

Phospho-Olivine Cathodes for Lithium-Ion Batteries

by Arumugam Manthiram

Lithium ion batteries have revolutionized the portable electronics market and are being intensively pursued for hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications. Although the concept of rechargeable lithium batteries was initially demonstrated with a transition metal sulfide cathode TiS_2 in the early 1970s,¹ the poor cyclability and safety concerns of metallic lithium anodes, along with the limited cell voltage (< 2.5 V) of the chalcogenide cathodes, was an impediment to realize commercial rechargeable lithium batteries. The pioneering work of Goodenough's group on lithium-containing insertion oxide cathodes^{2,3}—such as layered LiCoO_2 and spinel LiMn_2O_4 , at the University of Oxford in the early 1980s, to increase the cell voltage to as high as 4 V vs Li/Li^+ along with the successful development of carbon anodes by Sony Corporation,⁴—made the present-day lithium ion battery technology (based on lithium insertion/extraction hosts as both anodes and

Nevertheless, significant progress is being made in recent years and spinel LiMn_2O_4 remains a serious contender for high power applications.

Although simple oxides such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 with highly oxidized redox couples ($\text{Co}^{3+/4+}$, $\text{Ni}^{3+/4+}$, $\text{Mn}^{3+/4+}$ respectively) were able to offer high cell voltages of ~ 4 V in lithium ion cells, they are prone to release oxygen from the lattice in the charged state at elevated temperatures due to the chemical instability of highly oxidized species such as Co^{4+} and Ni^{4+} . One way to overcome this problem is to work with lower-valent redox couples like $\text{Fe}^{2+/3+}$. However, a decrease in the oxidation state will raise the redox energy of the cathode and lower the cell voltage. Recognizing this and to keep the cost low, Manthiram and Goodenough^{6,7} focused on oxides containing polyanions such as XO_4^{2-} ($\text{X} = \text{S}, \text{Mo}, \text{W}$) as lithium insertion hosts in the 1980s while the Delmas group⁸ was also pursuing polyanion hosts

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Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries

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ABSTRACT

Reversible extraction of lithium from LiFePO_4 (triphylite) and insertion of lithium into FePO_4 at 3.5 V vs. lithium at 0.05 mA/cm² shows this material to be an excellent candidate for the cathode of a low-power, rechargeable lithium battery that is inexpensive, nontoxic, and environmentally benign. Electrochemical extraction was limited to ~ 0.6 Li/formula unit; but even with this restriction the specific capacity is 100 to 110 mAh/g. Complete extraction of lithium was performed chemically; it gave a new phase, FePO_4 , isostructural with heterosite, $\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4$. The FePO_4 framework of the ordered olivine LiFePO_4 is retained with minor displacive adjustments. Nevertheless the insertion/extraction reaction proceeds via a two-phase process, and a reversible loss in capacity with increasing current density appears to be associated with a diffusion-limited transfer of lithium across the two-phase interface. Electrochemical extraction of lithium from isostructural LiMPO_4 ($\text{M} = \text{Mn}, \text{Co}, \text{or Ni}$) with an LiClO_4 electrolyte was not possible; but successful extraction of lithium from $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ was accomplished with maximum oxidation of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ occurring at $x = 0.5$. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple was oxidized first at 3.5 V followed by oxidation of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ couple at 4.1 V vs. lithium. The Fe^{2+} - O - Mn^{2+} interactions appear to destabilize the Mn^{2+} level and stabilize the Fe^{2+} level so as to make the $\text{Mn}^{2+}/\text{Mn}^{3+}$ energy accessible.

cathodes) a commercial reality following the initial launch by Sony in the early 1990s. Although most of the lithium ion cells used in portable electronic devices such as cell phones and laptop computers are based on layered oxide cathodes containing cobalt and a carbon anode, the high cost and toxicity of cobalt as well as the chemical instability and safety concerns at deep charge arising from a significant overlap of the $\text{Co}^{3+/4+}$:3d band with the top of the O^{2-} :2p band⁵ prevent the use of cobalt-rich cathodes in large batteries for HEV and PHEV applications.

