

Electronic structures of LiFePO_4 and related materials^a

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

^a**Ph. D. thesis work of Ping Tang, with help from Yaojun Du and Xiao Xu.** Supported by NSF grants DMR-0405456 and DMR-0427055.

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

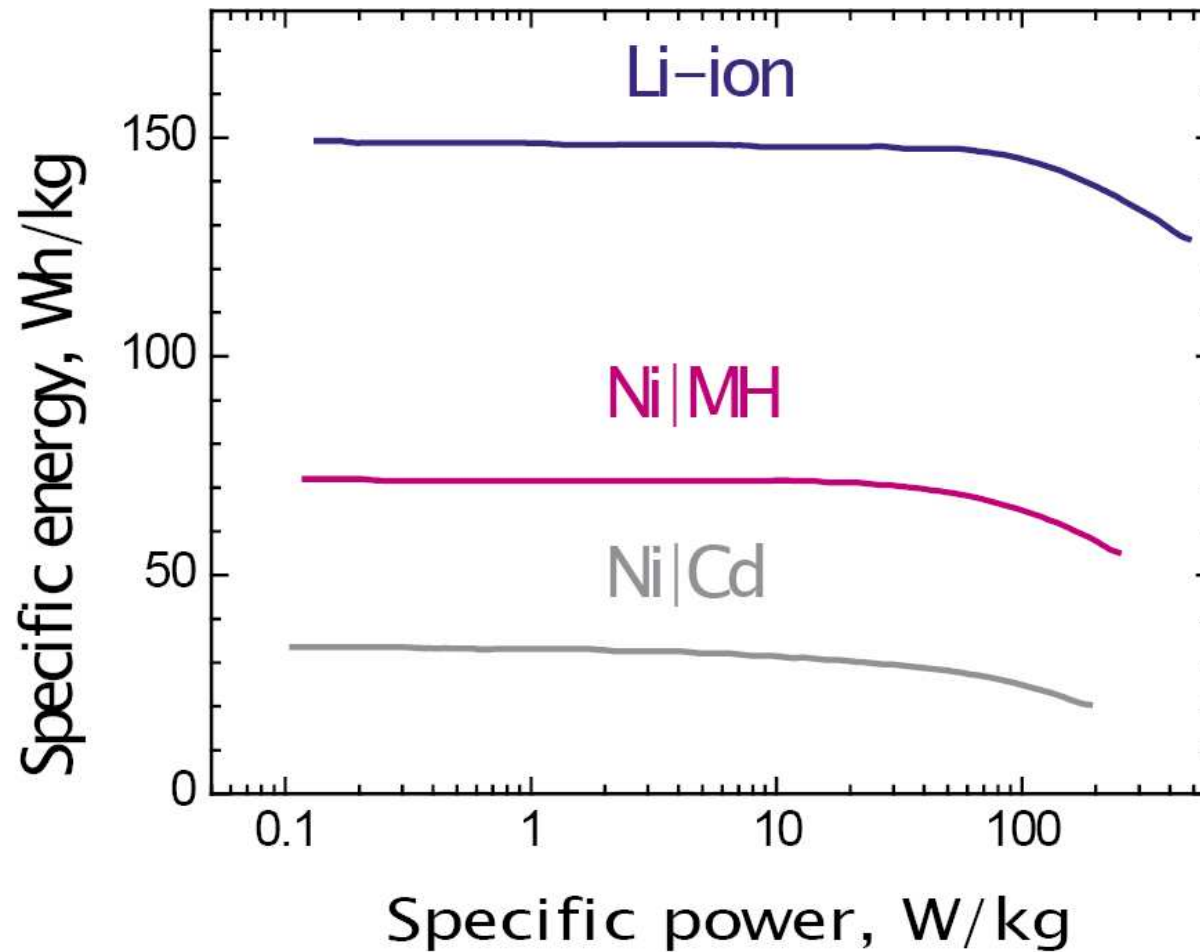
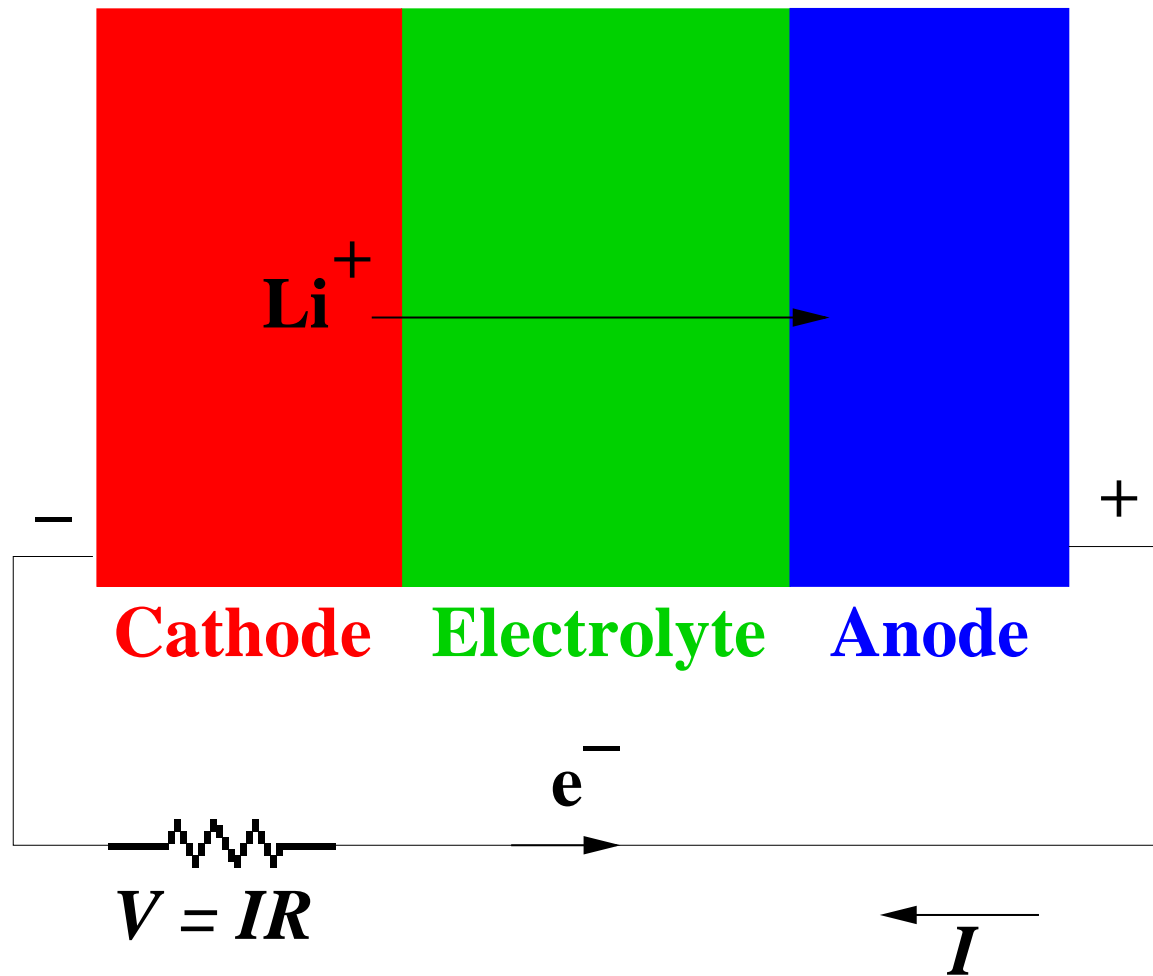


