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Thermal Stabilities of Delithiated Olivine MPO$_4$ (M=Fe,Mn) Cathodes investigated using First Principles Calculations

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Abstract

We present an analysis of the thermal reduction of delithiated LiMnPO$_4$ and LiFePO$_4$ based on the quarternary phase diagrams as calculated from first principles. Our results confirm the recent experimental findings that MnPO$_4$ decomposes at a much lower temperature than FePO$_4$, thereby potentially posing larger safety issues for LiMnPO$_4$ cathodes. We find that while substantial oxygen is released as MnPO$_4$ reduces to Mn$_2$P$_2$O$_7$, the mixed valence phases that form in the decomposition process of FePO$_4$ limit the amount of oxygen evolved.

Keywords: thermal stability, olivine, cathode, LiMnPO$_4$, LiFePO$_4$, MnPO$_4$, FePO$_4$, density functional theory, phase diagrams

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1. Introduction

The olivine LiMPO₄ materials (M=Fe,Mn,Ni,Co) form a promising class of cathode materials for rechargeable Li batteries. LiFePO₄[1], in particular, has already found widespread applications in industry due to its reasonable theoretical capacity of 170mAhg⁻¹, low cost and low toxicity. In recent years, there has been increasing interest in LiMnPO₄, LiCoPO₄ and LiNiPO₄ which could potentially deliver higher theoretical energy densities than LiFePO₄ due to their higher measured/predicted voltages of 4.1V, 4.8V and 5.1V vs Li/Li⁺ respectively.[2, 3, 4]

Of these promising alternatives, LiMnPO₄ has garnered the most interest because its voltage of 4.1V is higher than LiFePO₄ (3.5V) but well within the limitations of current organic electrolytes. While focus has been on understanding LiMnPO₄’s poor rate performance due to low ionic and electronic conductivities,[5] a high surface energy barrier for Li diffusion,[6] or significant volume change at the phase boundary[7, 8, 9], it has been tacitly assumed that the charged compound, MnPO₄, would match the excellent thermal stability of FePO₄, which is a major contribution to Li-ion battery safety. Two recent investigations by Kim et al.[10] and Chen et al.[11] have cast doubt on that assumption by demonstrating that while fully lithiated LiMnP₀₄ remains stable up to fairly high temperatures, delithiated MnPO₄ decomposes at temperatures of around 150-200°C, evolving O₂ and heat in the process. This is in stark contrast to delithiated FePO₄ which has been shown to be stable for temperatures up to 500-600°C.[12]

In this work, we constructed the oxygen grand potential phase diagrams for the Li-M-P-O (M=Fe,Mn) systems using the methodology developed in
our previous work.\[13\] We were able to confirm the lower stability of MnPO$_4$, and demonstrate that the difference in the relative stabilities of the delithiated MPO$_4$ phases can be explained in terms of the competing phases present in the phase diagrams.

2. Methodology

2.1. Thermodynamic Methodology

In our previous work\[13\], we outlined a thermodynamic methodology in which oxygen grand potential phase diagrams can be constructed from first principles. Interested readers are referred to that paper for further details. Such phase diagrams represent phase equilibria in an isothermal, isobaric system that is open with respect to oxygen, which is representative of conditions during synthesis and operation of LiMPO$_4$ cathodes.

In the open Li-M-P-O system at temperatures of interest (\(\approx 200\)-1000K), most phase equilibria changes are solid-state reactions involving the absorption or loss of oxygen. We may therefore make the simplifying assumption that the reaction entropy is dominated by the oxygen entropy. The effect of temperature and partial pressure is mostly captured by changes in the oxygen chemical potential, as follows:

\[
\mu_{O_2}(T, p_{O_2}) = \mu_{O_2}(T, p_0) + kT \ln \frac{p_{O_2}}{p_0} \tag{1}
\]

\[
= E_{O_2} + kT - T S_{O_2}^{T,p_0} + kT \ln \frac{p_{O_2}}{p_0} \tag{2}
\]

where \(p_{O_2}\) is the oxygen partial pressure, \(p_0\) is a reference oxygen partial pressure, \(S_{O_2}^{T,p_0}\) is the oxygen entropy, \(E_{O_2}\) is the oxygen energy, and \(k\) is
Boltzmann’s constant. Equation 2 is obtained by writing the chemical potential as a Legendre transform of the internal energy, with an ideal gas assumption made for the PV term.

