Material Design Concept of Lithium-Excess Electrode Materials with Rocksalt-Related Structures for Rechargeable Non-Aqueous Batteries

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Abstract: Dependence on lithium-ion batteries for automobile applications is rapidly increasing, and further improvement, especially for positive electrode materials, is indispensable to increase energy density of lithium-ion batteries. In the past several years, many new lithium-excess high-capacity electrode materials with rocksalt-related structures have been reported. These materials deliver high reversible capacity with cationic/anionic redox and percolative lithium migration in the oxide/oxyfluoride framework structures, and recent research progresses on these electrode materials are reviewed. Material design strategies for these lithium-excess electrode materials are also described. Future possibility of high-energy non-aqueous batteries with advanced positive electrode materials is discussed for more details.

Keywords: lithium, sodium, batteries, anionic redox

1. Development of Lithium-Ion Batteries with Stoichiometric Layered Oxides

In the past four decades, rechargeable lithium batteries (so-called lithium-ion batteries) were extensively studied, and now its technology was highly sophisticated after first commercialization in 1991. Now, more than a million of electric vehicles equipped with an electric motor and lithium battery have been sold per year in the global market. For a long time, the transportation system was depending on the technology of internal combustion engines. The lithium batteries are starting to substitute greener and sustainable energy resources for fossil fuels. Gravimetric energy density of the lithium batteries is 2–3 times greater when compared with batteries with aqueous electrolyte (e.g., metal hydride batteries).[1] Nevertheless, the demand for further increase in energy density is still growing to reduce the size of batteries.

The lithium batteries consist of two lithium insertion materials, i.e., positive and negative electrode materials, which reversibly store both lithium ions and electrons on charge/discharge processes.[2] The first generation of lithium batteries consisted of LiCoO2[3] and carbonaceous materials as positive and negative electrode materials, respectively. A theoretical capacity of LiCoO2 is calculated from the following reaction:

\[
\text{LiCoO}_2 \rightarrow \square \text{CoO}_2 + \text{Li}^+ + e^- \tag{1}
\]

Herein, \(\square\) denotes vacancy created by lithium extraction in the host structure. A trivalent Co ion as cationic species in LiCoO2 is oxidized to a tetravalent state, and lithium ions are extracted from the host structure to maintain charge neutrality. Theoretical capacity of LiCoO2 is calculated to be 274 mAh g\(^{-1}\) from the equation 1 (a practical reversible capacity is limited to \(\sim 200 \text{mAh g}^{-1}\)). LiCoO2 is still widely used in state-of-the-art lithium-ion batteries, especially for portable electronic devices because of high volumetric energy density.

For electric vehicle applications, LiMn\(_2\)O\(_4\) and its derivatives, whose crystal structure is classified as a spinel-type structure, were used as positive electrode materials. For LiMn\(_2\)O\(_4\), MnO\(_6\) octahedra share edges, forming a threedimensional framework structure, in which Li ions are located...
at tetrahedral sites (Figure 1). Nearly all of Li ions are reversibly extracted from the crystal structures as a 4-volt class electrode material without the destruction of the framework structure. However, a reversible capacity is limited to ~120 mAh g⁻¹ as shown in Figure 1, and available energy density is limited to 450–500 Wh kg⁻¹ on the basis of metallic lithium. To increase the energy density, Ni-based layered materials are now used for electric vehicles. Typical charge/discharge curves of stoichiometric LiNiO₂ are also shown in Figure 1. A crystal structure of stoichiometric LiMO₂ (M = transition metal ions) is classified as a rocksalt-related layered structure with the cubic close-packed (ccp) lattice of oxide ions. Li and M ions are ordered into alternate layers perpendicular to [111] of the original rocksalt lattice, forming the layered structure with a rhombohedral lattice. LiCoO₂ and LiNiO₂ are isostructural, leading the formation of solid solution in the entire composition, LiCoₓNi₁₋ₓO₂ (0 ≤ x ≤ 1).[4] A reversible capacity of stoichiometric LiNiO₂ exceeds 200 mAh g⁻¹ even though operating voltage is slightly lowered compared with the spinel-type manganese oxide. Energy density as positive electrode materials reaches 700–750 Wh kg⁻¹. Since stoichiometric LiNiO₂ is thermally unstable after charge,[5–7] other transition metal ions are partially substituted for nickel ions. The Co/Al-substituted system, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂,[8] is currently used for practical applications. In addition, the Mn/Co-substituted system was also extensively studied as positive electrode materials.[9–12] Charge/discharge curves of LiNi₀.₈Mn₀.₁Co₀.₁O₂ are also compared with stoichiometric LiNiO₂ in Figure 1. Average operating voltage is slightly higher than the pure Ni system, and voltage plateaus associated with phase transitions are less pronounced for LiNi₀.₈Mn₀.₁Co₀.₁O₂. Metal substitution disturbs lithium/charge ordering in the layered structure.[13] Although the Ni-based layered materials are currently used for electric vehicles, available energy density is restricted below 800 Wh kg⁻¹ based on metallic lithium. The development of high-capacity positive electrode materials, which outperform the Ni-based layered materials, is indispensable to further increase energy density of commercial lithium-ion batteries.

![Figure 1. Comparison of charge/discharge curves of representative lithium insertion materials used as positive electrode materials for lithium-ion batteries. Schematic illustrations of spinel-type and layered-type oxides are also compared in the inset.](Image)

2. Material Design Concept of Li-Excess Rocksalt Oxides

Since theoretical capacities of positive electrode materials depend on lithium contents in the host structure, substitution of lithium ions for transition metal ions in LiMO₂ (Li₁₊ₓM₁₋ₓO₂) is important strategy to design high-capacity positive electrode materials. In the past decade, Li₂O₃-type layered materials (M = Mn⁴⁺, Ru⁴⁺ and other tetravalent ions), which are also classified as the cation-ordered rocksalt-type structure,[14] have been extensively studied as potential high-capacity electrode materials.[15–23] Both compositions are found in a Li–M–O triangular phase diagram on a rocksalt tie-line shown in Figure 2. Li₂M₂O₄ is reformulated as Li₂M₂O₄ when the oxygen content in the chemical formula is normalized to two. Since the lithium content is enriched from conventional layered materials, these oxides are often called “lithium-excess” and “lithium-rich” materials. Among the Li₂M₂O₄-type oxides, a Mn-system, Li₂MnO₃ and its derivatives have been the most widely studied as electrode materials. A theoretical capacity of Li₂MnO₃ is calculated from the following reaction;

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**Personal Account**

Naoaki Yabuuchi is a professor at Yokohama National University. He completed his PhD at Osaka City University in 2006 and his postdoc at MIT, with research expertise in the development of new electrode materials and study on reaction mechanisms for high energy Li/Na batteries. He has over 90 publications in these areas. He is the recipient of First International Award, “Science Award Electrochemistry” by Volkswagen and BASF, The 2nd ISSI Young Scientist Award, and ISE Prize for Applied Electrochemistry, The Young Scientists’ Prize from the Minister of Education, Culture, Sports, Science and Technology, Japan among other honors.
Li$_2$MnO$_3$ → □$_2$MnO$_3$ + 2Li$^+$ + 2e$^-$  

