Electrochemical Performance of LiMnPO$_4$ Synthesized with Off-Stoichiometry

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<th>Citation</th>
<th>Kang, Byoungwoo, and Gerbrand Ceder. Electrochemical Performance of LiMnPO$_4$ Synthesized with Off-Stoichiometry. Journal of The Electrochemical Society 157, no. 7 (2010): A808. © 2010 ECS - The Electrochemical Society</th>
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<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1149/1.3428454">http://dx.doi.org/10.1149/1.3428454</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>The Electrochemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Wed Mar 16 19:03:56 EDT 2016</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/79714">http://hdl.handle.net/1721.1/79714</a></td>
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The family of LiMPO₄ compounds is of interest as cathode materials for rechargeable lithium batteries. LiFePO₄ has been intensely studied and several techniques such as carbon coating, coating with a metallic conducting layer,¹ and doping with supervalent charge/discharge,¹⁰ or the high activation barrier for Li to cross the electronic conductivity.⁴ Although LiMnPO₄ shows a higher potential⁵-⁷ than LiFePO₄, the higher energy density of LiMnPO₄ can only be achieved at a very slow rate.⁸ Previous studies suggested several possible culprits for the poor activity: strong polarons,⁶ very poor electronic conductivity (2.7 × 10⁻³ S cm⁻¹ at 300°C),⁸ the instability of MnPO₄³⁻, the distortion of the Jahn–Teller active Mn¹⁴⁺,⁹ the large volumetric charge change with LiMnPO₄ and MnPO₄, lower charge/discharge,¹⁰ or the high activation barrier for Li to cross the surface.¹¹ Good electrochemical performance was recently observed for thin platelet carbon-coated LiMnPO₄ with a small particle size synthesized by a polyol process¹²,¹³ or a sol–gel process.¹⁴ In this paper, we report on an alternative way to create small particles of LiMnPO₄ with reasonable performance. The approach is similar to our recently developed approach to synthesize small LiFePO₄ particles through a simple solid-state reaction by starting with the proper off-stoichiometry of precursors.¹⁵ As this off-stoichiometric LiFePO₄ showed excellent rate performance, we applied the same strategy to LiMnPO₄.

**Experimental**

The materials with the nominal formula LiMn₀.₉P₀.₉₅O₄₋₀.₅ were synthesized from the appropriate mix of Li₂CO₃, MnC₂O₄·2H₂O, and NH₄H₂PO₄ using heat-treatments at 350°C for 10 h and at 700°C for 10 h under Ar or air atmosphere. Before heat-treatment at 350°C, the precursors were ballmilled in acetone with zirconia balls. The structure and morphology was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The X-ray patterns were obtained on a Rigaku diffractometer using Cu Kα radiation. The lattice parameters were determined by Rietveld refinement using the X’pert High Score Plus software. SEM was performed on a FEI Philips XL30 Field Emission Gun (FEG) Environmental Scanning Electron Microscopy (ESEM). The samples on the stainless holder were coated with gold/palladium to avoid charging effects.

Electrodes were prepared by manually mixing the active material, carbon (Super P from M.M.M.), and the binder (polyethylene-tetrafluoride) in a weight ratio of 80, 15, and 5%, respectively. The cells were assembled in an argon-filled glove box and tested on a Maccor 2200 operating in the galvanostatic mode using lithium metal as an anode, nonaqueous electrolyte [1 M LiPF₆ in ethyl carbonate/dimethyl carbonate (1:1) from Merck], and Celgard 2500 as a separator in a Swagelok-type cell. All cells were tested at room temperature. The loading density of electrodes was 3–5 mg cm⁻². The current density at 1C was based on a capacity of 170 mAh g⁻¹. All cell tests had 1 min open-circuit rest at the end of each charge and discharge.

**Results and Discussion**

**Characterization of the off-stoichiometric LiMnPO₄.**—Figure 1 shows the XRD pattern of LiMnPO₄ and LiMn₀.₉P₀.₉₅O₄₋₀.₅ synthesized at 700°C under Ar. The pattern in Fig. 1b indicates the formation of LiMnPO₄ despite the large off-stoichiometry in the starting materials. This result is similar to what is observed when off-stoichiometric LiFePO₄ is prepared. Rietveld refinement using LiMnPO₄ as the structural model gives lattice parameters of a = 10.4366(4) Å, b = 6.0994(2) Å, and c = 4.7430(2) Å for the off-stoichiometric sample and a = 10.4367(5) Å, b = 6.0991(3) Å, and c = 4.7436(2) Å for the stoichiometric sample. These values are consistent with previously reported values,⁶ confirming that the crystalline phase in the off-stoichiometric sample is close to stoichiometric LiMnPO₄.

The crystallite size obtained from the XRD pattern is ~340 Å for the off-stoichiometric sample and ~337 Å for the stoicho-
metric sample. The SEM images in Fig. 2 show a spherelike morphology and particle size less than 50 nm for both samples.

