Phase Separation Tendencies of Aluminum-Doped Transition-Metal Oxides (LiAl$_{1-x}$M$_x$O$_2$) in the α-NaFeO$_2$ Crystal Structure

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First-principles methods are used to calculate the miscibility of eight aluminum-doped transition-metal oxides in the layered α-NaFeO$_2$ structure. This study finds that for all Li(Al,M)O$_2$ compounds investigated (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu) the enthalpy of mixing is positive. In addition, detailed analyses were performed on LiAl$_{1-x}$Co$_x$O$_2$ and LiAl$_{1-x}$Cr$_x$O$_2$ by calculating full temperature-composition phase diagrams. For the Li(Al,Co)O$_2$ system, we find regions of immiscibility below −173°C and above 600°C. For both Li(Al,Co)O$_2$ and Li(Al,Cr)O$_2$ above 600°C, Al-doping is limited by the formation of γ-LiAlO$_2$.
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There has recently been considerable interest in Al doping of lithium intercalation oxides. Al substitution of the transition-metal cation has been shown theoretically and experimentally to increase the cell voltage.[1] In addition, Chiang *et al.*[2] have demonstrated the positive effect of Al substitution on the cycle-life and high-temperature stability of spinel Mn-based insertion oxides. Ohzuku *et al.*[3] used Al to limit overcharging of LiNiO$_2$ and found beneficial effects on the thermal stability of charged LiNiO$_2$. Some other obvious advantages of doping with Al are that it is light, nontoxic, and inexpensive.

Because of the interest in Al doping of lithium insertion electrodes, we investigated the miscibility of Al in a number of transition-metal oxides. Although our results for most systems are based on only a few calculations, we find large positive enthalpies of mixing between LiAlO$_2$ and half of the lithium transition-metal oxides studied (Ti, V, Mn, and Fe), indicating that Al miscibility is limited. For Li(Al,Co)O$_2$ and Li(Al,Cr)O$_2$, in which mixing enthalpies are small, we calculated the full temperature-composition phase diagrams. For the Al-doped Co system, full miscibility in the range from −173 to 600°C is predicted. In both systems, Li(Al,Co)O$_2$ and Li(Al,Cr)O$_2$, the formation of γ-LiAlO$_2$ causes decreasing Al solubility with temperatures above 600°C. We expect this phenomenon to occur in other Al-doped lithium-metal oxides as well.

Enthalpies of Mixing

The tendency for two compounds to mix can be estimated from their enthalpy of mixing, *i.e.*, the enthalpy difference between the mixture and the pure compounds. The enthalpy of mixing for LiAlO$_2$ with another LiMO$_2$ compound is

$$\Delta H_{\text{mix}}(\text{LiAl}_{1-x}\text{M}_x\text{O}_2) = H_{\text{Li(Al}_{1-x}\text{M}_x)\text{O}_2} - xH_{\text{LiMO}_2}$$
$$- (1-x)H_{\text{LiAlO}_2} \quad [1]$$

Positive enthalpies of mixing represent a tendency for phase separation. Negative values indicate the formation of ordered compounds. Only positive values of the mixing enthalpy were obtained for LiAlO$_2$ with all eight transition metal oxides studied. However, even when a system has a positive enthalpy of mixing, it may still form a solid solution if the temperature is high enough for the entropy contribution to the free energy to compensate for the positive enthalpy. In practice, the enthalpy of mixing (ΔH) can be replaced by the internal energy (ΔU) of mixing, since the $p\Delta V$ term is usually very small for solid-state reactions ($H = U + pV$). Note that we consider mixing for an overall stoichiometry of LiAl$_{1-x}$M$_x$O$_2$. The conditions of oxygen partial pressure needed to achieve this average oxidation states for the cations is not computed. When the oxygen partial pressure does not lead to an average valence of 3+

for the cations, other compounds with different valence may form and prohibit mixing. This effect is not investigated here.

First-principles methods can give insight into miscibility in a system by providing the energies of the mixed and unmixed compounds. Energies for a series of Li(Al$_{1-x}$M$_x$)O$_2$ compounds were calculated with the *ab initio* pseudopotential method. The Vienna Ab initio Software Package (VASP) pseudopotential program[4,5] used here solves the Kohn-Sham equations within the local density approximation using ultrasoft pseudopotentials.[6,7] All crystallographic degrees of freedom were optimized such that the minimum ground state energy was obtained. Details of this method can be found in the references cited.