A theoretical capacity is calculated to be 459 mA h g$^{-1}$ when two electrons and lithium ions are successfully and reversibly extracted from the host structure. This value is much higher than those of stoichiometric layered oxides. Nevertheless, for a long time, Li$_2$MnO$_3$ was regarded as electrochemically inactive because of difficulty of oxidation of tetravalent Mn ions into higher oxidation states. However, the fact is that Li$_2$MnO$_3$ is electrochemically active associated with the contribution of anions (oxide ions) for the charge compensation process.[18,20] Detailed reaction mechanisms of Li$_2$MnO$_3$ are found in the literature.[24] Historically, charge compensation by non-cationic species has been already known in sulfides before 1990.[25] Sulfide ions are relatively soft and easily polarizable, and oxidation of sulfide ions (S$^{2-}$) and the formation of disulfide (persulfide) ions (2 S$^{2-}$) is a well-known process in many chemical/biological processes. Ligand hole stabilization has been also known associated with charge transfer from the oxide ion to the transition metal ions for a heavily hybridized system with oxygen 2p orbital, for example Fe$^{4+}$ in SrFeO$_3$.[26] Similarly, the possibility of charge transfer from oxygen 2p to Co$^{4+}$ in Li$_2$CoO$_2$ was also discussed in 1999.[27] If such ligand holes are directly and/or indirectly created by the electrochemical oxidation for the lithium-excess system, this process is classified as “anionic” redox.

Although a crystal structure of Li$_2$MnO$_3$ is essentially the same with LiCoO$_2$ (a difference is only found in additional lithium ions in transition metal layers as shown in Figure 3). Further enrichment of lithium contents in the structure is also possible by combining transition metals ions with higher transition metal ions. For instance, Li$_2$NbO$_4$ with pentavalent niobium ions,[28] Li$_2$MoO$_4$ with hexavalent molybdenum ions,[29] and Li$_2$ReO$_4$ with heptavalent rhenium ions[30] are found in the literature. These oxides are also classified as cation-ordered rocksalt-type structures (Figure 3) with the common ccp lattice of oxide ions, and found in the rocksalt tie-line in Figure 2. Although niobium and molybdenum as 4d-transition metal ions and rhenium as 5d-transition metal ions are heavier ions, theoretical capacities of these oxides are attractive as electrode materials as summarized in Table 1. These transition metal ions with high oxidation states and lithium ions are located at octahedral sites in the ccp lattice of oxide ions, but arrangement of these ions are different from each other as shown in Figure 3. The theoretical capacity reaches 526 mA h g$^{-1}$ for Li$_4$MoO$_5$ when anionic redox is utilized. However, these lithium-excess materials consist of transition metal ions without conductive d-electrons and are essentially insulators and/or semiconductors. Therefore, anionic redox reaction cannot be activated. Lithium insertion materials require both high ionic and electronic conductivity.
To induce electronic conductivity, partial substitution of transition metals for these oxides is the effective strategy to design high-capacity positive electrode materials. Two possible scenarios for metal substitutions are shown in Figure 4. Since Li$_3$NbO$_4$ (similarly reformulated as Li$_{1.5}$Nb$_{0.5}$O$_2$), layered/rocksalt Li$\text{M}$O$_2$ with trivalent transition metal ions (Mn$^{3+}$, Fe$^{3+}$, V$^{3+}$ etc.), and rocksalt MO with divalent transition metal ions (Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$ etc.) have the common ccp lattice of oxide ions, the formation of solid solution among these phases is anticipated. Theoretical capacities calculated with $M$=Mn are also plotted in Figure 4 as hypothetical materials. Here, theoretical capacities are calculated on the basis of the pure anionic redox (red lines, which also correspond to the highest reversible capacities in the entire composition) and one-, two-, and three-electron redox with cationic species (blue lines). For the case of divalent metal substitution, a large reversible capacity cannot be obtained for one-electron redox reaction for cationic species. A theoretical reversible capacity is limited to $\sim 200$ mAh g$^{-1}$, indicating that the use of anionic redox and/or more than two-electron redox for cationic redox is required to design high-capacity electrode materials. For the case of trivalent metal substitution, since lithium contents in the structure remain high enough in the entire composition, more flexible material designs are possible in this system. Therefore, high-theoretical capacities, over 300 mAh g$^{-1}$, are expected with different material design strategies for both anionic/cationic redox as shown in the latter sections.

### Table 1. Comparison of theoretical capacity on the basis of lithium contents in structures for different lithium-excess materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>LiCoO$_2$</th>
<th>Li$_2$MnO$_3$</th>
<th>Li$_3$NbO$_4$</th>
<th>Li$_4$MoO$_5$</th>
<th>Li$_5$ReO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (mAh g$^{-1}$)</td>
<td>274</td>
<td>459</td>
<td>452</td>
<td>526</td>
<td>423</td>
</tr>
</tbody>
</table>

Figure 4. Theoretical capacity for Li$_3$NbO$_4$–LiMO$_2$ (top) and Li$_3$NbO$_4$–MO (bottom) binary systems. See the text for more details. The same oxygen contents (Li$_{1.5}$Nb$_{0.5}$O$_2$, Li$\text{M}$O$_2$, and M$_2$O$_2$) are used in the calculation for simplicity.

3. Li$_3$NbO$_4$- and Li$_2$TiO$_3$-Based Systems; Reversible and Irreversible Anionic Redox

Although pure Li$_3$NbO$_4$ is electrochemically inactive, the substitution of 3$d$ transition-metal ions for Nb/Li ions effectively induces conductive electrons as mentioned above. Such 3$d$ transition-metal ions can accept electrons from oxide ions, leading to the activation of anionic redox coupled with cationic redox. After metal substitution, cation ordering observed for pure Li$_3$NbO$_4$ is lost, and a cation-disordered rocksalt-type structure is formed. Historically, cation-disordered rocksalt oxides was regarded as electrochemically inactive as electrode materials because of absence of Li migration path in a bulk structure. Nevertheless, facile lithium migration is possible for lithium-excess cation-disordered rocksalt (Li$_{1+x}$Me$_{1-x}$O$_2$) associated with the formation of percolative network for lithium migration in the host structure.