Analysis of the secondary-phase components.— Considering the significant deviation from the stoichiometric composition, the off-stoichiometric sample should have secondary phases present as LiMPO₄ cannot accommodate such a large compositional deviation. For LiFePO₄, Wagemaker et al.¹⁶ and Meethong et al.¹⁷ reported that a single phase could only be retained for less than 5 mol % deviation from stoichiometry in the overall sample.

Assuming that a near stoichiometric LiMnPO₄ is formed in the off-stoichiometric sample, the balance of products should be phases containing Li–P–O. According to the Li–Mn–P–O phase diagram obtained through first-principles calculations, the off-stoichiometric material forms either Li₃P₂O₇, Li₄P₂O₇, Li₃MnPO₄, or a combination of these as secondary phases depending on the oxidation conditions and the range of composition in which these phases exist.¹⁸ Although the first-principles calculations assume stoichiometric compounds, it is possible that these secondary phases are not stoichiometric, particularly given their amorphous or poorly crystallized nature. We indeed see some of these secondary phases when the material is fired at 700°C under air. Figure 3 indicates that crystalline Li₃PO₄ and Li₃P₂O₇ appear in the XRD pattern, whereas the LiMnPO₄ phase is unchanged. Rietveld refinement of the air-synthesized off-stoichiometric sample gives the weight percentage of LiMnPO₄ as 95 wt %.

The amorphous nature of the secondary phases when synthesis is performed under Ar can be understood by the fact that phosphorus, like silicon or boron, is also a network former. Alkali, earth alkali, or transition-metal oxides act as network modifiers in silicon, boron, and phosphate glasses. Therefore, the phosphate network in the glasses is likely to depend on manganese oxide contents. As the manganese oxide content increases, the phosphate network changes from a chain or ring structure, such as in metaphosphates (PO₃⁻), through the diametric pyrophosphate (P₂O₇²⁻), to the isolated orthophosphate (PO₄³⁻).²⁰,²¹ Hence, a high Mn to P ratio such as in

![Figure 2](image2.png)

**Figure 2.** SEM images of (a) LiMnPO₄ and (b) LiM₃PO₄PO₃O₄ synthesized at 700°C under Ar.

LiMnPO₄ leads to a crystalline compound, whereas under the same conditions, the secondary phase with a low Mn to P ratio may be noncrystalline. The crystallinity of these phases also depends on synthesis conditions²¹,²² such as temperature and atmosphere. The poorly crystallized phase induced by the off-stoichiometry is likely to be responsible for the small particle size. As stoichiometric LiMnPO₄ forms, it rejects the balance of composition into a secondary phase, which sits at the surface and between the grains of LiMnPO₄. A similar observation was made in off-stoichiometric LiFePO₄.²³ Possibly, this secondary phase prevents grain growth by limiting the diffusion between particles or grains similar to the role of carbon in carbon-coated LiFePO₄ compound²⁴–²⁶ or by reducing the surface energy of the material.²⁷

Electrochemical performance.— The theoretical capacity of stoichiometric LiMnPO₄ is 171 mAh/g. The theoretical capacity of the off-stoichiometric sample is more difficult to assess. If we assume that the LiM₃PO₄PO₃O₄−δ sample consists of LiMnPO₄ and a phase with composition Li₃P₂O₇, the theoretical capacity would be 166 mAh/g. Using, however, the refined phase fractions from the sample synthesized at 700°C in air, the theoretical capacity would be 162 mAh/g, assuming that only the LiMnPO₄ fraction is active. The voltage profiles of the stoichiometric and the off-stoichiometric samples at C/20 are shown in Fig. 4. The off-stoichiometric sample (Fig. 4b) shows a flat potential around 4.15 V vs Li/Li⁺, which is the typical redox potential of Mn²⁺/Mn⁴⁺ in the olivine structure²³ and achieves 145 mAh/g (87–89% of theoretical capacity) in the constant current mode for both charge and discharge. However, the stoichiometric sample in Fig. 4a shows a sloping voltage profile with only ~80 mAh/g capacity at the same rate.

Figure 5 shows the capacity retention of the off-stoichiometric and stoichiometric samples at 1C rate. Both materials show good capacity retention with cycling. The off-stoichiometric sample achieves 65 mAh/g at 1C, about twice the capacity of LiMnPO₄. The capacity of the off-stoichiometric sample at 1C is similar to that of the stoichiometric sample at C/20, indicating a remarkable improvement of rate capability by creating LiMnPO₄ in an off-stoichiometric sample.

![Figure 3](image3.png)

**Figure 3.** (Color online) XRD pattern of LiM₃PO₄PO₃O₄−δ synthesized at 700°C under air. LiMnPO₄, Li₄P₂O₇, and Li₃P₂O₇ are present.

