Electrochemistry and Solid-State Chemistry of Layered Oxides for Li-, Na-, and K-Ion Batteries

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ABSTRACT
Since reversible lithium (de)intercalation of layered LiCoO2 and its high-voltage operation were discovered by Mizushima, Goodenough, and coworkers in 1980, layered lithium transition metal oxides have been mainly used as positive electrode materials for Li-ion batteries. Since 2010, layered sodium transition metal oxides have been further considered for Na-ion batteries, and new materials have also been developed. Recently, layered potassium transition metal oxides have attracted attention for their potential use in K-ion batteries. This article summarizes our studies on layered transition metal oxides as positive electrode materials for Li-, Na-, and K-ion batteries. The correlation between their crystal structures and electrochemical properties is also discussed. Comprehensive and systematic studies of intercalation materials based on the three alkali metals will provide insight into the unique chemistry and development of new layered oxide materials for next-generation batteries.

Keywords : Electrochemistry, Solid-State Chemistry, Energy Storage Materials, Insertion Materials

1. Introduction
Among commercial rechargeable batteries, Li-ion batteries, named and commercialized by Sony in 1991, exhibit the highest energy density and power and have been widely utilized in electronic devices, electric vehicles, and stationary energy storage systems worldwide.1-4 Following these remarkable developments, the 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino for their contributions to the development of Li-ion batteries. The Li-ion battery market is rapidly growing across the world, and further fast growth is expected. The large-scale demand for batteries for electric vehicles and energy storage systems has resulted in the research priorities shifting from performances to production costs. Thus, minor metal-free or low-cost materials that can be derived from more abundant resources have become increasingly desirable. Since the reversible lithium (de)intercalation of layered LiCoO2 and its high-voltage operation were discovered by Mizushima, Goodenough and coworkers in 1980,5 layered lithium- and cobalt-containing transition metal oxides have been mainly employed as positive electrode materials for Li-ion batteries. In the last 20 years, Ni-rich Li[Ni1-xMnxCo1/2]O2, Li[Ni1/2x1/2MnxCo1/2]O2, and Li-rich Li[Li, Mn, Co, Ni]O2 materials have been investigated and developed as high-capacity and high-energy positive electrode materials, respectively, for next-generation Li-ion batteries. Na-ion batteries have been extensively studied as potential candidates for stationary energy storage systems,6 because of the abundant sodium resources evenly distributed in the Earth’s crust and seawater.7 Studies of room-temperature Na-ion batteries have started in the 1970s, and the electrochemical properties of a Na//Na2CoO2 cell were reported in 1980,8 when those of Li//LiCoO2 were also reported for the first time.9 In the industrial field, Allied Corp. (USA), Showa Denko K. K. (Japan), and Hitachi, Ltd. (Japan) carried out collaborative work on Na-ion batteries and filed patents for Na-Pb alloy // γ-Na2CoO2 cells9-12 exhibiting good cycle stability; however, they never commercialized Na-ion batteries. On the other hand, the Komaba group (Tokyo University of Science) reported hard carbon//NaNi1/2Mn1/2O2 full cells with acceptable cycle stability in 2009,13 and the results were published in 2011.14 While the good electrode performance of Co-Ni-free NaFe1/2Mn1/2O2 was reported in 2012,15 after these developments, Na-ion batteries have attracted much attention in the field and have been widely investigated and developed worldwide. More recently, electrochemical studies on layered oxide materials have been extended to layered potassium oxides, after Ceder’s team and our group reported the electrochemical properties of a K//K2CoO2 cell in 2017.16,17 This comprehensive article briefly summarizes our fundamental studies on layered transition metal oxides as positive electrode materials for Li-, Na-, and K-ion batteries, based on our previous...
and present research. Our viewpoint on future perspectives in this field is also presented.