Galvanostatic charge/discharge curves of Mn$^{3+}$ and Fe$^{3+}$ substituted Li$_3$NbO$_4$, i.e., Li$_{1.5}$Nb$_{0.5}$Fe$_{0.5}$O$_2$ and Li$_{1.5}$Nb$_{0.5}$Fe$_{0.5}$O$_2$, are compared in Figure 5. Both samples deliver $\sim 350$ mAh g$^{-1}$ of initial charge capacities with a voltage plateau at 4.1–4.3 V. However, a clear difference is noted for discharge. Polarization on discharge is much larger...
for the Fe substituted sample, and the second charge curve is completely different from initial charge. The voltage plateau is observed only for the initial charge. In contrast, profiles of the initial and second charge are similar for the manganese-substituted sample with a slope region (3–4 V) followed by a voltage plateau at 4.3 V. 300 mAh g\(^{-1}\) of the reversible capacity is observed for the Mn substituted sample with relatively high voltage on discharge. The discharge capacities observed are much larger than that of the theoretical capacities calculated based on the Mn\(^{3+}/Mn^{4+}\) cationic redox. The results suggest that charge compensation is, therefore, realized by anionic redox. Similar to Li\(_{1.2}\)NbO\(_4\), Li\(_{1.2}\)TiO\(_3\) is also used as host structure for anionic redox, and charge/discharge curves of Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) (\(M=\text{Mn}^{3+}\) and \(\text{Fe}^{3+}\)) are also shown in Figure 5. Niobium- and tatanium-based oxides show similar voltage profiles, and similar reaction mechanisms for both systems are anticipated.

To examine charge compensation mechanisms and the contribution of oxide ions on the charge process, soft X-ray absorption spectroscopy (XAS) was utilized for Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) (Figure 6).\(^{[37]}\) On charge, no change is observed for Ti L-edge XAS spectra, suggesting that Ti is not responsible for charge compensation. In the slope region (3 to 4 V on charge), shift of Mn L-edge XAS spectra to the higher energy region clearly indicates oxidation of Mn\(^{3+}\) to Mn\(^{4+}\) while no change is found on charge in the voltage plateau region. In contrast, a new peak appears at 530 eV for O K-edge XAS spectra, and systematic changes as a function of charge capacities are observed during charge in the plateau region. Moreover, this process is reversible, and coming back to its original position after discharge. Such a new peak after charge is also evidenced for Li\(_{1.3}\)Mn\(_{0.3}\)O\(_2\)-based electrode materials,\(^{[38,39]}\) but more clear changes are noted for Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) and Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{0.4}\)O\(_2\). When it is assumed that charge compensation is realized by anionic redox, formal oxidation states changes from Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{3}\)O\(_{2}\) for the as-prepared sample to Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{4}\)O\(_{2}\) for the fully charged state. The origin of the new peak has been debatable for a long time.\(^{[40]}\) Recently, this peak has been explained by results of the oxidation of \(\pi\)-like bonds between Mn\(^{4+}\) (\(t_{2g}\)) and O 2p orbitals.\(^{[41]}\) After the oxidation of oxygen, holes are energetically stabilized by \(\pi\)-type interaction with Mn\(^{4+}\), which is accompanied by rehybridization of molecular orbitals, and probably accounts for trend observed in the XAS spectra.

Figure 5. Comparison of charge/discharge curves of Li\(_{1.3}\)Nb\(_{0.3}\)Mn\(_{0.4}\)O\(_2\) and Li\(_{1.2}\)Ti\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) (\(M=\text{Mn}^{3+}\) and \(\text{Fe}^{3+}\)). Reprinted with permission from ref 24. Copyright 2017 The Chemical Society of Japan.
As shown in Figure 5, the iron-substituted samples, Li$_{1.3}$Nb$_{0.3}$Fe$_{0.4}$O$_2$ and Li$_{1.2}$Ti$_{0.4}$Fe$_{0.4}$O$_2$, show the completely different trend. These results suggest that irreversible phase transition occurs on initial charge. Soft XAS spectra of the Fe-substituted Li$_3$NbO$_4$ sample, Li$_{1.3}$Nb$_{0.3}$Fe$_{0.4}$O$_2$, on initial charge and discharge are shown in Figure 7. In O K-edge XAS spectra, a new peak at 527.5 eV appears after charge to the point b (120 mA h g$^{-1}$) in Figure 7. The energy position is clearly different from the manganese systems. Nevertheless, since no change is observed from Fe L-edge XAS spectra, oxygen contributes for the charge compensation process. A similar change was also reported for Li$_{1.19}$Ti$_{0.38}$Fe$_{0.42}$O$_2$.[42] Additionally, this new peak disappears on further charge to 4.8 V. This fact indicates that this intermediate species is energetically unstable, leading to oxygen loss by electrochemical oxidation. Such oxygen loss results in the reconstruction of particle morphology and formation of nanosized particles, and this fact is clearly evidenced in TEM images of Figure 7. After oxygen loss on charge, iron is electrochemically reduced from the trivalent to divalent state on initial discharge, as clearly observed in the Fe L-edge XAS spectra.[57] Instability of anionic redox results in huge polarization observed in Figure 5 for the Fe systems. Similarly, oxygen loss was also found to be the domimative process for Li$_{1.33}$Sb$_{0.33}$Fe$_{0.33}$O$_2$.[43]

For the case of oxides with Fe$^{3+}$, covalency is relatively high, and therefore, the Fermi level is consisting of both iron and oxygen.[37] After charge, both iron and oxygen are oxidized. Nevertheless, Fe$^{4+}$ is chemically less stable, and therefore oxygen donates electrons to reduce iron ions. As a result, oxygen is further oxidized, leading to oxygen release. In contrast, Mn–O bond has a relatively high ionic character, and Mn$^{4+}$ is chemically more stable. The holes created by oxidation is isolated in the structure (small interaction with

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**Figure 6.** Changes in electronic structures for Li$_{1.2-x}$Ti$_x$Mn$_{0.4}$O$_2$ on initial charge/discharge; Ti L-edge, Mn L-edge, and O K-edge XAS spectra. The points where XAS spectra have been collected are also shown.
manganese ions), and therefore high reversibility is achieved for the manganese system.

4. Activation of Anionic Redox by Chemical Bonds with High Ionic Characters

Each oxide ion in conventional and stoichiometric layered LiMO₂ is coordinated by three transition metal ions and three lithium ions. For the Li-excess layered oxides, Li₂MO₃, oxide ions are coordinated by two transition-metal ions and by four lithium ions. Coordination numbers of lithium ions are increased by Li enrichment. Since a bonding character of Li/C₂O is essentially ionic, the increase in the coordination numbers of lithium ions influences electronic structures of oxide ions. Oxide ions gain more electrons from Li ions, and a net oxidation number approaches its formal oxidation number, two minus. Recently, a rational explanation about such consideration has been provided by the DFT study for the lithium-excess oxides. The lithium-excess oxide contains the Li–O–Li configuration, and the Li–O–Li configuration is essentially unhybridized with transition-metal ions. The energy of this unhybridized state is lower than those of hybridized O 2p states with transition-metal ions, and thus, oxide ions are more easily oxidized for the lithium-excess oxides.

