

High Throughput Electrochemical Observation of Structural Phase Changes in LiFe_{1-x}Mn_xPO₄ during Charge and Discharge

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Electrochemical lithium extraction and insertion in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ has been investigated by high throughput cyclic voltammetry on an array of samples with different degrees of carbon coating to assist electron transfer. A linear decrease in the capacity was observed with an increase in the value of x and was explained by a gradual loss of electronic conductivity due to the manganese substituent. Slow scan voltammograms show differences in peak shapes corresponding to a heterogeneous (two-phase) reaction in LiFePO₄ and a homogeneous (one-phase) reaction of iron in LiFe_{0.2}Mn_{0.8}PO₄, illustrating a general interpretation of voltammograms to differentiate these mechanisms.

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High throughput techniques have been developed by many groups as methods of rapidly screening potential lithium battery electrodes.^{1,2} This work employs the postsynthesis array transfer (PoSAT) high throughput method^{3,4} in the study of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples with various degrees of carbon coating produced by sucrose pyrolysis.⁵

LiFePO₄ is of great interest as a safe, environmentally acceptable positive electrode for lithium-ion batteries but suffers from a low intrinsic electronic conductivity.^{6,7} Its properties may be considerably enhanced by doping the material or by applying a conducting carbon coating to the particles. Several authors have successfully introduced pyrolytic carbon from sucrose⁸ and other precursors after synthesis as a means of enhancing the surface conductivity and therefore the rate performance of LiFePO4. A synthesis method combining the carbon coating step with a pyrolytic sol-gel synthesis of LiFePO₄ (with optional doping) from a mixed salt solution precursor has been recently investigated in this laboratory.⁴ In this case, sucrose also acted as a viscosity enhancing additive to suppress the crystal growth of individual precursor components during the initial drying process, suppressing elemental segregation before the pyrolysis step. A relatively low calcination temperature was found to be sufficient to produce the required phase without any solid-state mixing or grinding. Results of galvanostatic cycling showed state-ofthe-art values for capacity and rate performance.

Other systems with the same structure as LiFePO_4 that have also been studied include $\text{LiCoPO}_4^{,9,10}$ $\text{LiNiPO}_4^{,9}$ and $\text{LiMnPO}_4^{,6}$ One of the most extensively investigated of these is LiMnPO₄, which gives a higher voltage than LiFePO₄ with approximately the same capacity and therefore has a higher theoretical energy density. However, this material has extremely low conductivity, and the reported electrochemical performance has been poor. In the initial work by Padhi et al., a capacity of only 6 mAh g^{-1} was reported,⁶ and the capacity was found to linearly decrease with the value of x in $LiFe_{1-r}Mn_rPO_4$ in Padhi et al.⁶ and in Yao et al.¹¹ An improved performance of up to 160 mAh g⁻¹ has been reported at slow rates (C/100) for some preparations that form extremely small particles.^{12,13} A detailed study of this material by Yamada et al.¹⁴ demonstrated 160 mAh g^{-1} for the composition LiMn_{0.6}Fe_{0.4}PO₄ at slow rates and resolved the reaction mechanism according to a twophase charge-discharge reaction in LiFePO₄ moving to a one-phase behavior on the substitution of Fe for Mn.^{14,15} Further work by Kobayashi et al. has shown a shift in the redox potential of Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} as the value of x in $LiFe_{1-x}Mn_xPO_4$ is

altered. 16 This shift was attributed to the inductive effect in the M–O–P bonding, increasing the ionic character of the transition-metal atoms.

The aims of the present work are to assess the viability of our sucrose-based preparation in the synthesis of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ over the whole composition range, to demonstrate the use of the PoSAT high throughput method applied to a complex electrochemical system with electrochemical properties that change with composition, to investigate the effect of increasing levels of carbon coating to compensate for the decrease in electronic conductivity on substitution of Mn for Fe in LiFePO₄, and to investigate how the change in reaction mechanism affects the electrochemical response in high throughput cyclic voltammetry.