2. Stable AMeO₂ (A = alkali metal) Crystal Structures

LiMnO₂ (Me = transition metal) compositions and layered rocksalt type structures are known to be theoretically suitable as positive electrode materials for lithium-ion batteries, because of their high lithium content in the pristine state, high Me⁴⁺/Li⁺ redox potential, and high-density structures, which lead to a large volumetric energy density.¹⁸ LiCoO₂, LiNi₀.₅Co₀.₅Al₀.₅O₂, and LiNi₁ₓMn₁₋ₓO₂, which are commonly used in commercialized lithium-ion batteries, are isosstructural with α-NaFeO₂. The layered rocksalt type structures with R-3m space group are classified as α-NaFeO₂ type. The α-NaFeO₂ type structures possess MeO₂ slabs consisting of edge-shared MeO₆ octahedra, stacked along the c-axis with cubic close-packed oxygen atoms as AB CA BC arrays; alkali metal ions are accommodated at octahedral sites in the interslab space, as shown in Fig. 1a. The layered structure is stabilized by the different ionic radii of the alkali metal and transition metal ions, which result in the separation of an alkali metal layer and a transition metal slab along the (111) direction in a cation-disordered NaCl type structure (Fig. 1b). The ionic radius of Li⁺ in octahedral coordination is 0.76 Å, similar to those of transition metal ions.¹⁹ Thus, lithium ions are often mixed with transition metal ions, resulting in the formation of NaCl type (Fig. 1b) or cation-ordered γ-LiFeO₂ type materials (Fig. 1c). Several α-NaFeO₂ type materials crystallize as LiMnO₂ (M° = Co, Ni, Cr, and V), as shown in Fig. 1d. When lithium ions are replaced by larger alkali metal ions such as Na⁺ (1.02 Å) and K⁺ (1.38 Å), a wider variety of transition metal ions are available to crystallize the α-NaFeO₂ type layered AMeO₂ (A = alkali metal) (Fig. 1d).²⁰⁻²³

3. Layered LiFeO₂ and LiMnO₂

The stable crystallization of layered oxides is advantageous for enhancing the structural stability of the materials during their synthesis and electrochemical charge/discharge reactions in batteries. Furthermore, lighter and low-cost transition metal oxides with abundant resources are desirable for practical applications. Based on the latter requirements, layered LiFeO₂ and LiMnO₂ would be ideal materials; however, their unstable structures hinder their direct synthesis by conventional solid-state reactions. We synthesized α-NaFeO₂ type LiFeO₂ by Li⁺/Na⁺ exchange from α-NaFeO₂ nanoparticles, based on a reported synthesis procedure.²⁴⁻²⁵ Although the obtained material contained 36 wt.% of ordered rocksalt type γ-LiFeO₂, it delivered a reversible capacity of ca. 100 mAh g⁻¹ (Fig. 2a), which was much larger than the 5–9 mAh g⁻¹ values reported previously.²⁵ However, irreversible structural changes into a LiFeO₂ spinel-like phase could not be avoided during the initial charge and subsequent discharge/charge cycles (Fig. 2b).²⁶ The practical use of α-NaFeO₂ type LiFeO₂ is still challenging.

