Combustion Synthesis of Nanoparticulate $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$)

Carbon Composites

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Abstract

A combustion synthesis technique was used to prepare nanoparticulate $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$)/carbon composites. Powders consisted of carbon-coated particles about 30 nm in diameter, which were partly agglomerated into larger secondary particles. The utilization of the active materials in lithium cells depended most strongly upon the post-treatment and the Mg content, and was not influenced by the amount of carbon. Best results were achieved with a hydrothermally treated $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4/\text{C}$ composite, which exhibited close to 50% utilization of the theoretical capacity at a C/2 discharge rate.

Introduction

LiMnPO_4 is of potential interest as a cathode material for lithium ion batteries. It is isostructural with the technologically important phospho-olivine LiFePO_4 , but discharges at a potential approximately 0.5V higher, resulting in a 15% increase in the theoretical specific energy. It has, however, proven challenging to obtain good electrochemical performances from this compound. The difficulties have been variously attributed to poor transport properties in either the bulk LiMnPO_4 or MnPO_4 phases,^{1,2} instability of the MnPO_4 phase itself,³ or surface effects.⁴ Currently, efforts to improve this material have focused on reduction of particle size to the nanoscale to ameliorate these issues. Methods used to make nanoparticulate LiMnPO_4 include low temperature synthesis,⁵ sol-gel techniques,^{6,7} and solvothermal methods.⁸ Carbon is generally added after preparation of the LiMnPO_4 phase to improve the poor electronic conductivity,⁹ and utilization in Li cells has been shown to scale strongly with the particle size of sol-gel prepared samples.¹⁰ Excellent results have recently been obtained using nanometric LiMnPO_4 prepared by a solvothermal process, in which particles were embedded in a carbon matrix.¹¹ Additionally, partial substitution of Mn with Mg has recently been shown to improve performance.¹² These results provide encouragement that LiMnPO_4 with good electrochemical properties can be prepared in spite of the difficulties mentioned above, provided that particle size is tightly controlled to minimize diffusion distances and there is intimate contact with carbon to ensure good electronic transport.

It was our intention in this work to investigate the feasibility of using a simple combustion technique to prepare electroactive $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4/\text{C}$ nanocomposites.

Such methods have been widely used to prepare nanoparticulate metal oxides,¹³ and recently considered for preparation of LiFePO_4 .¹⁴ We present our preliminary results as well as suggestions for further improvements.

Experimental

Materials Preparation

LiMnPO_4/C composites were prepared by combustion synthesis using citric acid (ACS, 99.5+%, Alfa Aesar) or glycine (Aldrich), LiNO_3 (lithium nitrate, Mallinckrodt) $\text{Mn}(\text{NO}_3)_2$, 45-50 wt. % in dilute nitric acid (manganese nitrate solution, Aldrich) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ammonium phosphate monobasic, Aldrich) precursors. Several different fuel/nitrate ratios were used, ranging from 0.4-1.0. For Mg-substituted materials, either a 9:1 or 8:2 molar mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) were used depending upon the desired stoichiometry. Approximately 1M solutions of the nitrate and phosphate precursors were prepared by dissolving them in water, and the desired amount of citric acid was then added. This solution was then poured or sprayed into a stainless steel beaker used as a reaction container, which was pre-heated on a hot plate. After evaporation of the water, the solution became viscous and started to foam. Subsequent auto-ignition of the precursors was accompanied by the evolution of a large volume of gaseous by-products. The self-propagating combustion was completed in a few minutes. The black powder obtained after combustion was collected, wet ball-milled with acetone for one hour, and heat-treated at 500- 700°C under a nitrogen atmosphere for varying lengths of time up to 5 hours. (Most materials were treated at 600°C for three hours.) Some samples were then treated hydrothermally in a 125 mL Parr Teflon-lined

stainless steel autoclave. For this, about 1.5 g of combusted sample was suspended in 80 mL of water. The autoclave was sealed and heated at 190 °C for 24 hours. The product was then filtered and dried for at least 6 hrs above 100°C.