From cost and environmental points of view, cathodes based on elements like Mn and Fe will be desirable. In this regard, spinel LiMn_2O_4 is appealing, as Mn is inexpensive and environmentally benign, and the 3-dimensional spinel structure with a good structural stability supports high rate capability necessary for HEV and PHEV applications. However, spinel LiMn_2O_4 is plagued by severe capacity fade at elevated temperatures due to the dissolution of manganese from the spinel lattice and consequent attack of the carbon anode by the dissolved manganese, resulting in a rise in cell impedance.

during this time. Although the $\text{Fe}^{2+/3+}$ couple in a simple oxide like Fe_2O_3 would normally operate at a voltage of < 2.5 V vs. Li/Li^+ , surprisingly the polyanion-containing $\text{Fe}_2(\text{SO}_4)_3$ host was found to exhibit 3.6 V vs Li/Li^+ while both $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{WO}_4)_3$ were found to operate at 3.0 V vs Li/Li^+ (Fig. 1). These $\text{Fe}_2(\text{XO}_4)_3$ hosts have the Nasicon-related framework structures in which the FeO_6 octahedra share corners with the XO_4 tetrahedra, resulting in Fe-O-X-O-Fe linkages. The lack of direct Fe-Fe or Fe-O-Fe interaction results in poor electronic conductivity and low rate capability despite good lithium ion conduction in the Nasicon-based frameworks.

The remarkable increase in cell voltage on going from a simple oxide such as Fe_2O_3 to polyanion hosts like $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$ and a difference of 0.6 V between the isostructural $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$ polyanion hosts, all operating with the same $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, was attributed to the influence of inductive effect and consequent differences in the location of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox levels relative to the Li/Li^+ redox level⁷ as seen in Fig. 1. In the Nasicon-related $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$ hosts with corner-shared FeO_6 octahedra and XO_4 tetrahedra

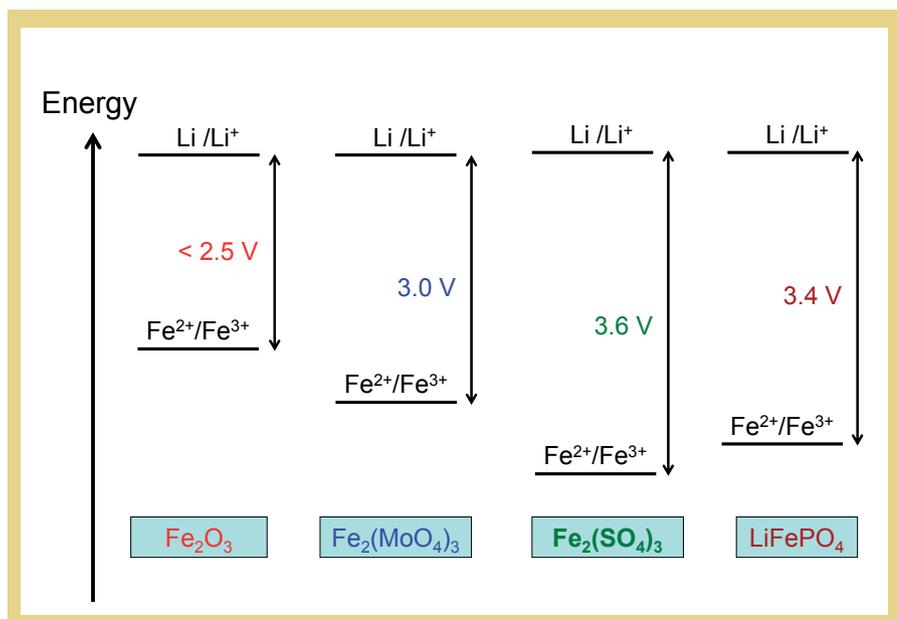


Fig. 1. Positions of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox energies relative to that of Li/Li^+ in various Fe-containing lithium insertion hosts and consequent changes in cell voltages, illustrating the role of polyanions.

