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Review—Li-Rich Layered Oxide Cathodes for Next-Generation Li-Ion Batteries: Chances and Challenges

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Since their commercialization Li-ion batteries have relied on the use of layered oxides (LiMO₂) as positive electrodes. Over the years, via skilful chemical substitution their performances have drastically improved in terms of safety and capacity, which has nearly doubled (280 mAh/g) with the recent arrival of Li-rich NMC, i.e. layered LiCoO₂ in which Co has been simultaneously replaced by Mn, Ni and Li. This review will aim to describe the chemical rationale which has led to this material evolution prior to focus on Li-rich NMC phases which are sources of excitement but challenges as well. The benefits of going back to fundamentals to rationalize and understand the new science at work with these Li-rich NMC phases will be stressed and illustrated by the discovery of a new reversible anionic redox process. Issues regarding voltage fade and limited rate capability which are plaguing their present utilization in commercial Li-ion cells will be addressed as well and solutions proposed. Owing to such advances, layered oxides which are over performing spinel or polyanionic-based compounds have a bright future.

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Lithium batteries first and then Li-ion batteries have been the subject of intensive research ever since 1976 when Exxon reported the first observation of reversible Li intercalation in Li_xTiS₂.¹ However, for safety reasons associated with the dendritic growth of Li, the commercialization of the non-aqueous Li-based technology was stopped. Attempts to circumvent this issue led to the emergence of the Li-ion concept in the 1980's² and the commercialization of the LiCoO₂/C Li-ion technology by Sony in 1991. The current state-of-the-art positive electrodes use either LiCoO₂ or its derivatives, spinel-like compounds such as LiMn₂O₄ or polyanionic compounds among which LiFePO₄ is poised to play a major role in the near future.

Today's research is divided into two schools; one, favoring safety and cost at the expense of energy density, which is sacrificed due to the dead weight of polyanions; the other prioritizes energy density, driven by myriad tweaks to the LiCoO₂ chemistry. Even though both have led to rich discoveries, this review focuses on the latter, that is on layered oxide chemistry.

Let us recall that for reliable operation, the delithiation process in LiCoO₂/C Li-ion cells must be limited to 0.5 Li, which means that solely 50% (~140 mAh/g) of the total material capacity (275 mAh/g) is used. Attempts to go beyond such a limit result in electrode degradation owing to the strong repulsion between CoO₂ layers which are no longer sufficiently screened by the presence of the Li ions. Over the years, materials scientists have tried to push this limit further via chemical substitution aiming to stabilize the layered framework. This has led to two great advances illustrated in Figure 1. The first one, over the 2001–2008 period, was the partial replacement of Co³⁺ with Ni²⁺ and Mn⁴⁺, which led to the Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ layered oxides coined as NMC, a very attractive class displaying higher capacities (200 mAh/g) than both the three-dimensional (LiMn₂O₄, LiNi_{0.5}Mn_{1.5}O₄) spinels (140 mAh/g) and the best performing polyanionic compound LiFePO₄ (170 mAh/g). Such NMC electrodes are now widely used in numerous applications.

Further explorations of lithium substitution in the layered oxide systems, dating back to ~2003 with the pioneering works of Thackeray's and Dahn's groups independently, have led to materials termed as "Li-rich NMC" which combine the beneficial effects of Ni, Co and Mn with some Li in the transition metal layers, in addition to the Li present in the Van der Waals gap, and showing capacities exceeding 280 mAh/g. However, poor kinetics and large voltage decay

upon cycling plague their implementation in practical Li-ion cells. Although many research groups can reproduce the performance of Li-rich NMC phases, the reasons for the origin of the extra capacities or of the voltage decays upon cycling were not clearly understood until recently.

This review will be structured to describe first the chemical rationale of the aforementioned advances which have led to the wide commercialization of NMC electrodes whose compositions in either Co, Ni or Mn are still evolving to cope with new market opportunities dictated by evolving portable electronics, automotive and grid applications. It is not intended to give an exhaustive review about this family of compounds, already covered by numerous well-written reviews, but rather to focus on providing the basic understanding of structure/electrochemistry/composition relationships in this class of materials. Then, using this materials platform, we will focus on the Li-rich NMC phases by addressing various issues (voltage and capacity fade upon cycling, irreversibility in the first cycle, . . .) which are still blocking their wide use. The aim being to focus on the precise understanding of bulk properties, their origin and to show how to tune them, for conciseness the works related to surface chemistry which does not directly affect bulk properties and which are already reviewed, will not be taken into account.

LiMO₂ Layered Compounds

To set the scientific platform necessary for making the rest of this document understandable we will first recall the main structural characteristics of layered oxides phases. They adopt the α -NaFeO₂ structure (Figure 2)³ which is considered as the prototype structure of AMO₂ layered materials. It corresponds to the ordered occupancy of the octahedral sites of a Face Centered Cubic network of anions, which, described using a hexagonal cell (space group R-3m), corresponds to the stacking of MO₂ layers built up with edge-sharing MO₆ octahedra in between which A species are located. The nature and amount of A (essentially in our case Li and Na) and M, lead to several ways of stacking the MO₂ layers for designing stable oxygenated surroundings to host A species while minimizing the repulsive effect between the different layers. Delmas et al.⁴ proposed a classification of the different polymorphs that can be obtained, in which the chemical composition of the layered compound is preceded by i) a majuscule letter indicating the surrounding of the interlayer alkali species (O for octahedral, T for tetragonal, P for Prismatic) and ii) a value equal to the number of MO₂ layers needed to recover the periodicity. As an

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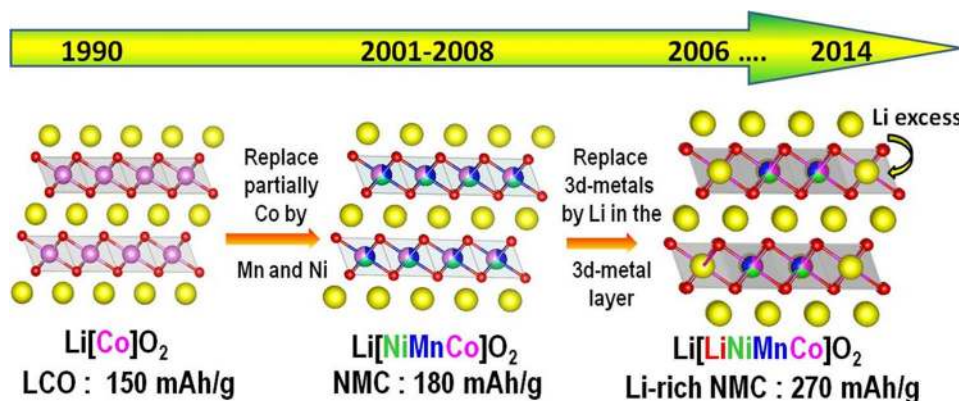


Figure 1. Chronological evolution of the layered oxide LiCoO_2 chemistry fueled by cationic substitution within the metal layers (left) with i) partial replacement of Co with Ni and Mn (NMC phase) within the metal layer (purple) and ii) more recently with Li (yellow) to form Li-rich NMC phases.