Another set of samples was prepared hydrothermally, as described in reference 15. For one sample, 12 mL of polyethylene glycol (M.W. 1000) was used as a surfactant to reduce particle size as described in reference 16.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Philips X'Pert diffractometer equipped with an X'Celerator detector, using CuK α radiation ($\lambda=1.54178$ Å) over the range of $2\theta=10-70^\circ$. The GSAS/EXPGUI package was used to carry out Rietveld refinements of the X-ray powder diffraction patterns. The theoretical pattern of LiMnPO₄ shown in Figure 1 was constructing using PowderCell 2.4 by W. Kraus and G. Nolze (Federal Institute for Materials Research and Testing, Berlin, Germany). *Ex situ* XRD powder patterns were obtained on samples of electrodes removed from coin cells and covered with Kapton films to prevent reaction with atmospheric water.

Luvak, Boylston, MA performed carbon and hydrogen analyses, used to determine H/C ratios, on selected samples. The morphologies of the powders were studied by scanning electron microscopy (SEM) using a Zeiss Gemini Ultra-55. The transmission electron microscopy (TEM) study was performed using a JEOL 2100F, equipped with an energy-dispersive X-ray microanalysis system.

Raman spectra were obtained on composite powders using the integrated Raman microscope system “Labram” made by ISA Groupe Horiba. Particle size distributions

were measured with a Beckman Coulter LS230 laser diffraction particle size analyzer, with a measurement range between ~ 0.04 and $2000\ \mu\text{m}$. Samples were prepared by dispersing $0.10\ \text{g}$ of powder in $100\ \text{mL}$ distilled water, to which 5 drops of Darvan C was added; this mixture was then ultrasonicated for fifteen minutes.

Composite positive electrodes were prepared by thoroughly mixing the active material (75 wt.%) with Chevron acetylene black (8 wt.%), Timcal SFG-6 graphite (8 wt.%) and Kureha polyvinylidene fluoride (PVdF, 9 wt.%) dissolved in N-methylpyrrolidinone (NMP). The electrode slurries were then cast onto carbon-coated aluminum current collectors (Intelicoat Technologies) and dried for 24 h in air followed by 12 h in a vacuum oven at $120\ ^\circ\text{C}$. Cathodes with an area of $1.8\ \text{cm}^2$ were punched from the cast electrode and typically contained $2.5\text{--}4.8\ \text{mg}/\text{cm}^2$ active material. 2032 coin cells were assembled in a helium filled glove box using lithium metal foil (Chemetal) as the counter electrode and Celgard 3401 separators. Either 1 M LiPF_6 in 1:2 v/v ethylene carbonate/ dimethyl carbonate electrolyte solution or 1 M LiPF_6 in propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1:3 v/v/v) (both from Ferro) was used as the electrolytic solution. Cells were subjected to electrochemical cycling on a VMP3 multichannel potentiostat (Biologic). A constant current constant voltage (CCCV) protocol was used for charging to 4.3-4.4V (unless otherwise specified). After C/25 rate charging to the potential cutoff, the voltage was held until the current dropped to 25% of the initial value or 25 hours had passed. Discharges were carried out at various rates to 2.5V. For the purposes of this study, C-rate was defined as the current required to discharge the full theoretical capacity ($170\ \text{mAh}/\text{g}$ for LiMnPO_4) in one hour.

Results and Discussion

Synthesis and Physical Characterization

$\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1$, and 0.2) carbon composites prepared using citric acid as the fuel ranged from fully amorphous to partially crystalline after combustion. Heating improved the crystallinity, judging from the increases in peak intensities, with best results obtained after about 3 hours at 600°C . Heating at $500\text{--}600^\circ\text{C}$ for less than five hours did not result in grain growth, as evidenced by the lack of peak broadening in the XRD patterns. In a few samples, small amounts of Li_2CO_3 and/or Li_3PO_4 were observed, but otherwise no impurities were detected in the XRD experiments (with the exception of a sample prepared with a fuel/nitrate ratio of 0.4). Figure 1 shows a comparison of XRD patterns obtained on two LiMnPO_4 samples prepared hydrothermally, and one of a LiMnPO_4/C composite prepared by combustion synthesis prior to calcination (second from bottom). The theoretical pattern of LiMnPO_4 is also shown as a reference. The broad peaks in the pattern of the combusted material are evidence of the small primary particle size produced by this synthesis method, estimated to be about 30 nm using the Scherrer equation. In contrast, crystallite sizes for the hydrothermally prepared sample shown at the top of Figure 1 are about 140 nm in the a direction and 110 nm in the b direction, estimated from the peak widths of the 200 and 020 reflections, respectively. Use of a surfactant during the hydrothermal synthesis (pattern shown 2nd from the top in Figure 1) reduces these dimensions somewhat, to 100 and 85 nm .

