A comparison of destabilization mechanisms of the layered NaxMO2 and LixMO2 compounds upon alkali de-intercalation

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A Comparison of Destabilization Mechanisms of The Layered Na$_x$MO$_2$ and Li$_x$MO$_2$ Compounds upon Alkali De-intercalation

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Abstract

To understand the difference in reversible energy storage capacity between the O3-type layered Na and Li compounds, we use first principles calculations to study and contrast the effect of two well-known destabilization mechanisms, transformation into the spinel-type structures and cation mixing due to transition metal migration. This study is performed on the layered oxides at A$_{0.5}$MO$_2$ composition, where A = (Na, Li) and M is a 3d transition metal. We find that while all Li$_{0.5}$MO$_2$ compounds have strong driving forces and low energy kinetic paths to transform to the spinel structure, Na$_{0.5}$MO$_2$ compounds do not have thermodynamic driving forces to transform to spinel type structures. We also find that transition metal mobility is higher in Li-compounds than in Na-compounds because of the unusual activated state for transition metal hopping. For many compounds, migration

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goes along an oct-tet-oct path, but transition metal migration in the same path needs to be assisted by alkali migration into a tetrahedral site forming activated $A_{\text{tet}}-M_{\text{tet}}$ defects; substituting Na for Li in the layered structure results in increased transition metal migration barriers due to the larger size of Na$^+$ ions. Overall, our findings indicate that Na compounds in the layered O3 structure have fundamentally different destabilization mechanisms to those of Li compounds. This distinction allows superior battery electrode performance in many Na compounds and offer optimistic perspective on finding many high energy density Na electrodes that cycle with stable high capacity.
Introduction

Interest in Na-ion batteries is rapidly growing.1-6 The relatively unexplored Na-ion chemistry creates an opportunity to find novel intercalation cathodes. The low raw materials cost and abundance of sodium provide a potential cost advantage, although it is not clear whether this is significant enough to reduce total battery cost. A recent computational study shows that Na-ion battery cathode materials can be competitive with those of Li-ion battery in terms of voltage, stability and alkali ion diffusivity.5 In this paper, we demonstrate that the intrinsic difference between Na+ and Li+ ions may lead to the layered intercalation electrodes with higher practical capacity.

Li-transition metal oxides in the layered O3 structure form the cornerstone of the Li-ion battery industry as they have among the highest practical energy density. It is therefore of interest that recent experimental reports for many chemistries show that Na materials in the layered O3 structure demonstrate superior structural stability to their iso-structural Li counterparts. For example, NaVO₂ reversibly cycles up to 0.5 Na per formula unit, while LiVO₂ spontaneously transforms into a spinel structure upon delithiation.7,8 A similar difference in reversible capacity has been reported for NaMnO₂ and LiMnO₂.9,10 The reversible intercalation capacity of NaCrO₂ is over 100mAh/g while micron-sized LiCrO₂ becomes inactive after the first cycle.11 Only when synthesized in particle size below 25nm has LiCrO₂ shown intercalation capacity over 80mAh/g.12 In addition, some layered O3 compounds which cannot be made in their Li version do form in the Na versions. Synthesis of layered O3 LiTiO₂ has not been reported while NaTiO₂ has been synthesized and studied electrochemically.13 O3-LiFeO₂ has been synthesized only by a Li+/Na+ ion exchange reaction from stable NaFeO₂ compounds.14 This compound, however, has been reported to result in structural instability and in the creation
of oxygen vacancies in LiFeO$_2$ instead of oxidation of Fe$^{3+}$ to Fe$^{4+}$ during electrochemical delithiation.$^{15}$ In contrast, NaFeO$_2$ does show Fe$^{3+}$/Fe$^{4+}$ redox activity upon electrochemical de-intercalation.$^{16}$ These examples suggest that fundamental differences exist in structural stability during cycling of O3-Na and O3-Li compounds. This study aims at understanding this difference in terms of the possible destabilization mechanisms for the layered O3 structure upon alkali removal.

