amounts of water reacting with the electrolyte attack the
The poor rate capability of LLOs, caused by the low Li diffusion rate in the Li₂MnO₃ component, leads researchers to synthesize smaller particles, which tend to be less dense. These smaller particles have a higher surface area, which leads to increased reactivity with the electrolyte, a thicker SEI layer, increased oxygen loss, and enhanced layered-to-spinel transformation, which speeds up voltage decay.

A myriad of solutions have been attempted in order to improve the volumetric energy density by increasing the particle density or by minimizing the capacity fade. Two simple methods, stepwise precycling and the use of electrolyte additives, do not require altering the LLO material at all. Electrochemical precycling has been mentioned before as a way to reduce the IRC, but the process also reduces capacity fade. Studies by Ito et al. and Nakahara et al. have shown that stepwise traversing of the oxygen-loss plateau can reduce microcrack formation at the surface and may promote the reversible oxidation of oxide ions, both of which enhance cyclability.

In order to fully activate the Li₃MnO₄ component of LLOs, cells must be cycled above 4.5 V, which is outside of the electrolyte stability window, so it decomposes and reacts with the cathode, leading to capacity fade and other negative outcomes. Electrolyte additives have been studied extensively in order to reduce this issue, as they are a relatively inexpensive and simple method of improving the cyclability of LLOs. They are often large organic molecules, and some examples are lithium organo-phosphates and lithium organo-borates. They promote better electrochemical performance by inhibiting electrolyte decomposition derived from both the high voltage and reactions with the superoxide ions created during the oxygen-loss plateau, acting as an HF scavenger in order to suppress TM dissolution, and forming a more stable and less insulating SEI layer.

Another approach to decreasing the capacity fade is by surface coating. The topic of surface coating should be familiar to the reader by now, as it has previously been discussed how surface coating can alleviate the LLO issues of poor rate capability and large first cycle IRC. With regards to capacity fade, however, surface coating is effective because it reduces electrolyte decomposition, which leads to the creation of a thinner and more robust SEI layer containing less Li⁺ ions. It also impedes surface attacks, such as TM dissolution, etching, and pitting that lead to material loss, by absorbing HF molecules. There are numerous examples of coatings that reduce the capacity fade, including the previously discussed carbon-based, metal phosphates, AlF₃, and metal oxides. One drawback to coatings, however, is that they often reduce the energy density compared to the pristine material.

Moreover, the volumetric energy density can also be increased by altering the synthesis method or parameters in order to minimize the capacity fade or to create larger and denser particles without sacrificing rate capability. Researchers have frequently found that producing particles that are more uniform in size, morphology, and composition, as well as more crystalline, leads to an increase in cyclability. The common methods of LLO synthesis are co-precipitation and sol-gel; however other techniques, such as combustion, organic co-precipitation, and hydrothermal-assisted synthesis can enhance cyclability. Zheng et al. used a hydrothermal-assisted synthesis method with great success. Energy dispersive spectroscopy (EDS) showed that Ni segregated to particle surfaces in the samples made by co-precipitation and sol-gel synthesis. In the hydrothermal-assisted materials, there was a uniform distribution of Ni throughout the particles, which led to decreased side reactions with the electrolyte and excellent cyclic stability.

A more promising area of research is in hierarchical structures, which are micrometer-sized secondary particles composed of nano-sized primary particles. The aim of these structures is to combine the often enhanced rate capability of nanoparticles with the decreased electrode/electrolyte side reactions and higher density of the micrometer-sized particles. Several studies have found novel ways of synthesizing hierarchical structures with varying degrees of success of producing high discharge capacity, rate capability, and cyclability. Oh et al. utilized an ionic interdiffusion method to synthesize uniform spherical secondary particles composed of nanoplates preferentially oriented to expose planes with facile Li⁺ diffusion paths, which lead to superior cyclic stability and rate capability. Oh et al. used a co-precipitation method followed by hydrazine surface treatment to create dense 10 micrometer particles made of flake-like primary particles. The hydrazine treatment formed a spinel-like phase on the surface, and the material exhibited excellent density and electrochemical performance. Some representative images and electrochemical data of Zhang and Oh’s hierarchical structures can be seen in Figure 10.

4. Conclusions and Future Directions

This report has provided a brief account of the progress made in recent years and the challenges associated with both Ni-rich layered oxide and Li-rich layered oxide cathodes. A summary of the progress made and future directions are briefly given in the next sections.