It was also possible to prepare composites of Mg-substituted materials with low impurity levels using citric acid as the fuel. Figure 2 shows XRD patterns of typical

LiMnPO₄, LiMg_{0.1}Mn_{0.9}PO₄ and LiMg_{0.2}Mn_{0.8}PO₄ composites after three hours of calcination at 600°C, and Table 1 summarizes the unit cell parameters obtained from Rietveld refinement of these patterns. Results for materials made by combustion synthesis are similar to those previously reported on LiMnPO₄ made by conventional methods,¹⁷ and fell between those previously reported for hydrothermally prepared samples.^{12, 15}

The carbon contents and H/C ratios of the composites were highly variable and depended upon the preparation method with values ranging from about 6-21 % w/w and 0.023-0.089, respectively. Thermal and hydrothermal treatments reduced both of these compared to the as-made materials. H/C ratios were above 0.05 for the as-combusted materials, but decreased to between 0.023-0.05 after thermal treatment. Usually, higher fuel/nitrate ratios resulted in greater carbon contents and lower H/C ratios, although carbon contents were low for fuel/nitrate ratios of 0.75-0.8. The lower H/C ratios suggest that more complete combustion is achieved, consistent with rising reaction temperatures as the fuel content is increased.¹⁸ Although lower H/C ratios are correlated with improved structure and conductivity of the carbon, the high carbon content (>20%) of materials made with fuel:nitrate ratios above about 0.8 reduces the practical energy density of the composites. Thus, most samples for this study were prepared with intermediate fuel/nitrate ratios of 0.7-0.8, which generally resulted in lower carbon contents and acceptable H/C ratios.

In contrast to materials made by the citric acid combustion method, LiMnPO₄/C composites prepared using glycine as the fuel always contained significant amounts of Mn₂P₂O₇ and Li₃PO₄ impurities and had low carbon contents (<0.5%), no matter

what the fuel:nitrate or Li:Mn ratios were. Calcination did not reduce the amount of impurities. The electrochemical properties of these materials were poor, and they will not be discussed further here.

Figure 3 shows SEM images of typical powders produced by combustion synthesis. An image of a hydrothermally prepared sample is included for comparison. Particles of the latter have a plate-like morphology (Figure 3a), whereas combusted samples are made up of spherical particles (Figures 3b-f) approximately 30 nm across, consistent with the XRD data. These are heavily agglomerated and, in some portions of the samples, the primary particles appear to have fused together during the thermal treatment (this is especially evident in Figure 3e). In other parts of the samples, the primary particles appear to be well separated (e.g., Figure 3f). The particle morphologies and sizes were unaffected by the hydrothermal treatment (compare 3b and c to 3d and e) and did not change with Mg substitution.

Particle size analyses on several combusted samples prepared with differing fuel/nitrate ratios and calcined at 600°C for three hours all showed similar results. Particle size distributions were narrow, with 90% or more of particles between 1.5 and 2.3 μm in diameter and the majority about 2 μm across. Periods of ultrasonication longer than about 15 minutes resulted in a bimodal distribution, with a significant fraction of submicron sized particles produced. This suggests that the small primary particles observed in the SEM images are somewhat loosely aggregated into larger secondary particles, and that some of these agglomerates can be broken apart with moderate effort.

Figure 4a shows a high resolution TEM image of a $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ particle after

3 hours of calcination at 600°C. This sample contained 17.4% carbon and had a H/C ratio of 0.0347. The olivine structure is clearly observable, as is an amorphous layer of carbon approximately 5 nm thick on the particle surface. The Raman microprobe spectrum taken of the powder (Figure 4b) show broad bands at 1339 and 1577 cm^{-1} attributable to the D and G bands of the disordered carbon structure, respectively.¹⁹ The small peak at 943 cm^{-1} corresponds to a stretching mode of the PO_4^{3-} anion in the olivine phase.²⁰

