Electronic structures of 
LiFePO$_4$ and related materials$^a$

Natalie Holzwarth 
Wake Forest University, Winston-Salem, NC, USA

- Introduction and motivation
- Calculational methods
- Electronic structure results
- Summary and Conclusions

Performance comparison of different rechargeable AA-size (or equivalent) batteries at 20° C. (Figure from Interface 15:1, 18 (2006).)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\end{figure}
Diagram of discharge operation for a Li-ion battery

\[ V = IR \]
### Some battery materials

#### Cathodes
- LiCoO$_2$
- LiMn$_2$O$_4$
- LiFePO$_4$

#### Electrolytes
- LiPF$_6$ (liquid)
- PEO & other polymers
- LiPON (Li$_3$PO$_4$ glass)

#### Anodes
- Li metal
- LiAl alloy
- LiC$_6$
Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries

A. K. Padhi,* K. S. Nanjundaswamy,** and J. B. Goodenough

Center for Materials Science and Engineering, The University of Texas at Austin, Austin, Texas 78712-1063, USA

ABSTRACT

Reversible extraction of lithium from LiFePO₄ (triphylite) and insertion of lithium into FePO₄ 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, FePO₄, isostructural with heterosite, Fe₉₋₅Mn₃₋₅PO₄. The FePO₄ framework of the ordered olivine LiFePO₄ 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 LiMPO₄ (M = Mn, Co, or Ni) with an LiClO₄ electrolyte was not possible; but successful extraction of lithium from LiFeₓ₋₀.₅MnₓPO₄ was accomplished with maximum oxidation of the Mn²⁺/Mn⁴⁺ occurring at x = 0.5. The Fe³⁺/Fe²⁺ couple was oxidized first at 3.5 V followed by oxidation of the Mn³⁺/Mn⁵⁺ couple at 4.1 V vs. lithium. The Fe³⁺/O-Mn⁵⁺ interactions appear to destabilize the Mn²⁺ level and stabilize the Fe³⁺ level so as to make the Mn³⁺/Mn⁵⁺ energy accessible.

Introduction

Since the demonstration of reversible lithium intercalation between the layers of TiS₂,¹ considerable effort has been devoted to the identification of other lithium-intercalation compounds that can be used as the cathode for a secondary lithium battery. The desired material would have a relatively flat open-circuit voltage over a large lithium solid solution within the voltage range of 2.5 < V₀ < 4.0 V and be inexpensive, easy to fabricate, environmentally benign, and safe in handling and operation. Reversible lithium insertion/extraction has been performed on a variety of compounds containing different transition-metal cations and structural architectures. The sulfides have too low a V₀, and the halides too low an electronic conductivity, so particular attention has been given to transition-metal oxides. These efforts have resulted in the development of rechargeable lithium batteries that now serve as state of the art power sources for consumer electronics.

Among the known Li-insertion compounds, the layered rock salt systems Li₅₋₃CoO₂,² Li₆₋₃NiO₂,³ and the manganese-spinel framework system Li₅₋₃[Mn₂]O₄,⁴ are now

Accumulated number of papers on LiFePO$_4$

(Estimated from the number of citations of the original articles:
Commercial use of LiFePO$_4$???
(pure speculation)

In 2001, Professor Yet-Ming Chiang, Department of Materials Science and Engineering, M. I. T. co-founded A123Systems, a startup company involved with developing, manufacturing, and marketing batteries based on lithium metal phosphate. (http://www.a123systems.com)

Watertown, Mass. November 2, 2005: A123Systems, developer of a new generation of Lithium-ion batteries, today unveiled its technology and announced that it is delivering batteries with unprecedented power, safety, and life as compared to conventional Lithium technology. A123Systems first battery is now in production and being delivered to the Black & Decker Corporation (NYSE: BDK). It will be first utilized by the corporation’s DEWALT brand, a leading manufacturer of power tools.
What can computer simulations do to advance our understanding of LiFePO$_4$ materials?

The role of computation in electrochemical research is not as prominent as it is in the semiconductor and catalysis fields. Our work was inspired by a talk given by Professor Gerbrand Ceder of M. I. T. given at the Fourteenth Annual Workshop on Recent Developments in Electronic Structure Methods – ES2002 in which he summarized his pioneering work on the cathode materials LiCoO$_2$, LiNiO$_2$, and LiMn$_2$O$_4$. (More recently, Ceder and his group have made major advances in the understanding of the LiFePO$_4$ family as well.)

