Stability of Prismatic and Octahedral Coordination in Layered Oxides and Sulfides Intercalated with Alkali and Alkaline-Earth Metals

Maxwell D. Radin and Anton Van der Ven*

Materials Department, University of California, Santa Barbara, California 93106, United States

Supporting Information

ABSTRACT: Many layered oxide and sulfide intercalation compounds used in secondary batteries undergo stacking-sequence change phase transformations during (de)intercalation. However, the underlying reasons why different intercalants result in different stacking-sequence changes are not well understood. This work reports on high-throughput density functional theory calculations on the prototype systems A\textsubscript{x}CoO\textsubscript{2} and A\textsubscript{x}TiS\textsubscript{2} (where A = [Li, Na, K, Mg, and Ca]), which show that a few simple rules explain the relative stability among the O1, O3, and P3 stacking sequences. First, for large intercalants (Na, K, and Ca), P3 stacking is favorable at intermediate concentrations (x ∼ 0.5) as its intercalant site topology minimizes in-plane electrostatic repulsion. At the extreme compositions (x ∼ 0 and x ∼ 1), O1 or O3 are stable, with more ionic compounds preferring O3 and covalent ones O1. These rules explain why stacking-sequence changes are much more common in Na materials than Li ones.

INTRODUCTION

Many intercalation electrode materials for batteries are layered compounds with formula A\textsubscript{x}MX\textsubscript{y}, where A is an alkali or alkaline earth metal, M is a transition metal (or alloy of transition metals), and X is oxygen or sulfur. This class includes the canonical cathode material LiCoO\textsubscript{2} and the derived NCM and NCA compounds widely used in state-of-the-art commercial Li-ion batteries,\textsuperscript{1,2} as well as novel Na-ion\textsuperscript{3,4} and Mg-ion\textsuperscript{5,6} battery materials.

Layered intercalation compounds often undergo phase transitions between crystal structures that differ only in the stacking of their layers upon the insertion or removal of the A-species.\textsuperscript{5,7} The layered O1, O3, and P3 crystal structures, for example, can be converted into each other through a simple gliding of adjacent MX\textsubscript{x} slabs.\textsuperscript{7,8} This occurs in LiCoO\textsubscript{2} where the removal of Li transforms the compound from O3 to O1.\textsuperscript{9–12} The thermodynamically preferred stacking sequence is known to vary on the identity of the elements A, M, and X.\textsuperscript{13,14}

Stacking-sequence changes can strongly affect electrochemical performance in several ways. First, different layered structures may exhibit quite different electrochemical behavior. For example, intercalant migration mechanisms\textsuperscript{4,15,16} and intercalant ordering\textsuperscript{15} that occur only in particular stacking sequences could have important implications for diffusion kinetics. Additionally, transition-metal migration from the transition-metal layer to the intercalant layer (a common degradation mechanism in O3 layered oxide electrodes\textsuperscript{1,2}) may be slower in P3 structures for transition metals that tend to prefer the octahedral coordination over prismatic coordination.

Perhaps more importantly, stacking-sequence-change phase transformations driven by (de)intercalation may hinder the kinetics of cation removal and insertion and also lead to the degradation of the electrode. Kinetic limitations arise from the motion of phase boundaries through the electrode particles as the material undergoes a first-order phase transformation.\textsuperscript{2,18} The migration of these interfaces can slow charge and discharge rates and increase polarization as it is a dissipative kinetic process that, together with cation diffusion, consumes chemical free energy that could otherwise be converted to useful electrical work. High mechanical stresses due to differences in the lattice parameters at the interfaces that mediate stacking-sequence phase changes\textsuperscript{19} may also trigger degradation by inducing local crack initiation and growth.\textsuperscript{19–21}

Although the thermodynamics of stacking sequences are critical to electrochemical energy storage, relatively little is known about the driving force for stacking-sequence changes during (de)intercalation. The purpose of this work is to use high-throughput density functional theory (DFT) calculations to provide insight into the trends in stacking sequence thermodynamics. We focus on the A\textsubscript{x}CoO\textsubscript{2} and A\textsubscript{x}TiS\textsubscript{2} (where A = [Li Na, K, Mg, and Ca]) family of materials in the O1, O3, and P3 stacking sequences; this represents a generalization of two canonical Li-ion battery materials, LiCoO\textsubscript{2} and LiTiS\textsubscript{2}. These materials are good prototypes for studying layered oxides and sulfides because they are not complicated by the strong charge localization and Jahn–Teller effects seen in other compounds (e.g., layered nickel oxides\textsuperscript{22,23}).