**Structural Competition for the Layered O3 Structures**

1. **Layered O3 Structure**

Delmas et al.$^{17}$ identified several crystal structures of layered transition metal oxides and labeled them according to the anion environment around the alkali metal and the size of the repeat unit perpendicular to the alkali metal layer. For example, O3 refers to a structure with octahedrally coordinated alkali ions and a stacking of the oxygen layers such that the stacking perpendicular to the alkali layers repeats after three O-A-O-M-O layers. Here, A indicates one of the two alkali metal species of interest, (Li, Na), and M indicates a 3d-transition metal species (Ti, V, Cr, Mn, Fe, Co, Ni) unless otherwise stated. Transition metal oxides in the layered O3 structure have been subject of numerous experimental$^{18-21}$ and theoretical$^{22-25}$ studies. All compounds of interest in the general formula AMO$_2$ have been synthesized for both Na and Li, except for LiTiO$_2$. In this work, we include the hypothetical O3 LiTiO$_2$ for completeness.

2. **Transition metal migration**

Some of the degradation mechanisms of O3 LiMO$_2$ materials upon Li-cycling are reasonably well understood. In several layered O3 materials, transition metals migrate into the alkali metal
layer upon removal of alkali metals.\textsuperscript{8,10,26,27} This phenomenon has been experimentally observed in many layered O\textsubscript{3} compounds including LiVO\textsubscript{2}, LiCrO\textsubscript{2}, LiMnO\textsubscript{2} and Li(Li\textsubscript{0.2}Cr\textsubscript{0.4}Mn\textsubscript{0.4})O\textsubscript{2} by using magnetic susceptibility measurements,\textsuperscript{27} in-situ XRD,\textsuperscript{28} ex-situ XRD,\textsuperscript{28} and in-situ XAFS.\textsuperscript{26} Transition metal migration is either partially reversible or irreversible, and has been claimed to cause capacity loss,\textsuperscript{20} lower Li\textsuperscript{+} ion diffusivity\textsuperscript{29} and possibly increase electronic resistance.\textsuperscript{30} 

Aspects of the capacity loss due to transition metal migration are understood. In Li\textsubscript{1-z}Ni\textsubscript{1+z}O\textsubscript{2} with (Li\textsubscript{1-z}Ni\textsubscript{z})\textsubscript{interslab}(Ni\textsubscript{z}\textsuperscript{II}Ni\textsubscript{1-z}\textsuperscript{III})\textsubscript{slab}O\textsubscript{2} ionic distribution, Li sites next to Ni\textsuperscript{2+} ions in the Li layer are not or only very slowly occupied upon lithiation.\textsuperscript{20} This is rationalized from the shrinkage in the layer spacing near Ni\textsuperscript{2+} due to the electrostatic interaction between Ni\textsuperscript{2+} and O\textsuperscript{2-}. It is likely that this capacity loss mechanism occurs for all systems where transition metal ions migrate into alkali metal layers.\textsuperscript{29} A second effect is the reduction of alkali mobility as the presence of transition metal ions in the alkali layer contracts the oxygen layers around them. This contracted oxygen layer spacing has been shown to lead to a dramatic decrease in alkali metal ion mobility.\textsuperscript{29} This effect is most pronounced between the A\textsubscript{0.5}MO\textsubscript{2} and AMO\textsubscript{2} composition. In extreme cases, such as for O\textsubscript{3}-LiMnO\textsubscript{2}, Mn ion migration leads to an almost complete transformation to the spinel structure with significant change in the voltage profile.\textsuperscript{10,31}

The key mechanism for transition metal migration has been clarified with first principles calculations.\textsuperscript{32} Transition metals migrate into the Li layer through intermediate tetrahedral sites; in this migration process, each M\textsubscript{oct} \rightarrow M\textsubscript{tet} defect is stabilized by one Li\textsubscript{oct} \rightarrow Li\textsubscript{tet} defect immediately below the vacated transition metal site.\textsuperscript{24} This defect configuration, consisting of M\textsubscript{tet}-M\textsubscript{vac}-Li\textsubscript{tet}, is called a dumbbell defect and forms in five connected steps. These five steps are labeled from A to E in Figure 1.
Figure 1. Modeled reaction coordinates (A – E) for dumbbell defect formation. M indicates the transition metal.