and Fe-O-X-O-Fe (X = S, Mo, or W) linkage, the strength of the X-O bond can influence the Fe-O covalence and thereby the relative position of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox energy. The stronger the X-O bonding, the weaker is the Fe-O bonding and consequently the lower is the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox energy relative to that in a simple oxide like Fe_2O_3 . The net result is a higher cell voltage in going from Fe_2O_3 to $\text{Fe}_2(\text{MoO}_4)_3$ or $\text{Fe}_2(\text{SO}_4)_3$. Comparing $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$, a stronger S-O covalent bonding in $\text{Fe}_2(\text{SO}_4)_3$ compared to the Mo-O bonding in $\text{Fe}_2(\text{MoO}_4)_3$ leads to a weaker Fe-O covalence in $\text{Fe}_2(\text{SO}_4)_3$ compared to that in $\text{Fe}_2(\text{MoO}_4)_3$, resulting in a lowering of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox energy in $\text{Fe}_2(\text{SO}_4)_3$ compared to that in $\text{Fe}_2(\text{MoO}_4)_3$ and a consequent increase in cell voltage by 0.6 V on going from $\text{Fe}_2(\text{MoO}_4)_3$ (3.0 V vs Li/Li^+) to $\text{Fe}_2(\text{SO}_4)_3$ (3.6 V vs Li/Li^+). Thus, the replacement of simple O^{2-} ions by XO_4^{n-} polyanions was recognized to offer a viable approach to tune the position of redox levels in solids and consequently to realize higher cell voltages with chemically more stable lower valent redox couples like $\text{Fe}^{2+/3+}$. This approach was subsequently pursued with several phosphates with two graduate students at the University of Texas at Austin in the late 1980s and in 1990s.^{9,10}

Although the above findings in the late 1980s demonstrated an important fundamental concept in tuning the redox energies in solids, the cathode hosts pursued ($\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$) did not contain any lithium, so they could not be combined with the carbon anode in a lithium ion cell. With an establishment of the advantage of the inductive effect in polyanion containing hosts to raise the cell voltage,^{6,7,9} Goodenough's group, now relocated to the University of Texas at Austin, focused on lithium-containing polyanion hosts in the 1990s. This led to the identification in 1997 of LiFePO_4 crystallizing in the olivine structure (Fig. 2) as a facile lithium extraction/insertion host that could be combined with a carbon anode in lithium ion cells.¹¹ They also identified other olivine LiMPO_4 (M = Mn, Co, and Ni) as lithium insertion/extraction hosts. Since its identification as a potential cathode, LiFePO_4 has created intensive studies both from scientific and technological points of view and some of the more prominent follow-up activities are briefly discussed below.

The initial work was able to extract only < 0.7 lithium ions from LiFePO_4 even at very low current densities, which corresponds to a reversible capacity of < 120 mAh/g.¹¹ As the lithium extraction/insertion occurred by a two-phase mechanism with LiFePO_4 and FePO_4 as end members without much solid solubility, the limitation in capacity was attributed to the diffusion-limited transfer of lithium across the two-phase interface. Nevertheless, as Fe is abundant, inexpensive, and environmentally benign, olivine LiFePO_4 attracted immense interest as a potential cathode. Recognizing that the limited reversible capacity and low rate capability may be linked to the poor electronic conductivity arising from corner-shared FeO_6 octahedra and localized Fe^{2+} or Fe^{3+} ions, initial work following the identification of LiFePO_4 as a lithium insertion host concentrated on coating the LiFePO_4 powder with conductive carbon.¹² However, other early investigations^{13,14} suggested that both intimate contact with conductive carbon and particle size minimization are necessary to optimize electrochemical performance. LiFePO_4 is a one-dimensional lithium ion conductor

with the lithium ion diffusion occurring along edge-shared LiO_6 chains (*b* axis) as seen in Fig. 2. With a reduction in particle size and coating with conductive carbon, reversible capacity values of ~ 160 mAh/g could be realized.^{13,14}