Our results show that the trends in stacking-sequence stability are determined by two simple rules: (1) The more...
ionic compounds adopt the O3 structure, while the more covalent compounds prefer the O1 structure at high and low intercalant compositions \((x \sim 0\) or \(x \sim 1\)). (2) The P3 structure is often preferred at intermediate concentrations \((x \sim 1/2)\) for intercalants that are large enough to support prismatic coordination as the honeycomb topology of the A sites in P3 minimizes intercalant—intercalant electrostatic repulsion.

These results imply that, in general, phase transformations are inherently more prevalent for large intercalants (Na, K, and Ca) that stabilize P3 at intermediate concentrations than small intercalants (Li, Mg). Stacking-sequence changes are therefore likely to play a much larger role in the performance of batteries based on Na, K, and Ca intercalation than they do in traditional Li-ion batteries.

### CRYSTALLOGRAPHY

The O1, O3, and P3 structures (Figure 1) are fundamental building blocks for layered oxides and sulfides. Transformations between them can occur readily during (de)intercalation because the gliding of MX2 slabs does not require bonds to break. Although we restrict our analysis to O1, O3, and P3, other stacking sequences have been observed. These include hybrid-stacking sequences that combine features of the pure stacking types. For example, the H1–3 phase in Li2CoO2 consists of alternating O1-like and O3-like layers. Other important stacking types include the O2/P2 family. These differ from the O1/O3/P3 family in that every other MX2 layer is reflected across a plane perpendicular to the crystallographic axis, resulting in BA oxygen stacking rather than AB oxygen stacking. While many battery materials can be synthesized in P3, these cannot transform to O1/O3/P3 through a simple gliding of slabs.

We can identify three crystallographic factors that play important roles in determining relative stabilities among O1, O3, and P3: (i) the presence or absence of face-sharing cation sites, (ii) triangular vs honeycomb intercalant site topology, and (iii) prismatic vs octahedral intercalant coordination.

### Cation Face Sharing.

The stability of a particular stacking sequence is affected by the proximity of the transition metal ions to the A-sites; Pauling’s third rule states that face-sharing between cations tends to reduce stability due to electrostatic repulsion. While in the O3 structure no A sites share faces with transition metals, the intercalants and transition metals share one face in P3 and two faces in O1 (see Figure 1). As discussed below, this tends to favor O3 during intercalation, especially when the bonding is highly ionic. However, when bonding is more covalent, O1 is often preferred; this has been attributed to the lesser repulsion between oxygen p orbitals in the van der Waals gap in O1 as compared to O3.

### Topology of Intercalant Sites.

The topology of the two-dimensional intercalant lattices between adjacent MX2 slabs also affects the relative stability among hosts: while the intercalant sites in O1 and O3 form triangular sublattices, those in P3 form honeycomb lattices consisting of two triangular sublattices that we will label \(\alpha\) sites and \(\beta\) sites. (Note that although the term honeycomb lattice is commonly used, honeycombs are not lattices in the crystallographic sense.)

The DFT calculations to be described below show that the presence of additional sites in P3 plays a critical role in stabilizing the structure because it allows for intercalant orderings that minimize intercalant—intercalant repulsion. This becomes evident with a comparison of low energy cation orderings at \(x = 1/2\) on the triangular and honeycomb lattices. A common ordering at \(x = 1/2\) over the triangular A-site lattices of O3 and O1 consists of rows of A-cations alternated by rows of vacancies (Figure 2, left panel). The availability of two triangular sublattices in the honeycomb lattice offers more flexibility allowing for a zigzag ordering (Figure 2, right panel). While the O1 and O3 hosts are frustrated at \(x = 1/2\) in the sense that geometric considerations force intercalants to occupy adjacent sites, P3 permits orderings in which the closest occupied neighbors are farther away by a factor of \(2/3 \approx 1.15\).