FIG. 3. Specific energy vs. specific power or Ragone plots, for three common rechargeable batteries. Ref: Handbook of batteries, D. Linden, T. B. Reddy, Eds., McGraw-Hill, New York (2002), 3rd Edition.

Diagram of discharge operation for a Li-ion battery



Some battery materials

Cathodes

LiCoO₂

LiMn₂O₄

LiFePO₄

Electrolytes

LiPF₆ (liquid)

PEO & other polymers

LiPON (Li₃PO₄ glass)

Anodes

Li metal

LiAl alloy

LiC₆

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, $\text{Fe}_{0.65}\text{Mn}_{0.35}\text{PO}_4$. 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 (M = Mn, Co, 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 $\text{Mn}^{3+}/\text{Mn}^{2+}$ occurring at $x = 0.5$. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple was oxidized first at 3.5 V followed by oxidation of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple at 4.1 V vs. lithium. The Fe^{3+} -O- Mn^{2+} interactions appear to destabilize the Mn^{2+} level and stabilize the Fe^{3+} level so as to make the $\text{Mn}^{3+}/\text{Mn}^{2+}$ energy accessible.

Introduction

Since the demonstration of reversible lithium intercalation between the layers of TiS_2 ,¹ considerable effort has been devoted to the identification of other lithium-insertion 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 $2.5 < V_{oc} < 4.0$ 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 V_{oc} 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 $\text{Li}_{1-x}\text{CoO}_2$,² $\text{Li}_{1-x}\text{NiO}_2$,³ and the manganese-spinel framework system $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ ⁴ are now

