Dilute Mixing Thermodynamics in $Li_xM^A_{1-y}M^B_yPO_4$ (M=Mn,Fe,Ni) from First Principles Calculations

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Introduction:

For Li-ion cathodes, lithium metal phosphate materials have demonstrated excellent durability, both as particle cores [1,2] and more recently as particle surface coatings.[3,4,5] Pure $LiMPO_4$ materials can be actively tailored by introducing dopant atoms, or may passively absorb atoms from adjacent phases. In either case, electrochemical properties may be impacted, and so it is desirable to understand these defect formation thermodynamics, as well as to characterize the behavior of these defects in the electrochemical cell.

We present results from Density Functional Theory (DFT) calculations, quantifying the dilute mixing themodynamics of olivine $Li_xM^A_{1-y}M^B_yPO_4$ (M=Mn,Fe,Ni) phases. We show energies for lithium-vacancy mixing and for M^A - M^B transition metal mixing, and we quantify the effects of dilute transition metal mixing on delithiation potentials. We relate these results to prior computational work[6] and to technological questions, including Mn containment, cathode coating delithiation, and core-coating chemical stability.

Results and Discussion:

Our calculations show dilute mixing energies that are positive for all binary $LiM^A_{1-y}M^B_yPO_4$ (M=Mn,Fe,Ni) systems. For each system, the mixing energies are approximately symmetric, meaning solubility of M^A in LiM^BPO_4 is similar to solubility of M^B in LiM^APO_4. At room temperature, we predict complete solubility for the $LiMnPO_4$–$LiFePO_4$ system; whereas for the $LiMnPO_4$–$LiNiPO_4$ system we predict a miscibility gap up to approximately 500 K. In experimental studies, $LiMnPO_4$ core materials have been coated with $LiFePO_4$.[3,4] Our calculations suggest that $LiNiPO_4$ would be more effective than $LiFePO_4$ at containing Mn in the particle core; this discovery could be especially relevant for long-term cyclability. Compared to the Mn–Fe and Mn–Ni systems, the $LiFePO_4$–$LiNiPO_4$ system exhibits intermediate solubility.

The delithiated $M^A_{1-y}M^B_yPO_4$ systems exhibit less symmetry in dilute mixing energies. We predict that the $FePO_4$–$NiPO_4$ and $FePO_4$–$MnPO_4$ systems have weakly positive mixing energies, consistent with complete solubility at room temperature. We find that the $MnPO_4$–$NiPO_4$ dilute mixing energies are strongly negative. This ordering tendency could be explained by charge disproportionation: $Mn^{3+} + Ni^{3+} \rightarrow Mn^{4+} + Ni^{2+}$. However, delithiated $NiPO_4$ is not accessible within today's electrolyte voltage windows.

Finally, we calculate the impact of dilute transition metal mixing on the delithiation potentials of these transition metal atoms. For example, if an Fe atom is substituted into a $LiNiPO_4$ host, we calculate the energy required to remove a Li atom from a Li site adjacent to that Fe atom. For the Ni–Fe system, we find that these transition metals interact weakly. For example, the delithiation potential of Fe in $LiNiPO_4$ is similar to the delithiation potential of Fe in $LiFePO_4$. For the Ni–Mn and Fe–Mn systems, the atoms interact more strongly to give intermediate delithiation potentials. For example,

the delithiation potential of Ni in a $LiMnPO_4$ host is near to the mean of the delithiation potentials for pristine $LiMnPO_4$ and $LiNiPO_4$.

References:
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[6] Malik et al., *Physical Review B* 79, 214201 (2009)