### Intercalant Coordination.

The intercalant coordination plays an important role in the relative stability of different stacking sequences: while the A sites in O1 and O3 are octahedrally coordinated by anions, A sites in P3 are prismatically coordinated. The shorter anion–anion distance in prismatic coordination tends to raise the energy of P3 relative to O1 and O3. This can be seen from the simple geometric considerations shown in Figure 3. Here, the cation–anion distance is assumed to be fixed by the ionic radii of the cation and anion \(r_c\) and \(r_a\), and the inter-plane anion–anion distance fixed by the anion ionic radius. In this approximation, the distance between anions across the intercalant layer will always be shorter in prismatic environments than octahedral ones.

Importantly, the anion repulsion across the intercalant layer becomes stronger for smaller cations, such as Li and Mg (Figure 4), because the anion–anion distances will be shorter. For example, Li is almost never observed in trigonal prismatic coordination. This is due to the stronger electrostatic repulsion at short distances and possibly also the size of...
anions: when the ratio $r_{+}/r_{-}$ falls below $\sqrt{3}/3 \approx 0.53$, the cation is too small to keep the anions on each side of the layer separated.

### COMPUTATIONAL METHODOLOGY

Using the appropriate electronic structure method is critical for capturing the key physics in layered transition-metal oxides and sulfides. The optB86b-vdW exchange-correlation functional was chosen to ensure that van der Waals dispersion interactions were accounted for as these effects play a critical role in the interlayer bonding in the deintercalated state. Although conventional wisdom holds that DFT+$U$ gives an improved description of transition-metal oxides, we chose not to use on-site Hubbard corrections because a number of studies indicate that it can actually lead to qualitatively incorrect results in layered cobalt oxides. For example, the addition of a typical $U$ correction will stabilize O3 in CoO$_2$. In contrast, DFT without $U$ gives an improved description of transition-metal oxides, and introduce spurious phases in the P2$\bar{1}$-Na$_x$CoO$_2$ phase diagram. In contrast, DFT without $U$ has been shown to predict accurately the phase diagrams and voltage curves of Li$_x$CoO$_2$, Mg$_x$TiS$_2$, and Mg$_x$TiS$_2$.

DFT calculations were performed with the Vienna ab initio simulation package (VASP) with projector augmented-wave (PAW) pseudopotentials. The pseudopotentials used were Li, Na$_{pv}$, K$_{sv}$, Mg, Ca$_{sv}$, Ti$_{sv}$, Co, O, and S. All calculations were spin polarized, employed plane-wave basis sets with 530 eV energy cutoffs and sampled the Brillouin zone with a k-point mesh density of 38 Å or more. Relaxations used Gaussian smearing of width 0.1 eV and were converged to within a force convergence criterion of 0.02 eV/Å; these were followed by single-point calculations using the tetrahedron method with Blöchl corrections in order to obtain accurate energies.

Calculations were performed on all symmetrically unique orderings of intercalants in A$_x$MX$_2$ ($0 < x < 1$) with supercell volumes no greater than four times the formula unit. Calculations on the P3 host were restricted to orderings in which there are no nearest-neighbor intercalant pairs because the nearest-neighbor sites are too close to accommodate intercalants. This represents 50 O1 orderings, 48 O3 orderings, and 86 P3 orderings for each combination of elements, for a grand total of 1840 DFT calculations. Because some configurations are mechanically unstable, the intercalant ordering and host type (O1, O3, and P3) of each relaxed structure was determined using a mapping score that accounts for lattice deformation and atomic displacements. Also, calculations that failed to meet electronic or ionic convergence criteria were discarded.

### RESULTS

The calculated zero-temperature phase diagrams of Figure 5 show that each compound exhibits a very different sequence of phase transformations. (The calculated formation energies and convex hulls leading to these predictions of phase stability are provided in Figures S1 and S2 of the Supporting Information.)

The TiS$_2$ and CoO$_2$ compounds without any intercalating A-cations favor O1 in agreement with experiments. Fully intercalated ACoO$_2$ is stable in O3 for all cation species, while ATiS$_2$ in contrast prefers O1 for Li and Mg and O3 for Na, K, and Ca. This is in agreement with experimental observations for Li$_2$ and Na compounds.