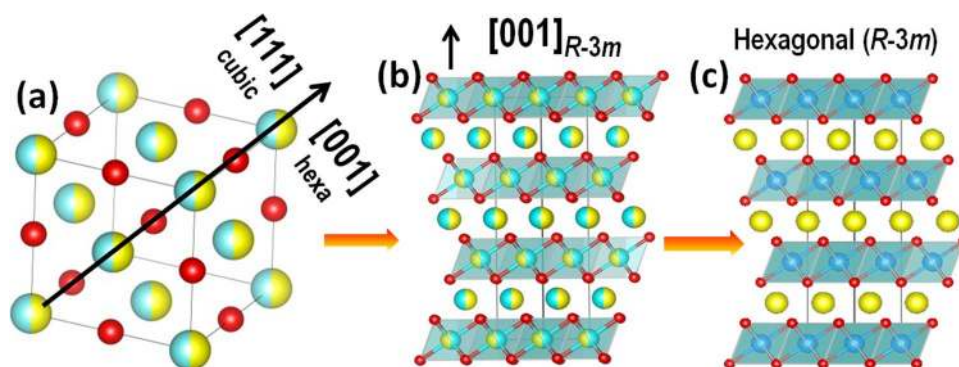


Figure 2. Structural representation of the layered oxides crystallizing in a O3-type structure with their relation to rocksalt FCC networks (a \rightarrow b via a rotation) and their evolution as a function of the cationic Li segregation (b \rightarrow c) leading to M and Li layers (with the courtesy of G. Rousse).

example, using this classification LiCoO_2 is written as O3- LiCoO_2 , because Li sits in octahedral site and 3 CoO_2 layers are needed to describe the unit cell.

LiCoO₂.— Thanks to the large difference between the size of ions ($r\text{Li}^+ = 0.76 \text{ \AA}$; $r\text{Co}^{3+} = 0.545 \text{ \AA}$), LiCoO_2 is considered as a pure 2D material i.e. without partial mixing of cations. The structural changes occurring during Li extraction were deeply investigated with i) the onset of a hexagonal-monoclinic transformation near $x \sim 0.5$ and ii) the feasibility to reach an O1-type structure (ABAB stacking sequence) for the fully delithiated and highly reactive CoO_2 phase.⁵⁻¹⁰ Deeper investigations were carried out to understand how such a structure could be stabilized in spite of the strong repulsive effect between oxygen from adjacent layers no longer screened by Li^+ ions. As magnetic measurements indicated the presence in the fully charge sample of remaining Co ions in +3 valence state, the existence of an extra redox process was suggested to account for the full extraction of Li^+ ions. It has then been proposed that at high voltage the oxidation of oxygen is activated thus decreasing the repulsive effect due to lower charge carried out by the anions.¹¹ The migration of the 3d band of TM ions into the 2sp band of oxygen (Figure 3) is proposed as an explanation to the activation of the anionic redox couple. It is expected to lead to an extreme situation in which the cations become more electronegative than the anion so that electrons are poured into the d band leaving behind sp holes which simply indicate the formation of ligand holes and to the extreme of oxygenated redox species.¹¹

This idea was highly controversial although this type of chemistry had been developed by J. Rouxel (for example Ref. 12) ten years earlier within the sulfurs and also heavily discussed in the high Tc compounds which, like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$, show a high mixing of the p and d bands at the Fermi level.¹³ Whatever, as we will see later such

a controversial hole-redox chemistry will find all of its meaning with the emergence of the Li-rich NMC oxides.

LiNiO₂.— Back to the 1990's, isostructural LiNiO_2 was eagerly considered by J. Dahn et al., at that time in Moly Energy, as an alternative to LiCoO_2 because of its lower cost, higher reversible capacity (ca. 200 mAh/g) and better environmental compatibility.^{14,15} However, the spontaneous reduction of Ni^{3+} to Ni^{2+} during synthesis leads to the formation of non-stoichiometric $\text{Li}_{1-z}\text{Ni}_{1+z}\text{O}_2$ compounds, the $z\text{Ni}^{2+}$ excess being located in the Li^+ layer which is detrimental for cell performances.¹⁶⁻²¹ Then, this large capacity is

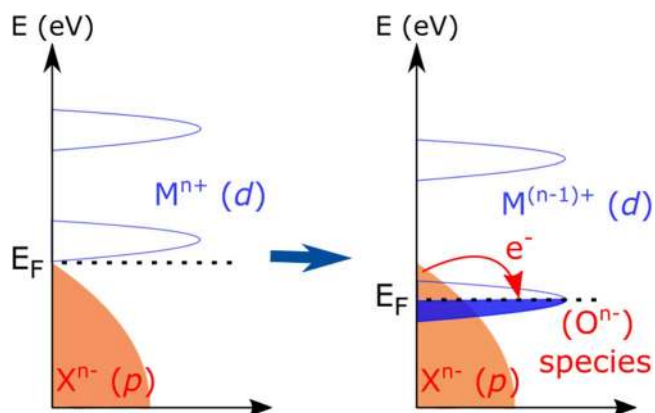


Figure 3. Schematic band diagram illustrating the anionic redox process. Left: way classical systems operate; Right: hybridization of the d-p bands needed to trigger the formation of $(\text{O}_2)^{n-}$.

solely obtained for nearly stoichiometric specimens ($z \leq 0.05$),^{19,22,23} made via suitable synthetic routes. Nevertheless, for safety reasons, it turns out that such material could not compete with LiCoO_2 as confirmed by DSC measurements which indicated a lower thermal stability of delithiated state in presence of electrolyte i.e. a lower decomposition temperature and a greater energy released.^{24–27} Mainly for this reason non-substituted LiNiO_2 electrodes were abandoned by battery manufacturers.

LiMnO₂.— With the scope of finding an attractive material from an economical and environmental point of view, LiMnO_2 has been deeply investigated. However, the low radii difference between Mn^{3+} in high spin configuration (0.65 Å) and Li^+ (0.76 Å) prevents the direct stabilization of layered LiMnO_2 to the expense of another thermodynamically stable form of LiMnO_2 which shows poor electrochemical activity.²⁸ Nevertheless, the preparation of metastable layered LiMnO_2 , has been achieved using ion exchange of the stable layered NaMnO_2 with Li^+ .^{29–31} Unfortunately, on charge Li_xMnO_2 converts into the more stable LiMn_2O_4 spinel structure resulting in poor electrochemical performances.^{32–33} This transformation, which will be of great importance when dealing with Mn-derived LiMO_2 phases, is facilitated by the fact that both O3-LiMnO_2 and LiMn_2O_4 adopt the same oxygen network, hence little energy is required for the diffusion of cationic species. Moreover, such materials can be the source of an internal redox process $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$ favored by the contact with the electrolyte; this latter generates mobile Mn^{2+} which can easily diffuse from Mn to Li layer.^{34,35} Some attempts to stabilize LiMnO_2 layered compounds with different oxygen layers stacking sequences (such as O2 type instead of O3 type) to prevent the transformation into spinel led to compounds with poor electrochemical performances.³⁶

Binary Li(M,M')O₂ and Ternary Li[M,M']O₂

Owing to the rich chemistry of layered oxides, chemical substitution at the metal (M) site has been intensively explored and several combinations including either two or three 3d metals were realized with the ultimate goals being cost reduction and enhanced safety and energy density. An illustration of such a chemical substitution approach is next given by presenting the main achievement in studying Ni/Co and Ni/Mn binary oxides before turning to present most attractive ternary $\text{Li}[\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z]\text{O}_2$ NCA and $\text{Li}[\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z]\text{O}_2$ NMC compounds.