Outline of our work

- Introduction to the general features of the electronic structures of the electrochemically active forms of LiFePO$_4$ and FePO$_4$.

- Comparison of the electrochemically active form of FePO$_4$ with 3 other meta-stable crystalline structures.

- Beginning work on Li-ion diffusion mechanisms in Li$_3$PO$_4$. 
# Calculational methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PAW</strong>&lt;br&gt;\textit{pwpaw} - pwpaw.wfu.edu&lt;br&gt;\textit{socorro} - dft.sandia.gov/socorro&lt;br&gt;\textit{abinit} - <a href="http://www.abinit.org">www.abinit.org</a></td>
<td>Works well for moderately large unit cells, but variable unit cell optimization not yet implemented in \textit{pwpaw} and \textit{socorro}. Need to construct and test PAW basis and projector functions.</td>
</tr>
<tr>
<td><strong>LAPW</strong>&lt;br&gt;\textit{wien2k} - <a href="http://www.wien2k.at">www.wien2k.at</a></td>
<td>Works well for smaller unit cells; variable unit cell optimization not implemented. Need to choose non-overlapping muffin tin radii and avoid “ghost” solutions.</td>
</tr>
<tr>
<td><strong>PWscf</strong>&lt;br&gt;\textit{pwscf} - <a href="http://www.pwscf.org">www.pwscf.org</a></td>
<td>Works well for large unit cells and includes variable unit cell optimization. Need to construct and test soft pseudopotential functions.</td>
</tr>
</tbody>
</table>
## Secret recipe of calculational parameters

<table>
<thead>
<tr>
<th></th>
<th>$r_c$ (bohr)</th>
<th>Atomic basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAW*</td>
<td>1.90</td>
<td>$3s, 4s, 3p, 4p, 3d, \epsilon_d$</td>
</tr>
<tr>
<td>PWscf†</td>
<td>1.90</td>
<td>$3s, 4s, 3p, 4p, 3d, \epsilon_d$</td>
</tr>
<tr>
<td>LAPW</td>
<td>1.95</td>
<td>$3s, \epsilon s, 3p, \epsilon p, \epsilon d$</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAW*</td>
<td>1.41</td>
<td>$2s, \epsilon s, 2p, \epsilon p$</td>
</tr>
<tr>
<td>PWscf†</td>
<td>1.40</td>
<td>$2s, \epsilon s, 2p, \epsilon p$</td>
</tr>
<tr>
<td>LAPW</td>
<td>1.28</td>
<td>$2s, \epsilon s, \epsilon p$</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAW*</td>
<td>1.51</td>
<td>$2s, 3s, 2p, 3p$</td>
</tr>
<tr>
<td>PWscf†</td>
<td>1.50</td>
<td>$3s, \epsilon s, 3p, \epsilon p, \epsilon d$</td>
</tr>
<tr>
<td>LAPW</td>
<td>1.38</td>
<td>$\epsilon s, 2p, \epsilon p$</td>
</tr>
</tbody>
</table>

* PAW basis and projector functions generated by *atompaw* code.

† Ultra-soft pseudopotentials generated by *uspp* code of David Vanderbilt.
Details on constructing the PAW basis and projector functions

For each all-electron basis function $\phi_i(r)$, we need to construct corresponding pseudo-basis functions $\tilde{\phi}_i(r)$ and projector functions $\tilde{p}_i(r)$. Two slightly different variations:

- Blöchl’s scheme (PR B 50, 17953 (1994)): choose shape of $\tilde{p}_i(r)$ and derive $\tilde{\phi}_i(r)$.
- Vanderbilt’s scheme (PR B 41, 7892 (1990)): choose shape of $\tilde{\phi}_i(r)$ and derive $\tilde{p}_i(r)$.

Example for 3d functions of Fe:

Basis and projector functions

$$F(q) \equiv \tilde{p}(q)\tilde{\phi}(q)q^2$$
Other computational details

• Spin polarized calculations performed assuming full crystal symmetry ("ferromagnetic" spin configuration).