Dumbbell defect formations begin with partially de-intercalating alkali metals from the structure in step A. In step B, three alkali metal vacancies collect to create an empty tetrahedral site in the A layer that is not face-sharing with any alkali metal octahedron. This is needed to avoid the strong electrostatic repulsion between alkali metal ions and the migrating transition metal ion. C is the activated state where the migrating transition metal is at the center of an oxygen triangle shared between its vacated octahedral site, and the tetrahedral site created in step B. The small area of the triangle confined by three oxygen atoms suggests that step C is the bottleneck in the migration reaction and this is often found to be the case in first principles calculations.\textsuperscript{32,33} In step D, the migrating transition metal has passed through the oxygen triangle and occupies the tetrahedral site. At step D, there is a transition metal defect in the A layer, and a negatively charged vacancy in the M layer. In step E, the alkali metal ion immediately below the M vacancy migrates into the tetrahedral site that is face sharing with the vacated transition metal site. While these steps are shown sequentially in Figure 1, it is possible and likely that some migrations occur collectively.
3. **Transformation into the spinel**

If transition metals are very mobile, a complete conversion of the layered O3 structure to a spinel type structure can take place upon de-intercalating the alkali metal. Transformation to the spinel structure has been reported for O3 Li₅VO₂,⁴ and Li₅MnO₂¹⁰ and at elevated temperature for Li₃NiO₂.⁵ Even for LiCoO₂, some spinel transformation is observed after extended cycling of Li.⁶,⁷ This structural transformation involves a cation rearrangement within the oxygen fcc sublattice. To form the spinel structure, one quarter of the transition metal ions need to migrate to the octahedral sites in the alkali metal layer, and all the alkali metal ions at A₀.₅MO₂ composition need to move to tetrahedral sites. First principles calculations have shown that the thermodynamic driving force for this transformation is large in many Li compounds, even for the materials known to be stable upon numerous lithiation-delithiation cycles.³⁸ In addition, the critical kinetic step in this transformation is identified from first principles calculations to be the formation of dumbbell defects described in the previous section.²⁴ The dumbbell defect configuration therefore serves as the transformation pathway from the layered O3 to the spinel and spinel-related structures, such as the partially inverse spinel and inverse spinel structures. For this reason, the energetics of the dumbbell defect will be a focus of this paper.

4. **Spinel, partially inverse spinel and inverse spinel structures**

The spinel, partially inverse spinel and inverse spinel structures share a chemical formula AM₂O₄, and an identical fcc oxygen sublattice with the O3 layered structure. The three structures differ only by the cation distribution over octahedral and tetrahedral sites. Figure 2 illustrates the three spinel type structures. In the partially inverse spinel structure, one half of the alkali metal ions and three quarters of the transition metal ions occupy octahedral sites. The remaining cations occupy tetrahedral sites such that the structure can be viewed as a crystalline form of the
dumbbell defects. In the inverse spinel structure, all the alkali metals ions and half of the transition metals occupy octahedral sites while the remaining half of the transition metals occupy the tetrahedral sites.

![Spinel type structures with different cation arrangements in interstitial sites](image)

Figure 2. Spinel type structures with different cation arrangements in interstitial sites; [A]_{tet} indicates alkali metal ions (A) in the tetrahedral sites and [M]_{oct} means transition metal ions (M) in the octahedral sites.

5. **P3 competition for Na compounds**

Some sodium compounds including Na_xCrO_2, Na_xCoO_2 and Na_xNiO_2 in the layered O3 structure transform into the layered P3 structure upon de-intercalating Na⁺ ions. In the layered P3 structure, sodium ions occupy trigonal prismatic sites while transition metals ions occupy octahedral sites. Each Na prism shares one triangular face with the neighboring transition metal octahedron, deviating from the Pauling’s third rule.

Although the layered P3 structure also has a repeat unit of three O-A-O-M-O layers, it differs from the layered O3 structure by its oxygen stacking sequence. Figure 3 shows the repeat unit of the layered O3 and P3 structures after labeling each distinct oxygen plane as A, B and C. In order to achieve the transformation from the layered O3 to the P3 structure in Figure 3, four oxygen
planes in the repeat unit each glide in a direction parallel to the $a$ (or equivalently $b$) crystallographic direction. This direction is equivalent to the [111] direction in cubic close packed oxygen sublattice. During this process, the $\text{MO}_2$ slabs are maintained, without breaking any M-O bond.