To isolate the effect of metal chemistry from the effect of different structures, we chose to compute the formation energies for a series of compounds with different choices of M but all in the same α-NaFeO$_2$ structure. For half the metals examined, including LiCoO$_2$, a well-studied and commercially used cathode compound[8,9] this is the equilibrium structure. The same structure was used for the other compounds, even when it is not the experimentally observed ground state, in order to isolate the chemical effects from structural factors. Eight metals were examined: Ti, V, Cr, Mn, Co, Fe, Ni, and Cu. Note that whenever LiMO$_2$ does not crystallize in the layered α-NaFeO$_2$ structure, our calculated enthalpies of mixing relative to the true experimental structure are underpredicted (*i.e.*, too small). This is because in this case the experimentally observed LiMO$_2$ structure would have a lower (more negative) enthalpy than layered LiMO$_2$. Hence from Eq. 1, the enthalpy of mixing would be higher. While our results only apply directly to mixtures in the layered state, they may also give an indication of the sign of the enthalpy of mixing in other host structures.

Hewston and Chamberland[10] extensively reviewed the crystal structures of the first row of transition-metal LiMO$_2$ compounds. Four (V, Cr, Co, and Ni) of the eight transition-metal oxides studied here and LiAlO$_2$, are stable at room temperature in the layered rhombohedral α-NaFeO$_2$ (space group *R3m*) crystal structure. Ni is stable in a Jahn-Teller distorted variant of this structure and generally has some site disorder between the Li and Ni sites.[11] The other four metals, Ti, Mn, Fe, and Cu, have different experimentally observed ground states.

The results of the mixing energy calculations are shown in Table I. The structures chosen to evaluate the enthalpy of mixing had the smallest unit cells possible (8 or 12 atoms) for the composition studied. In addition, these structures had the lowest energy in the Li(Al,Co)O$_2$ system, where a more extensive set of structures was investigated. All the formation energies are positive, indicating that thermodynamically, LiAl$_{1-x}$M$_x$O$_2$ favors phase separation into LiAlO$_2$ and LiMO$_2$ at low temperature. It is possible, although unlikely, that ordered compounds with larger unit cells or a different

Table I. Computed formation energies, in meV per formula unit, for LiAl$_{1-x}$M$_x$O$_2$ in the α-NaFeO$_2$ (*R3m*) crystal structure.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$x = 0.3333$	337	249	1	148	94	13	25	18
$x = 0.5000$	299	228	14	131	70	28	3	47
$x = 0.6666$	253	229	7	111	44	9	11	17

stoichiometry have negative formation energies. Several additional structures were investigated in the Li(Al,Co)O$_2$ system, and all had positive formation energies as well. This implies that the material forms a low-temperature miscibility gap, separating into the two different compounds. At higher temperatures the material is expected to transform into a solid-solution state.

The temperatures at which a complete Al-M solid solution can be achieved depend on the mixing enthalpies and may be above the decomposition temperature of the oxide for large positive enthalpies. We can approximately predict the transition temperatures from the calculated formation energies. To do this, a nearest-neighbor lattice model was fit to the enthalpies of mixing for each of the eight transition metals to obtain the first nearest-neighbor pair interactions (V_1). Once the nearest-neighbor interaction has been obtained, the transition temperature can be approximated following the method outlined by de Fontaine[12] for a triangular lattice

$$T_c = \frac{0.6062 \cdot 6 \cdot |V_1|}{k_B} \qquad [2]$$

The eight predicted transition temperatures are shown in Fig. 1. These results allow us to extrapolate a rule of thumb for the triangular lattices of the layered structure: full miscibility occurs when $k_B T > 0.9 \ \Delta H$ (at $x = 0.5$). The rough prediction of T_c for Li(Al,Co)O$_2$ from Eq. 2 agrees well with the more exact result from the calculated phase diagram described in more detail below; they differ by roughly 15%. This confirmation suggests that our approximate approach provides a reasonable estimate of the temperature at which complete solid solution can be reached.