• Exchange-correlation functionals –
  
  
Fluorite structure

NaCl structure

Tetrahedral molecule

Note: This kind of consistency is generally not possible with parameters taken “off the shelf”.

Test results for simple oxides
Introduction to general features of the electronic structures of the electrochemically active forms of LiFePO$_4$ and FePO$_4$

FePO$_4$ and LiFePO$_4$ in olivine (Pnma) structure
LSDA partial densities of states for olivine materials

**FePO$_4$**

**LiFePO$_4$**

N(E) (states/(eV • spin • sphere))

E (eV)

-10 -5 0 5 10

16
Partial densities for majority spin FePO$_4$ states

I: $-9.9 \leq E \leq -6.2$ eV

II: $-6.2 \leq E \leq -2.3$ eV

III: $-2.3 \leq E \leq -0.1$ eV
Partial densities for majority spin LiFePO$_4$ states

I: $-11.1 \leq E \leq -7.7$ eV
II: $-7.7 \leq E \leq -3.4$ eV
III: $-3.3 \leq E \leq -1.2$ eV
Summary of results for FePO$_4$ and LiFePO$_4$

FePO$_4$ – Fe$^{+3}$ $\iff$ Fe $3d_\uparrow^5$; strong hybridization of Fe $3d_\uparrow$ and O $2p_\uparrow$ bands

LiFePO$_4$ – Fe$^{+2}$ $\iff$ Fe $3d_\uparrow^5 d_\downarrow^1$; Fe $3d$ states form narrow bands with very little O $2p$ character
Comparison of the electrochemically active form of FePO$_4$ with 3 other crystalline structures

Summary of experimental situation:

- FePO$_4$ in its “olivine” structure is the delithiated product of LiFePO$_4$, known as a promising cathode material for rechargeable Li ion batteries. (Padhi, Nanjundaswamy, Goodenough, *J. Electrochem. Soc.* 144, 1188 (1997))

- Yang, Song, Zavalij, and Whittingham (*Electrochem. Comm.* 4, 239 (2002)) showed that olivine FePO$_4$ irreversibly transforms to a quartz-like structure at $\approx 600^\circ$C.

- Song, Zavalij, Suzuki, and Whittingham (*Inorg. Chem.* 41, 5778 (2002)) investigated the structural and electrochemical properties of several crystalline forms of FePO$_4$.

- Iyer, Delacourt, Masquelier, Tarascon, and Navrotsky (*Electrochem. Solid-State Lett.* 9, A46 (2006)) showed that the olivine structure is more stable than the quartz structure.
Computational challenge

1. Can we reliably predict the most stable structure?

2. If so:
   (a) Can we understand what factors control the structural stability?
   (b) Can we understand what factors control the electrochemical activity? can we understand what determines its structural stability?
Crystal structures

“Olivine”
Space group: Pnma
Mineral names: olivine, heterosite
Properties: Li ion cathode (LiFePO₄)

“Quartz”
Space group: P3121
Mineral names: α-quartz, berlineite
Properties: Catalyst, electrochemically inactive
Forms at 600° C from olivine phase
“CrVO₄-type”
Space group: Cmcm
Synthesized at high pressure from quartz form
Properties: Electrochemically inactive
Arroyo-de Dompablo, Gallardo-Amores, Amador,

“Monoclinic”
Space group: P2₁/n
Synthesized by dehydrating phosphosiderite
Properties: Partial electrochemical activity
Song, Zavalij, Suzuki, Whittingham,
*Inorg. Chem.* 41, 5778, 2002
## Crystal volumes – optimized and experimental

(in units of å^3/FePO_4)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>LDA</th>
<th>GGA</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>67.5</td>
<td>74.5</td>
<td>67.9</td>
</tr>
<tr>
<td>(PAW)</td>
<td>68.1</td>
<td>74.0</td>
<td></td>
</tr>
<tr>
<td>(PWscf)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>79.9</td>
<td>91.9</td>
<td>82.4</td>
</tr>
<tr>
<td>(PAW)</td>
<td>79.8</td>
<td>91.3</td>
<td></td>
</tr>
<tr>
<td>(PWscf)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrVO_4-type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>62.3</td>
<td>68.6</td>
<td>64.2</td>
</tr>
<tr>
<td>(PWscf)</td>
<td>62.8</td>
<td>68.6</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>81.3</td>
<td>91.4</td>
<td>82.1</td>
</tr>
<tr>
<td>(PWscf)</td>
<td>81.9</td>
<td>88.4</td>
<td></td>
</tr>
</tbody>
</table>
## Internal Energy Differences