In light of the aforementioned results, it is obvious that the best electrochemical performances are obtained when using compounds having both the typical $\alpha\text{-NaFeO}_2$ structure type and no migration of TM ions in the Li layers. The comparison of various parameters shows that the relative size of TM ions against alkaline species is the main parameter governing structural aspects in layered oxides. This message is highlighted in Figure 4 which shows that among the three widely used TM ions only Co and Ni in their +3 valence state enable strictly 2D layered Li-based oxides. The large size of Mn^{3+} in its high spin configuration implies to use larger Na^+ alkaline ion to stabilize the 2D layered structure. This structure can then act as a precursor to obtain, via chemical exchange at low temperature, the metastable 2D layered LiMnO_2 . Further exploiting this comparison, the 2D layered structure of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ can be explained owing to the presence of small Mn^{4+} ions. This indicates that the TM valence state stability can be considered as a second parameter for predicting the feasibility of stabilizing 2D structure. As observed for Ni, the spontaneous $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$ reduction associated to an increase of ionic radius size, while keeping the layered character, induces a partial migration of the latter in the Li layers thus limiting Li^+ diffusion and decreasing the initial capacity. On this basis, despite cost penalty, the benefit of using Co^{3+} as a stabilizing agent for ensuring layered structure is evidenced and confirmed by the wide acceptance of both NCA and NMC materials.

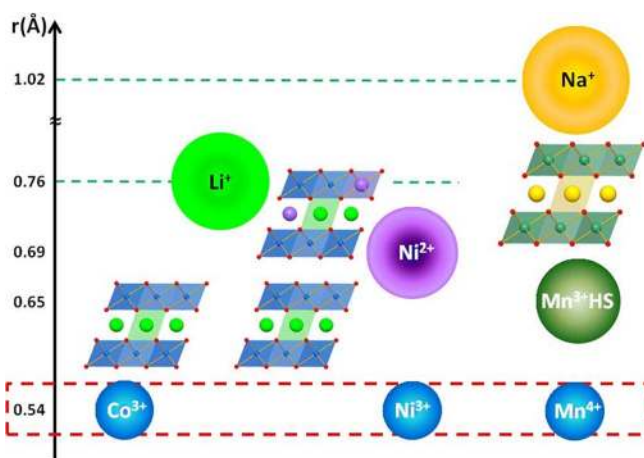


Figure 4. Comparison of ionic radii of alkaline species and TM ions in their stable valence states at synthesis operating temperatures and their influence on the 2D layered characters of AMO_2 phases. Dashed red rectangle shows ions leading to strictly 2D layered LiMO_2 structure and the partial cation mixing due to Ni reduction is schematically represented.

From LiNiO_2 to $\text{Li}[\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z]\text{O}_2$ (NCA) compounds.— To prevent the spontaneous reduction of Ni^{3+} to Ni^{2+} and its migration within the Li layers, the substitution of Co^{3+} for Ni^{3+} has been investigated. The stability of Co in its +3 valence state even at high temperature minimizes the formation of Ni^{2+} species and its radius (0.545 Å) smaller but close to that of Ni^{3+} (0.56 Å) favors the formation of $\text{Li}(\text{Ni},\text{Co})\text{O}_2$ solid solution. In addition, its difference with that of Li^+ (0.76 Å) is large enough to promote the ordering of the M/Li occupancy leading to the stabilization of layered compounds.^{5,19,37–40} A full $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ solid solution could indeed be prepared and members having Co content (y) greater than 0.3 exhibit Li-layers free of Ni^{2+} . The best electrochemical performance is obtained beyond this 0.3 threshold value with namely a capacity of 180 mAh/g associated to the removal of 0.7 Li and corresponding to the sequential oxidation of Ni then Co.^{39,41–43} Moreover, in the absence of drastic structural changes within this domain of Li composition,^{39,42,44–46} such Co-doped samples show better stability in the charged state.^{47–48}

Turning to non-electrochemically active substituent elements for Ni, aluminum appears to be the most promising to increase the electrode thermal stability.^{49–51} Al^{3+} cations were shown to occupy octahedral sites in the NiO_2 layers, hence acting as structural pillars due to stronger Al-O than Ni-O bonding.^{52,53} Obviously, the addition of electrochemically dead Al reduces the electrode capacity but in contrast enhances both the electrode stability at high voltage and its cycling lifetime.^{50,53}

To cumulate the benefits of Co to stabilize its layered character and Al to enhance its thermal stability, researchers have pursued the dual substitution approach which has led to $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$ electrodes, coined NCA, having enhanced safety and capacity retention.⁵⁴ Among the various NCA members, the $\text{Li}[\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ and more recently $\text{Li}[\text{Ni}_{0.81}\text{Co}_{0.10}\text{Al}_{0.09}]\text{O}_2$ compositions have been carefully selected to meet safety criteria without sacrificing the energy, power, or cost advantages of Ni-based cathodes. The former composition shows a reversible capacity of 200 mAh/g⁵⁵ together with an enhanced thermal stability at high potentials⁵⁰ and attractive power rate capability since 155 mAh/g can be obtained at 10 C rate for the latter composition.⁵⁶

From LiNiO_2 to $\text{Li}[\text{Ni}_{1-y-z}\text{Co}_y\text{M}_z]\text{O}_2$ (NMC) compounds.— Early reported in the 1990's as a poorly attractive electrode,⁵⁷ the $\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$ ($y \leq 0.5$) system was revisited in 2001 and the performances improved when such materials are prepared using synthesis temperatures greater than 800°C.^{58,59} By operating at such

temperatures, issues regarding cationic distribution between the M and Li layers and the presence of stacking faults could be mastered⁶⁰ even though ca 10% of Ni²⁺ located in the Li layer cannot be easily avoided thus impeding the diffusion of Li⁺ ions.⁶¹ Nevertheless, despite the remaining Ni⁺² ions, at low C rates, LiNi_{0.5}Mn_{0.5}O₂ compositions present a reversible capacity as high as 200 mAh/g with small capacity fading and high thermal and structural stability,⁶² as well as greater inhibition of side reaction with the electrolyte.^{63,64}