Also plotted in Fig. 1 is the ionic size for each transition metal in the 3+ valance state.[13] The larger the ion, the greater the size difference between it and the Al ion. A large size difference with the substituting ion causes more lattice strain and therefore a greater tendency for phase separation. As can be seen from the plot, a definite correlation exists between the transition temperature and ionic size: the four largest ions, Ti, V, Mn, and Fe, have the highest transition temperatures. Chemical effects, such as electronic bonding and magnetic effects, alter the interactions as well so that T_c is not exactly determined by the physical size of the ions. For example, Cu^{3+} is much smaller than Cr^{3+}, Co^{3+}, or Ni^{3+}, and yet Li(Al,Cu)O$_2$ has a higher T_c than any of them. Mn^{3+} and Fe^{3+} are the same size but they also differ in transition temperature. However, an overall correlation clearly exists between ionic size and transition temperatures.

LiAl$_{1-x}$Co$_x$O$_2$ System

While zero temperature energy calculations can give indications of (im)miscibility, a complete temperature-composition calculation of the free energy is required to predict the temperature dependence of solubility limits. For LiAl$_{1-x}$Co$_x$O$_2$ we have performed a complete phase-diagram calculation.

Experimentally, α-LiAlO$_2$ is observed to crystallize in the α-NaFeO$_2$ structure below 600°C.[14,15] Above this temperature, γ-LiAlO$_2$ is stable in the tetragonal crystal structure with the $4_1 2_1 2$ space group. The major difference between the two structures is that the Al ions are tetrahedrally coordinated in the γ structure while they are octahedrally coordinated in the a structure. LiCoO$_2$ forms in the layered α-NaFeO$_2$ crystal structure for all temperatures.[10]

When LiAlO$_2$ and LiCoO$_2$ are mixed below 600ºC it is reasonable to assume that the α-NaFeO$_2$ crystal structure is maintained so
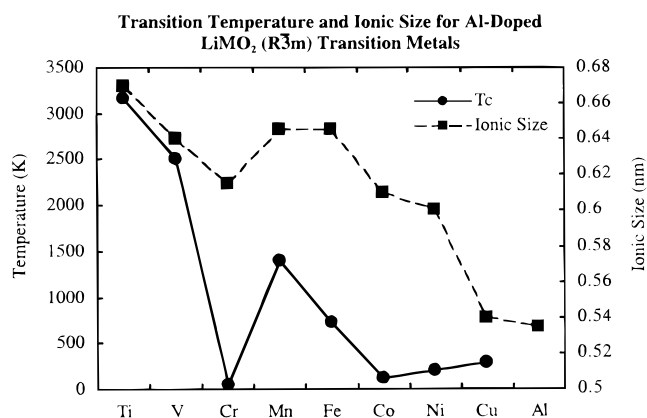

Figure 1. Estimated temperature above which complete solid solution can be reached in layered Li(Al,M)O$_2$ plotted next to ionic size of the M^{3+} ions.[13]

that Al and Co mix only on the (111) planes of the rock salt structure, while the Li plane remains perfect in composition. The formalism to calculate the free energy of systems with binary disorder from first-principles is well known[16-18] and consists of parameterizing the dependence of the energy on the distribution of ions in a given host structure. We parameterized this dependence using a cluster expansion, which is a standard technique to study substitutional disorder in metals, oxides, and semiconductors.[16,19-21] In the case of layered LiAl$_{1-x}$Co$_x$O$_2$ the disorder of Al and Co was restricted to a two-dimensional triangular lattice of sites. Adding interplane interactions in the cluster expansion did not significantly change the results; hence, these were neglected. In addition, no disorder between the Al$_{1-x}$Co$_x$ plane and the lithium plane was allowed. More details on the method can be found in the references.[16-21]

The calculated energies for nine different compositions of LiAl$_{1-x}$Co$_x$O$_2$ in the α-NaFeO$_2$ structure were used to create a cluster expansion with three pairs and two triplets for the layered material. The formation energies of these structures are plotted in Fig. 2. The formation energy of a given structure, as opposed to the total energy, reflects the relative stability of that structure with respect to phase separation. The two energies are related by Eq. 1, with enthalpies replaced by energies. The formation energies for this system are positive but quite small.