We note that the phase diagrams in Figure 5 should be interpreted qualitatively only. Since our calculations include supercells containing up to four formula units, we have not considered more complex orderings that form in larger supercells. The honeycomb lattice, for example, exhibits a devil’s staircase of low energy orderings made of triangular islands separated by antiphase boundaries. We have also not considered hybrid structures, consisting of mixtures of pure stacking sequences. However, based on the evidence for hybrid O1/O3 stacking in LiCoO$_2$ and hybrid O1/P3 stacking in...
NaTiS$_2$, we speculate that intercalating other cations in CoO$_2$ and TiS$_2$ will also result in hybrid stackings.

The results for $x > 0.5$ for divalent cations (Mg and Ca) should be taken cum grano salis: these layered phases may be unstable relative to other compounds because Ti and Co would be nominally reduced to $2+$. However, the electrochemical reduction of Ti to $2+$ in Li$_2$TiS$_2$ suggests that the formation of MgTiS$_2$ and CaTiS$_2$ may be possible.

Trends in the energy differences between the three host structures provide insight into the origins of their relative stability. Figure 6 shows the energies of the most stable O1 and P3 orderings at different compositions relative to the energy of the most stable O3 ordering at the same composition. Points above the horizontal line represent structures which are less stable than O3, while points below represent structures that are more stable than O3.

The energy differences shown in Figure 6 support the hypothesis that the topology of intercalant sites is crucial in stabilizing P3 for large cations (Na, K, and Ca) at intermediate compositions ($x \sim 1/2$). When the occupancy in each P3 layer is constrained to one of the two triangular sublattices constituting the honeycomb lattice (e.g., the $\alpha$ sites), P3 is no longer more stable than O3 for any of the materials considered. This can be seen in the data for Na, K, and Ca intercalation in Figure 6. The yellow lines, which represent the lowest energy P3 orderings, pass below zero around $x \sim 1/2$, indicating that P3 is more stable than O3 at that composition. In contrast, the purple lines, which represent the energy of P3 when intercalants are restricted to just one sublattice in each layer, never pass below zero because P3 is less stable than O3 when the mixed occupation of both sublattices is excluded. This demonstrates the importance of the honeycomb site topology in minimizing intercalant–intercalant repulsion and stabilizing P3.

The fact that Li and Mg do not exhibit P3 in either CoO$_2$ or TiS$_2$ can be attributed to their smaller size, which destabilizes prismatic coordination. This manifests in Figure 6 as a greater destabilization of P3 relative to O3 at $x = 1$ for Li and Mg as compared to Na, K, and Ca. The less ionic bonding in Li and Mg as compared to Na, K, and Ca (discussed in more detail below) may also play a role in preventing the transformation to P3 upon deintercalation: weaker intercalant–intercalant repulsion reduces the energetic benefit of the honeycomb lattice. This can be seen in Figure 6 as a more shallow dip in the energy of P3 relative to O3 around $x \sim 1/2$ in Li and Mg compounds as compared to Na, K, and Ca compounds.

The variation in the relative stabilities of P3 and O3 upon substitution of chemical elements can be attributed to the strength of electrostatic repulsion between cations. At $x = 1$, P3 is more unstable in A$_x$CoO$_2$ than A$_x$TiS$_2$. We attribute this to the greater degree of ionicity in the oxide due to the high electronegativity of oxygen, which results in a larger energy penalty for the face-sharing of intercalant and transition-metal sites. At $x = 1/2$, however, the P3 has a greater stability relative to O3 in A$_x$CoO$_2$ than in A$_x$TiS$_2$. This can be attributed to the stronger intercalant–intercalant repulsion in more ionic materials (as discussed below) which increases the favorability of the honeycomb site topology. The stronger intercalant–intercalant repulsion in more ionic compounds can also explain why the P3 stability relative to O3 at $x = 1/2$ is larger for K than for Na.