Lowering $\mu_{O_2}$ corresponds to more reducing environments brought about by higher temperatures, lower oxygen partial pressures or the presence of reducing agents. In this work, we have set the reference oxygen chemical potential to be zero at the room temperature air (298K, 0.21atm) value obtained with the calculated value of $E_{O_2}$ in equation 2. This calculated value has been corrected for the $O_2$ binding energy error and GGA error associated with adding electrons to the oxygen $p$ orbital when $O^{2-}$ is formed through a constant -1.36eV shift.[14] Experimental entropy data for $O_2$ at 0.1MPa were obtained from the JANAF thermochemical tables.[15]

2.2. Computational Methodology

We calculated the energies of all structural prototypes in the Li-Fe-P-O and Li-Mn-P-O systems in the 2006 version of the Inorganic Crystal Structure Database[16] for both the Fe and Mn compositions. Compounds having partial occupancies were related to the ordered structure with lowest electrostatic energy[17, 18] at the same or close composition from a group of representative structures enumerated with a technique similar to that proposed by Hart et al.[19]

All energies were calculated using the Vienna ab initio Simulation package[20] within the projector augmented-wave approach[21], using the Perdew-Burke-Ernzerhof generalized-gradient functional[22] and the GGA+U extension to it.[23] $U_{\text{effective}}$ values of 3.9 eV and 4.0eV were used for Mn and Fe respectively, following Wang’s method [14] of fitting the calculated binary oxide for-
mation enthalpies to experimental values from the Kubachewski tables.[24] A plane wave energy cut-off of 520eV and $k$-point density of at least $500/(\text{number of atoms in unit cell})$ were used for all computations. All calculations were spin-polarized starting from a high-spin ferromagnetic configuration for Fe and Mn.

3. Results

3.1. Phase Diagrams at Critical $\mu_{O_2}$ for Reduction

To investigate the stability of delithiated MnPO$_4$ and FePO$_4$, we have constructed the phase diagrams at various $\mu_{O_2}$. Increased temperature leads to a more reducing condition, i.e. more negative $\mu_{O_2}$. Hence, the critical temperature for reduction of the MPO$_4$ corresponds to an $\mu_{O_2}$ below which the compound decomposes. The equilibrium reduction products are given by the phases stable below this critical $\mu_{O_2}$. Figure 1 show the oxygen grand potential phase diagrams for the Li-Fe-P-O and Li-Mn-P-O systems at $\mu_{O_2}$ just below that required for the reduction of the delithiated olivine MPO$_4$ phase. It should be noted that the delithiated olivine is not the ground state structure for the FePO$_4$ composition, and the trigonal ground state phase and all phases lower in energy than the olivine phase[25] have been removed from the dataset to determine the non-equilibrium reduction pathway. We will discuss the consequence of this removal in the next section.