Figure 3. Repeat units of the layered O3 and P3 structures, with the relative position of the oxygen planes labeled as A, B and C

This structural transformation is reversible during electrochemical cycling of Na$^+$ ions in Na$_x$CrO$_2$, Na$_x$CoO$_2$ and Na$_x$NiO$_2$ for various $x$. Na$_x$VO$_2$ on the other hand maintains the layered O3 structure within the $0.5 < x < 1$ range. The transformation has not been observed in any of the Li compounds.

In this paper, we will computationally investigate the energy difference between the layered O3, layered P3, spinel-type structures, the dumbbell configuration, and the transition path to the dumbbell configuration. We will especially contrast the Na and Li chemistries, so as to better understand the relation between structure, chemistry, and cycling stability.


**Methods**

We investigate the stability of partially de-intercalated layered O3 structures by comparing it to the spinel, partially inverse spinel and inverse spinel structures. We also examine the formation energies of the dumbbell defect configuration and migration barrier for each transition metal migration involved in dumbbell defect formation, in order to assess the low energy kinetic path for the phase transformations. For the layered O3 Na compounds, we also investigate the relative stability of the layered P3 structure.

All of our analysis is performed for the A_{0.5}MO_2 composition. For the Li-vacancy arrangement in the layered O3 structure at this composition, we use the linear vacancy ordering reported in previous experimental and theoretical studies for Li_xCoO_2 and Li_xNiO_2.\textsuperscript{42-45} Tests of five distinct orderings confirm that this ordering has the lowest energy within the error limits of our calculations. The exact P3 structure for all Na_{0.5}MO_2 has not been reported, and we used the Na-vacancy configuration that has been identified for Na_{0.5}CoO_2 for all the layered P3 compounds.\textsuperscript{46}

All energies are calculated using density functional theory as implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{47} The projector-augmented wave method\textsuperscript{48} and Perdew-Burke-Ernzerhof spin-polarized generalized-gradient approximation (GGA)\textsuperscript{49} functional were used with GGA+U extensions. GGA+U\textsuperscript{50} corrects for the self-interaction errors in GGA, and accurately captures possible oxidation state changes between different configurations of the transition metals, which have been shown to be critical for their mobility.\textsuperscript{32} The values of U for transition metals were computed according to Wang et al.’s scheme.\textsuperscript{51}
An energy cutoff of 520 meV and $k$-point density of at least 500 / (number of atoms in unit cell) were used. All calculations were initialized from a high-spin ferromagnetic configuration, except for the Co$^{3+}$ ions which were initialized with low spin configuration. For systems in which the transition metal ions have mixed valence, symmetry was explicitly broken by imposing different initial magnetic moments on the different transition metals in the cell. All ionic coordinates and cell parameters were allowed to fully relax, except in the defect calculations used in modeling transition metal ion migration.

For defect calculations, supercells consisting of 12 primitive cells of A$_{0.5}$MO$_2$ and a $k$-point grid of $2 \times 2 \times 4$ were used. The lattice parameters of this supercell were set to those of the undefected layered O3 A$_{0.5}$MO$_2$ (A=Li, Na) (M=Ti, V, Cr, Mn, Fe, Co, Ni). Ionic coordinates were allowed to fully relax except for configuration C described in Figure 1. For configuration C, where a transition metal ion sits at the center of an oxygen triangle, selective dynamics was used to limit the movement of the confined transition metal in the $c$ crystallographic direction. Jahn-Teller distortions were allowed by explicitly breaking the symmetry.