Layered LiMnO₂ has a NaNiO₂ type monoclinic structure with C2/m space group, due to the cooperative Jahn-Teller distortion caused by Mn⁴⁺ ions (3d⁴ in the high-spin state).²⁷,²⁸ Monoclinic layered LiMnO₂ (m-LiMnO₂) was previously prepared through Li⁺/Na⁺ exchange from NaNiO₂ type α-NaMnO₂.²⁴⁻²⁷,²⁸ As reported by Armstrong et al., m-LiMnO₂ irreversibly and gradually transforms into a LiMnO₂ spinel-like phase during charge/discharge cycles.²⁹ In fact, the author and colleagues also synthesized m-LiMnO₂ via Li⁺/Na⁺ exchange from NaNiO₂ type NaMnO₂ (Fig. 2c) and confirmed that discharge voltage plateaus at ca. 4.0 and 3.0 V, corresponding to the characteristic plateaus observed for spinel LiMnO₂, gradually appeared during charge/discharge cycles, as shown in Fig. 2d. Surprisingly, even cation-disordered NaCl type cubic LiMnO₂ (c-LiMnO₂),³⁰ which was synthesized at 1300°C and 4 GPa for 30 min with LiF flux (Fig. 2c), displayed a gradual appearance of the characteristic plateaus at ca. 4.0 and 3.0 V during cycling, as shown in Fig. 2d. Another high-pressure phase of ordered rocksalt (γ-LiFeO₂) type, tetragonal LiMnO₂ (t-LiMnO₂),³¹ was recently re-evaluated in comparison to the β-NaMnO₂ type, corrugated-layered orthorhombic LiMnO₂ (o-LiMnO₂) precursor.²⁵ Both LiMnO₂ materials showed the characteristic discharge voltage plateaus and irreversible transformation into a spinel-like phase during charge/discharge cycles.³¹ Therefore, all LiMnO₂ polymorphs, including m-LiMnO₂, c-LiMnO₂, t-LiMnO₂, and o-LiMnO₂, irreversibly transform into a LiMnO₂ spinel-like phase (Fig. 2e), as previously proposed for α-LiMnO₂³¹ and m-LiMnO₂.²⁹ Note that Sato et al. recently reported nanocrystalline c-LiMnO₂ prepared by mechanical milling of o-LiMnO₂, which delivered a large reversible capacity of ca. 250 mAh g⁻¹ with negligible transition into the spinel-like phase.³² The defect content and crystallite/particle sizes can influence the electrochemical properties of LiMnO₂. The present author highlighted the importance of these effects based on studies of layered Li₃MnO₄.