Reduction of FePO$_4$ takes place at a much lower $\mu_{O_2}$ of $-1.72eV$ ($\approx 700^\circ C$ under air) compared to MnPO$_4$ which reduces at $\mu_{O_2}$ of $-0.83eV$ ($\approx 370^\circ C$). From the phase triangle bounding the MPO$_4$ compositions, we determine
Figure 1: Li-M-P-O Phase Diagrams for $\mu_{O_2}$ just below critical values where delithiated MPO$_4$ olivine decomposes. The composition of MPO$_4$ is marked with an X.
that FePO$_4$ and MnPO$_4$ undergo the following initial reduction reactions:

\[
\begin{align*}
\text{FePO}_4 & \quad \rightarrow \quad 0.1 \text{Fe}_3(\text{P}_2\text{O}_7)_2 + 0.1 \text{Fe}_7(\text{PO}_4)_6 + 0.1 \text{O}_2 \\
\text{MnPO}_4 & \quad \rightarrow \quad 0.5 \text{Mn}_2\text{P}_2\text{O}_7 + 0.25 \text{O}_2
\end{align*}
\]

The predicted reduction temperatures and products are in fairly good agreement with experimental findings. Delacourt et al.[12] have previously reported the formation of the mixed valence Fe$_7$(PO$_4$)$_6$ phase for Li$_x$FePO$_4$ ($x << 1$) at 500-600°C. Kim et al.[10] and Chen et al.[11] also reported that the decomposition of MnPO$_4$ leads to the formation of Mn$_2$P$_2$O$_7$ at 150-200°C. The calculated temperatures may differ from experimentally measured temperatures for several reasons. Firstly, a 100K temperature difference corresponds to about 10meV, well within the errors of our DFT calculations and entropy approximations (refer to our previous work[13] for a more detailed discussion). Secondly, the presence of reducing agents such as the electrolyte and carbon under experimental conditions will tend to decrease the actual decomposition temperatures. We also observe that in MnPO$_4$ decomposition, the Mn/P ratio stays constant and only O$_2$ release takes place, while for FePO$_4$, longer range transport will be needed to create phases with Fe/P ratio different from 1.

### 3.2. O$_2$ evolved versus Temperature

Figure 2 summarizes the O$_2$ evolution versus temperature for the reduction paths of FePO$_4$ and MnPO$_4$. Both the non-equilibrium paths and the equilibrium paths are shown for FePO$_4$. The non-equilibrium path corresponds to the likely reaction path if the FePO$_4$ olivine is unable to transform to the lowest energy trigonal structure[26, 27] (space group $P3_121$) due to
Figure 2: $O_2$ evolved vs temperature for delithiated $\text{MPO}_4$ (M=Fe,Mn)
kinetic limitations, and proceeds to reduce into other phases with the evolution of oxygen. The equilibrium path assumes that olivine FePO$_4$ is able to transform first into the trigonal phase before undergoing reduction.

For FePO$_4$, O$_2$ evolution takes places at a much lower temperature for the non-equilibrium path as compared to the equilibrium path. The path taken depends on the relative kinetics, which is affected by experimental conditions and Li content. Stability investigations by Yang et al. and Rousse et al.[26, 27] have shown that orthorhombic FePO$_4$ transforms irreversibly to trigonal FePO$_4$ only at fairly high-temperatures of 600-700°C, though there is some controversy as to the transition temperature for this structural transformation.[25] Regardless, the fact that the mixed valence Fe$_7$(PO$_4$)$_6$ was observed by Delacourt et al.[12] during Li$_x$FePO$_4$ ($x << 1$) decomposition at 500-600°C suggests that at least some degree of non-equilibrium decomposition does take place under certain experimental conditions. For MnPO$_4$, the olivine phase is the lowest energy structure. Nonetheless, the critical temperature for the onset of O$_2$ evolution in non-equilibrium FePO$_4$ reduction is still much higher than that for MnPO$_4$.

From Figure 2, we may also observe that initial reduction of FePO$_4$ evolves 0.1 moles of oxygen per mole of cathode, compared to 0.25 moles for initial reduction of MnPO$_4$. Hence, not only does MnPO$_4$ reduce at a much lower temperature than FePO$_4$, it also evolves 2.5 times the amount of O$_2$. Even at higher temperatures between 1100°C and 1300°C, FePO$_4$ only evolves 0.17 moles of oxygen per mole of cathode, significantly less than MnPO$_4$. This greater amount of O$_2$ evolved for MnPO$_4$ presents a significant safety hazard as O$_2$ released can ignite the organic electrolytes used in
rechargeable Li batteries.