Additionally, Nb⁵⁺ and Ti⁴⁺ are also highly ionized ions compared with the late transition metal ions. The mixing
between metal d orbitals and oxygen 2p orbitals is less pronounced, and thus similar to the lithium enrichment in the structure, the character of oxide ions becomes more ionic. This fact is beneficial to activate anionic redox, leading to lowering the electrochemical potential. Initial charge/discharge profiles of the conventional lithium-excess oxide, \( \text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2 \), and \( \text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_2 \) in Li cells are compared in Figure 8. Well-defined voltage plateaus are observed for both samples, but voltage related to anionic redox is 0.15 V lower for \( \text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_2 \) than that of \( \text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2 \). Oxide ions are more easily oxidized with a lower electrode potential for \( \text{Li}_{1.2}\text{Ti}_{0.4}\text{Mn}_{0.4}\text{O}_2 \). By the presence of \( \text{Nb}^{5+} \) and \( \text{Ti}^{4+} \), anionic redox is more easily accessed when compared with the lithium-excess oxides containing the late transition metal ions. Moreover, for \( \text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2 \), the voltage plateau is lost for the second charge process, as shown in Figure 8 because the partial oxygen loss and structural reconstruction processes cannot be avoided on initial charge.\(^{[22,23,45–47]} \) Nevertheless, as pointed out by the recent article,\(^{[41]} \) a nature of chemical bonds between oxygen and ions without valence electrons, like \( \text{Nb}^{5+} \) and \( \text{Ti}^{4+} \), is essentially a non-bonding state, and therefore these ions cannot stabilize the redox reaction of oxide ions. Therefore, anionic redox would be stabilized by tetravalent manganese ions through \( \pi \)-type interaction with oxygen.

5. \( \text{Li}_4\text{MoO}_5 \) as Host Structure of Lithium-Excess Compounds

\( \text{Li}_4\text{MoO}_5 \) has been also studied as a host structure of high-capacity positive electrode materials. To extract lithium ions from \( \text{Li}_4\text{MoO}_5 \), divalent nickel ions are partly substituted for lithium and molybdenum ions based on \( x\text{Li}_4\text{MoO}_5-(1-x)\text{NiO} \) binary system with two different rocksalt-type related structures. Synthesis of single-phase samples is achieved in the entire range in this binary system.\(^{[48]} \) An XRD pattern of the 1:1 mixture of \( \text{Li}_4\text{MoO}_5 \) and \( \text{NiO} \), i.e., \( \text{Li}_4\text{NiMoO}_6 \) is shown in Figure 9a. Similarly, \( \text{Li}_4\text{NiMoO}_6 \) is also reformulated as \( \text{Li}_{4/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2 \). The crystal structure of \( \text{Li}_4\text{NiMoO}_6 \), was analyzed by the Rietveld analysis, and it is found that the crystal structure is related to that of \( \text{Li}_5\text{ReO}_6 \). Rhenium ions at 2a sites in \( \text{Li}_5\text{ReO}_6 \) are replaced by molybdenum ions. Additionally, one nickel ion is substituted for one Li ion, resulting in the chemical formula of \( \text{Li}_4\text{NiMoO}_6 \). Nickel and lithium ions are nearly randomly distributed at the same octahedral sites whereas perfect ordering is evidenced for Mo ions as shown in a schematic illustration of the crystal structure in Figure 9a inset.

Electrochemical properties of \( \text{Li}_{4/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2 \) with different cut-off voltages for the charge (oxidation) process are shown in Figure 9b. A large initial charge capacity is observed by charge to 4.8 V, but the polarization as electrode materials is large. Electrode reversibility is improved by lowering the cut-off voltage even though reversible capacity is inevitably lowered. No capacity loss was observed for continuous 15 cycles in the range of 1.5–4.11 V (Figure 9c). When the cut-off voltage is increased from 4.11 to 4.5 V, a discharge (reduction) voltage profile changes. A clear voltage plateau at 2 V appears after charge above 4.5 V, which is clearly different from the voltage profile observed for 4.11 V cycle. To examine the difference in voltage profiles for 4.11 and 4.5 V cycles, \( \text{ex-situ} \) XRD patterns were collected after electrochemical cycles. Diffraction lines related to the Mo ordering, observed in a two theta range of 20–35°, have disappeared after the 4.5 V cycle, and major diffraction lines on the XRD...
pattern can be assigned as a cation-disordered rocksalt structure. This observation suggests that an irreversible phase transition, at least including Mo migration in the bulk structure, occurs on the 4.5 V cycle. Clear difference is observed on the XRD pattern for the 4.11 V cycle. Diffraction lines related to the Mo ordering are still observed after charge to 4.11 V, suggesting partial oxygen loss on oxidation to above 4.11 V.

Similarly, a binary system, $x\text{Li}_4\text{MoO}_5-(1-x)\text{LiFeO}_2$, is studied as electrode materials for rechargeable lithium batteries. A sample of single phase is obtained at $x=0.5$, and it is found that $\text{Li}_{1.42}\text{Mo}_{0.29}\text{Fe}_{0.29}\text{O}_2$ ($x=0.5$) also crystallizes into $\text{Li}_5\text{ReO}_6$-type structure. Although an initial charge capacity of $\text{Li}_{1.42}\text{Mo}_{0.29}\text{Fe}_{0.29}\text{O}_2$ reaches 350 mAh g$^{-1}$, irreversible phase transition associated with oxygen loss and molybdenum migration on charge is evidenced by X-ray diffraction and X-ray absorption spectroscopy. The irreversible phase transition inevitably results in large polarization on discharge as electrode materials in Li cells. For late transition metals, such as iron, cobalt and nickel ions, competition of cationic and anionic redox reactions cannot be avoided associated with relatively high covalent natures. The holes created in oxygen are destabilized by charge transfer to cationic species, leading to oxygen loss as the irreversible process.

6. Li$_3$RuO$_3$ System; Extremely Reversible Anionic Redox

Although irreversible anionic redox was evidenced for the late 3d-transition metal ions, an exception is found in Li$_3$RuO$_3$ ($\text{Li}_4\text{Ru}_3\text{O}_7$). Ruthenium as the 4d-transition metal ion have a much higher covalent nature with oxide ions. However,
chemical stability of ruthenium ions with higher oxidation states is relatively high when compared with 3d-transition metal ions, and therefore unfavorable charge transfer from oxygen on charge is effectively suppressed. In addition, anionic redox is easily activated associated with high electronic conductivity of Li$_2$RuO$_3$,\(^{[15]}\) leading to highly reversible anionic redox. Typical charge/discharge curves of Li$_2$RuO$_3$ is shown in Figure 10 collected at 50 °C. A reversible capacity of 300 mA h g$^{-1}$, which corresponds to $>90\%$ of the theoretical capacity, is observed, and surprisingly nearly 2 moles of lithium ions are reversibly extracted from Li$_2$RuO$_3$ with the cationic/anionic redox, forming $\square_2$RuO$_3$ after charge to 4.8 V. Moreover, such electrode properties are obtained from the highly dense particles with large size of $\sim 15\mu$m as shown in the SEM image of Figure 10. No capacity fading is observed even at 50 °C. Since XRD density is also higher than Ni-based layered materials, both gravimetric/volumetric energy density clearly outperforms stoichiometric layered materials. The only problem is found in material cost of ruthenium as electrode materials.

