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 quaternary 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.

1. Introduction

The olivine LiMPO$_4$ materials (M = Fe, Mn, Ni, Co) form a promising class of cathode materials for rechargeable Li batteries. LiFePO$_4$ [1], in particular, has already found widespread applications in industry due to its reasonable theoretical capacity of 170 mA h g$^{-1}$, low cost and low toxicity. In recent years, there has been increasing interest in LiMnPO$_4$, LiCoPO$_4$ and LiNiPO$_4$ which could potentially deliver higher theoretical energy densities than LiFePO$_4$ due to their higher measured/predicted voltages of 4.1 V, 4.8 V and 5.1 V versus Li/Li$^+$, respectively [2–4].

Of these promising alternatives, LiMnPO$_4$ has garnered the most interest because of its voltage of 4.1 V which is higher than LiFePO$_4$ (3.5 V) but well within the limitations of current organic electrolytes. While focus has been on understanding LiMnPO$_4$'s poor rate performance due to low ionic and electronic conductivities [5], significant volume change at the phase boundary [7–9], it has been tacitly assumed that the charged compound, MnPO$_4$, would match the excellent thermal stability of FePO$_4$, 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 LiMnPO$_4$ remains stable up to fairly high temperatures, delithiated Mn$_2$PO$_4$ decomposes at temperatures of around 150–200 °C, evolving O$_2$ and heat in the process. This is in stark contrast to delithiated FePO$_4$ 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 (≈200–1000 K), 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:

\[ \mu_{O_2}(T, p_{O_2}) = \mu_{O_2}(T, p_0) + kT \ln \frac{p_{O_2}}{p_0} + E_{O_2} + \Delta S_{O_2}^{ref} + kT \ln \frac{p_{O_2}}{p_0} \]  

(1)

where \( p_{O_2} \) is the oxygen partial pressure, \( p_0 \) is a reference oxygen partial pressure, \( E_{O_2} \) is the oxygen energy, and \( k \) is Boltzmann's constant. Eq. (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 (298 K, 0.21 atm) value obtained with the calculated value of \( E_{O_2} \) in Eq. (2). This calculated value has been shifted by −1.36 eV to correct for the \( O_2 \) binding energy error and GGA error associated with adding electrons to the oxygen p orbital when \( O^2- \) is formed. Experimental entropy data for \( O_2 \) at 0.1 MPa 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 and Forcade [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]. Ultimate values of 3.9 eV and 4.0 eV were used for Mn and Fe, respectively, following Wang's method [14] of fitting the calculated binary oxide formation enthalpies to experimental values from the Kubachewski tables [24]. A plane wave energy cut-off of 520 eV 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 MnPO4 and FePO4, 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 MnPO4 corresponds to an \( \mu_{O_2} \) below which the compound decomposes. The equilibrium reduction products are then given by the phases stable below this critical \( \mu_{O_2} \). Fig. 1 shows 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 MPO4 phase. It should be noted that the delithiated olivine is not the ground state structure for the FePO4 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 FePO4 takes place at a much lower \( \mu_{O_2} \) of −1.72 eV (≈700°C under air) compared to MnPO4 which reduces at \( \mu_{O_2} \) of −0.83 eV (≈370°C). From the phase triangle bounding the MPO4 compositions, we determine that FePO4 and MnPO4 undergo the following initial reduction reactions:

\[ \text{FePO}_4 \rightarrow 0.1 \text{Fe}_3(\text{PO}_4)_{12} + 0.1 \text{Fe}_7(\text{PO}_4)_6 + 0.1 \text{O}_2 \]  

\[ \text{MnPO}_4 \rightarrow 0.5 \text{Mn}_2\text{P}_2\text{O}_7 + 0.25 \text{O}_2 \]

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\(/\text{PO}_4\)\(_x\) phase for LiFePO\(_4\) (\(x < 1\)) at 500–600°C. Kim et al. [10] and Chen and Richardson [11] also reported that the decomposition of MnPO4 leads to the formation of MnPO\(_3\) at 150–200°C. The
calculated temperatures may differ from experimentally measured temperatures for several reasons. Firstly, a 100 K temperature difference corresponds to about 10 meV, 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 MnPO₄ decomposition, the Mn/P ratio stays constant and only O₂ release takes place, while for FePO₄, longer range transport will be needed to create phases with Fe/P ratio different from 1.