4. Discussion

Our results show that delithiated FePO$_4$ is inherently more thermally stable than MnPO$_4$, and the amount of O$_2$ evolved upon initial decomposition is also much less. The greater stability of FePO$_4$ over MnPO$_4$ may be explained through ligand field theory.[28] It is well-known that in an octahedral environment such as MO$_6$ in olivines, half-filled high-spin $t_{2g}^3e_g^2$ is a highly stable electronic configuration due to the exchange stabilization arising from the five parallel-spin electrons. We would therefore expect that Fe$^{3+}$ and Mn$^{2+}$, both of which have the high-spin $t_{2g}^3e_g^2$ half-filled configuration, to have greater stability as compared to Fe$^{2+}$ and Mn$^{3+}$ respectively. Indeed, there is a greater proportion of Mn$^{2+}$ phases relative to Mn$^{3+}$ in the Li-Mn-P-O phase diagram, whereas the situation is reversed in the case of Fe. Furthermore, LiMnPO$_4$ is stable over a much wider range of oxygen chemical potentials ($-0.56eV < \mu_{O_2} < -7.02eV$) than LiFePO$_4$ ($-2.36eV < \mu_{O_2} < -6.24eV$). A similar argument has been used to explain why the LiFePO$_4$ voltage is unusually low.[2]

The key factor influencing the amount of O$_2$ evolved is the competing phases present in the system, which is also related to the relative stabilities of the +2 and +3 oxidation states. In the Fe system, the relative stability of the Fe$^{3+}$ oxidation state leads to the presence of the mixed valence Fe$_7$(PO$_4$)$_6$ and Fe$_3$(P$_2$O$_7$)$_2$ phases, which results in a smaller amount of O$_2$ evolved. On the other hand, MnPO$_4$ immediately reduces to Mn$_2$P$_2$O$_7$ which has the Mn$^{2+}$ oxidation state, resulting in significantly higher O$_2$ evolution.
Huggins[29] has previously performed a thermodynamic analysis of the relationship between equilibrium Li voltages and oxygen partial pressure for a number of ternary oxide systems. He found that extrapolation of the observed trends indicates high values of equilibrium \( O_2 \) partial pressures in high voltage materials. Our results similarly suggest that there could be some tradeoff between higher voltage and thermal stability of the charged cathode. However, the voltage of a rechargeable Li battery cathode material is related to the difference in energies between the delithiated and lithiated phases.[2] Therefore, a higher voltage can come from either a more stable lithiated phase, or a less stable delithiated phase. So this tradeoff between higher voltage and thermal stability of the charged cathode may not be absolute. We also note that coating strategies have been successfully employed to stabilize the charged cathode in LiCoO\(_2\) batteries[30, 31], and similar strategies could possibly be developed for the olivine cathodes to mitigate safety concerns.

5. Conclusion

In this work, we have analyzed the thermal stabilities of delithiated FePO\(_4\) and MnPO\(_4\) by constructing the oxygen grand potential phase diagrams of the Li-M-P-O (M=Fe,Mn) systems using first-principles calculations. Our observations indicate, in agreement with recent experiment findings,[10, 11] that MnPO\(_4\) reduces with substantial oxygen release at a much lower temperature than FePO\(_4\). Hence, the Mn system may trade off its somewhat higher energy density with considerably lower safety. The difference in relative stabilities of FePO\(_4\) and MnPO\(_4\) may be explained by the competing
phases present in the phase diagrams and relative stabilities of the $M^{2+}$ and $M^{3+}$ as explained by ligand field theory. The technique outlined in this paper can conceivably be extended to other similar systems, e.g. Li-Co-P-O and Li-Ni-P-O.

6. Acknowledgements

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