For the conventional layered oxides, e.g., LiCoO$_2$ and LiNiO$_2$, extraction of 1.0 mol of Li ions from host structures results in the formation of O1 phase\(^{[50]}\) (additionally, some stacking faults are noted for Li$_2$NiO$_2$\(^{[51]}\)), and thus drastic shrinkage of interlayer distances cannot be avoided. This fact is generally used to account for insufficient cyclability for LiCoO$_2$ and LiNiO$_2$ when all Li ions are extracted from oxides. As layered materials, a similar drawback was anticipated for Li$_2$RuO$_3$. Nevertheless, no degradation on electrochemical cycles is evidenced in this system. Further studies on reaction mechanisms for the Ru system as model materials of the anionic redox are needed to explain outstanding experimental observation. Similar to Li$_2$RuO$_3$, if 2 moles of lithium ions are reversibly extracted from Li$_2$MO$_3$ (4/3 moles of lithium ions from Li$_{4/3}$M$_{2/3}$O$_2$) with chemistry of 3d-transition metal ions, available reversible capacity possibly exceeds 400 mA h g$^{-1}$ as the electrode materials.

7. Li$_3$NbO$_4$-LiMO$_2$ System ($M=V^{3+}$ and Mo$^{3+}$); Pure Cationic Redox

Another group of the lithium-excess compounds is found in vanadium and molybdenum chemistry. Unavoidable competition of cationic/anionic redox often results in oxygen loss for the late 3d-transition metal ions. Since energy of d-electrons for vanadium/molybdenum ions low enough compared with p-electrons of oxygen, such completion of cationic/anionic redox is avoided, and pure cationic redox is, therefore, used as electrode materials. Electrochemical properties of Li$_{1.25}$V$_{0.25}$V$_{0.5}$O$_2$, which is found in Li$_3$NbO$_4$-LiVO$_2$ binary system, are shown in Figure 11. In this binary system, both end members crystallize into cation-ordered rocksalt structures, in which lithium, niobium, and vanadium ions are located at distinct octahedral sites. In contrast, Li$_{1.25}$V$_{0.25}$V$_{0.5}$O$_2$ crystallizes into essentially cation-disordered rocksalt structure and cations are located at the same octahedral sites\(^{[52]}\). The highest theoretical capacity is expected for the sample of Li$_{1.2}$Nb$_{0.2}$V$_{0.6}$O$_2$ in this binary system based on two-electron redox for V ions (see also Figure 4). However, synthesis of a single phase sample was not successful by conventional calcination.

For Li$_{1.2}$V$_{0.25}$V$_{0.5}$O$_2$, good capacity retention as electrode materials is evidenced, and such high reversibility is advantageous to use two-electron redox reaction of vanadium ions for...
battery applications. Moreover, reversible capacity is further enhanced at elevated temperatures. \( \text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_{2} \) delivers a large capacity of approximately 300 mAh g\(^{-1}\) at 50 °C, at least for 15 cycles as shown in Figure 11. Energy density available reaches 770 mWh g\(^{-1}\). Li metal, and this value exceeds those of conventional layered oxides and phosphates. Experimentally observed reversible capacity nearly corresponds to that of the theoretical capacity based on two-electron redox of vanadium ions, indicating that 1.0 mol of Li ions are reversibly extracted from the host structure. Rate-capability of the carbon composite \( \text{Li}_{1.25}\text{Nb}_{0.25}\text{V}_{0.5}\text{O}_{2} \) sample is also shown in Figure 11. Discharge capacity observed at a low rate of 10 mA g\(^{-1}\) reaches 230 mAh g\(^{-1}\) at room temperature, and the sample delivers 150 mAh g\(^{-1}\) at a rate of 2000 mA g\(^{-1}\). Inferior rate-capability was expected for the cation-disordered rocksalt phase. However, the sample shows good rate-capability as shown in Figure 11, probably because of good electronic conductivity for the vanadium system.

The theoretical capacity with cation redox is further increased by the use of three-electron redox as shown in Figure 4. Historically, three-electron redox of transition metals is reported for \( \text{Cr}^{3+}/\text{Cr}^{6+} \), e.g., \( \text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_{2} \).[53] However, chemical compounds containing \( \text{Cr}^{6+} \) are toxic and restricted in use. Three-electron redox reaction of \( \text{Mo}^{3+}/\text{Mo}^{5+} \) is, therefore, targeted for a new series of electrode materials. Since a conventional layered system, \( \text{LiMo}_3\text{O}_6 \) has one mole of Li in the formula unit, only one-electron redox of \( \text{Mo}^{3+}/\text{Mo}^{4+} \) is used.[54] As a proof of concept, \( \text{Mo}^{5+} \) is diluted in \( \text{Li}_3\text{NbO}_4 \) and tested as a model material to form a binary system with the chemical formula of \( x \text{LiMoO}_2-(1-x) \text{Li}_3\text{NbO}_4 \). Crystal structures of \( \text{LiMoO}_2 \)[54] and \( \text{Li}_3\text{NbO}_4 \)[54] are classified as rocksalt-type superstructures, indicating that both oxides consist of a common cubic close-packed (ccp) oxygen lattice, and a difference is found only in cation distribution in octahedral sites. Therefore, similar to other binary systems, the formation of solid solution samples is anticipated. The highest reversible capacity (based on \( \text{Mo}^{3+}/\text{Mo}^{5+} \) redox) is expected when \( x=0.6 \) (reformulated as \( \text{Li}_{0.37}\text{Nb}_{0.27}\text{Mo}_{0.37}\text{O}_2 \)). If all Li ions are reversibly extracted/re-inserted from/into the crystal lattice with the three-electron redox of Mo, the theoretical capacity reaches 317 mAh g\(^{-1}\). Nevertheless, all our trials to synthesize samples by conventional calcination failed.[55] Phase segregation into \( \text{Li}_3\text{NbO}_4 \) and \( \text{LiMoO}_2 \) has been evidenced, and a narrow solid solution range is anticipated in this binary system. \( \text{Li}_{0.37}\text{Nb}_{0.27}\text{Mo}_{0.37}\text{O}_2 \) was not identified as a thermodynamically stable phase.