4. Lithium-rich Layered Li₂MnO₃

In contrast to the metastable nature of NaNiO₂ type layered m-LiMnO₂, layered Li₂MnO₃ is thermodynamically stable and can be synthesized by a conventional solid-state reaction.¹⁹ Its crystal structure is basically derived from that of layered rocksalt α-NaFeO₂ type compounds, and Li₂MnO₃ can be alternatively described as Li[(Li₁₋ₓMnₓ)₂O₃]O₂, in layered notation. Additional lithium ions occupy the transition metal sites in the slab, which results in a superstructure with in-plane honeycomb Li/Mn ordering in the [Li₁₋ₓMnₓ]₂O₃ slab, as shown in Fig. 3a. Lithium-rich layered...
transition metal oxides, which correspond to the solid solution phases between LiMeO$_2$ and Li[Li$_{1-2/3}$Mn$_{2/3}$]O$_2$, exhibit a characteristic flat plateau-like region starting from 4.4 V vs. Li/Li$^+$ in the initial charge cycle. However, this process is irreversible and does not occur in the initial discharge or subsequent cycles. After the activation of the Li$_2$MnO$_3$ component in lithium-rich layered materials, a large discharge capacity is obtained along the voltage plateau above 4.4 V in the initial charging process. Similar to the lithium-rich layered compounds, Li$_2$MnO$_3$ exhibits a characteristic voltage plateau at 4.4 V in the initial charging process, although manganese ions are tetravalent in the pristine state. As reported by Yu et al., the initial charge and discharge capacities strongly depend on the crystallite (primary particle) size of Li$_2$MnO$_3$. Li$_2$MnO$_3$ samples with particle sizes of 250–500 nm delivered initial charge and discharge capacities of ca. 50 and 35 mAh g$^{-1}$, respectively (Figs. 3b and 3c). On the other hand, a Li$_2$MnO$_3$ sample with a particle diameter of ca. 50 nm exhibited an extremely large initial charge capacity of ~750 mAh g$^{-1}$ and a discharge capacity of ~320 mAh g$^{-1}$ (Figs. 3d and 3e). Several reaction mechanisms were proposed for the activation process in the initial charge, such as oxidation to Mn$^{5+}$ and simultaneous oxygen extraction, as supported by the oxygen gas generation observed by gas chromatography. Using X-ray absorption spectroscopy, Yu et al. confirmed that tetravalent manganese ions were retained during the initial charging process and then reduced during the following discharge process. Okamoto estimated the stable structure of Li$_2$MnO$_3$ by first-principles calculations and proposed that the 8j sites are favorable for the introduction of oxygen vacancies. These results indicate that a certain amount of oxygen is extracted in the first charging process, and that the oxygen-extracted phase might contribute to the high discharge/charge capacities after activation.
the initial cycle. The author and coworkers assumed that the high capacity of the lithium-rich layered materials is due to oxygen extraction from the parent lattice, together with the reconstruction process to a phase capable of delivering high capacity during the initial charging process. Based on this hypothesis, we attempted to synthesize an oxygen-deficient phase from Li$_2$MnO$_3$ using hydride compounds as strong reducing agents. The NaH and CaH$_2$ reducing agents were reported to be efficient for producing metastable materials with structures characterized by the exotic coordination environments and/or valence states of transition metals. The oxygen-deficient SrFeO$_2$ perovskite, with infinite-layer structure and square-planar coordination, was obtained from the cubic perovskite SrFeO$_2$ using CaH$_2$ as a reducing agent.\textsuperscript{42} The CaH$_2$ reducing agent heterogeneously extracted oxygen from Li$_2$-MnO$_3$,\textsuperscript{43,44} while the stronger LiH reducing agent led to more homogeneous oxygen extraction and formation of the oxygen-deficient Li$_2$MnO$_{3-x}$.\textsuperscript{38} Elemental analysis and synchrotron X-ray diffraction (XRD) Rietveld refinements revealed a lattice volume expansion upon the introduction of oxygen vacancies at the $\delta$ sites, without significant changes in the original layered structure after the reduction process, which was in good agreement with the results of first-principles calculations.\textsuperscript{44} The high-resolution transmission electron microscopy (TEM) image of Li$_2$MnO$_{3.25}$ (Fig. 3f) shows that no significant changes occurred in the particle size after the reduction process with LiH, although slightly disordered domains were observed. Nevertheless, the charge/discharge curves were substantially different after the LiH-reduction process. In contrast to pristine Li$_2$MnO$_3$ (Fig. 3e), no significant voltage plateau at 4.4 V was observed during the initial charging process for the oxygen-deficient Li$_2$MnO$_{3-x}$ phase, as shown in Fig. 3g. This indicates that the initial charging process of pristine Li$_2$MnO$_3$ is related to oxygen extraction and induces structural reconstruction, producing a structure suitable for extremely high charge/discharge capacities. Detailed structural analysis revealed that the oxygen-deficient Li$_2$MnO$_{3-x}$ phase contained partial disruption of in-plane Li/Mn ordering as shown in Fig. 3h.\textsuperscript{38} The partial disruption of the Li/Mn ordering suppressed the strong interaction between [Li$_{1/2}$Mn$_{1/2}$]$_2$O$_2$ slabs (\(0\) = vacancy) at the end of the charge process, resulting in a suppression of drastic structural reconstruction and enhanced cycle stability. The obtained oxygen-deficient phase consisted of metastable nanoparticles. The practical use of Li$_2$MnO$_3$ and lithium-rich layered compounds is still challenging. Optimization of the in-plane Li/Me ordering and stacking sequence would further enhance their electrode performances for future Li-ion battery applications.

5. Layered Polytypes of A$_x$MeO$_2$

In 2013, the present author joined Komaba’s group at the Tokyo University of Science and extended his research from lithium to sodium and potassium layered transition metal oxides as positive electrode materials for Na- and K-ion batteries. As discussed above, the ionic radius of sodium is larger than that of lithium, and various transition metals can be simultaneously employed to form solid solutions, which is advantageous for optimizing the composition of layered sodium transition metal oxides suitable for Na-ion batteries. Furthermore, unlike Li$_x$MeO$_2$, sodium- and potassium-deficient layered oxides such as Na$_x$MeO$_2$ and K$_x$MeO$_2$ are thermodynamically stable and have a wider variety of layered structures. For example, $\alpha$, $\beta$, and $\gamma$-Na$_x$CoO$_2$ (0.5 $\leq x \leq 1$) were reported to crystallize as layered oxides with different oxygen packing sequences.\textsuperscript{45-47}