Experimental

PoSAT array preparation .- Two 500 mL solutions were prepared, the first containing 0.625 M of LiCH₃COO·2H₂O (Aldrich), Fe(NO₃)₃·9H₂O (Aldrich), and H₃PO₄ (85 wt %, Aldrich) and the second containing 0.4 M LiCH₃COO·2H₂O (Aldrich), Mn(CH₃COO)₂·4H₂O (Aldrich), and H₃PO₄ (85 wt %, Aldrich). Aliquots of the two solutions were mixed down the rows of an array of quartz tubes so that each row contained a different value of x in $LiFe_{1-x}Mn_xPO_4$ (x = 0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9, 1). A 100 mL solution of 2 M sucrose was then prepared and added in different amounts to each column so that from left to right each column contained a sucrose-to-phosphate ratio (SPR) of 0.10, 0.15, 0.2, 0.22, 0.24, 0.27, 0.30, and 0.35. These solutions were then agitated using a Fischer "Whirlimix" vortex mixer to ensure homogeneity before being placed in an oven at 70°C for 12 h to remove the water. The array of precursor solids was then calcined in an argon atmosphere at 700°C using a large bore (80 mm diameter) tube furnace (Lenton). After cooling, the products were crushed to a powder using a glass rod attached to a drill. Composite electrode preparation began by adding two inks, 4% poly(vinylidene fluoride)-cohexafluoropropylene (PVDF-HFP, Aldrich) and 4% acetylene black (AB, Shawinigan, Chevron Phillips Chemical Co. LP) in cyclopentanone (CP), to the active material powders with five 1 mm zirconia beads placed in each tube. The inks were added to give a final mass ratio of 10% PVDF-HFP, 25% AB, and 65% active material and were then mixed using the vortex mixer. Then, 14 µL aliquots of each ink were deposited onto the appropriate position on the array of aluminum current collectors and spread across the surface to form an even film of ink. At the same time, a 40 µL sample of each ink was deposited onto a second array of alumina microcrucibles for a thermogravimetric analysis, as detailed below. The CP was evaporated from both arrays at room temperature before drying at 80°C followed by evacuation. The samples on both arrays were then accurately weighed using a balance with a digital output for automated recording.

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Figure 1. XRD pattern for products formed from selected samples. The SPR used in this column was 0.35. The value of *x* in LiFe_{1-x}Mn_xPO₄ is shown. Also shown are the standard measurements of (\bullet) LiFePO₄⁵ and (\times) LiMnPO₄¹⁹

Determination of active masses by thermogravimetric analysis.— The array of samples deposited in alumina microcrucibles was heated to 800°C in air to burn off carbon and the binder. After allowing the array to cool to room temperature, each sample was weighed again to accurately measure the mass of the fully oxidized active material. The percentage of active materials in each element of the electrode array was calculated by assuming that the compositions of samples were identical with corresponding positions in the two arrays and by considering any weight gain from oxidation of LiFePO₄.

High throughput XRD.— For X-ray phase analysis, we used a combinatorial X-ray diffractometer (Bruker AXS C2, Cu K α radiation) that automatically records X-ray patterns of the 64 composite electrodes using a general area diffraction detection system (GADDS). The scan time was 20 min for each sample, i.e., about 24 h to record diffraction patterns across the whole array.

High throughput electrochemical evaluation of 64 electrode arrays.— The cell construction and instrumentation has been reported previously.¹⁷ The electrode array was cycled between 2.5 and 4.5 V vs Li at the following scan rates: 0.05, 0.1, 0.4, 0.8, and 1.6 mV s⁻¹.

Bulk sample preparation.— Several bulk preparations were also undertaken for comparison. The same synthesis method was used for the array except that the volumes were scaled up to give a total volume of 20 mL. LiFePO₄, LiFe_{0.7}Mn_{0.3}PO₄, LiFe_{0.5}Mn_{0.5}PO₄, and LiMnPO₄ were all prepared with an SPR of 0.25. These solutions were then dried and placed in ceramic crucibles and were heated under the same conditions. The active materials were then prepared into composite poly(tetrafluoroethylene)-bound films, as described previously, and were galvanostatically cycled at various C-rates between 2 and 4.5 V.

Results and Discussion

XRD patterns.— The X-ray diffraction (XRD) patterns recorded for the array indicated the minimum SPR required to form the olivine phase by ensuring full reduction of Fe³⁺ from the iron precursor. Accordingly, a minimum SPR of 0.15 was required for the ironrich (x < 0.5) samples, whereas an SPR of 0.10 was sufficient for samples with x > 0.5.

Figure 1 shows XRD patterns for materials formed using 0.35 SPR. Selected XRD patterns shown in Fig. 1 indicate that as x



Figure 2. Unit cell volume of $LiFe_{1-r}Mn_rPO_4$.

increased from 0 to 1, there is a gradual shifting of the peak position related to a change in the unit cell parameters. To quantify this effect, the peaks were indexed and the unit cell volume was calculated; the results are shown in Fig. 2.

The linear increase in the unit cell volume with x is seen in Fig. 2, indicating Vegard's shift and suggesting a solid solution mixing of the iron and manganese. Yamada et al.¹⁴ and Padhi et al.⁶ reported a similar result, with slightly different minimum cell volumes of 291–292 A³. The discrepancy is attributed to the problems of scatter due to the GADDS.