A deeper investigation of the science at work in this compound shows that in its pristine state Ni is in +2 and Mn in +4 valence state, so that Ni²⁺ is the main active element contributing for 2 electrons during the redox process. Herein, Mn⁴⁺ which is Jahn-Teller free stabilizes the structure and prevents the transformation to spinel structure by avoiding the creation of mobile Mn²⁺ species.⁶⁵ The redox potential of Li_xNi_{0.5}Mn_{0.5}O₂, although it should be lower, is very similar to that of Li_xNiO₂ because of the partial contribution of redox processes associated to Mn and O⁶⁶ or by repulsive/attractive electrostatic interactions between Mn and Ni taking place during lithium extraction and insertion respectively.⁶⁷

To enhance the rate capability O3-LiNi_{0.5}Mn_{0.5}O₂ was prepared from O3-NaNi_{0.5}Mn_{0.5}O₂ via an exchange reaction including either solution (LiCl in hexanol) or molten salt (LiNO₃) at low temperature.⁶⁸ The large difference of Na⁺ ionic radius (1.02 Å) with that of Ni²⁺ (0.69 Å) favors the 2D character and prevents the localization of Ni²⁺ in alkaline layer. During the ion exchange, there is no migration of Ni²⁺ ions. Such experimental protocol leads then to compounds with Li layers free of Ni⁺²,⁶⁹⁻⁷¹ thus enabling both high reversible capacity (183 mAh/g at 6C rate) and enhanced capacity retention.

At this stage, as demonstrated by the study of Li(Ni,Co)O₂ system, the use of Co⁺³ metal substituent is another way of reducing the amount of Ni²⁺ in the Li layer and is the reason why the ternary Li[Ni_{1-y-z}Mn_yCo_z]O₂ system has been highly surveyed. The hope here was to reunite within the same compound the positive attributes of Co, Ni and Mn substitutions which respectively enhance performances in terms of rate capability, capacity and structural stability.

Among all the compositions studied, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ has shown particularly promising electrochemical performances with a reversible capacity of 150 mAh/g when cycled between 2.5 V and 4.2 V vs Li⁺/Li⁰ which is enhanced to 200 mAh/g when charged up to 4.6 V.⁵⁸ It shows good rate capabilities like 150 mAh/g at 1600 mA/g⁷³ and high stability of the compound charged at high potential thus enhancing safety.⁷⁴ The exact reasons for such improvements are controversial. Some authors claim that in addition to Ni⁴⁺/Ni²⁺ redox couple, charge compensation could arise from oxygen oxidation⁷⁵⁻⁷⁷ while others report that Co³⁺ to Co⁴⁺ oxidation occurs at high voltage without any anionic redox activity.⁷⁸⁻⁸⁰ Equally, there is no consensus on the Li-NMC pristine structure which seems to depend upon the sample heating history with several possibilities enlisting i) perfect disordering of the Ni, Mn, Co ions in the layers,⁸¹⁻⁸³ ii) existence of local ordering^{77,84-86} or iii) long range ordering of the cations leading to a superstructure.^{58,79,87}

Whatever the science beyond it is commonly agreed that Li-NMC electrodes offer precious safety advantages as witnessed by DSC measurements which show a higher exothermic decomposition temperature associated to a lower release of energy, as compared to any other layered oxides. It is even claimed that by partially substituting Al for Co, these materials can reach safety aspects which can rival those offered by LiFePO₄ and LiMn₂O₄ electrodes.⁸⁸

Aside from safety, today for large volume applications battery makers are pushing research directions toward lower dollars/kWh, which in short means designing low cost and high energy density materials. Owing to their composition versatility, NMC's materials provide an attractive playground. Further surveying the Ni composition in Li-NMC has resulted in the feasibility to prepare Ni-rich materials such as Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ which exhibit, when cycled in the range 3.0 V – 4.3 V, a reversible capacity of 200 mAh/g compared to 150 mAh/g for Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂.⁸⁹ However, the penalty associated with the instability of the Ni⁴⁺ rich charged compound leads to poor capacity retention.⁹⁰ The effects of Ni, Co and Mn in NMC materials

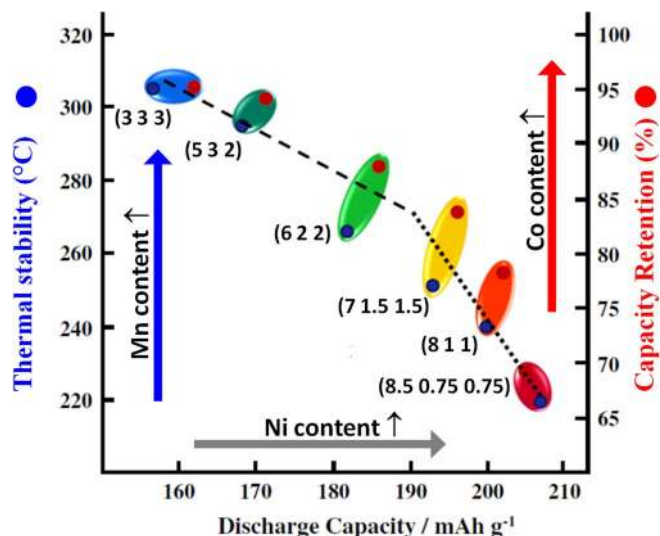


Figure 5. A map of relationship discharge capacity (black), thermal stability (blue) and capacity retention (red) of Li/Li[Ni_xCo_yMn_z]O₂ compounds with number in brackets corresponding to the composition (Ni Mn Co). The positive effect of Ni on capacity, Mn on thermal stability and Co on capacity retention and rate performances is underlined (adapted from Ref. 91).

are summarized in the Figure 5 showing that Ni governs capacity, Mn thermal stability and Co rate capabilities.⁹¹ To overcome this latter phenomenon a core/shell strategy has been successfully developed. It consisted in using a core made of a poorly thermally stable but high capacity Ni-rich NMC phase (Li[Ni_{0.64}Co_{0.18}Mn_{0.18}]O₂) and a shell made of low capacity but high thermal stability Mn-rich NMC phase (Li[Ni_{0.46}Co_{0.23}Mn_{0.31}]O₂). Such particles were prepared by making a core-shell of the corresponding hydroxide phases via solution chemistry which was treated to high temperature in presence of Li-salts.⁹²⁻⁹³

Such electrodes were shown to deliver reversible capacities of 209 mAh/g as for Li-NMC but with a much better capacity retention and thermal resistance (96.5% capacity retention after 500 cycles in conventional use) even under aggressive test profile (96% capacity retention at 55°C and charged up to 4.4 V).⁹⁴ Although very attractive this core-shell concept still presents a weakness that is the progressive delamination of the core-shell interface upon long cycling due to strains similar to a certain extent, but quite less tragic, to that experienced with solid state batteries. This has been an impetus to successfully design, via a clever pH-driven aqueous low temperature precipitation process followed by a high temperature firing, layered oxide particles showing a Ni, Co, and Mn concentration gradient so as to mitigate the negative effect of physical interfaces while ensuring the better electrochemical stability and equal safety.^{95,96} Nevertheless, the most efficient approach to drastically increase the energy density, once again, relies in further playing with the chemical composition of the material to adjust its physical properties / electrochemical performances as described next.