Therefore, an alternate route was selected, i.e., synthesis of a metastable phase, and mechanical milling was used for material synthesis.[55] Figure 12a shows X-ray diffraction patterns of the samples before and after the mechanical milling. The diffraction lines of \( \text{LiMoO}_2 \) and \( \text{Li}_3\text{NbO}_4 \) in a 2θ range of 15–37° are gradually disappeared by mechanical milling, and new peaks are appeared at 38, 42, and 63°, which are assigned as the cation-disordered rocksalt structure. This fact indicates that a mixture of \( \text{Li}_3\text{NbO}_4 \) and \( \text{LiMoO}_2 \) is gradually changed into the cation-disordered rocksalt structure. A single phase sample is successfully obtained after mechanical milling. The heating of the rocksalt sample results in the phase segregation into \( \text{Li}_3\text{NbO}_4 \) and \( \text{LiMoO}_2 \), indicating that this rocksalt phase is a metastable phase.

Electrochemical properties of \( \text{Li}_{0.37}\text{Nb}_{0.27}\text{Mo}_{0.37}\text{O}_2 \) are also shown in Figure 12b. The sample delivers a reversible capacity of > 280 mAh g\(^{-1}\), which corresponds to approximately 85 % of the theoretical capacity based on the three-electron redox of Mo ions. No degradation is observed for continuous 30 cycles as shown in Figure 12c. Similarly,

![Figure 11.](image-url)
Li$_2$TiO$_3$ and Li$_4$MoO$_5$ are used as starting materials for three-electron redox of molybdenum ions, and solid solution samples with LiMoO$_2$ are obtained by mechanical milling. Reversible capacity exceeds 300 mA h g$^{-1}$ for Li$_4$MoO$_5$-LiMoO$_2$ binary system as shown in Figure 12b, and this system, Li$_{4/3}$Mo$_{6}^{4+/5+}$Li$_{2/9}$Mo$_{3}^{4+/5+}$O$_2$ is reformulated as Li$_2$MoO$_3$, in which average oxidation state of Mo is calculated to be “four”. Electrochemical properties of Li$_2$MoO$_3$ prepared by mechanical milling are much better than that of bulk Li$_2$MoO$_3$ prepared by conventional calcination, and reversible capacity observed reaches >90% of theoretical capacity on the basis of Mo$^{4+/5+}$ redox and the lithium content in the structure. Mechanical milling is effective technology to synthesize metastable materials, and electrode performance of samples is drastically improved by nanosizing of materials.

8. Lithium-Excess Metal Oxyfluorides; LiF-LiM$_2$O$_2$ System

Metal fluorides, such as FeF$_3$, has been extensively studied as positive electrode materials. A fluoride ion, which is the most electronegative element, effectively increases the electrochemical redox potential, and thus relatively higher operating voltage is achieved for FeF$_3$ with a redox couple of Fe$^{2+}$/Fe$^{3+}$. However, FeF$_3$ contains no lithium ions in the structure, and therefore fabrication of a full cell with graphite as a negative electrode is impossible. Additionally, FeF$_3$ crystallizes into a distorted ReO$_3$-type structure, and a non-close packed structure reduces the volumetric capacity as electrode materials. Lithium-containing close packed structures are, therefore, preferable as positive electrode materials. Similar to layered LiM$_2$O$_2$, as a fluoride counterpart, LiM$_2$F$_2$ is considered as potential electrode materials (also see Figure 13). However, in this case, oxidation states of M ions are decreased to monovalent, and therefore material designs are restricted to limited chemistry. Moreover, sacrifice of electronic conductivity is also unavoidable for the pure fluoride system. One possible strategy is the use of mixed-anion systems, i.e., metal oxyfluorides, LiMOF with divalent transition metal ions. As a lithium-free metal oxyfluoride, FeOF with a rutile structure, which is a distorted close packed structure, is known and is prepared by heating of a mixture of FeF$_3$ and Fe$_2$O$_3$. Lithium ions are reversibly inserted into Fe$_3^{4+/5+}$OF, ideally forming LiFe$_2^{4+/5+}$OF. Lithium-containing metal oxyfluorides, LiM$_2^{4+/5+}$OF, are attractive candidates as potential positive electrode materials. LiM$_2^{4+/5+}$OF is also regarded as solid solution of LiMO$_2$ and LiM$_2$F$_2$ as shown in Figure 13. Theoretical capacities of lithium-containing metal oxyfluorides are also shown in Table 2. These oxyfluorides are, unfortunately, not thermodynamically stable, and synthesis is not easy by conventional routes. Nevertheless, it has been reported that synthesis of LiFeOF is possible by mechanical milling.
milling, and nearly one mole of lithium ions are reversibly extracted from the crystal lattice with Fe$^{2+}$/Fe$^{3+}$ redox. Similarly, lithium-excess metal oxyfluorides are obtained by mechanical milling. Li$_2$VO$_2$F has been reported as a first lithium-excess metal oxyfluoride, and Li$_2$MO$_2$F is also found in a phase diagram between Li$_2$MO$_3$ and Li$_2$MF$_3$ (Figure 13). Li$_2$VO$_2$F (Li$_{1.33}$V$_{0.67}$O$_{1.33}$F$_{0.67}$) delivers large reversible capacity of 350 mA h g$^{-1}$ in Li cells on the basis of V$^{3+}$/V$^{5+}$ two-electron redox. However, in general, solubility of fluorides into carbonate solvents is higher than that of oxides, and therefore improvement of cyclability is needed for battery applications.

Recently, our group has extended the concept of three-electron redox of Mo$^{3+}$/Mo$^{6+}$ to the oxyfluoride, and relatively low electrochemical potential of Mo redox (2–3 V vs. Li) is effectively increased by partial substitution of fluoride ions for oxide ions. Lithium molybdenum oxyfluorides were prepared from a mixture of LiMoO$_2$ and LiF. Crystal structures of LiMoO$_2$ and LiF are also classified as rocksalt-type (super)structures consisting of a common cubic close-packed (ccp) anion lattice, and a difference is found only in cation distribution in octahedral sites. Therefore, the formation of solid solution samples (Li$_{1+x}$MoO$_x$F$_{3-x}$ or Li$_{1+x}$Mo$_{1-x}$O$_{2-x}$F$_{2+x}$) is anticipated, and the highest reversible capacity (based on the Mo$^{3+}$/Mo$^{6+}$ redox) is expected for Li$_2$MoO$_2$F (x=2). Indeed, a uniform distribution of Mo/O/F is clearly noted by EDX mapping after mechanical milling as shown in Figure 15, and the formation of a single phase sample with low crystallinity is further confirmed by XRD. If all lithium ions are reversibly extracted from the crystal lattice with the three-electron redox of Mo, the theoretical capacity reaches 430 mA h g$^{-1}$. Li$_{1+x}$MoO$_x$F$_x$ samples with different compositions deliver large reversible capacities of over 250 mA h g$^{-1}$ in lithium cells. The highest reversible capacity is obtained for x=1, Li$_2$MoO$_2$F, and the sample delivers more than 300 mA h g$^{-1}$ (Figure 14). Moreover, operating voltage is increased in comparison to the non-fluorine substituted sample, which is also prepared by mechanical milling, as shown in Figure 14. Energy density observed

Table 2. Comparison of theoretical capacity for rocksalt-related metal oxyfluorides and oxynitrides. M=Mn is assumed for the calculation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Capacity (mA h g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMOF</td>
<td>277</td>
</tr>
<tr>
<td>Li$_2$MO$<em>x$F$</em>{3-x}$</td>
<td>447</td>
</tr>
<tr>
<td>LiMON</td>
<td>292</td>
</tr>
<tr>
<td>Li$_2$MO$<em>x$N$</em>{3-x}$</td>
<td>467</td>
</tr>
</tbody>
</table>

Figure 13. A materials design concept for stoichiometric/lithium-excess fluorides, nitrides, oxyfluorides, and oxynitrides with rocksalt-related structures. See the text for more details.