Results

Driving force to transform into the spinel type structures

Figure 4 shows the computed difference in the energy per atom between the LiM$_2$O$_4$ spinel-type structures and the layered O3 Li$_{0.5}$MO$_2$ structure for various transition metals. For all Li compounds from Figure 4, the spinel structure is the lowest energy structure among those considered. This is in good agreement with previous ab initio reports and experimental studies. During Li cycling, spontaneous transformation into the spinel structure has been
observed for the layered O3 Li$_{0.5}$VO$_2$ and Li$_{0.5}$MnO$_2$ at room temperature.$^{8,10,31,53}$ Partially de-intercalated Li$_x$NiO$_2$ transforms into the spinel structure at elevated temperature,$^{35,54}$ and Li$_x$CoO$_2$ slowly transforms after numerous intercalation cycles,$^{36,37}$ indicating that both compounds are kinetically limited for the transformation process. Synthesis of the spinel structure has not been reported for Li$_x$CrO$_2$, suggesting that LiCrO$_2$ may decompose by a different mechanism. For LiFeO$_2$, there have been a limited number of studies and the delithiated structures are not well-understood.$^{15,55}$

Figure 4. Difference in energy per atom between the LiM$_2$O$_4$ spinel-type structures (spinel, partially inverse spinel and inverse spinel) and the layered O3 Li$_{0.5}$MO$_2$ structure, i.e. $E_{\text{spinel-type}} - E_{\text{layered O3}}$ energy for various transition metals
No system shows any significant driving force to form the inverse spinel, even though it contains transition metals on the tetrahedral sites. The partially inverse spinel where transition metals on the tetrahedral sites are accompanied by Li$_{tet}$, on the other hand, is in some cases below the layered O3 structure energy, and never has a higher energy than the inverse spinel. This suggests that the alkali metal may play an important role in stabilizing the transition metal ions on the tetrahedral sites.

![Graph showing energy differences](image)

**Figure 5.** Difference in energy per atom between NaM$_2$O$_4$ spinel-type structures (spinel, partially inverse spinel and inverse spinel) and the layered O3 Na$_{0.5}$MO$_2$ structure, i.e. $E_{\text{spinel}} - E_{\text{layered O3}}$ energy for various transition metals.
Figure 5 shows that the energetics of the spinel-type structures is substantially different for the Na compounds as compared to the Li compounds. In general, the layered O3 structure has the lowest energy among the four structures and therefore has no driving force for transformation into the spinel-type structures. Experimentally, no spinel structure with sodium in the tetrahedral site has been reported in the Inorganic Crystal Structure Database (2011).\textsuperscript{56} It is noted from Figure 5 that Na\textsubscript{0.5}TiO\textsubscript{2} in the layered O3 structure is not stable with respect to the spinel transformation. This agrees with an experimental observation that Na\textsubscript{1-x}TiO\textsubscript{2} reversibly intercalates up to $x = 0.3$ Na per formula unit, with further extraction of Na resulting in irreversible behavior.\textsuperscript{13}

**Driving force for dumbbell defect formation**

![Graph showing formation energies of dumbbell defects](image)

Figure 6. Formation energy of a dumbbell defect with respect to the layered O3 a) Li\textsubscript{0.5}MO\textsubscript{2} and b) Na\textsubscript{0.5}MO\textsubscript{2} structure energy for various transition metals, i.e. $E_{\text{Dumbbell}} - E_{\text{Layered}}$ energy

Figure 6 shows the formation energies of the dumbbell defects a) for Li\textsubscript{0.5}MO\textsubscript{2} and b) for Na\textsubscript{0.5}MO\textsubscript{2} compounds. For Li\textsubscript{0.5}MO\textsubscript{2} where M = Ti, V, Mn, Fe, there exists a thermodynamic driving force to form dumbbell defects. For Li\textsubscript{0.5}CrO\textsubscript{2}, the dumbbell defect formation energy is
only 46meV/defect, and metastable dumbbell defects are likely to form due to entropic effects. For Li\textsubscript{0.5}CoO\textsubscript{2} and Li\textsubscript{0.5}NiO\textsubscript{2}, however, we observe that dumbbell defects are unlikely to form with their formation energies as high as 308meV/defect and 152meV/defect respectively. This result is consistent with the kinetically limited spinel transformation during cycling and with previous \textit{ab initio} calculations\textsuperscript{32}. Figure 6b also shows that the dumbbell defect formation energies for all the Na\textsubscript{0.5}MO\textsubscript{2} compounds are significantly higher than those of Li\textsubscript{0.5}MO\textsubscript{2}. The dumbbell defect formation energies for all the Na compounds range from 166meV/defect up to 2200meV/defect, giving an indication that transition metal migration will be much more difficult in Na compounds.