(in units of eV/FePO$_4$)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>LDA</th>
<th>GGA</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td>0.12*</td>
</tr>
<tr>
<td>(LAPW)</td>
<td>0.09</td>
<td>−0.35</td>
<td></td>
</tr>
<tr>
<td>(PAW)</td>
<td>0.05</td>
<td>−0.27</td>
<td></td>
</tr>
<tr>
<td>(PWscf)</td>
<td>0.09</td>
<td>−0.25</td>
<td></td>
</tr>
<tr>
<td>CrVO$_4$-type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>−0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PAW)</td>
<td>−0.11</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>(PWscf)</td>
<td>−0.07</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LAPW)</td>
<td>0.02</td>
<td>−0.19</td>
<td></td>
</tr>
<tr>
<td>(PAW)</td>
<td>−0.01</td>
<td>−0.16</td>
<td></td>
</tr>
<tr>
<td>(PWscf)</td>
<td>−0.02</td>
<td>−0.17</td>
<td></td>
</tr>
</tbody>
</table>

LDSA partial densities of states for FePO$_4$

N(E) (states/(eV\cdot spin\cdot sphere))

Olivine
Quartz
Monoclinic
CrVO$_4$

E (eV)
LSDA band gaps and widths for FePO$_4$ crystals

(Band widths refer to Fe $3d$ majority spin states)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Band gap (eV)</th>
<th>Band width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>0.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.8</td>
<td>5.2</td>
</tr>
<tr>
<td>CrVO$_4$-type</td>
<td>0.0</td>
<td>8.9</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>0.4</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Results so far for FePO$_4$

1. Can we reliably predict the most stable structure? **no**

2. If not, what is missing from our simulations?
   (a) We suspect the electron self-interaction error to be the most important contribution, especially for the very localized Fe 3$d$ states.
   (b) Possibly, electron correlation effects could also be significant.
Li-ion diffusion mechanisms in electrolyte material $\text{Li}_3\text{PO}_4$

$\text{LiFePO}_4$
(cathode)

$\gamma$-$\text{Li}_3\text{PO}_4$
(electrolyte)
Li$^+$ diffusion by possible interstitial mechanism in $\gamma$- Li$_3$PO$_4$

Relaxed structures about two meta-stable interstitial sites. (Arrows indicate magnitude and direction of distortion relative to perfect crystal. Darker green ball indicates interstitial position.)
Li$^+$ diffusion by possible vacancy mechanism in $\gamma$- Li$_3$PO$_4$

Relaxed structures about two meta-stable vacancy sites. (Arrows indicate magnitude and direction of distortion relative to perfect crystal, scaled by 2$\times$ relative to interstitial case. Light green ball indicates vacancy position.)
Results so far for Li-ion diffusion mechanisms in $\gamma$-Li$_3$PO$_4$

- Found several meta-stable interstitial and vacancy configurations.
- Currently investigating the barriers for diffusion between these sites along several likely paths.
Summary

- With careful attention to calculational details, we are able to obtain nearly identical results using independent software packages.

- Investigated general features of the electronic structures of the electrochemically active forms of LiFePO$_4$ and FePO$_4$.

- Compared of the electrochemically active form of FePO$_4$ with 3 other meta-stable crystalline structures. *Need to estimate electron self-interaction error.*

- Currently studying Li-ion diffusion mechanisms in the electrolyte material Li$_3$PO$_4$. 
Acknowledgments

Collaborators:

Ph. D. Thesis: Ping Tang
Postdoc: Yaojun Du
Beginning Grad. Student: Xiao Xu

Funding:

• NSF DMR-0405456
• NSF DMR-0427055

Graphics software:

• XCrySDen (http://www.xcrysden.org), written by Anton Kokalj
• dx (http://www.opendx.org) (based on Data Explorer, a general purpose visualization package originally developed at IBM.)