Free energies for all compositions in the layered phase were determined by Monte Carlo simulations using the grand canonical ensemble on a system of 576 (Co, Al) sites. At each temperature and chemical potential, 1000 Monte Carlo passes per lattice site were performed, after which sampling occurred over an additional 4000 Monte Carlo passes. Free energies were found by performing ther-
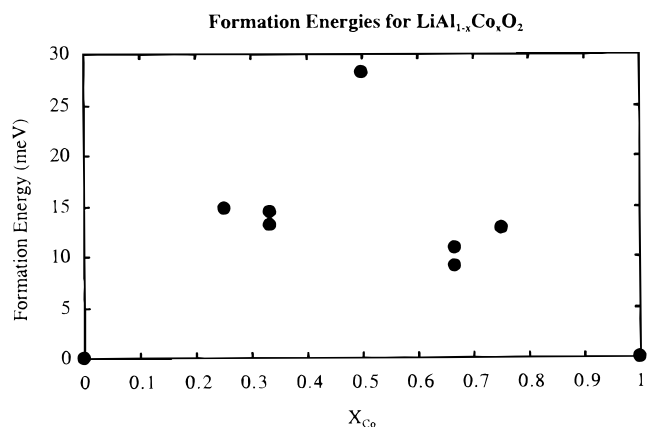

Figure 2. Computed formation energies, in meV, for LiAl$_{1-x}$Co$_x$O$_2$ in the α-NaFeO$_2$ (*R3m*) crystal structure.

modynamic integration of the chemical potential as a function of composition.

In principle, a separate cluster expansion is required for the tetragonal parent lattice of γ-LiAlO$_2$. However, we calculated the energy for substituting Co in the tetragonal structure and found the energies for these compounds to increase very rapidly with x_{Co}. The formation energies for mixed tetragonal Li(Al,Co)O$_2$ ranged from 300 to 800 meV and the free energies for tetragonal structures were greater by 850-1500 meV than the free energies of the layered structures at the same composition. We therefore concluded that LiCoO$_2$ and LiAlO$_2$ are not miscible in the tetragonal phase and that γ-LiAlO$_2$ can be treated as a stoichiometric line compound.

To obtain the free energy of γ-LiAlO$_2$ relative to α-LiAlO$_2$, the total energies at zero K were compared. The calculated difference is 165 meV. The entropy difference between these two phases was determined by requiring the difference in free energy at the transition temperature, 600°C, to be equal to zero. Assuming that the heat capacities of α-LiAlO$_2$ and γ-LiAlO$_2$ are the same, the free energy for the tetragonal phase (with respect to α-LiAlO$_2$) is

$$F_{\gamma\text{-LiAlO}_2} = 165 \text{ meV}\left(1 - \frac{T}{873 \text{ K}}\right) \qquad [3]$$

The phase diagram obtained by combining Eq. 3 with the free energies for the layered phase obtained from Monte Carlo is given in Fig. 3.

Within the Li(Al,Co)O$_2$ phase diagram, the lower temperature miscibility gap is symmetric and peaks at about −180°C. Due to the low temperature of this miscibility gap there is obviously no experimental data with which to compare this part of the result. At 600°C, the transformation of layered α-LiAlO$_2$ to the tetragonal γ-phase in which no Co dissolves creates a new two-phase region on the Al-rich side. Note that above 600°C the solubility of LiCoO$_2$ and LiAlO$_2$ actually decreases with temperature due to the increasing stability of γ-LiAlO$_2$. Such a case of retrograde solubility, while unexpected, is not all that uncommon.

Initial experiments on the Li(Al,Co)O$_2$ system done by Nazri *et al.*[22] found the solubility limit for formation of solid solutions of Al in LiCoO$_2$ to be around 25% when processed at 750°C. However, because γ-LiAlO$_2$ was one of the starting materials, it is difficult to assess if a true solubility limit was reached or whether the material had not been treated long enough to reach equilibrium. A second study, by Alcántara *et al.*[23] agrees with our results; they found no traces of γ-LiAlO$_2$ at 700°C with composition up to 70% Al. Recent experiments by Jang *et al.*[24] at 800°C have confirmed the existence of a two-phase region at LiAl$_{0.75}$Co$_{0.25}$O$_2$ and a solid solution at LiAl$_{0.25}$Co$_{0.75}$O$_2$. They also found traces of the tetragonal phase at 50% Co, where the results of this study show that the two-phase region ends at about 30% Co at this temperature. Because the results of the experimental studies disagree with each other and with our calculated results, it is difficult to decide whether these differences are due to our calculations or experimental discrepancies, such as incomplete equilibration. Further experimental investigation of the phase diagram in this region is therefore warranted.