To further elucidate the structural differences among layered A$_x$MeO$_2$ materials, Delmas and coworkers proposed a systematic notation system.\textsuperscript{48,49} According to this notation, $\alpha$-NaFeO$_2$ and $\alpha$-NaCoO$_2$ are categorized as O3 type materials, whereas $\beta$- and $\gamma$-Na$_x$CoO$_2$ are P3 (including P$'3$) and P2 type materials, respectively. Schematic illustrations of typical layered structures of sodium transition metal oxides, drawn using the VESTA program,\textsuperscript{50} are shown in Fig. 4a–c.\textsuperscript{51} The O3 type ($\alpha$-NaFeO$_2$ type) structure is made up of MeO$_2$ slabs consisting of edge-shared MeO$_6$ octahedra stacked along the $c$-axis, with cubic close-packed oxygen atoms arranged in AB CA BC arrays and alkali metal ions accommodated at octahedral sites in the interslab space (Fig. 4a). Three MeO$_2$ slabs are contained in the hexagonal unit cell. Namely, the “O” in the O3 label indicates the octahedral form of alkali metal ions, and the following “3” denotes the number of MeO$_2$ slabs in the hexagonal unit cell. When the lattice symmetry is lowered to monoclinic or orthorhombic, a prime symbol is added between the letter and number, but the number of MeO$_2$ slabs is counted using a pseudo-hexagonal unit cell, e.g., O3’ type (NaNiO$_2$ type) NaMnO$_2$ with a monoclinic lattice (C2/m space group).\textsuperscript{52} Unlike Li$_x$MeO$_2$, Na$_x$-MoO$_2$ and K$_x$MeO$_2$ crystallize in P3 and P2 type alkali metal-deficient phases (0.3 $\leq x \leq 1$). Large alkali metal ions such as K$^+$ and Rb$^+$ generally prefer prismatic sites with larger available volume than octahedral ones, resulting in the formation of P-type layered oxides such as P3 and P2 ($\beta$-RbSeO$_3$) ones.
In P3 type layered structures (Fig. 4b), the alkali metal ions occupy prismatic sites in the interslab space between MeO2 slabs stacked in AB BC CA oxygen packing sequence along the c-axis, and three MeO2 slabs are contained in a hexagonal unit cell with R3m space group. On the other hand, in the P2 type (β-RbRh2O4 type) structure (Fig. 4c), the alkali metal ions occupy prismatic sites in the interslab space between MeO2 slabs stacked in AB BA AB oxygen packing sequence along the c-axis, and the hexagonal unit cell with space group P63/mmc contains two MeO2 slabs.

Most O3 type NaMeO2 materials generally transform in the O3 → P3 → O3 (→ O1) sequence by gliding of the MeO2 slab during Na extraction in the charging process. The P3 type phase is thus identified as an alkali metal-deficient and intermediate phase related to O3 type oxygen packing. On the other hand, P2 type NaMeO2 compounds generally transform in the P2 → P2-O2 intergrowth (including OP415) → O2 sequence by gliding of MeO2 slabs without breaking Me-O bonds. However, to the best of our knowledge, the electrochemical structural transformation to O2 type K2MnO3 has not been reported to date. This is probably due to the large ionic size of the potassium ion, which maintains a large interslab space and displays a marked preference for P-site occupation.17