Figure 14. (top) SEM/EDX images of a mixture of LiMoO$_2$ and LiF (x=2 in LiF–LiMoO$_2$) before/after the mechanical milling. Uniform contrast for Mo, O, and F is clearly evidenced for the EDX map after mechanical milling. (bottom) Comparison of charge/discharge curves of Li$_2$MoO$_3$ and Li$_2$MoO$_2$F (x=1 in LiF–LiMoO$_2$) prepared by mechanical milling. Operating voltage is increased by fluorine-substitution. Reprinted with permission from ref 60. Copyright 2017 Elsevier B.V.
reaches 750 mWh g\(^{-1}\) based on Li metal, and is comparable to layered positive electrode materials with nickel and cobalt. Although redox potential of molybdenum ions is relatively low as positive electrode materials, operating voltage is effectively increased by LiF substitution through an inductive effect\(^{[61]}\) by electronegative fluoride ions. Nevertheless, the reversible capacities decrease by further enrichment of fluoride ions. The observed reversible capacity for \(x = 2\) is limited to only 60% of the theoretical capacity. This observation is expected to originate from the inferior electronic conductivity for the fluorine-rich phases.

Electrode performance of other lithium-excess metal oxyfluorides, Li\(_2\)VO\(_2\)F\(^{[59]}\) and Li\(_2\)CrO\(_2\)F,\(^{[62]}\) collected at room temperature is also compared with Li\(_2\)MoO\(_2\)F in Figure 15. Both samples were similarly prepared by ball milling. The vanadium system shows slightly higher operating voltage compared with the molybdenum-system. Moreover, operating voltage is further increased for the chromium-system, but polarization on discharge is larger compared with vanadium-/molybdenum-system. Irreversible migration of Cr ions would be responsible for the polarization as observed in a lithium-excess layered oxide containing Cr ions.\(^{[63]}\) Very recently, a manganese system, Li\(_2\)MnO\(_2\)F, has been already reported. The sample delivers a reversible capacity of nearly 300 mAh g\(^{-1}\), which partly originates from the anionic redox reaction.\(^{[64]}\) In addition, it has been reported that Li\(_2\)Mn\(_{2/3}\)Nb\(_{1/3}\)O\(_2\)F also delivers a reversible capacity of approximately 300 mAh g\(^{-1}\) in lithium cells on the basis of Mn\(^{2+}\)/Mn\(^{4+}\) redox coupled with partial anionic redox.\(^{[65]}\)

Theoretical capacities, experimentally observed reversible capacities, and average operating voltage of lithium-excess rocksalt oxides/oxyfluorides shown in this manuscript are plotted and compared in Figure 16. As shown in this manuscript, now, reversible capacities of 300 mAh g\(^{-1}\) are realized for many chemistries with cationic/anionic redox. For the case of ruthenium system, Li\(_2\)RuO\(_3\), the observed reversible capacity is very close to that of the theoretical capacity (also see Figure 10). In contrast, for the manganese-based oxides/oxyfluorides, observed reversible capacities are clearly smaller than those of theoretical capacities, and observed reversible capacities are possibly further increased by further optimization of electrode materials. Average operating voltage of vanadium-/molybdenum-based electrode materials is relatively low (ca. 2.5 V vs. lithium metal) as positive electrode materials, but high safety with moderate energy density is anticipated. In contrast, nickel-based system, high average operating voltage is attractive even though observed reversible capacity is currently limited. If reversibility of anionic redox is improved for the nickel-based system, available energy density would be significantly improved.

![Figure 15](image_url)  
**Figure 15.** Comparison of charge/discharge curves of lithium-excess metal oxyfluorides; Li\(_2\)VO\(_2\)F, Li\(_2\)CrO\(_2\)F, and Li\(_2\)MoO\(_2\)F.

![Figure 16](image_url)  
**Figure 16.** Comparison of observed reversible capacity (mAh g\(^{-1}\)), average operating voltage (V), and calculated energy density (Wh kg\(^{-1}\)) based on metallic lithium for different lithium-excess metal oxides and oxyfluorides. Theoretical capacity on the basis of lithium contents in the structure is also shown.

Similar to the oxyfluorides, the concept of is extended to a nitride system as shown in Figure 13, but the requirements of metals with high oxidation states results in the difficulty of material designs with rocksalt-related structures. Among expected compounds shown in Figure 13, LiMoN\(_2\) with layered structure was synthesized and tested as electrode...
In contrast to fluorine-substitution, LiMoN$_2$ has significantly low resistivity, and nitride-substitution is an effective strategy to increase the electronic conductivity as electrode materials. Although LiMoN$_2$ crystallizes into a non-close packed structure (molybdenum ions are located at prismatic sites), lithium ions are indeed extracted by electrochemical oxidation. Lithium ions are also inserted into a metal oxynitride, NbON with a baddeleyite-type (ZrO$_2$) structure, and NbON is used as potential negative electrode materials. Since fluoride/nitride ions have unique functionality compared with oxide ions, such mixed anion systems potentially open a new direction to design electrode materials in the future.