It is interesting to note that this two-phase region with γ-LiAlO$_2$ occurs in other Al-doped layered oxides as well. Chiang *et al.* found that in Li(Al,Mn)O$_2$[2,25] small amounts of Al can be incorporated into the layered structure, but at greater Al concentrations γ-LiAlO$_2$ forms. Their results indicate a solid solubility of Al in the layered phase of about 5-7% at 950-1000°C. Aluminum solubilities more similar to our results for Li(Al,Co)O$_2$ have been found for LiCrO$_2$. In Li(Al,Cr)O$_2$, 60% Al substitution was reached for processing temperatures up 920°C.[26] Above this temperature, γ-LiAlO$_2$ forms. An Al solid-solubility limit between 20 and 30% was found for Li(Al,Ni)O$_2$[27] at 700°C, again much smaller than for Li(Al,Co)O$_2$.

For Li(Al,Cr)O$_2$ a phase diagram can be easily calculated. Since the mixing enthalpies in the layered structure (Table I) are particularly small in this system, the free energy of the layered phase may be approximated with an ideal solution model, without any significant loss in accuracy. Combining these energies with Eq. 3 for the free energy of γ-LiAlO$_2$ results in the phase diagram of Fig. 4. As in Li(Al,Co)O$_2$, the solubility at high temperature is limited by the stability of γ-LiAlO$_2$. This agrees very well with experiment. Poeppelmeier *et al.*[26] found that at 60% Al content the material remains a layered solution below 920°C, while above this temperature it decomposes to γ-LiAlO$_2$ and the layered solid solution Li(Al,Cr)O$_2$. This result is therefore in good agreement with our calculation, which gives a 55% Al solubility limit at the same temperature.

Interestingly, our calculation for Li(Al,Co)O$_2$ shows complete solubility at intermediate to low temperatures. This realization may pave the way for LiAl$_{1-x}$Co$_x$O$_2$ mixtures with a high degree of Al substitution. Al reduces the total theoretical capacity by moving some of the voltage to a very high potential,[1] but currently commercial batteries based on the LiCoO$_2$ system use only about half the theoretical capacity. Substitution of the nonoxidized fraction of Co ions by Al should result in significant cost and weight savings. Obviously, the material needs to possess other features such as long cycle life and long-term stability in order to become practical as an electrode. In addition, Alcántara *et al.*[23] have speculated that at low Al substitution, tetrahedral occupation of Al in LiAl$_{1-x}$Co$_x$O$_2$ may limit the material's reversibility. Though we have not been able to confirm these results using first-principles methods, Al migrating to tetrahedral positions would result in a decrease in lithium ion diffusivity and, consequently, the observed poor reversibility. Preliminary calculations indicate that Al occupation of tetrahedral sites is not energetically favorable.
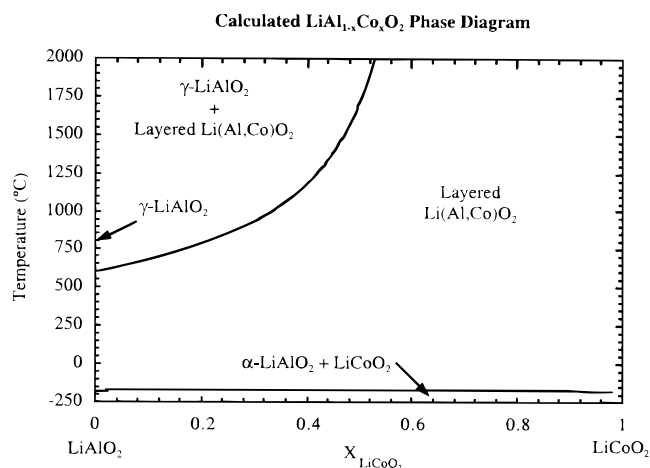