The relative preference for O1 vs O3 in the deintercalated state can be rationalized in terms of the degree of ionicity, with more ionic bonding favoring O3 and more covalent bonding favoring O1. This is clearly demonstrated by the strong correlation between relative O1/O3 stability and the difference in cation and anion electronegativities shown in Figure 7. For example, O3 is predicted to be more stable than O1 for TiO$_2$ and MnO$_2$ compounds exhibiting a very large difference in electronegativity between the transition metal and oxygen. In contrast, the more covalent CoS$_2$ and NiS$_2$ compounds, having
a small difference in electronegativity between sulfur and the transition metal, are substantially more stable in O1 than in O3. However, other factors also affect the O1/O3 relative stability to some degree. This is evident in Figure 7 where CoO_2 and CoS_2 favor O1 more than NiO_2 and NiS_2, respectively, despite the fact that Co and Ni have very similar electronegativities.

Figure 6 shows that O3 generally becomes more stable relative to O1 upon intercalation. This can be attributed to the energy penalty for cation face-sharing in O1, as discussed above. The strength of this effect appears to depend on the degree of ionicity: for TiS_2, intercalating highly electropositive elements like Na, K, and Ca stabilizes O3, while O1 is retained upon intercalation of the relatively less electropositive elements Li and Mg. In A_xCoO_2, which is more ionic than A_xTiS_2 due to the high electronegativity of oxygen, O1 is unstable relative to O3 for all intercalants when x > 0.

The strength of short-range intercalant–intercalant repulsion (which determines the steepness of the equilibrium voltage curve) correlates well with the degree of ionicity. One metric of the interaction strength between intercalant cations is the depth of the convex hull to the calculated formation energies at x = 1/2 (Figure 8). Negative formation energies for A_xMX_2 (when using MX_2 and AMX_2 as reference states) are a result of ordering tendencies among A cations and vacancies, which are driven by repulsive cation–cation interactions. The calculated convex hull depths indicate that intercalants repel more strongly in CoO_2 than in TiS_2 which can be attributed to the greater degree of ionicity in CoO_2 because of the high electronegativity of oxygen. Similarly, the degree of repulsion also increases with increasing electropositivity of the intercalant (K > Na > Li and Ca > Mg) and charge state (Ca > Li).

**FIGURE 8.** Depth of convex hulls for intercalating different cations into CoO_2 (blue) and TiS_2 (yellow). A deeper convex hull (more negative value) corresponds to stronger intercalant–intercalant repulsion and a more sloping voltage curve.

Using the fact that Co and Ni have very similar electronegativities.

**DISCUSSION**

As the battery community looks beyond lithium for battery materials, it is important to recognize that the crystallography of intercalation in layered materials is very different for other cations. Our results indicate that large intercalants (Na, K, and Ca) behave fundamentally differently from small cations (Li and Mg) because they are compatible with prismatic coordination. As a result, Na, K, and Ca tend to have more stacking sequence changes than Li and Mg: in addition to transforming between two octahedral end members (e.g., O3 to O1), P3 will exist at intermediate compositions where intercalant–intercalant electrostatic repulsion is minimized by the honeycomb intercalant site sublattice of the P3 host. This predisposition toward stacking sequence changes suggests that, broadly speaking, phase transformations may play a much more important role in the electrochemical performance for Na, K, and Ca battery materials than for Li and Mg materials.

We hypothesize that these trends, especially the stability of P3 at intermediate compositions for large intercalants, apply broadly to other layered oxides and sulfides besides TiS_2 and CoO_2. Indeed, ion size, degree of ionicity, and degree of intercalation have long been recognized to correlate empirically with stacking-sequence preference. For example, transformations from O3 to P3 during Na deintercalation have been observed in a wide range of layered sulfides (Na_xTiS_2, Na_xVS_2, and Na_xCoO_2) and layered oxides (Na_xVO_2, Na_xCrO_2, Na_xCoO_2, and Na_xNiO_2). Prior DFT calculations have also predicted P3 to be more stable than O3 at x = 1/2 for some of these compounds. However, transformations to P3 appear not to occur in Na_xTiO_2, Na_xMnO_2, and Na_xFeO_2. We speculate that the absence of P3 in Na_xTiO_2 and Na_xMnO_2 could be due to the larger energy penalty for cation face sharing in more ionic compounds (Pauling’s third rule). However, experiments cannot always be directly compared to the equilibrium phase diagram because stacking-sequence changes are sometimes kinetically inhibited at room temperature.