Over-Lithiated Layered Li_{1+x}M_{1-x}O₂: Li-Rich Compounds

Back to 2006, further explorations of the layered oxides systems by Thackeray and J. Dahn groups independently have led to materials made of Ni, Co and Mn with Li in excess. These compounds also termed as Li-Rich-NMC, show staggering capacities exceeding 270 mAh/g. Such findings generated great excitement among materials makers with mainly two companies, BASF and 3M, getting on board to implement these materials onto the next generation of high energy density Li-ion batteries. Owing to the foreseen importance of these phases, we will recall their structural and electrochemical aspects prior to rationalize the scientific strategy that has led to their full fundamental mastering prior to envision future ameliorations.

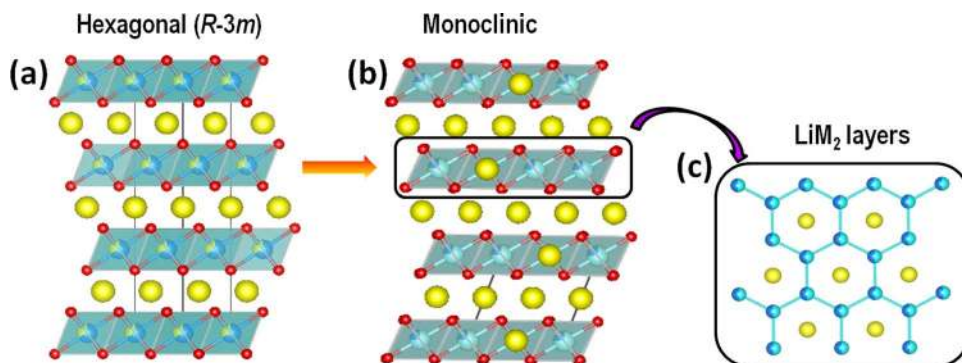


Figure 6. Structural representation of (a) O3-type layered oxides; (b) the overall cell of Li-rich layered oxides described as monoclinic and (c) M / Li ordering within LiM₂ layer leading to a honeycomb pattern (with the courtesy of G. Rousse).

The structure of Li-rich compounds derives from that of parent lamellar LiMO₂ by considering a progressive substitution of excess Li⁺ for M³⁺ in the [MO₂] layers (Figures 6a-6b). The charge compensation is insured by an increase of the valence state of the remaining M elements following the general equation $Li[M_{1-2x}^{3+}M_x^{4+}Li_x^+]O_2$. A first limit occurs for $x = 1/3$ (M solely in +4 valence state) and corresponds to the formula Li[Li_{1/3}M_{2/3}]O₂ alternatively noted Li₂MO₃. Among the numerous compounds with Li-rich Li₂MO₃ structure type (M = Mn, Ru, Ti, Zr, Sn, Pt . . .), Li₂MnO₃ is the most studied so far. It exhibits an O3-type structure described in the monoclinic system (space group C2/m) to take into account the distortion induced by the ordered distribution of the Mn⁴⁺/Li⁺ cations in the mixed [Li_{1/3}Mn_{2/3}]O₂ layer⁹⁷ so that lithium ions are surrounded by six M to form a honeycomb pattern (Figure 6c).⁹⁸⁻¹⁰¹

Electrochemically-wise, Li₂MnO₃ was initially considered as inactive due to the impossibility i) to release Li⁺ on charge as Mn⁴⁺ in octahedral surrounding cannot be oxidized further and ii) to uptake additional Li⁺ ions on discharge due to the absence of free accessible site for extra lithium. However using chemical acid treatment¹⁰² or electrochemical oxidation at high voltage¹⁰³ it has been shown that Li₂MnO₃ presents electrochemical performances better than those of LiMnO₂. This electrochemical activation has been ascribed to a partial loss of Li₂O to form Li_{2-x}MnO_{3-x/2} with the enhanced stability associated to the existence of a composite structure built up with Li₂MnO₃ domains in a LiMnO₂ matrix. The latter was considered as the electrochemically active component while the former electrochemically transparent in the working voltage range used (2 V – 4.4 V) was supposed to act as a stabilizer of the structure. In light of such a finding research on materials with nominal composition xLi₂MnO₃-(1-x)LiMO₂ (where M = Mn, Ni, Co, Cr, Fe) has been intensified leading to a tremendous amount of studies aiming at a better understanding of the behavior of the Li-rich NMC compounds.

When cycled vs. Li, all Li-rich compounds present a stair-case charge profile which differs from the discharge one which shows a S-shape profile (Figure 7a). Afterwards, the S-shape voltage profile is preserved on subsequent charge/discharge cycles. Their capacity exceeds the one calculated considering the exchange of 1 electron per TM even taken into account the capacity loss observed after the first charge. Unfortunately, they also have inherent drawbacks such as important voltage decay upon cycling (Figure 7b) which presently prevents their commercial use. The origin of both, the extra capacity and voltage decay, has been the source of a prolific but not conclusive literature. Few scenarios involving either i) O²⁻ migration from the bulk to the surface,¹⁰⁶⁻¹⁰⁸ ii) transition metal cation migration from the surface to the bulk¹⁰⁹⁻¹¹² iii) reversible oxygen oxidation¹¹³⁻¹¹⁵ and iv) transition metal-over-oxidation, have been proposed to account for the extra capacity while the creation of spinel like domains, still very controversial, was advanced to explain the capacity fade.^{111,112,116,117}

To overcome some of these issues, as for the NMC phases, surface chemistry approaches have been proposed among which one of the

most efficient improvements of cathode material is the covalent coating method using carbon, oxides, fluorides and even more stable materials such as phosphates. Most of the time, it targets the improvement of lifetime and safety properties through the reduction of interfacial reaction between electrolyte and active materials. It also results in the improvement of transports properties by preventing the formation of poorly conductive interfacial layers and in the enhancement of capacity retention through the protection from HF attack thus limiting the dissolution of TM ions. In the case of Li-rich compounds, a variety

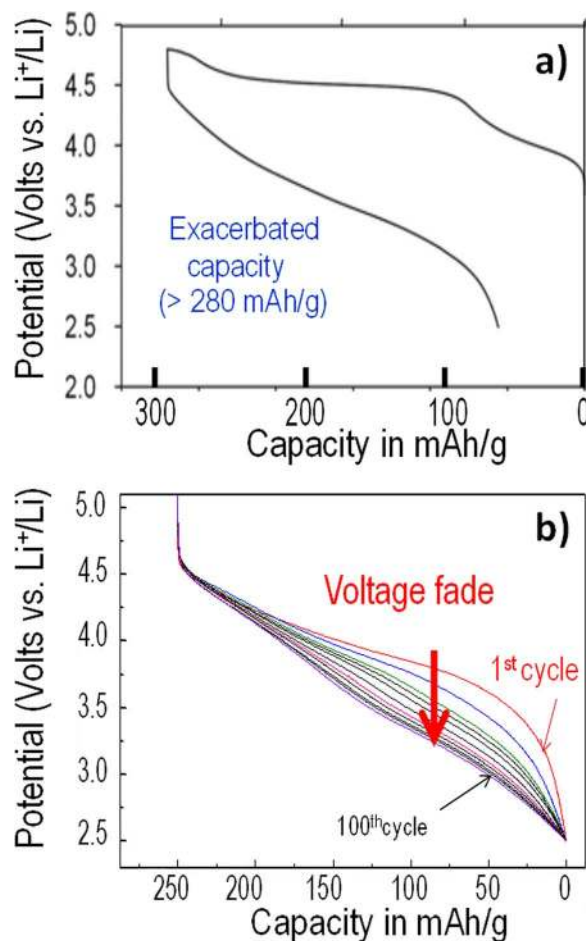


Figure 7. Voltage-composition profile for Li-rich NMC compounds showing in a) a stair-case trace on oxidation and a S-shape on the following reduction and in b) the voltage fading of the Li-rich compounds upon cycling.