We observe that the transition metal dependence of the dumbbell defect formation energies is the same for Na and Li compounds; the defect formation energies are the largest for M = Cr, Co, Ni, and are the smallest for M = Mn, Fe. We could hypothesize from these results that the contribution of the transition metal to the dumbbell energy is similar in Li and Na compounds, which is consistent with a previous \textit{ab initio} study that this component is largely controlled by the electronic structure of the transition metal ion and its ligands\textsuperscript{32}. 

Transition metal migration barrier

![Energy change along the reaction path for Cr ion migration along the defect states shown in Figure 1 (A-E)](image)

Figure 7. Energy change along the reaction path for Cr ion migration along the defect states shown in Figure 1 (A~E)

We now evaluate in more detail the migration path for transition metal ions in Na and Li compounds. As an example, figure 7 depicts the calculated energy along the path for Cr migration in A0.5CrO2. In our modeled migration path, the maximum energy for both Na and Li compounds occur in configuration C, where M is at the triangular face between A and M layers. This activated state was identified in previous work of our group. However, it is noticed that the Cr migration barrier in Na0.5CrO2 is significantly higher than that for Li0.5CrO2. The computed migration barriers are 2.01eV and 1.10eV for Na0.5CrO2 and Li0.5CrO2 respectively. At room temperature, and assuming a vibrational pre-factor (ν) between 10^{12}/s and 10^{13}/s, these energy barriers translate to a Cr hopping rate of 1.8 × 10^{-23} − 1.8 × 10^{-22} s^{-1} for the Na compound and 4.25 × 10^{-6} − 4.25 × 10^{-5} s^{-1} for the Li compound. Therefore, while dumbbell defects are likely to form in Li0.5CrO2 on the time scale at which typical battery experiments are performed,
they will not in Na\textsubscript{0.5}CrO\textsubscript{2}. This indicates that Cr can escape from its layer in O3-Li\textsubscript{0.5}CrO\textsubscript{2} but not in Na\textsubscript{0.5}CrO\textsubscript{2}.

A similar calculation was performed for all the transition metal ions. Table 1 shows the computed migration barriers for the transition metal migration in both Na and Li compounds. The result is in good agreement with a previous \textit{ab initio} study on Li compounds.\textsuperscript{24} We may observe that compounds with high transition metal migration barriers are stable against cation mixing behavior. For the Co system, the barriers are very high for both Na and Li compounds, consistent with the strong inherent stability of the layered A\textsubscript{x}CoO\textsubscript{2} upon cycling. Transition metal migration barriers in many Na\textsubscript{0.5}MO\textsubscript{2} compounds are very high, except for Na\textsubscript{0.5}MnO\textsubscript{2}. The migration barrier for Na\textsubscript{0.5}MnO\textsubscript{2} is similar to that of Li\textsubscript{0.5}VO\textsubscript{2}, which readily transforms into spinel. A large amount of cation mixing is therefore expected in Na\textsubscript{0.5}MnO\textsubscript{2}. However, a recent experimental study reports that NaMnO\textsubscript{2} cycles up to 140mAh/g for over 10 cycles.\textsuperscript{58} This observation suggests that Na\textsubscript{0.5}MnO\textsubscript{2} achieves stability against cation mixing by a different mechanism.

Table 1. Computed migration barriers for transition metal motion in the layered O3 A\textsubscript{0.5}MO\textsubscript{2} compounds

<table>
<thead>
<tr>
<th>Migration Barrier (eV / defect)</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{0.5}MO\textsubscript{2}</td>
<td>1.45</td>
<td>1.50</td>
<td>2.01</td>
<td>0.82</td>
<td>1.10</td>
<td>2.45</td>
<td>1.61</td>
</tr>
<tr>
<td>Li\textsubscript{0.5}MO\textsubscript{2}</td>
<td>0.98</td>
<td>0.78</td>
<td>1.23</td>
<td>0.44</td>
<td>0.55</td>
<td>1.62</td>
<td>1.10</td>
</tr>
</tbody>
</table>
Driving force to transform into the layered P3 structure

![Graph showing the difference in energy per formula unit between the layered P3 Na$_{0.5}$MO$_2$ structure and the layered O3 Na$_{0.5}$MO$_2$ structure, i.e. $E_{P3} - E_{O3}$ energy for various transition metals.]