4.1. Ni-Rich Layered Oxides

Ni-rich layered oxides are being pursued as next generation Li-ion battery cathodes because of their high discharge capacity (200–220 mAh g⁻¹) and lower cost than current Li-ion battery cathodes. They are derived from LiNiO₂, which possesses the typical rhombohedral layered oxide structure. Some challenges associated with LiNiO₂, however, are the difficulty in maintaining all Ni ions in the 3+ oxidation state as some tend to reduce to Ni²⁺, and the consequent presence of Ni²⁺ ions in the Li layer, which affects the layerenedness of the structure and reduces the rate capability. It was found that doping with other cations could improve the structural stability, discharge capacity, and thermal stability. Researchers then found that the substitution of two or more metal ions can provide even greater performance improvement. The two most successful combinations of dopant ions are Co/Al and Mn/Co. The addition of Mn and Co to LiNiO₂ is particularly beneficial, as Mn exists in the 4+ state, which allows for the formation of more Ni²⁺ ions.
While the Mn$^{4+}$ ions are electrochemically inactive and enhance structural stability, the Ni$^{2+}$ ions and their presence in the Li layer lowers the rate capability. Researchers have tried to combat these issues with a variety of approaches. The simplest is to add a surface coating to the cathode oxide particles. Surface coating can mitigate many of the issues facing Ni-rich layered oxides, including raising the rate capability through an increase in electrical conductivity and Li-ion diffusivity, improving capacity retention, and reducing thermal instability. The capacity retention and thermal stability enhancements are due to the altered interface with the electrolyte. The coatings decrease side reactions between the active material and the electrolyte and act as an HF scavenger. Some of the more successful coatings are metal phosphates and metal oxides.

Altering the particle morphology has also been found to mitigate some of the issues with Ni-rich layered oxides. Synthesizing nanorod primary particles that are radially aligned to the outer shell significantly improve cyclic retention because they reduce the number and size of voids that the electrolyte can fill. By reducing the interfacial area between the active material and the electrolyte, side reactions are reduced, leading to superior cyclability.

Another method of improving Ni-rich layered oxide performance is through the use of compositional heterogeneity. The first form of this was to synthesize a high capacity Ni-rich core inside of a Mn-rich shell that provided structural and thermal stability. During cycling, however, the different rates of expansion led to cracks between the core and shell and material failure. To overcome this problem, Sun's group has synthesized shell layers that had concentration gradients throughout them. This enhanced the capacity and cyclability of the materials, but the thermal stability was still an issue. This led to full concentration gradient materials, where the composition varied throughout the entire particle, which are currently being intensely pursued.

Overall, it remains challenging to achieve both a high capacity and excellent stability because of the different characteristics of individual TM ions. There is a trade-off relationship among capacity, cyclability, and thermal properties in Ni-based layered cathode materials. Therefore, effective mitigation of these problems requires exploration of the best compositions, which satisfy application-specific goals. Combining at least two compositions (e.g., layered-layered or spinel-spinel) seems to be a better approach to realize the goals through material design, including the synthesis method, morphology, composition, and charge balance, involving new concepts from nano- to microscale modification. Lithium-ion batteries are indispensable power sources in the mobile market, and they could also become critical for mid- to large-scale applications.

### 4.2. Li-Rich Layered Oxides

LLOs are a candidate to replace the current crop of Li-ion battery cathodes due to their large discharge capacity of 250–300 mAh g$^{-1}$. They have a complex structure, as they can be viewed as a combination of Li$_2$MnO$_3$ and LiMO$_2$, and, depending on synthesis conditions and composition, they can form either a single phase solid solution or a nanocomposite. LLOs also possess a very unique two-part first charge profile that consists of an initial region where the TM ions are oxidized,
which is followed by a long plateau, where oxide ions are oxidized. Some oxide ions are irreversibly oxidized and lost from the structure, while others are reversibly oxidized and contribute to the high discharge capacity. Some of the oxygen and Li vacancies created during the first charge are then eliminated through TM migration, which leads to a large first cycle IRC, creation of reduced Mn$^{3+}$ ions, and a gradual transformation of the material to a spinel-like phase and subsequent voltage decay.