![Figure 4](image4.png)

**Figure 4.** (Color online) (a) Voltage profiles of LiMnPO₄ at C/20 and (b) LiM₃PO₄PO₃O₄−δ at C/20.
The discharge profile of LiFe0.9P0.95O4−δ and LiMn0.9P0.95O4−δ at 2C are compared in Fig. 7. Although LiFe0.9P0.95O4−δ shows a flat discharge profile at 3.4 V, LiMn0.9P0.95O4−δ shows a clear nucleation barrier and a sloping voltage profile, indicating that the two materials may have fundamentally different transformation kinetics.

Figure 6. (Color online) Rate capability of LiMn0.9P0.95O4−δ synthesized at 700°C under Ar. The cell was charged at C/20 and held at 4.8 V until the current reached C/100, and then discharged at various rates. The discharge test at 2C was the first cycle. The sequence of the discharge tests: 2C → C/10 → 1C → C/5. The voltage window is 3.0–4.8 V.

Figure 7. (Color online) Comparison of the discharge behavior of LiMn0.9P0.95O4−δ and LiFe0.9P0.95O4−δ. Both materials were discharged at 2C. The LiMnPO4 data are the same as in Fig. 6. The off-stoichiometric LiFePO4 was charged at C/5 and held at 4.3 V until the current reached C/20.

The discharge profile of LiFe0.9P0.95O4−δ and LiMn0.9P0.95O4−δ at 2C are compared in Fig. 7. Although LiFe0.9P0.95O4−δ shows a flat discharge profile at 3.4 V, LiMn0.9P0.95O4−δ shows a clear nucleation barrier and a sloping voltage profile, indicating that the two materials may have fundamentally different transformation kinetics.

Discussion

LiMnPO4 shows a rather limited electrochemical activity even with a small particle size obtained by a variety of processes.6,11 Even at a very low rate such as C/100 or C/20, the capacity is well below the theoretical capacity. As in LiFePO4, creating a Mn/P 2:1 deficiency improves the rate capability, obtaining up to 100 mAh/g at 2C. Although the small particle size likely contributes to the enhanced rate capability, it is not the only factor with comparable particle size6,12 and the stoichiometric samples achieve less capacity at 1C than LiMnPO4 created in our off-stoichiometric sample.

The improvement of the rate capability using off-stoichiometry was not as substantial for LiMnPO4 as that observed in LiFePO4. This result could point at fundamentally different kinetics of the two compounds. Unfortunately, no precise model exists for the kinetics of phase transition in LiFePO4 or LiMnPO4. The voltage profiles of LiFePO4 and LiMnPO4 also point at a substantial difference between the two materials. The LiFePO4 compound shows a flat potential, whereas a sloping voltage12,15 is observed in LiMnPO4. The sloping voltage profile can arise from several factors. Gaberscek et al.30 claims that the sloping voltage arises from transport limitations in the electrode, not from the material. However, formulating the electrode with 65 wt % carbon (Fig. 8) to facilitate electron transfer did not lead to any significant im-
and discharged in constant current mode. The loading density of the material itself is rate-limiting. This evidence, together with the different benefits in rate capability from reducing its loading density in the LiMnPO₄ synthesized from an off-stoichiometric mixture has improved electrochemical performance over stoichiometric samples: 145 mAh/g discharge capacity at C/10 and ~100 mAh/g at 2C after a CCCV charge mode. The capacity retention at 1C charge/ discharge was excellent without degradation of the capacity for 50 cycles. Unlike LiFeO₃PO₃O₆, the LiMnP₀₄ compound shows less benefits in rate capability from reducing its loading density in the electrode by increasing the carbon content, indicating that the material itself is rate-limiting. This evidence, together with the different shape of the overpotential between LiFePO₄ and LiMnP₀₄ points at fundamentally different transformation kinetics in the two materials.

**Conclusion**

We synthesized LiMnP₀₄ with small particles using the proper off-stoichiometry to create a poorly crystallized second phase. LiMnP₀₄ synthesized from an off-stoichiometric mixture has improved electrochemical performance over stoichiometric samples: 145 mAh/g discharge capacity at C/10 and ~100 mAh/g at 2C after a CCCV charge mode. The capacity retention at 1C charge/discharge was excellent without degradation of the capacity for 50 cycles. Unlike LiFeO₃PO₃O₆, the LiMnP₀₄ compound shows less benefits in rate capability from reducing its loading density in the electrode by increasing the carbon content, indicating that the material itself is rate-limiting. This evidence, together with the different shape of the overpotential between LiFePO₄ and LiMnP₀₄ points at fundamentally different transformation kinetics in the two materials.

**Acknowledgment**

This work was supported by the BATT program under contract no. DE-AC02-05CH1123 (subcontract no. PO6806960) and by the U.S. National Science Foundation through the Materials Research Science and Engineering Centers program under contract no. DMR-0819762.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

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