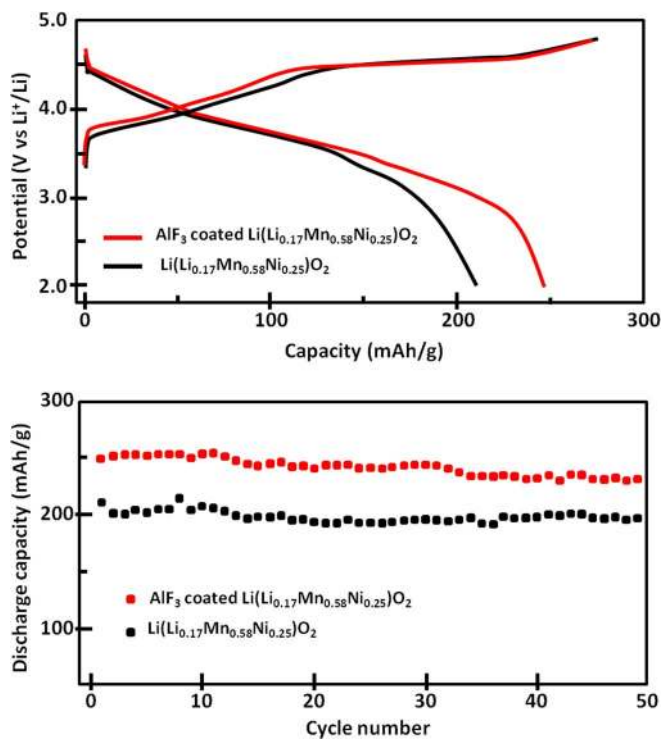


Figure 8. (a) 1st charge-discharge curves (b) cycle performance of AlF₃ coated Li(Li_{0.17}Ni_{0.29}Mn_{0.58})O₂ at 0.2C rate (from Ref. 126).

of materials such as C, ZrO₂, TiO₂, Al₂O₃, MgO, and Ni and Mn composite oxides have been used for surface coating and shown improved performance in capacity retention and rate performances.^{118–124}

The AlF₃ coating,^{125–129} which is one of the most efficient against HF attack due to strong Al-F bonds, leads, when applied onto Li(Li_{0.17}Ni_{0.29}Mn_{0.58})O₂, to a better electrode coulombic efficiency (from 76% to 90%) during the first cycle and a 20% increase of the capacity after 50 cycles (Figure 8¹²⁶). Equally, coatings based on inert phosphates such as AlPO₄ or LiMPO₄^{130–135} were shown to be effective in improving initial capacity retention and rate capability of the Li-rich layered oxide composite 0.5Li₂MnO₃-0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O₂.¹³³ The application of a double layer coating (AlPO₄/Al₂O₃) onto Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ particles was even shown to lead to capacities as high as 295mAh/g.¹³¹

The literature on coatings is quite prolific with all the papers claiming successes but too frequently against poor reference samples. Whatever the claimed performances, coating processes raise extra issues dealing with the difficulty to achieve homogenous coatings both in thicknesses and in composition. Equally, controlling the crystalline-amorphous nature of the coated layer or the nature of the bulk-coating interface in terms of composition and chemical stability is quite complex. So far, neither of these coating approaches has limited the voltage decay. The reason for such a failure is nested in the absence of a real understanding of the specific behavior of this family of compounds in terms of capacity and voltage decay. This is often the case with new discoveries until the fundamental science is not understood. The difficulty in rationalizing the science at work in these materials was mainly rooted in the complexity of these materials which involve 3 redox centers (Ni, Co and Mn). To circumvent these issues, model materials were needed to reach a fundamental mastering of the Li-rich phases.

So far, most of the pursued approaches were nicely tackling the synthesis aspects of these compounds enlisting either various sample annealing temperatures and cooling processes as well as different reactants or many changes/combinations in the Li/Co/Ni/Mn ratio. By contrast, limited attempts, if any, have attacked the problem from the structural/chemical point of view; that is departing both from the LiMO₂ structure and from the nature of the 3d elements (Ni, Co and Mn) used so far. Back to 2012, works were devoted to address the aforementioned bottlenecks by the exploration of related Li₂MO₃ deviating from the classical approach by using 4d (Ru and Sn) rather than 3d metals. These new Li₂Ru_{1-y}Sn_yO₃ phases exhibit similar capacities of 280 mAh/g as Li-rich NMC, but do not present the undesirable potential fading upon cycling.¹⁴³ This chemical trick has provided a textbook material for fundamental studies as it contains just a single redox active cation (Ru), rather than three separate redox active cations (Ni, Co and Mn) for the complex Li-rich NMC phases. By coupling this chemical approach with complementary X-ray photoemission spectroscopy (XPS), operando electron paramagnetic resonance (EPR) and in situ EPR imaging measurements, the first experimental evidence for Li-driven reversible formation of peroxo-superoxo (O₂)ⁿ⁻ species in these materials was proposed (Figure 9).^{143–144}

On that basis, the high capacity of such materials is explained as due to cumulative cationic (Mⁿ⁺ ↔ Mⁿ⁺¹) and anionic (2O²⁻ ↔ (O₂)ⁿ⁻) reversible redox processes. The strong overlapping of the M(nd)-O(sp) bands is put forward as the driving force for Li-driven reversible formation of (O₂)ⁿ⁻ species (i.e., creation of holes on the oxygen) in these materials. The existence of anionic network redox activity in intercalation compounds is then clearly established thus enabling to achieve capacities surpassing the previously believed limit of 1 e- per transition metal.