Figure 8. Difference in energy per formula unit between the layered P3 Na$_{0.5}$MO$_2$ structure and the layered O3 Na$_{0.5}$MO$_2$ structure, i.e. $E_{P3} - E_{O3}$ energy for various transition metals.

The above results indicate that transition metal migration is much less likely in the O3 Na compounds than in their Li versions. As Na ions often occupy prismatic sites in layered oxides, however, we also investigate the driving force to form the layered P3 structure from the O3 Na$_{0.5}$MO$_2$ compounds. The computed results shown in Figure 8 suggest that Na$_{0.5}$MO$_2$ with M = Mn, Co, Ni, have a strong driving force to transform into the P3 structure while Na$_{0.5}$TiO$_2$ and Na$_{0.5}$VO$_2$ energetically favor the layered O3 structure. This agrees with the experimental studies that during electrochemical cycling of Na$^+$ ions, Na$_x$VO$_2$ remains as the O3 structure up to Na$_{0.5}$VO$_2$ while Na$_{0.5}$CoO$_2$ transforms into the P3.\cite{7,40} During electrochemical cycling, Na$_x$CrO$_2$
and Na$_x$NiO$_2$ are known to transform into the layered P3 structure at high sodium compositions ($x \approx 0.8$) and have not been characterized at $x = 0.5$ to our best knowledge.

**Discussion**

In this work, we try to understand the remarkable stability of the O3-Na$_x$MO$_2$ compounds when desodiated, as compared to their iso-structural Li counterparts. We focus particularly on one instability mode which involves migration of the transition metal, as in most cases this leads to degradation of capacity and/or rate capability.

The difference between Na and Li compounds may at first be surprising as de-alkalination leads to a more and more similar composition and structure for Na$_x$MO$_2$ and Li$_x$MO$_2$ and one would expect similar structural instabilities. We find in this paper that the key in the Li/Na difference lies in the role the alkali metal plays in stabilizing the transition metal in its activated state. To migrate between octahedral sites in a close-packed oxygen lattice, a cation needs to pass through a tetrahedral site. Direct octahedral-octahedral migration through a shared edge is in general very high in energy.\textsuperscript{25,32} While the octahedral-to-tetrahedral site energy change is strongly influenced by its electronic configuration,\textsuperscript{32} it is generally positive (as evidenced by the high energy of the inverse spinel), unless it can be accompanied by the migration of an alkali into a tetrahedral site. For Li compounds, we find that this migration is highly favorable, while it is not for Na. Therefore, it is the alkali ion which is the factor controlling whether the transition metal migrates or not.

Ultimately, the different behavior between Na and Li compounds can be traced back to the ionic size difference between Na$^+$ and Li$^+$ ions. In six-fold coordination, Na$^+$ ions (102pm) are
approximately 34% greater than Li$^+$ ions (76pm). Pauling’s first rule suggests that in an ideally ionic solid, Na$^+$ ions would be coordinated by six oxygen ions while Li$^+$ ions be coordinated by either four or six oxygen ions. When applied to the layered O3 structure, where there are only octahedral and tetrahedral interstitial sites in the fcc oxygen framework, Pauling’s first rule suggests that Na$^+$ ions occupy octahedral sites while Li$^+$ ions may occupy either octahedral or tetrahedral sites. We observe from our calculations that this rule is followed very well for the structures we considered. The structures with tetrahedrally coordinated Na$^+$ ions, including the spinel structure, partially inverse spinel structure and dumbbell configuration are noticeably higher in energy compared to their Li counterparts; Na$^+$ ions have a strong tendency to avoid tetrahedral sites in an oxygen fcc framework.