For the O3 (including P3) and P2 groups, the charge/discharge behavior of A3CoO2 polymorphs in Li, Na, and K half-cells are compared in Figs. 4d and 4e, respectively.56,57 Clear tendencies are observed for both groups: the layered A3CoO2 and P2 type Na3CoO2 and proposed that the electrostatic repulsion between the alkali metal ions (A–A–A) influences the Co–O bond-length.58 The larger sodium ions result in longer CoO3–O bonds in O3 type NaCoO2 compared to those of O3 type LiCoO2, therefore producing different working potentials of the redox reactions. In fact, the average Cr3–O bond lengths in the CrO6 octahedra are 1.9931, 2.0131, and 2.0360 Å for O3 type LiCrO2,59 O3 type NaCrO2,60 and O3 type KCrO2,60 respectively, showing an increase in the Cr3–O bond length with the size of the alkali metal ion. The starting voltages (i.e., open circuit voltages) for the charge/discharge cycles (Figs. 4d and 4e) decreased with increasing size of the alkali metal ion. Therefore, the low-voltage operation of P2 and P3 type Na3CoO2 and K1+xCo2O4 is expected to originate from the longer Co–O distances. This effect was attributed to the low Lewis acidity and large ionic size of the Na+ and K+ ions and to the strong Na+–Na+ and K+–K+ repulsion in the interslab space. Interestingly, the P3 and P2 type Na3CoO2 materials exhibit almost the same charge-discharge voltage behavior in Na and K cells (Figs. 4f and 4g, respectively). This indicates a relatively smaller effect of the interaction between A+ ions at prismatic sites in the large interslab space between MeO2 slabs, compared to the strong A+–A+ repulsion in the interslab.

The strong A+–A+ repulsion stabilizes the A+/vacancy ordering in A3MeO2 at the discrete A contents (x) of 3/4, 5/8, 2/3, 4/7, 1/2, etc., resulting in the stepwise voltage curves observed for the Na and K cells.17,53,61,62 Schematic illustrations of the typical sodium distribution in the interslab space are presented in Fig. 4g–j. In these structures, sodium ions are ordered in the interslab space, as predicted by DFT calculations62 and experimentally confirmed by XRD measurements.61,64 When such specific ordering is established, the stable structure produces voltage steps in the charge/discharge voltage curves, whereas smooth voltage curves are desired for the practical use of layered A3MeO2 in positive electrode materials. According to the insight obtained for Na3MeO2, smoother voltage curves can be partially realized in binary, ternary, and quaternary transition-metal systems,25 as well as by partial replacement with redox-inactive metals.55

6. O3 and P2 Type Na-containing Binary and Ternary Transition Metal Oxides

The number of 3d transition metal ions that can crystallize into layered LiMeO2 and KMeO2 phases are very limited in the case of single-transition metal systems, as found for the synthesizable α-NaFeO2 type (O3 type) oxides (Fig. 1d). However, the trend is quite different in binary and ternary transition metal (including p-block elements) systems. Many transition metals can be accommodated in the slabs of binary and ternary systems such as LiNi2/3Co3/2Al1/2O2 and LiNi1/3Mn1/3Co1/3O2.66 Obviously, a wider variety of transition metals is available for multi-transition metal NaMeO2 systems.23 O3 type α-NaFeO2 is thermodynamically stable and delivers a discharge capacity of 60–80 mAh g–1 with a flat voltage plateau at 3.3 V in an aprotic Na cell (Fig. 5a (top)).67 However, the Na extraction process is affected by irreversible migration of iron ions into the interslab space68 of oxygen evolution.69 On the other hand, O3 type α-NaCoO2 exhibits reversible extraction and insertion of Na with stepwise voltage curves, which are related to structural changes in the O3 → O3 → P3 → P3 → P3 → P3 sequence (Fig. 5a (bottom)).70,71 Upon mixing iron and cobalt, O3 type NaFe1/2Co1/2O2 delivers a reversible capacity of 160 mAh g–1 with smoother voltage curves and superior rate performance compared to the end members of NaCoO2 and NaFeO2 (Fig. 5a).71,72 Operando XRD measurements during the charging process revealed structural changes in the O3 → P3 → P3 → P3-O3 intergrowth sequence. P-type layered oxides have a wider interslab space, where alkali metal ions can diffuse faster between prismatic sites, compared to O-type ones.73 The narrow compositional range of O3 and O3 type phases for NaFe1/2Co1/2O2 on charge, as well as the direct O3-P3 transition (without the O3-O3* step), are expected to contribute to the high rate performance.71