Subsequently, doping of LiFePO_4 with polyvalent cations like Ti^{4+} , Zr^{4+} , and Nb^{5+} and organometallic precursors of the dopants was reported¹⁵ to increase the electronic conductivity by a factor of 10^8 . Although this report attracted significant interest, subsequent investigations suggested that the formation of a percolating nano-network of metallic iron phosphides may play a role in enhancing electronic conductivity.¹⁶

Recognition of the importance of both the decrease in particle size and improvement in electronic conductivity has also generated a flurry of activities on the solution-based synthesis of LiFePO_4 to minimize the particle size and on coating the LiFePO_4 particles with conductive species such as carbon and conducting polymers.¹⁷⁻²² Among them, hydrothermal synthesis^{17,18} has been particularly appealing, and Sud-Chimie Inc. is currently engaged in the scale up of this process to produce large quantities of LiFePO_4 for commercial cells. More recently, microwave-assisted hydrothermal and solvothermal approaches have been found to offer single crystal LiFePO_4 with high crystallinity at significantly low temperatures of 230-300°C in a relatively short reaction time of

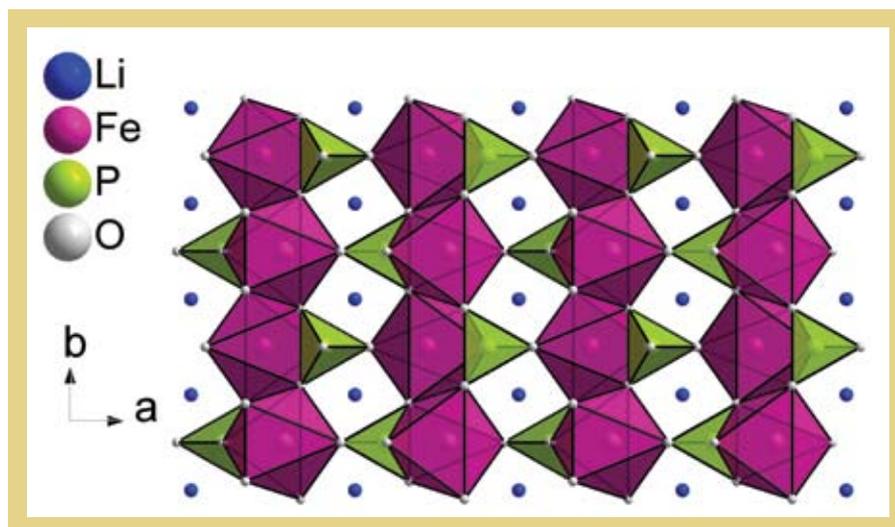


Fig. 2. Crystal structure of olivine LiFePO_4 with one-dimensional lithium diffusion channels.

5–15 min.²³ The products obtained by such approaches exhibit unique nanorod-like morphologies with excellent crystallinity (see the TEM fringe pattern) as seen in Fig. 3 with the easy lithium diffusion direction (*b* axis) perpendicular to the long axis, which is beneficial for achieving high rate capability. The nanocrystalline samples obtained by these solution-based approaches exhibit capacities close to the theoretical value (170 mAh/g) with excellent rate capabilities.^{20,23}

Although the initial work by Goodenough's group revealed a two-phase reaction mechanism with LiFePO_4 and FePO_4 as end members,¹¹ subsequent investigations have indicated several interesting observations.^{22,24–26} For example, the miscibility gap between the two phases has been found to decrease with increasing temperature, and the occurrence of a single-phase solid solution Li_xFePO_4 with $0 \leq x \leq 1$ has been reported at 450°C.²⁵ Similarly, the miscibility gap has been found to decrease with decreasing particle size,^{22,26} and complete solid solubility between LiFePO_4 and FePO_4 at room temperature has been reported for 40 nm size particles.²² Thus, what was originally found to be a two-phase reaction mechanism with micrometer-size particles¹¹ has now turned into a single-phase reaction mechanism with nano-sized particles. This is a clear demonstration of how nanoparticles can behave entirely different from their micrometer sized counterparts. Defect chemistry with the existence of cationic vacancies in the samples prepared by the low temperature approaches has been suggested to be partly the reason for this contrasting behavior of the nano-sized particles.