High throughput electrochemical measurements.— The cyclic voltammograms (CVs) (scan rate 0.05 mV s⁻¹) for the array are shown in Fig. 3. Significant currents were not detected for SPR values less than 0.15. For the high iron-content samples (x < 0.5), this is assumed to be due to the phase impurity, as detected in XRD, whereas for x > 0.5, the low currents were attributed to insufficient electronic conductivity.¹⁸ The highest currents were observed for samples containing high amounts of carbon (prepared using an SPR > 0.2) and low amounts of Mn ($x \le 0.5$). At high manganese contents (x > 0.5), a larger SPR was required to obtain significant currents even though the correct phase had formed.

The role of sucrose in this preparation has three functions: It suppresses the crystallization of the salts during drying, acts to reduce Fe(III) to Fe(II) during synthesis, and finally forms a pyrolyzed carbon residue on the surface of the product. In principle, the threshold amount of sucrose required for a percolating carbon coating can vary with Fe(III) and nitrate contents. However, the XRD data confirmed that all materials prepared at SPR values greater than 0.15 were pure phases, and the electrochemical results showed percolation of carbon even in the sample formed from the precursor with the highest Fe(III) nitrate. Materials prepared with lower amounts of Fe(III) nitrate should contain carbon well over the percolation threshold.

The dependence of specific capacity on SPR is shown in Fig. 4, which can be described as a set of percolation profiles showing the effect of an increase in the supply of electrons to the olivine particles via the carbon matrix. The effect of manganese on the conductivity can be seen as a reduction in the maximum capacity as *x* increases in LiFe_{1-x}Mn_xPO₄, as well as an increase in the amount of sucrose required to give the characteristic increase in capacity. This result cannot be reconciled with a carbon percolation effect because the latter should not depend on the conductivity of the olivine. Instead, we propose that the effect is due to the increasing surface coverage of carbon that would be required to make an effective contact to a material of decreasing conductivity. As a reference, the conductivity of LiFePO₄ is reported by Delacourt et al.¹⁸ as ~1.5



Figure 3. CVs (0.05 mV s^{-1}) for the 64 LiFe_{1-x}Mn_xPO₄ materials.

 $\times 10^{-9}$ S cm⁻¹ at 25°C, whereas LiMnPO₄ is ~3 $\times 10^{-9}$ S cm⁻¹ at 300°C. Using the quoted activation energy of 1.4 eV, we estimate a conductivity of 1.2×10^{-20} S cm⁻¹ at 25°C.

Figure 5 compares data from samples with an SPR value of 0.27, which is more than sufficient to form a percolating carbon network in each case. It shows a remarkably linear trend of decreasing capacity with Mn content, from 160 to 10 mAh g^{-1} , with *x* changing from 0 to 1. For comparison and validation of the high throughput method, a series of points recorded using a standard small cell test method from materials prepared in the bulk is shown. These points confirm the results seen using the high throughput method.

Expanded versions of the CVs at various scan rates are shown in Fig. 6 for selected electrodes on the array. The CVs in Fig. 6 show charge and discharge peaks around 3.5 and 4.0 V for Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} , respectively, with varying peak heights dependent on the degree of manganese substitution. The ratio between the Mn and Fe peak heights corresponds to the composition. This is confirmed in Fig. 7, where a linear trend is seen, which has a gradient of approximately 1, and intercepts the axis at the origin.

A change in the Fe^{2+}/Fe^{3+} peak shape with increased substitution of Mn is also noted in Fig. 6 and explained in Fig. 8 with schematic



Figure 4. Specific capacity vs sucrose:LiFe_{1-x}Mn_xPO₄ ratio for x values 0 (- \blacksquare -), 0.3 (- \blacktriangle -), 0.7 (- \bigstar -), and 1 (- \boxdot -) to investigate the percolation threshold of these materials. These capacities were calculated from the CVs shown in Fig. 3.



Figure 5. Specific capacity vs *x* in LiFe_{1-x}Mn_xPO₄ measured using standard battery techniques (SPR 0.27) (\blacktriangle) and combinatorial techniques (SPR 0.3) (\blacksquare). Also shown is a line of best fit for the combinatorial measurements (—). The standard materials were cycled between 2.5 and 4.5 V under galvano-static control at a rate of C/10.6. The CVs used to make the combinatorial measurements were cycled between 2.5 and 4.5 V at a scan rate of 0.05 mV s⁻¹; this equates to an approximate rate of C/11.1.



Figure 6. (Color online) LiFe_{1-x}Mn_xPO₄ CVs normalized by scan rate and shown for four different scan rates: 0.05 (black), 0.2 (red), 0.4 (green), and 0.8 (blue) mV s⁻¹. The SPR used for these preparations was 0.35.