Similar to the O3 type NaFe1/3Co1/3O2 material, O3 type NaNi2/3Mn1/3O2 delivers a large reversible capacity of 125–180 mAh g–1, with a O3 → O3 → P3 → P3 → O3 phase transition sequence during charge.74,75 The structural changes are different from those occurring in the O3 type NaMnO2 and O3 type NaNiO2 end members, as shown in Fig. 5b.71 In particular, the O3 type NaNiO2 end member does not transform into P3 or P3 type phases upon Na extraction during charge,74 while O3 type NaNiO2 changes to P3 type upon charging and then into the O3 type phase with an unusual wider interslab space.77 Both end members exhibit insufficient cycle stability due to irreversible structural changes. In contrast, O3 type NaNi1/2Mn1/2O2 exhibits superior cycle performance.74

These results show that O3 type binary transition metal Na(Me,Me’Me”O2) systems exhibit larger reversible capacity, better rate performance, and longer cycle life, along with smoother voltage curves in Na cells compared to single-transition metal systems. The smooth voltage curves indicate that the binary systems perturb the Na+/vacancy ordering due to the disordered distribution of transition metals in the slab. However, an obvious voltage jump is often observed at charging capacities of 100–120 mAh g–1, corresponding to a Na content x of 1/2 in Na(x,Me,Me’Me”)O2. We confirmed the Na*/vacancy ordering in Na1/3Fe1/2Co1/2O2 by ex situ synchrotron XRD measurements.73 As the voltage jump is also seen for Li1/3CoO2 in Figs. 4d and 4e, the A+/vacancy ordering is highly stabilized in the A1/3MeO2 composition. Many 3d transition metal ions contribute to redox reactions in the A1/3MeO2 composition and the high-voltage region, resulting in delocalization of electrons and stabilization of the Na+/vacancy ordering. To localize 3d electrons and suppress the ordering, Wang et al. employed titanium and chromium with different redox potentials.85 As a result, P2 type Na0.6Cr0.6Ti0.4O2 exhibited very smooth voltage curves and excellent rate performance in a Na cell. These results prompted us to employ electrochemically inactive ions in P2 type NaMeO2.
The Ti-substituted oxide, P2 type Na2Ti0.4O2, the smooth voltage curves indicate suppression of Na stability (Fig. 5c), while P2 type Na2Ni1-x/3Mn2/3O2 displayed better rate performance of (a) Na1-x/3Fe2/3O2 (top), Na1-x/3Co2/3O2 (bottom) and (b) Na1-x/3MnO2 (top), Na1-x/3Ni1/3Mn2/3O2 (middle), Na1-x/3NiO2 (bottom). *Detailed structural changes have never been reported for monoclinic P'3 type Na1-x/3O2 above 3.5 V. (c) Capacity retention and (d) rate performance of metal-substituted P2 type Na2/3Ni1/3Mn2/3O2 samples. TEM images of (e, f) non-substituted and (g, h) Al-substituted samples in the pristine state (e, g) and after 10 cycles in the 2.0–4.5 V region (f, h). Reproduced with permission from Ref. 23. Copyright 2018, Wiley-VCH.

Figure 5. Galvanostatic charge and structural evolution of (a) Na1-x/3Fe2/3O2 (top), Na1-x/3Co2/3O2 (middle), Na1-x/3Co2/3O2 (bottom) and (b) Na1-x/3MnO2 (top), Na1-x/3Ni1/3Mn2/3O2 (middle), Na1-x/3NiO2 (bottom).