Electrochemical Characterization

In general, utilization of the combusted olivine composites in lithium cells was less than predicted from the theoretical capacities even for low discharge currents and high charging voltage limits, but these varied considerably. There was no obvious correlation between carbon contents or the fuel/nitrate ratios used to prepare materials, and the delivered capacities or utilization. (Utilization is defined here as the percentage of theoretical capacity obtained in the composite; in other words, corrected for the carbon content. In contrast, specific capacities are reported per unit weight of composite, including the carbon). Higher carbon contents did not necessarily improve utilization, and gave low specific capacities, in part due to the large inert mass of the carbon. Likewise the H/C ratios of calcined samples (all of which were below 0.05) did not appear to influence the discharge properties. The electrochemical performances of materials not subjected to heat treatment were uniformly very poor; this is likely a consequence both of incomplete combustion of the carbon precursors, as evidenced by the high H/C ratios (above 0.05) and of the poor crystallinity of the olivine phase itself. These results indicate that there are multiple factors influencing the electrochemical behavior of the composites.

For many of the LiMnPO_4 and $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ materials, the discharge characteristics improved upon cycling, sometimes rather dramatically. Figure 5

shows the cycling behavior of a $\text{Li/LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ cell discharged at a C/25 rate as an example. The capacity nearly doubled after 68 cycles, and the voltage profile appears noticeably flatter, although there is still a sloping portion towards the end of discharge indicating that kinetic limitations remain. Utilization for this cell was still less than 1/3 of the available capacity, when corrected for the carbon content and the effect of the Mg substitution. The improvement upon cycling is a feature frequently seen in olivine/carbon composites and has been attributed to improved penetration of the electrolyte into particle interiors due to formation of cracks in the amorphous carbon layer.²¹

Lithium cells containing LiMnPO_4 composites made with a fuel/nitrate ratio of 0.8 as cathodes, exhibited an anomalous feature in their discharge profiles near 3.3V. The additional feature appeared during the first discharge (Figure 6) but disappeared after a few cycles. It is most readily observable in the derivative plots included to the right of each discharge profile in Figure 6. Although improvements in the electrochemical characteristics were still apparent upon cycling, as evidenced by the evolution of flatter voltage profiles, the capacity decreased upon cycling in contrast to LiMnPO_4 composites made with higher fuel/nitrate ratios (i.e., having higher carbon contents). This feature also dominates the voltage profiles of cells containing the uncalcined poorly crystalline LiMnPO_4/C composite cathodes (not shown). These observations suggest that the composites with relatively low carbon contents still contain an amorphous impurity that is electrochemically active but not reversible; this adds to the capacity initially, but its presence is undesirable because of the poor reversibility and low potential. The impurity levels, however, appear to be unaffected by increasing the calcination times at 600°C or by raising the temperature to 700°C (not shown). Hydrothermal treatment, in contrast, does remove the impurity, either by dissolving it in water or by promoting crystallization. The result is a higher discharge capacity initially and more stable cycling (Figure 6d). Interestingly, the amorphous

impurity was not observed in calcined composites having carbon contents above about 7 wt.%, suggesting a correlation between high carbon content and improved crystallinity.

The biggest influence on cathode utilization in lithium cells appears to be the level of Mg substitution in the olivine phase. Figure 7 shows rate capabilities of lithium cells containing calcined and hydrothermally treated LiMnPO_4 , $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$, and $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ carbon composites. For these experiments, separate cells were cycled until the capacities stabilized at the specified rate (all cells were charged galvanostatically at C/25 rate followed by a constant voltage step except for one cell charged and discharged at C/50, shown in Figure 7c). The best-performing material is $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4$, both in terms of specific capacity delivered (uncorrected for the carbon content) and in terms of utilization of the active phase. About 60% of the expected capacity was obtained at C/25 rate for this system. In contrast, utilization of the less highly substituted materials was lower, although $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ appears to be somewhat less rate-limited than LiMnPO_4 judging from the flatter discharge profiles. It is interesting to note that the hydrothermally treated $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ composite performed better than that shown in Figure 5, even though it contains much less carbon. Improvement in redox kinetics upon partial Mg substitution has previously been observed in hydrothermally prepared $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ compounds¹² and has been attributed to stabilization against strain associated with the Jahn-Teller distortion of Mn^{3+} ions in the delithiated phase as well as decreased volume changes upon cycling.

Mg substitution reduces the theoretical capacity from 170 mAh/g for LiMnPO_4 to 157 and 142 mAh/g for $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ and $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4$, respectively, but as seen above, improves the practical utilization. It also raises the average discharge potential at C/25 (Figure 8), which reflects the improved kinetics and/or a thermodynamic effect.