9. Anionic Redox Reaction for Rechargeable Sodium Batteries

The use of redox reactions of oxide ions is not limited to the Li system, and is easily extended to the system with different mobile ions, and the application of anion redox has been extended for sodium insertion materials. Na$_2$MnO$_3$, which is a hypothetical Na counterpart of Li$_2$MnO$_3$, is considered to be the host structure of high-capacity sodium insertion materials. Nevertheless, synthesis of Na$_2$MnO$_3$ (Na(Na$_{1/3}$Mn$_{2/3}$)$_3$O$_2$) as an isostructural phase with Li$_2$MnO$_3$ is difficult by conventional synthesis routes associated with a large gap in size of Na$^+$ and Mn$^{4+}$ ions. Instead, the use of Na(Li$_{1/3}$Mn$_{2/3}$)$_3$O$_2$ has been proposed in the literature. Although synthesis of the stoichiometric phase is difficult, a non-stoichiometric Na-deficient phase, Na$_{5/6}$(Li$_{1/4}$Mn$_{3/4}$)O$_2$, has been successfully obtained. Similar to Li$_2$MnO$_3$-based electrode materials, a well-defined voltage plateau is observed for Na$_{5/6}$(Li$_{1/4}$Mn$_{3/4}$)O$_2$ in the Na cell. Partial oxygen loss results in the disappearance of the plateau from the second cycle, but the sample delivers a large reversible capacity of 200 mA h g$^{-1}$ in the Na cell. Similarly, a large reversible capacity was reported for Na$_{x}$Lil$_{1/4}$Mn$_{3/4}$O$_2$ and such large capacity cannot be obtained without the contribution of anion redox. A reversible voltage plateau at 4.2 V vs. Na metal (4.5 V vs. Li metal), presumably associated with oxide ion redox, has been also reported for Na$_{0.6}$(Li$_{0.2}$Mn$_{0.8}$)O$_2$. Mg ions are substituted for Li ions in transition metal layers. Na$_{2/3}$(Mg$_{0.28}$Mn$_{0.72}$)O$_2$ delivers large reversible capacity of more than 200 mA h g$^{-1}$, and the contribution of reversible anionic redox has been reported.

Recently, the reversible redox reaction of oxide ions has been evidenced for Ru-based layered compounds. Similar to Li$_2$RuO$_3$, Na$_2$RuO$_3$ crystallizes into the α-NaFeO$_2$-type layered structure. Two layered polymorphs, in-plane Na/Ru ordered and disordered phases, exist and the anionic redox is activated only for the ordered phase. The origin of activation has been proposed to be the formation and stabilization of the intermediate phase, ilmenite-type NaRu$_2$O$_4$, associated with glide of layers. A similar phase is also found in the Li counterpart. This process involves the phase transition from ccp to hexagonal closed packing (hcp) for the oxygen arrangement. It has been also proposed that large distortion of RuO$_6$ octahedra for the ilmenite phase triggers the formation of O–O sigma antibonding state, and thus the anion redox is also activated.

Similar to Li$_3$NbO$_4$, Na$_3$NbO$_4$ has been also studied as a model host structure for high-capacity positive electrodes. Na and Nb ions are located at octahedral sites in a cubic-close packed (ccp) lattice of oxide ions, and clusters consisting of four Nb ions are surrounded by sodium ions (Figure 17a). If all Na ions are extracted/re-inserted from/into the crystal...
lattice, the theoretical capacity reaches 356 mAh g⁻¹. A binary system, Na₃NbO₄-NaMnO₂ has been examined as possible high-capacity positive electrode materials for sodium battery applications. However, synthesis of samples by conventional calcination is impossible. Phase segregation into Na₃NbO₄ and NaMnO₂ was evidenced, and a narrow solid solution range is expected in this binary system. Therefore, similar to other systems, mechanical milling was used to synthesize metastable phases. Figure 17a shows X-ray diffraction patterns of a mixture of Na₃NbO₄ and NaMnO₂ before and after the mechanical milling. The mixture gradually changes into a cation-disordered rocksalt-type structure. Color of powders also changes into black after the mechanical milling. Although the size of Na⁺ is much larger than those of Nb⁵⁺ and Mn³⁺, all cations are located at the same octahedral sites in the ccp lattice. The sample segregates into a mixture of Na₃NbO₄ and NaMnO₂ after heating, indicating that this phase is a metastable phase. From the scientific point of view, such a metastable phase is quite interesting and important as insertion materials. Nevertheless, from the practical point of view, the difficulty in the synthesis of these materials hinder the use for battery applications because of the cost limitation. Therefore, the research progress on synthesis of metastable phases, possibly the development of a continuous flow process with low cost, is needed to solve this practical problem in the future.

Electrochemical properties of the samples prepared by the conventional calcination and mechanical milling are compared in Figure 17b. A theoretical capacity reaches 311 mAh g⁻¹ when all Na ions are extracted from Na₁.₃Nb₀.₃Mn₀.₄O₂. However, the sample prepared by the conventional calcination delivers only 95 mAh g⁻¹, nearly corresponding to the theoretical capacity based on the Mn²⁺/Mn⁴⁺ redox. This result indicates that O²⁻ redox is not activated. In contrast, the sample obtained by the mechanical milling delivers a large reversible capacity of approximately 200 mAh g⁻¹ at 50 °C, indicating that anionic redox is effectively activated for the sodium-excess condition. Electrochemical voltage of the sample increases almost linearly with two different slope angles, which change at 3.2 V.

The potential profile of the sample is similar to the case of Li₂MnO₃-based electrode materials. However, a clear voltage plateau as observed for Li₁.₃Nb₀.₃Mn₀.₄O₂[31, 37] is not found for the Na counterpart. Moreover, cyclability of the sample in the Na cell is not acceptable for battery applications. Reversibility is completely lost after only 20 cycles.[74] Metastable phases prepared by mechanical milling consists of nanosize particles with low crystallinity, and therefore anionic redox is destabilized compared with submicrometer-sized particles. Indeed, reversibility as electrode materials is significantly improved for nanosize NaMnO₂ with the cation-disordered rocksalt structure prepared by mechanical milling.[75]

10. Conclusions and Future Perspectives

Lithium-excess compounds with rocksalt-related structures are attractive as positive electrode materials for rechargeable lithium/sodium batteries. Higher lithium (sodium) contents with fewer transition-metal ions in framework structures effectively increases theoretical capacities as positive electrode materials. A wide variety of material designs is possible with different chemistry on the basis of both cationic/anionic redox. In the past several years, many new positive electrode materials appeared. Moreover, the concept of the anion redox reaction, not only for the oxide system is extended to the sulfide system.[76] In addition, these concepts would be extended non-rocksalt system, e.g., Li₃Mn₂O₅[77] and Li₂O system.[78–80] Experimental and theoretical understandings of cationic/anionic redox are also further accelerated from the research progress on oxygen electrocatalysts as another important anionic redox system,[81] and a possible synergy between battery materials and electrocatalysts is anticipated.[82] Nevertheless, cyclability of anionic redox as electrode material is currently not enough for practical battery applications. The surface of electrode materials can be chemically reactive after the activation of anionic redox, probably leading to unfavorable side reactions with electrolyte and growth of impedance on electrochemical cycles. In contrast, pure cationic redox system, and the exception of Li₄RuO₃, shows much better cyclability, and will be used for battery applications soon. Further studies of degradation mechanisms are, therefore, encouraged to solve the cyclability problem of anionic redox. Indeed, stabilization of anionic redox has been recently proposed by fluorination.[83] Coordination numbers of transition metal ions with d-electrons to oxygen also significantly influence the reversibility of anionic redox through o-type interaction.[84] Further understanding results in the development of high energy electrode materials with highly reversible anionic redox in the future.

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