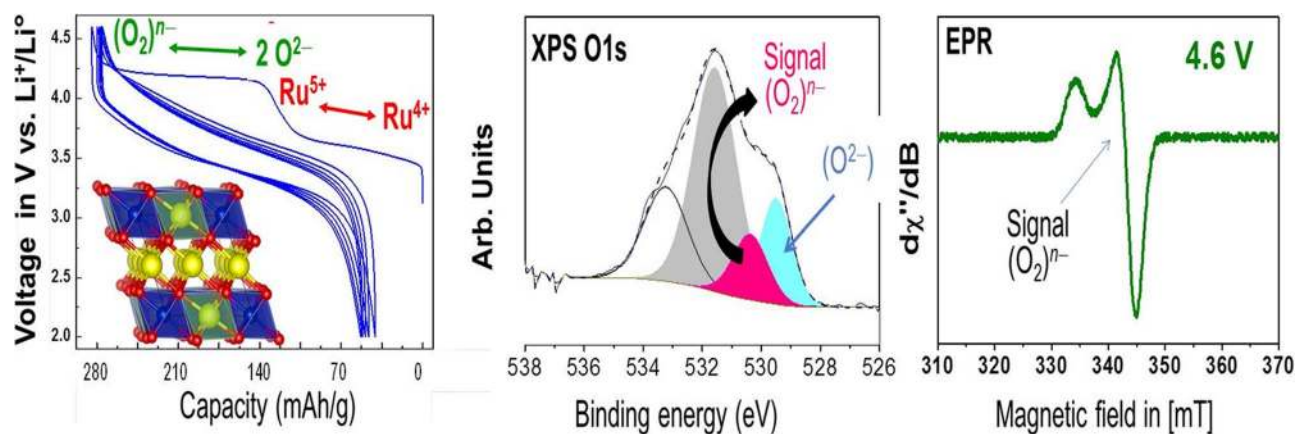


Figure 9. Voltage versus capacity curve (left) for Li₂Ru_{1-y}Sn_yO₃ highlighting both cationic and anionic reversible redox processes, along with an illustration of its layered structure. Middle: Oxygen 1s X-Ray photoemission spectroscopy (XPS) showing the signal of peroxo (O₂)ⁿ⁻ species (red) with at the right their electron paramagnetic resonance (EPR) signature (from Ref. 118).



Figure 10. HAADF-SEM imaging of $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ and $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ electrodes recovered on the discharged state after 150 cycles and 50 cycles, respectively. The right image shows the presence of Ti^{4+} ions (white arrows) in tetrahedral positions as shown on the center structure. Such capturing on ions in tetrahedral sites was shown to increase upon cycling (from Ref. 120).

Such finding calls for a different look at the transport mechanisms in Li-rich compounds to determine the kinetics of cations and anions transports as a function of current rates, potentials, resting times, electrolytes or temperatures as well as possible correlations between and also for the development of new analytical tools to spot radical species. To address these seminal questions and probe the redox mechanisms occurring at electrodes during their operation, electron paramagnetic resonance (EPR) has been used.¹⁵⁰ By monitoring operando the EPR of Ru^{5+} and paramagnetic oxygen species, it became feasible to prove the formation of reversible $(\text{O}_2)^{n-}$ species that contribute to their high capacity. In addition, by developing in situ EPR imaging with micrometric resolution, the authors could follow the zones of nucleation and growth of Ru^{5+} /oxygen species $(\text{O}_2)^{n-}$ at the positive electrode. From the exploitation of these images, a limitation of the anionic transport was deduced,¹⁵⁰ but this requires further studies owing to the importance that this could have application-wise besides voltage fade.

Chemical substitution approaches were pursued to grasp a better understanding of this phenomenon. The replacement of Ti for Sn was shown to lead to the formation of layered $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ materials, having similar capacities as the Sn compounds, but which display a voltage decay of similar amplitude as the Li-rich NMC compounds.¹⁴⁵ Ex-situ HAADF-STEM experiments using these Ti-substituted phases as a model, have evidenced the presence Ti^{4+} captured in tetrahedral sites with the amount trapped cations increasing with increasing cycle numbers. From this correlation together with DFT calculations which predict a lowering of the voltage associated to the partial occupancy of tetrahedral sites, the origin of the voltage decay in Li-rich NMC materials was established. It is mainly nested in ionic radii considerations and size bottleneck issues¹⁴⁵ (Figure 10), hence providing clues for the confection of Li-rich NMC systems free of voltage fade.

Application-wise, another issue with these new systems relying on the anionic redox processes regards the identification of the key parameter controlling the stability of Li-driven oxygenated $(\text{O}_2)^{n-}$ species against recombination into gaseous O_2 at high potential. To grasp further insight onto the $(\text{O}_2)^{n-}$ formation vs. O_2 release equilibrium, researchers went into a survey of Li_2MO_3 materials. We will only refer to key $\text{Li}_2\text{Ni}_{0.5}\text{Te}_{0.5}\text{O}_3$,¹⁴⁶ $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$,¹⁴³ $\text{Li}_2\text{Fe}_{0.5}\text{Sb}_{0.5}\text{O}_3$,¹⁴⁷ $\text{Li}_2\text{Fe}_{0.28}\text{Te}_{0.5}\text{O}_3$ ¹⁴⁸ and Li_2IrO_3 ¹⁴⁹ systems which add important aspects to our understanding of the role of oxygen during redox reactions in these layered oxides. From combined electrochemical and DEMS studies summarized and compiled in the Figure 11 it was deduced that $\text{Li}_2\text{Ni}_{0.5}\text{Te}_{0.5}\text{O}_3$ behaves like a classical insertion system solely relying on the $\text{Ni}^{+2}/\text{Ni}^{+4}$ redox. This differs with the electrochemical activity of $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$ which enlists both cationic and anionic redox processes without any O_2 evolution or of $\text{Li}_2\text{Fe}_{0.28}\text{Te}_{0.5}\text{O}_3$,¹⁴⁷ which solely involves the removal of O_2 . Apart from these systems, $\text{Li}_2\text{Fe}_{0.5}\text{Sb}_{0.5}\text{O}_3$,¹⁴⁷ shows a more complicated behavior owing to the initial formation of peroxy-species and their partial recombination into O_2 when the cell is charged to high potential.

Within this context of oxygen evolution, it is worth recalling that the value of the $E^\circ(\text{O}_2^{2-}/\text{O}_2)$ redox couple for inorganic compounds in aqueous media is nearly equivalent, after rescaling, to a potential of 4.3 V vs. $\text{Li}^+/\text{Li}^\circ$ (dashed line in Figure 11). On that basis, the absence of O_2 evolution upon oxidation noted for $\text{Li}_2\text{Ru}(\text{Ir})\text{O}_3$ compounds is not a surprise since their voltage profile falls below the $E^\circ(\text{O}_2^{2-}/\text{O}_2)$ redox line. Neither is the O_2 evolution observed for $\text{Li}_2\text{Fe}_{0.28}\text{Te}_{0.5}\text{O}_3$,¹⁴⁸ whose oxidation voltage is well above the $E^\circ(\text{O}_2^{2-}/\text{O}_2)$ redox dashed line. In contrast, the voltage profile for $\text{Li}_2\text{Fe}_{0.5}\text{Sb}_{0.5}\text{O}_3$,¹⁴⁷ crosses the $E^\circ(\text{O}_2^{2-}/\text{O}_2)$ redox line indicative of the creation of $(\text{O}_2)^{n-}$ species and partial recombination into O_2 in good agreement with DEMS experiment. This has led us to propose the high voltage formation of core-shell type particles with the bulk containing $(\text{O}-\text{O})^{n-}$ peroxy groups and the shell oxygen vacancies (O_2) release. Bearing in mind the position of the voltage trace with respect to $E^\circ(\text{O}_2^{2-}/\text{O}_2)$ redox for the Li-rich NMC phases, a similar situation enlisting the formation of core-shell particles is expected and was observed by TEM by several authors.