CVs for one- and two-phase insertion reactions. The one-phase reaction shows each redox reaction as a bell-shaped peak according to the lattice gas model of insertion/extraction in a solid solution (Fig. 8a), with some displacements due to kinetic and diffusional overpotentials as in Fig. 8b. The two-phase reaction shows a rapid current increase just beyond the equilibrium potential in each direction to a peak followed by a decay determined by mass transport processes as in Fig. 8c. The first CV, for LiFePO₄, indicates a phase change as expected. In LiFe_{0.8}Mn_{0.2}PO₄, the anodic peak at 3.6 V is similar to the pure material except for the small peak due to the manganese

reaction near 4 V. The cathodic peak at 3.3 V, however, shows a shoulder at 3.6 V, characteristic of a one-phase reaction before the main peak for the two-phase reaction, which can be extrapolated back to an onset of 3.5 V. (The peak position depends on a scan rate and should not be used as a measure of the phase-change potential. Therefore, the onset potential that does not depend on the scan rate should be used.) These results are consistent with Yamada's phase diagram,¹⁴ which we have reproduced in Fig. 9 to show the single-phase region in the charged materials containing manganese. The anodic reaction, heterogeneous lithium extraction with phase change



Figure 7. The linear relationship of the ratio of peak heights for Fe $[I_p (Fe)]$ and Mn $[I_p (Mn)]$ from CVs recorded at 0.05 mV s⁻¹ and the ratio of composition. This relationship is shown for both the charge (- \blacksquare -) and discharge (- \bullet -) peaks.

is shown by the dotted arrow and followed by homogeneous insertion into a single phase, which is inconspicuous due to the similar decay transients in both cases. The cathodic reaction, following the arrows in reverse, shows an initial homogeneous reaction followed by a sharp increase in current due to a phase nucleation at y = 0.6; the bold arrow indicates the heterogeneous two-phase insertion at 3.5 V.

According to the phase diagram, the manganese redox reactions should all be expected to follow a two-phase mechanism. Conversely, the proportion of the respective phase behaviors for the iron reactions should change with *x* until 60% of Fe is replaced by Mn, whereupon the charge from Fe^{2+}/Fe^{3+} is extracted by a complete one-phase reaction.



Figure 9. (Color online) A schematic phase diagram of the $\text{Li}_{v}(\text{Mn}_{1-x}\text{Fe}_{x})\text{PO}_{4}$ ($0 \le x, y \le 1$) system according to Yamada et al.¹⁴

Using the information from Fig. 8 and 9, the CVs from the array can be interpreted to observe these changes in the reaction mechanism, as shown in Fig. 10. This shows selected voltammograms for $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples superimposed on simulations based on linear combinations of the voltammograms of the end members LiFePO_4 and LiMnPO_4 , both showing a two-phase behavior. The comparison between the data and simulations emphasizes the changes toward the one-phase behavior.

Figure 10 shows that iron oxidation always begins by the twophase mechanism with an approximately constant onset potential of 3.5 V. However, the reduction of iron is increasingly pre-empted by the one-phase reaction on substitution with manganese. The manganese reduction peaks also concur with the phase diagram, showing relatively sharp transients before the peaks. The surprising result is





that a substantial degree of iron substitution of manganese causes a pre-emption of the oxidation of manganese with an initially shallow transient characteristic of a one-phase insertion reaction instead of a two-phase reaction with a composition dependent equilibrium potential, as reported by Yamada. A comparison with Yamada's study also shows a much lower separation between the anodic and cathodic peaks for manganese, especially close to x = 1, where our carbon coating and possibly a smaller particle size would have given the greatest benefit.

Conclusions

The synthesis of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ with varying degrees of carbon coating has been successfully demonstrated using the sucrose solgel method. A phase pure material was obtained from each case when the appropriate amount of sucrose was used, and a larger carbon coating was found to improve the capacity according to an increased contact area with the particles. This work has shown that $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ reacts with a heterogeneous two-phase mechanism at the extremes of charge and discharge but tends toward a homogeneous one-phase behavior in the intermediate region. The analysis also illustrates a general method of interpretation of results of cyclic voltammetry to complement phase information gained by diffraction methods.

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Figure 10. $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ CVs (exact compositions indicated on the graph). To indicate the change in shape of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$, discharge peaks in the solid solution CVs were simulated by combining the CVs for the pure LiFePO₄ and LiMnPO₄ and by normalizing the peak heights of each according to the amount of Fe or Mn. Simulated CVs are shown by the dotted (----), and real CVs are shown in the solid (----).

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4.5

4.0

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