In summary, recognition of the influence of inductive effect in tuning the relative position of the redox couples and the cell voltage has led to the identification of polyanion-containing phospho-olivine compound, LiFePO_4 , as a potential cathode for lithium ion batteries. The abundance and low cost of Fe, excellent thermal stability and safety offered by the covalently-bonded PO_4 groups, and the high rate capability realized with the nanoparticles coated with conductive carbon, have made LiFePO_4 as an attractive candidate for HEV and PHEV applications. LiFePO_4 is now intensively developed by companies such as A123 Systems Inc. for automotive applications. Thus, the identification of phospho-olivines as a lithium insertion/extraction host¹¹ has led to a profound scientific and technological impact in the field. Although the energy density of LiFePO_4 is currently limited due to its lower operating voltage (3.4 V) and the less dense olivine structure,

other phospho-olivines such as LiMnPO_4 (4.1 V), LiCoPO_4 (4.8 V), and LiNiPO_4 (5.2 V) with higher operating voltages are appealing for increasing the energy density. However many challenges including the development of more stable, robust electrolyte compositions remain to be addressed. ■

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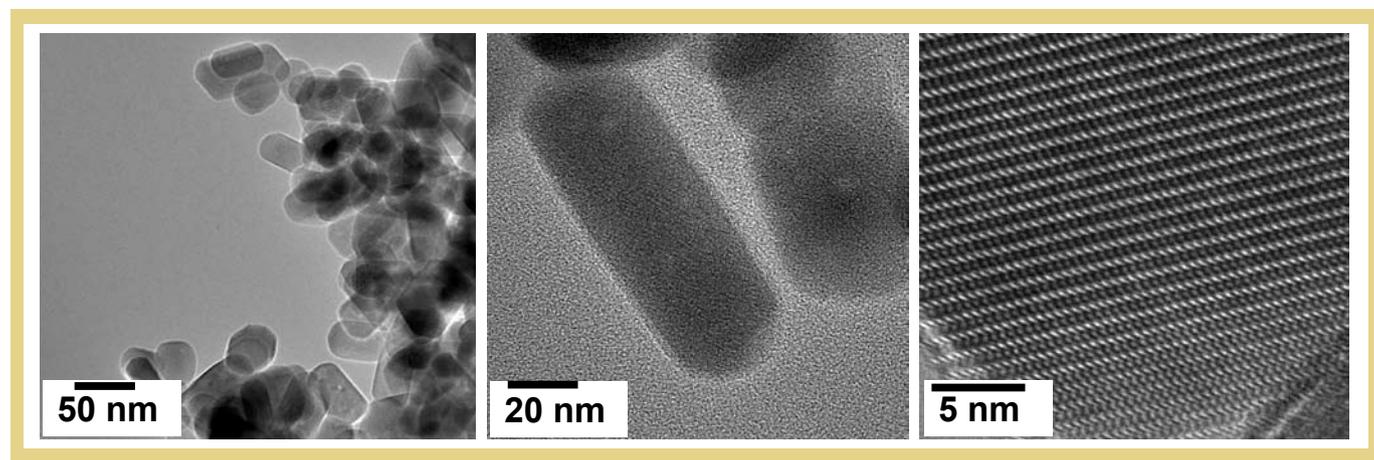


FIG. 3. TEM images of single crystal LiFePO_4 prepared by microwave-assisted solvothermal method at 300°C for 5 min, illustrating the highly crystalline nature of the synthesized sample.

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