However, there are considerable challenges inherent to LLOs, including the aforementioned voltage decay and IRC, as well as low rate capability due to the Li$_2$MnO$_3$ component and low volumetric energy density. Researchers have devised several strategies to resolve these issues. New synthesis methods have been developed to produce more homogenous particles and hierarchical structures that exhibit strong electrochemical performance and dense particles. The composition can be altered by adjusting the ratio of the Li$_2$MnO$_3$ and LiMO$_2$ phases or cation substitutions, which, when done intelligently, can have positive impacts on the voltage decay, IRC, and rate capability concerns. Surface modification through coating or chemical treatment can significantly enhance the electrochemical performance of LLOs by stabilizing the structural framework and protecting the particle surface from negative reactions with the electrolyte. Other solutions to mitigating the negative properties of LLOs include changing the cycling parameters, using electrolyte additives, and creating composite materials by blending LLOs with other compounds.

The approaches mentioned in this progress report have partially mitigated some of the challenges posed by the LLO materials; however, substantial improvements are still required in order for these materials to move to the commercial level. Multiple studies have investigated the local structure, but there is still no consensus among researchers. That disagreement is due in part to the various synthesis procedures and compositions used in the studies. A clearer understanding of the local structure, particularly the Li/TM ordering, with respect to synthesis conditions and composition is required. This will require a combination of characterization techniques, such as HAADF-STEM, neutron diffraction, Raman spectroscopy, and EDS. Once a thorough understanding of the local structure is gathered, it can inform the studies of the cycling mechanism and electrochemical properties. Completely elucidating the cycling mechanism, specifically the first charge-discharge cycle, is the next crucial step in LLO development because all of the electrochemical properties tie back to the unique first cycle behavior. Specifically, the prevalence and mechanism of reversible oxide-ion oxidation and how it is affected by local structure and composition is of prime importance. Other points of emphasis should be the fate of O$_2$ gas and oxide radicals upon removal from the cathode, figuring out how the various types of vacancies are created and eliminated, and the process of TM and Li migration in the structure. One potential method of investigating the cycling mechanism is to look further into the results of high temperature cycling. LLOs have exhibited discharge capacities of 310–350 mAh g$^{-1}$, which is above the theoretical limit, when cycled at 55 °C or above.$^{[96c,d,56]}$ If this unexpected capacity is not due to electrolyte oxidation or proton exchange, then this behavior could provide insight into the room-temperature mechanism as well.

Additionally, more work needs to be done to solve the major drawbacks of LLOs. Surface coating has repeatedly been shown to improve the discharge capacity, cyclic stability, and rate capability, while reducing the IRC, but it has not been as effective at mitigating the voltage decay phenomenon, meaning this process also takes place in the bulk material. Other methods need to be developed to combat the TM migration, vacancy elimination, and subsequent phase transformation in order to halt voltage decay. Additional synthesis of hierarchical structures with new morphologies should be pursued, as they have shown the most promise in raising the volumetric energy density of LLOs. Several newer areas of LLO research are also ripe for further exploration. Electrolyte additives were briefly discussed previously, but development of new additives could greatly enhance the electrochemical performance of these materials, particularly if they were electroactive and could collect oxygen ions before they partake in negative side reactions. It may be possible to find enhanced performance and new insights in materials that are not based on the Li$_2$MnO$_3$-LiMO$_2$ system, such as how Tarascon et al. have developed Li$_2$RuO$_3$-based materials.$^{[49c,d,56]}$ Thermal stability is another area that should be further explored in LLOs. When charged to high voltages, LLOs have poor thermal stability due to the oxygen lost from the structure.$^{[96]}$ This effect can be mitigated to some extent by synthesizing larger particles or coating the particles, both of which reduce the side reactions that lead to thermal runaway reactions.$^{[72a,96]}$ More in depth research, however, is required on this topic.

The number of full cell studies is limited, so more should be undertaken, as this is another obstacle towards commercialization and phenomena seen in half cells may not always match those seen in full cells.$^{[57,97]}$ Unfortunately, this may add to the list of LLO problems that need to be addressed. Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$ is often seen as the “base” LLO composition, so it is frequently the subject of advanced structural studies and new synthesis techniques. This composition has a lower capacity, however, due to the lack of Co substitution. Cation substitution can significantly affect local structure and particle morphology, so while it is certainly wise to understand the “base” material before modifying it, more analyses should be completed on Co-substituted compositions and other higher capacity LLOs, as they are more likely to be the materials that are of commercial interest. Exploring the synergistic effects of techniques presented in this report should also be pursued. For example, an electrolyte additive may eliminate the capacity fade found in a dense material with superior rate capability produced by a novel synthesis procedure, thus mitigating multiple shortcomings of LLOs. Interested readers can find further discussion of the current research on LLOs in other review articles.$^{[72a,96]}

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