Owing to the different oxygen packing from the O3 type, P2 type layered Na3MeO2 does not display significant irreversible structural changes accompanied by Me migration into the interslab space in the bulk. Thus, P2 type Na2/3MeO2, displaying cooperative Jahn-Teller distortion, exhibits excellent capacity retention in a Na cell.79 Before Wang’s report, we substituted titanium ions in P2 type Na3/2Ni1/2Mn1/2O2, which is air-stable and delivers a large reversible capacity of 160 mAh g−1,80 but also presents insufficient cycle stability due to a significant volume change during Na extraction/insertion.81 The Ti-substituted oxide, P2 type Na2/3Ni1/2Mn1/2Ti1/2O2, exhibited enhanced cycle stability with smooth voltage curves and a higher working voltage.82 Similar to P2 type Na2/3Mg1/2Ti1/2O2, the smooth voltage curves indicate suppression of Na+/vacancy ordering upon substitution of the redox-inactive titanium ions. Based on our previous study and Wang’s report, the influence of partial substitution with redox-inactive ions such as Mg2+, Cu2+, Al3+, and Ti4+ on the electrochemical properties was systematically examined in P2 type Na2/3[Me1/2Mn1/2O2]2 (Me = Mg, Al, Cu, and Ti; x + y = 1/18).23 P2 type Na2/3[Al1/3Ni1/3Mn2/3O2]2 and P2 type Na2/3[Mg1/13Ni1/3Mn2/3O2]2 exhibited superior cycle stability (Fig. 5c), while P2 type Na2/3[Al1/13Ni1/13Mn2/3O2]2 and P2 type Na2/3[Al1/13Ni1/13Mn2/3O2]2 displayed better rate performance (Fig. 5d). Substitution of even small amounts of the redox-inactive metals resulted in smoother voltage curves. Operando ex situ synchrotron XRD measurements revealed that substitution with divalent ions efficiently suppressed the significant volume changes during charge/discharge. However, this could not explain the improved performance of the Al-substituted sample. Obvious differences were observed in the TEM images (Fig. 5e–h), and suppressed surface degradation was found for the Al-substituted sample after 10 cycles,23 indicating that Al substitution stabilized the surface structure. The charge/discharge voltage behavior is indeed related to the structural changes caused by extraction/insertion of alkali metals. However, the battery performance is determined not only by the bulk properties, but also by the stability of the surface and the reactions taking place at the surface/electrolyte interface. In addition to the bulk and surface properties, comprehensive studies on positive and negative electrode materials, current collectors, binders, as well as electrolyte salts and solvents are required to enable the future commercialization of Na- and K-ion batteries.

7. Summary and Future Perspectives

Fundamental studies of layered transition metal oxide-based positive electrode materials for Li-, Na-, and K-ion batteries were reviewed based on the author’s previous research contributions. The review focused on the structural stability of the layered oxides and the correlation between crystal structures and electrochemical properties. The charge/discharge voltage behavior is strongly related to the bulk structure and the corresponding changes induced by alkali metal extraction/insertion. Nevertheless, the factors influencing the battery performance are complex; in addition, the surface stability and reactions at the surface/electrolyte interface are also related, as found in the studies of metal-substituted P2-Na2/3Ni1/2Mn2/3O2 materials discussed in the last section.

Comprehensive studies on the Li, Na, and K chemistry allowed highlighting the advantages and disadvantages of electrode materials and batteries. The similar ionic sizes of lithium and 3d transition metals facilitate irreversible cation mixing, which represents a serious issue for practical battery applications. However, the smaller ionic size of lithium leads to negligible lattice changes and weaker A⁺⁻A⁺ repulsion compared to sodium and potassium ions, resulting in smooth voltage curves and a high working voltage. On the other hand, the structural stability of layered Na3MeO2 and the presence of a wide variety of available transition metals in the slab are advantageous and represent the key to optimizing the characteristics of Na-ion batteries. Although potassium ions are too large to fully occupy the interslab space, the low Lewis acidity and weaker Coulombic interactions with anions lead to fast ionic diffusion not only in the electrolyte solution, but also in the electrode materials. Further performance improvements over Li-ion batteries are needed for Na-ion and K-ion batteries. It is clear that practical Na- and K-ion batteries will not be commercialized only because of their enhanced energy density or material abundance. As shown in Fig. 6, lifetime, safety, cost, market demand, economy, manufacturability, and productivity should also be considered. As academic researchers, we believe that interdisciplinary research such as that at the interface of solid-state chemistry and electrochemistry, as well as
comprehensive studies on various rechargeable batteries and battery materials, will have a positive effect on the fundamental understanding and development of sustainable energy technologies.

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