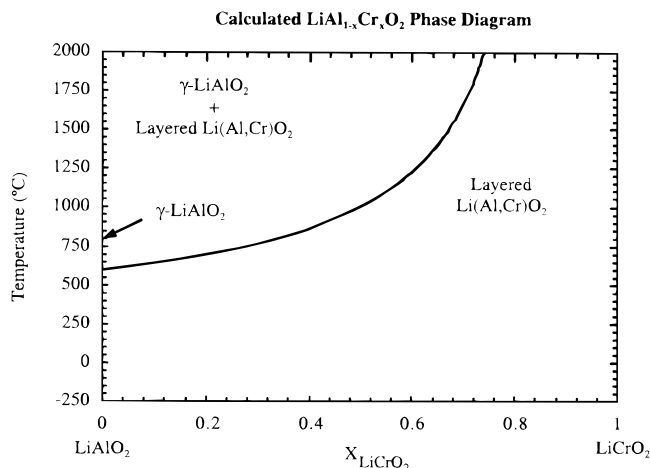**Figure 3**. Computed phase diagram for LiAl$_{1-x}$Co$_x$O$_2$.

Figure 4. Computed phase diagram for LiAl$_{1-x}$Cr$_x$O$_2$.

Another source for the discrepancy between theoretical and experimental results is the existence of oxygen defects. All calculations were performed assuming stoichiometric oxygen content. Experiments have shown, however, that oxygen vacancies can be formed during processing, notably in Li_xNiO_2 and in Li_xCoO_2 ($x < 1$).[28] It has been found that the higher the lithium content, the greater the temperature needed to promote oxygen liberation. Though these oxygen defects were not found in the fully lithiated compounds at the temperatures tested, the trends indicate that oxygen vacancies could form for fully lithiated $LiCoO_2$ at high enough temperatures. We calculated the defect energy for an oxygen vacancy in both $LiAlO_2$ and $LiCoO_2$ and found that the oxygen vacancy defect energies are much larger for α-$LiAlO_2$ and γ-$LiAlO_2$ than for $LiCoO_2$. Thus oxygen defects would more readily occur in $LiCoO_2$. Because the defect energy differs for the two end members, the incorporation of oxygen vacancies changes the free energy of the layered structure's nonuniformly as a function of composition.

We were able to qualitatively determine the effect on the phase diagram by combining these energies and the chemical potential for gaseous oxygen found using an ideal gas model. The free energy changes for the layered structure are very small for all compositions in the temperature ranges of interest. However, the effect of oxygen defects, a greater free energy, is much more pronounced on the Co-rich side. This increase in the free energies pushes the edge of the two-phase region closer to the Al rich side. However, the changes in the phase diagram occur only at high temperatures, above 2000°C. Our preliminary results show promise for modeling oxygen defects. Further investigations, both computational and experimental, need to be done to refine the defect model and determine the role of oxygen defects in these materials.

Conclusions

The energy calculations described here show that when $Li(Al,M)O_2$ is doped with Al, four of the eight transition-metal oxides studied (Ti, V, Mn, Fe) phase separate at normal processing temperatures. The other four (Cr, Co, Ni, Cu) have low-temperature miscibility gaps, but form solid solutions at room temperature. A full temperature-composition phase diagram was calculated for $LiAl_{1-x}Co_xO_2$. Complete miscibility is found between −173 and 600°C. Above 600°C, Al-doping in $LiCoO_2$ is limited by the formation of γ-$LiAlO_2$. A temperature-composition phase diagram was also calculated for $LiAl_{1-x}Cr_xO_2$. Complete miscibility is found below 600°C, as in $LiAl_{1-x}Co_xO_2$. Al-doping above 600°C is limited by the formation of γ-$LiAlO_2$. For all oxides which have substantial solubility with $LiAlO_2$ in the layered phase, reduced solubility should be expected above 600°C due to the formation of γ-$LiAlO_2$. In some materials such as $Li(Al,Mn)O_2$ where a minimal amount of Al is critical for the stability of the layered phase,[25] the relative stability of different polymorphs may therefore strongly depend on temperature through the solubility limit.

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