For the cell in Figure 7c, lowering the discharge rate to C/50 does not improve the utilization. Likewise, increasing the upper voltage limit to 4.5V rather than 4.4V vs. Li during charge increases the subsequent discharge capacity only slightly for these cells (results not shown). This suggests that a portion of each composite is, for all intents and purposes, not redox active. Another feature common to all the cells shown in Figure 7 is the relatively small decrease in delivered capacity when the current density is increased, indicating that the redox active portion has relatively good rate capability. It is reasonable to surmise that the redox active portions consist of the free carbon-coated nanoparticles like those pictured in Figures 3f and 4a, whereas fused agglomerates like those seen in Figure 3e may be inaccessible due to poor carbon coverage and increased diffusion pathlengths for lithium ions in the connected particles. Thus, improving the homogeneity of the carbon coverage and preventing agglomeration in which particles are fused together, are key to better electrochemical performances.

Cells made with $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ /carbon composites showed large coulombic inefficiencies on the first cycle, which decreased sharply on subsequent cycles. The first cycle efficiency (defined as $Q_{\text{discharge } 1}/Q_{\text{charge } 1}$) shows a strong inverse correlation with the carbon content in the composites, and a somewhat weaker one with the hydrogen content (Figure 9a and b). Inefficiencies did not necessarily increase as the upper potential limit was raised, suggesting that irreversible oxidation of electrolyte and/or current collector are not the main contributors. Instead, the side reactions are associated with the carbon, as has been previously observed.¹¹ The weak relationship with H content suggests that irreversible oxidation of residual functional groups on carbon may be partly responsible for the inefficiency. Another possible contribution comes from oxidation of the disordered carbon and concomitant intercalation of the PF_6^- anion. Partially reversible oxidative intercalation of PF_6^- into graphite is known to occur at potentials above about 4.5V vs. Li.^{22, 23} This process occurs at somewhat

lower potentials for disordered carbons and is much less reversible.²⁴ This indicates that the LiPF_6 electrolyte salt is partially consumed during the first charge. In configurations with minimal electrolytic solution, this may cause premature cell failure, but salt depletion did not occur in the cells tested for this study.

Ex situ powder XRD patterns were obtained on charged electrodes from disassembled cells covered with Kapton film to prevent reaction of the hygroscopic delithiated phase with atmospheric water.^{12, 25} These were consistent with the observations of coulombic inefficiencies on the first cycle (Figure 10). For these experiments, lithium cells containing $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ electrodes were charged to 4.4, 4.5, or 4.6V using a CCCV protocol. Although the coulometry suggested that the cathodes were anywhere from 65% to nearly 90% charged, the main phase discernible in all of the patterns is the original $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$. Weak peaks attributable to the delithiated phase, $\text{Li}_{0.1}\text{Mg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$, are barely detectable in the pattern of the electrode charged to 4.4V, but these become relatively stronger in the patterns of electrodes charged to higher voltages, indicating that the delithiation, although still not complete, has proceeded further. However, in cells charged to 4.5V, utilization upon subsequent discharge was only modestly better than for those charged to 4.4V, suggesting that not all of the delithiated phase produced in the cathode can be relithiated. The observation of delithiated material in the XRD patterns of electrodes taken from cells stopped at the end of discharge supports this observation (not shown). Thus, incomplete utilization in the cathode appears to be a function not only of inefficient charging due to competing reactions involving carbon, but also loss of some active material after charge.

Conclusions

The electrochemical properties of nanoparticulate $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$)/C composites are strongly dependent upon the degree of crystallinity and the

amount of Mg substitution in the olivine phase. Higher carbon contents do not necessarily improve utilization upon discharge, but do result in greater first cycle coulombic inefficiencies due to side reactions involving residual functional groups and, possibly, oxidative intercalation of PF_6^- anions. Because of this, and because the practical capacity is reduced, it is desirable to minimize the amount of carbon in the composites. Achieving better rate performance of the nanocomposites in lithium cells is dependent upon improving the homogeneity of the carbon coverage and preventing agglomeration of the nanoparticles.

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Tables

Table 1. Unit cell parameters of $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$) carbon composites.