Furthermore, we speculate that the minimization of electrostatic repulsion in honeycomb lattices may play a role in other layered compounds beyond the O1/O3/P3 family. For example, O2 Na layered oxides and sulfides are widely observed to transform to P2 upon deintercalation. (However, this transformation is more complex than the O3–P3 transformation because in P2, unlike P3, the two triangular sublattices of the honeycomb lattice are not symmetrically equivalent.) Similar transformations from octahedral to prismatic coordination upon deintercalation have also been observed in Na_xNbS_2 which differs from the O1/O3/P3 and O2/P2 families in that the transition metal is primitively coordinated.

Our calculations provide some guidance for strategies to prevent stacking-sequence change phase transformations. For example, we speculate that Mg^2+ and Al^3+ could be effective dopants in the intercalant layer to suppress transformations to P3 as they are too small to support prismatic coordination. Furthermore, any cation that remains in the intercalant layer could prevent transformation to O1, with more electropositive elements being more effective (e.g., Ca^2+ being more effective than Mg^2+).

In terms of doping on the transition-metal site, our calculations suggest that the electronegativity of the dopant could be used to control the relative stability of O1 and O3. In particular, doping with more electropositive elements should stabilize O3, while less electropositive elements will stabilize O1. For example, replacing Co with a more electropositive dopant, such as Mn or Ti, could discourage transformation from O3 to O1.

Lastly, the relative strengths of intercalant–intercalant repulsion suggest that Na and K electrodes will have more steeply sloped voltage curves than their Li analogues, in the sense that (de)intercalation takes place over a wider voltage range. Experiments showing steeper voltage curves for Na compounds than Li compounds support the notion that Na–Na repulsion is stronger than Li–Li repulsion. For example,
essentially all of the Li in Li$_2$CoO$_2$ can be (de)intercalated over a voltage window of $\sim$0.7 V, but a voltage window of at least 1.2 V is needed to (de)intercalate just 0.7 Na in Na$_x$CoO$_2$. A similar trend is seen in other compounds, such as LiNiO$_2$ vs Na$_x$NiO$_2$, Li$_x$Ti$_2$O$_4$ vs Na$_x$Ti$_2$O$_4$, and Li$_x$V$_2$O$_5$ vs Na$_x$V$_2$O$_5$. A larger voltage range for (de)intercalation might be undesirable, as it could bring the potential outside of the electrolyte stability window.

■ CONCLUSIONS

The main result of this study is that layered intercalation materials with large cations (Na, K, and Ca) behave qualitatively differently in the O1/O3/P3 system from traditional Li insertion materials. Because large cations can support prismatic coordination, these compounds transform to P3 at intermediate compositions ($x \sim 0.5$) as its honeycomb topology of intertcalant sites minimizes intercalant–intercalant repulsion. This suggests that stacking-sequence-change phase transformations will in general play a much larger role in the performance of Na, K, and Ca intercalation batteries than in traditional Li intercalation batteries.

■ ASSOCIATED CONTENT

1 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b03454.

Convex hulls for intercalated CoO$_2$ and TiS$_2$ and interlayer spacing of ground states (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: avdv@engineering.ucsb.edu.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012583. We acknowledge support from the Center for Scientific Computing from the CNSI, MRL: an NSF MRSEC (DMR-1121053), Hewlett-Packard, and the National Energy Research Scientific Computing Center (NERSC), supported by the Office of Science and U.S. Department of Energy, under Contract Number DE-AC02-05CH11231.

■ REFERENCES


(15) Van der Ven, A.; Bhattacharya, J.; Belak, A. A. Understanding Li Diffusion in Li-Intercalation Compounds. Acc. Chem. Res. 2013, 46, 1216–1225.


(26) Croguennec, L.; Fouilliere, C.; Mansour, A. N.; Delmas, C. Structural Characterization of the Highly Deintercalated Li$_x$Ni$_{0.2}$O$_2$ Phases (with $x \leq 0.30$). J. Mater. Chem. 2001, 11, 131–141.