3.2. O₂ evolved versus temperature

Fig. 2 summarizes the O₂ evolution versus temperature for the reduction paths of FePO₄ and MnPO₄. Both the non-equilibrium paths and the equilibrium paths are shown for FePO₄. The non-equilibrium path corresponds to the likely reaction path if the FePO₄ olivine is unable to transform to the lowest energy trigonal structure [26,27] (space group P3121) due to kinetic limitations, and proceeds to reduce into other phases with the evolution of oxygen. The equilibrium path assumes that olivine FePO₄ is able to transform first into the trigonal phase before undergoing reduction.

For FePO₄, O₂ evolution takes place 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. [27] and Rousse et al. [27] have shown that orthorhombic FePO₄ transforms irreversibly to trigonal FePO₄ 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 Fe²⁺PO₄ₓ and Fe²⁺PO₄ₓ was observed by Delacourt et al. [12] during LiₓFePO₄ (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 MnPO₄, the olivine phase is the lowest energy structure. Nonetheless, the critical temperature for the onset of O₂ evolution in non-equilibrium FePO₄ reduction is still much higher than that for MnPO₄.

From Fig. 2, we may also observe that initial reduction of FePO₄ evolves 0.1 moles of oxygen per mole of cathode, compared to 0.25 moles for initial reduction of MnPO₄. Hence, not only does MnPO₄ reduce at a much lower temperature than FePO₄, it also evolves 2.5 times the amount of O₂. Even at higher temperatures between 1100 °C and 1300 °C, FePO₄ only evolves 0.17 moles of oxygen per mole of cathode, significantly less than MnPO₄. This greater amount of O₂ evolved for MnPO₄ presents a significant safety hazard as O₂ released can ignite the organic electrolytes used in rechargeable Li batteries.

4. Discussion

Our results show that delithiated FePO₄ is inherently more thermally stable than MnPO₄, and the amount of O₂ evolved upon initial decomposition is also much less. The greater stability of FePO₄ over MnPO₄ may be explained through ligand field theory [28]. It is well-known that in an octahedral environment such as MO₆ in olivines, half-filled high-spin t₂g eg is a highly stable electronic configuration due to the exchange stabilization arising from the five parallel-spin electrons. We would therefore expect that Fe²⁺ and Mn²⁺, both of which have the high-spin t₂g eg half-filled configuration, to have greater stability as compared to Fe³⁺ and Mn³⁺ respectively. Indeed, there is a greater proportion of Mn³⁺ phases relative to Mn²⁺ in the Li–Mn–P–O phase diagram, whereas the situation is reversed in the case of Fe. Furthermore, LiₓMnPO₄ is stable over a much wider range of oxygen chemical potentials (−0.56 eV < μ₀₂ < −7.02 eV) than LiₓFePO₄ (−2.36 eV < μ₀₂ < −6.24 eV). A similar argument has been used to explain why the LiₓFePO₄ voltage is unusually low [2].

The key factor influencing the amount of O₂ 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 Fe³⁺ oxidation state leads to the presence of the mixed valence Fe(x)PO₄ₓ and Fe(x)PO₄ₓ phases, which results in a smaller amount of O₂ evolved. On the other hand, MnPO₄ immediately reduces to Mn₂P₂O₇ which has the Mn³⁺ oxidation state, resulting in significantly higher O₂ 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 O₂ 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 LiCoO₂ 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 FePO₄ and MnPO₄ 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 MnPO₄ reduces with substantial oxygen release at a much lower temperature than FePO₄. Hence, the Mn system may trade off its somewhat higher energy density with considerably lower safety. The difference in relative stabilities of FePO₄ and MnPO₄ may be explained by the competing phases present in the phase diagrams and relative stabilities of the M²⁺ and M³⁺ 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.
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References