In addition, it should be noted that the considerably larger Na slab spacing than that of a Li slab creates distorted tetrahedral sites in the Na layer. This, in conjunction with the notion that alkali metal motions assist transition metal migrations, explains the large difference in energy between Li$_{0.5}$CrO$_2$ and Na$_{0.5}$CrO$_2$ at configuration D. The relaxed structure from configuration D shows that the CrO$_4$ tetrahedron in Na$_{0.5}$CrO$_2$ is distorted with two distinct Cr-O bond lengths (1.86Å and 1.95Å). In Li$_{0.5}$CrO$_2$, the Cr-O bond lengths are almost identical with an average value 1.85Å. This indicates that the distinct slab sizes of the Na layer and transition metal layer provides further inherent stability against transition metal ions occupying tetrahedral sites in the Na layer.

The energetics of the inverse spinel structure also provides further understanding of the alkali size effect on the stability of the layered O3 structure. While the inverse spinel structure does not involve tetrahedrally coordinated alkali metal ions, the Na inverse spinel compounds are much more unstable with respect to the layered structure than the Li equivalents. We believe that this
difference arises from the size difference between the Na and Li octahedrons; in the inverse spinel structure, alkali metal octahedrons edge-share with transition metal octahedrons and the large size difference between the two probably leads to strain. The fully relaxed inverse spinel structures in our calculations show that the average Na octahedron is 40% greater (14.28 Å³) than the transition metal octahedrons (10.22 Å³) while the difference between Li octahedrons (11.75 Å³) and transition metal octahedrons (10.94 Å³) is below 8%. In the layered structure, this size difference is not a problem as the octahedrons in each layer can relax largely independently of each other.

Our results on the stability of the layered O3 structure with respect to two specific transformation mechanisms, the layered to spinel transformation and cation inter-layer mixing, show very good agreement with the experimental results on reversibility of intercalation reactions. Several O3-Li compounds including Li₀.₅VO₂ and Li₀.₅MnO₂ transform to the spinel structure upon delithiation.¹⁰,₃¹,₃₄,₅³ Other Li compounds that remain stable upon delithiation at room temperature, Li₀.₅CoO₂ or Li₀.₅NiO₂, possess high dumbbell defect formation energies and high transition metal migration barriers. Sodium compounds, however, neither have the driving force to transform into the spinel structure, nor a low energy kinetic paths for the transition metal migration. The transition metal migration barriers are well above 1.1eV for many Na compounds and therefore, cation mixing is not expected to readily occur. We believe that Na₀.₅MnO₂ which has a fairly low Mn migration barrier, can avoid cation mixing destabilization mechanism by transforming into the layered P3 structure. In the layered P3 structure, there is no tetrahedral site available for transition metal ions to occupy, and trigonal prismatic sites in the Na layer are too large for transition metal ions. This analysis on the layered O3 Na compounds agrees with experimental observations that all NaMO₂ compounds have been shown to reversibly intercalate
Na⁺ ions except for NaTiO₂ and NaFeO₂ for which no recent literature exists on the cyclability of the intercalation reaction. The layered O₃ NaTiO₂ may make for a good anode material in Na-ion batteries because of its structural stability and predicted low potential.⁵ The only exception to our analysis is LiCrO₂. The compound possesses a transition metal migration barrier as high as LiNiO₂ but show no reversibility in intercalation reactions, indicating that the dominant degradation mechanism for LiCrO₂ may be different from other layered Li compounds.

**Conclusion**

We conclude from our analysis that Na compounds have enhanced structural stability in the layered O₃ structure compared to their Li counterparts at A₀.5MO₂ composition. While all Li compounds strongly favor the spinel structure at Li₀.5MO₂ composition, no such driving force exists for the layered Na compounds. In addition, transition metal migration is kinetically disfavored in Na systems as alkali displacement to a tetrahedral site is required to assist transition metal migration. Because of sodium’s higher energy in the tetrahedral site compared to Li, Na is less effective in assisting this migration. Some Na compounds have a driving force to transform into the layered P₃ structure, which would also inhibit transition metal migration, as it needs to cross the highly unfavorable prismatic sites in the Na layer. We believe that these findings offer an optimistic perspective on finding new high energy density Na electrodes. High energy density is best achieved with close packed oxides, as poly-anion systems take a disproportionately large hit on density on top of their lower gravimetric capacity.⁶ In such close packed oxides, migration of ions requires oct-tet-oct migrations. If Na⁺ ions more generally inhibit this migration, then it may be possible to find many Na-intercalation electrodes that cycle with stable high capacity.
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