Despite the above investigations, it was remaining impossible to visualize the deformation the oxygen sublattice resulting from the formation of the O-O peroxy-like dimmers. Such a failure was rooted i) in the fact that these compounds crystallized in the O3-type structure so that there are M atoms on top of the oxygen ones in contrast to an O1-type structure and ii) in the Li-driven motion of the metallic atoms upon oxidation. It is possible to circumvent this issue by enhancing the covalence of the LiM_2 layers via the replacement of Ru by a chemical element of a higher d number (Ir; 5d), the reason being that Ir 5d orbitals are more spatially expanded and less correlated than the Ru 4d orbitals, hence promoting covalence. LiIr_2O_3 and Sn derived

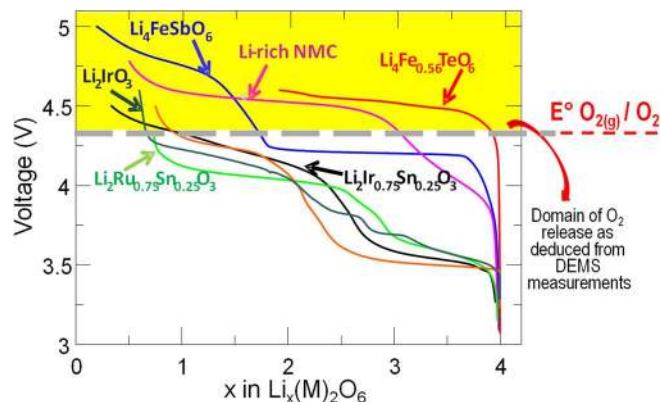


Figure 11. Charging voltage profile against Li for a variety of Li-rich layered oxide phases with the dashed line corresponding to the $\text{O}_2(\text{gas})/\text{O}_2^{2-}$ redox couple. The shaded yellow zone correspond to the range of potential over which $(\text{O}-\text{O})^{n-}$ are likely to recombine to liberate O_2 .

$\text{Li}_2\text{Ir}_{1-y}\text{Sn}_y\text{O}_3$ were synthesized and studied for their electrochemical properties.¹⁴⁹ Although such samples show extra-capacity similar to Li-rich compounds, their voltage profile drastically differs. The discharge curve is not any longer S-type but rather mirrors the charge curve. Moreover, there is no voltage fade upon cycling but a rapid capacity decay. The structural changes associated to the staircase voltage variation were studied by complementary XRD and microscopy measurements. The former reveals the appearance of a Li-driven structure transformation from O3 to O1 structure type upon oxidation which was confirmed by microscopy measurements. However, as opposed to most of the charged Li-rich samples so far investigated, TEM images show no migration of the Ir cation to the Li layers. This ideal situation enables, via the collection of ABF-STEM images, the direct visualization for the first time of the (O-O) peroxo-like dimmers, hence putting an end to an old problem initiated back to 1999.¹¹

This last study has provided a better understanding of the science at work in these systems with i) a clear demonstration that capacity fade and voltage fade have different origins, ii) direct evidence for connecting the appearance of S-type voltage profile to the massive migration of cations and iii) the role of electrochemically inert substituents in enhancing lattice elasticity. Thus they provide a chemical handle to better harvest the performances of this new class of Li-rich materials that remain to be further exploited via innovative chemistry and multi-faceted synthesis process to engineer particle compositions.

Conclusions/Perspectives

Humongous amounts of work have been dedicated to the layered oxides over the last 25 years. At the materials levels, chemical substitution has enabled a steady progression on the materials capacities which has passed from capacities of 140 mAh/g for LiCoO_2 to capacities of 200 mAh/g and >250 mAh/g for Li-NMC and Li-rich NMC phases respectively. A multitude of synthesis of either low or high temperatures approaches has been developed to tune the particle size, morphology and texture with the most practical results being the feasibility of spherical particles for increasing the material tapping density. Step-changes in terms of lifecycle or stability performances were also recently obtained by pursuing the core-shell approach or gradient concentration approach. Such layered oxide materials were ideal, for cost reasons, regarding portable electronics applications. Turning to large scale applications, there have been two schools favoring either layered or polyanionic compounds such as LiFePO_4 . Nowadays, the trend seems to favor layered oxides owing to the improvement in materials composition which has enabled to reduce cost, while polyanions inherently suffer from low packing density and hence low energy density associated to their poorest gravimetric density. Additionally, highly performing LiFePO_4/C Li-ion cells require high purity materials whose synthesis adds extra cost.

Turning back to the layered compounds, there exists a consequent number of compositions (LCO, NCA, NMC and its derivatives 214, 622, and Li-rich NMC), all having their associated advantages and drawbacks which are more suited for some applications than others. From performances analyses, NMC's and NCA's compounds will definitely compete for the years to come while both of them can gain from stability improvements to approach "zero risk" utilization. Tricks can be played to enhance this issue by wisely selecting coatings but this adds a cost issue. NMC is therefore the most attractive as we can change the Ni-Co-Mn ratio and no doubts that the Ni-rich NMC, namely the composition 622 which can deliver sustained capacities of 185 mAh/g, will certainly become the stellar material for EV's applications. Greater capacities up to 200 mAh/g can be obtained by increasing the Ni content, but here their use requires the coating with a Mn rich-NMC phase for stability purposes. Such core-materials are presently implemented in Li-ion cells.

At longer terms the Li-rich NMC phases with capacities exceeding 250 mAh/g are by all means the most attractive, although their commercialization is still hindered by their voltage upon cycling and their poor kinetics. We have seen that such materials present transformational changes with respect to classical electrodes owing to the

participation of the oxygen network to the overall redox-process. A great amount of progress has been made toward understanding their mechanistic and identifying the cause of voltage fade. Unfortunately, such advances have been made of materials including Ru, Ir which are far from being the most appealing materials cost-wise for applications. Implementing such learning to Li-rich NMC is presently being aggressively pursued. In parallel particles engineering involving core-shell, gradient-concentration approaches with a Li-rich NMC surrounded by a classical NMC or Ru-based films are explored as well with some success. In short it appears that issues related to these materials are solvable. No doubts that significant work is needed before the practical application of Li-rich NMC. Questions such as i) the long term stability of surface peroxo species in contact with electrolyte or ii) the interplay kinetics between cationic and anionic redox processes in the same material remain to be studied and understood. We must devote more intensive research to solve these burning problems which could enable to harvest the tremendous benefits of Li-rich NMC. So our ending note regarding the future of layered oxides, they will be here forever, owing to their rich and diversified chemistry.

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