<i>Formula</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>Cell volume, Å³</i>
LiMnPO_4	10.444	6.105(0)	4.744(0)	302.48
$\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$	10.427	6.093(0)	4.747(0)	301.59
$\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4$	10.389	6.071(0)	4.739(0)	298.90

Figure Captions

- 1) XRD patterns of LiMnPO_4 and LiMnPO_4/C materials. From top to bottom: hydrothermally prepared sample, sample prepared hydrothermally with a surfactant, LiMnPO_4/C composite prepared by combustion synthesis, and, at the bottom, the theoretical pattern. Expanded sections of the patterns showing the 002 and 020 reflections are shown to the right.
- 2) XRD patterns of $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$) carbon composites, taken after calcination for three hours at 600°C .
- 3) Scanning electron micrographs of a) a hydrothermally prepared sample of LiMnPO_4 , b) and c) LiMnPO_4 prepared by combustion synthesis and calcined for 3 hours at 600°C , d) and e), LiMnPO_4 prepared by combustion synthesis, calcined for 3 hours at 600°C and then hydrothermally treated, and f) $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ prepared by combustion synthesis, calcined for 3 hours at 600°C and hydrothermally treated.
- 4) a) High-resolution transmission electron micrograph of a $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ particle from a sample containing 17.4% carbon by weight. b) Raman spectrum of a $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4/\text{C}$ composite (17.4% C, H/C=0.0347).
- 5) Voltage profiles of a $\text{Li}/\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4/17.4\% \text{ C}$ cell discharged at C/25 rate ($0.027 \text{ mA}/\text{cm}^2$).
- 6) Voltage profiles of $\text{Li}/\text{LiMnPO}_4$ cells (left column) discharged at C/25 rates and the derivative plots of the discharges (right column). LiMnPO_4 samples were all prepared with fuel/nitrate ratios of 0.8 and contained about 7.3% carbon. They were subjected to heat or hydrothermal treatments after combustion as follows: a)

- 1 hour at 600°C, b) 3 hours at 600°C, c) 5 hours at 600°C, and d) 3 hours at 600°C followed by hydrothermal treatment as described in the text.
- 7) Rate capabilities of lithium cells containing a) $\text{LiMnPO}_4/7.3\% \text{ C}$, b) $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4/5.84\% \text{ C}$, and c) $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4/12.1\% \text{ C}$ composites. A rate of C/5 corresponds to a discharge current of 0.1 mA/cm^2 . Utilization (top x-axis) is corrected to account for carbon content, but specific capacity (bottom x-axis) is not.
  - 8) dQ/dV plots of discharge profiles (C/25 rate) of Li/LiMnPO₄, Li/LiMg_{0.1}Mn_{0.9}PO₄, and Li/LiMg_{0.2}Mn_{0.9}PO₄ cells. Positive electrode materials are the same as shown in Figure 7, and cells were cycled until capacities stabilized.
  - 9) First cycle coulombic efficiencies as a function of a) composite carbon content and b) composite hydrogen content for Li/LiMg_xMn_{1-x}PO₄ cells charged (using a CCCV protocol) and discharged at C/25 rate. The upper voltage limits used for the cells are indicated in the legend.
  - 10) a) Charge profiles of Li/LiMg_{0.1}Mn_{0.9}PO₄ cells, using different upper potential limits. Cells were charged at a C/25 rate to the limit and the voltage was then held until the current decayed to 1/100 of the initial value. b) *Ex situ* XRD patterns on electrodes recovered from the cells in 10a, covered with Kapton films to prevent reaction with atmospheric water. Cell components are marked with G (graphite) and Al, and peaks attributable to $\text{Li}_{0.1}\text{Mg}_{0.1}\text{Mn}_{0.9}\text{PO}_4$ are marked with an asterisk.

Figure 1.

Figure 2

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3

(a)

(b)

Figure 4

Figure 5

Figure 6

Figure 7. Rate capabilities of lithium cells containing a) $\text{LiMnPO}_4/7.3\%$ C, b) $\text{LiMg}_{0.1}\text{Mn}_{0.9}\text{PO}_4/5.84\%$ C, and c) $\text{LiMg}_{0.2}\text{Mn}_{0.8}\text{PO}_4/12.1\%$ C composites. A rate of C/5 corresponds to a discharge current of 0.1 mA/cm^2 . Utilization (top x-axis) is corrected to account for carbon content, but specific capacity (bottom x-axis) is not.

Figure 8

a)

b)

Figure 9

(a)

(b)

Figure 10