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

J. Electrochem. Soc. 144 1188, (1997)

Accumulated number of papers on LiFePO_4

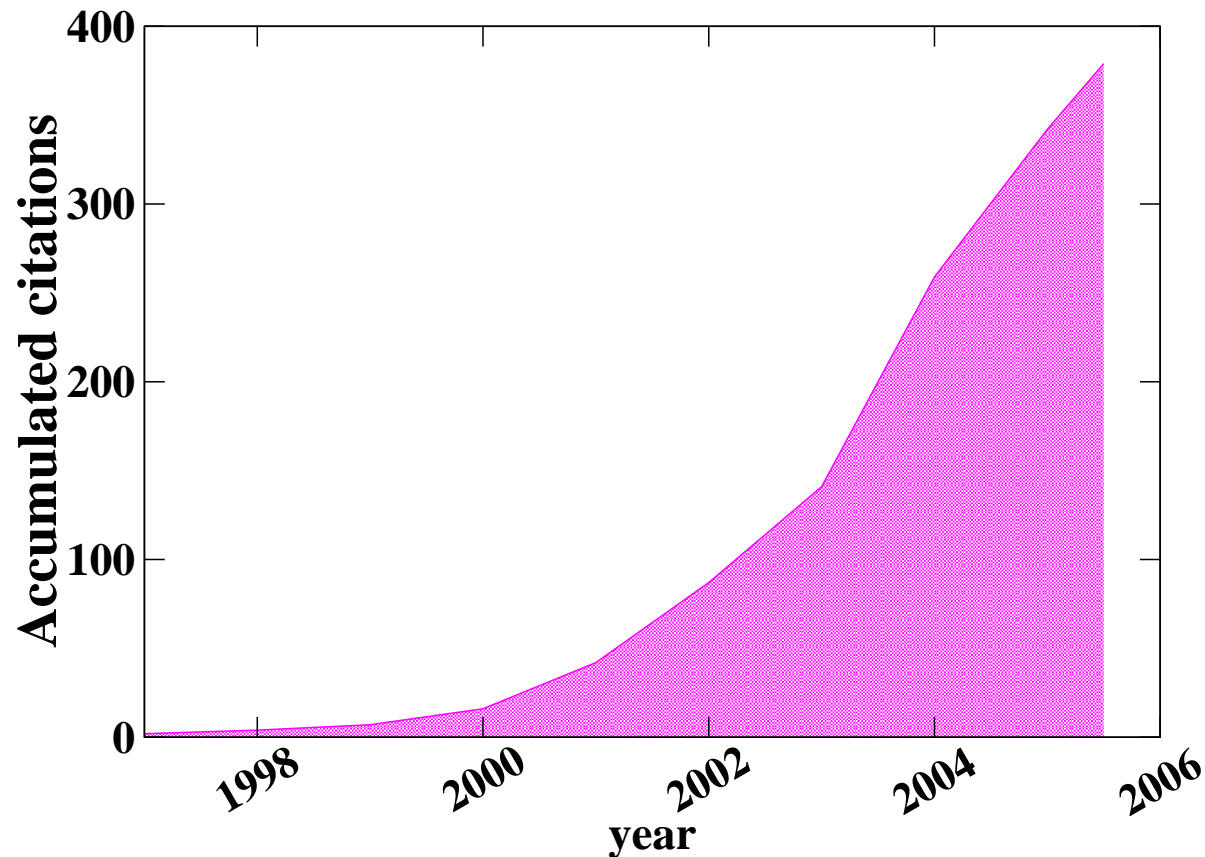
(Estimated from the number of citations of the original articles:

“Phospho-olivines as positive-electrode materials for rechargeable lithium batteries”, A. K.

Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J ECS* **144** 1188, (1997); “Effect of

structure on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in iron phosphates”, A. K. Padhi, K. S.

Nanjundaswamy, C. Masquelier, S. Okada, and J. B. Goodenough, *J ECS* **144** 1609, (1997)



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.



Best combination of Power, Safety, and Life

	Power Density (<3Ah cy cells)	Weight to discharge @1500W	Safety	Life at 100% DoD	Environmental friendliness
A123 M1	>3000 W/kg	0.9 lbs	✓	>1000	✓
High Power Li ion	1350 W/kg	2.75 lbs	✗	500	✗
NiMH	750 W/kg	4.4 lbs	✓	<1000	✓
NiCd	600W/kg	5.5 lbs	✓	<1000	✗

Based on: Novel nanoscale highly active materials (patent pending)
Low impedance cell design and electrolyte (patent pending)

Applications: Lawn and Garden, Power tools, Hybrid Vehicles, Medical Devices, Military...

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_2O_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_3PO_4 .

Computational methods

Method	Comments
PAW <i>pwpaw</i> - pwpaw.wfu.edu <i>socorro</i> - dft.sandia.gov/socorro <i>abinit</i> - www.abinit.org	Works well for moderately large unit cells, but variable unit cell optimization not yet implemented in <i>pwpaw</i> and <i>socorro</i> . Need to construct and test PAW basis and projector functions.
LAPW <i>wien2k</i> - www.wien2k.at	Works well for smaller unit cells; variable unit cell optimization not implemented. Need to choose non-overlapping muffin tin radii and avoid “ghost” solutions.
PWscf <i>pwscf</i> - www.pwscf.org	Works well for large unit cells and includes variable unit cell optimization. Need to construct and test soft pseudopotential functions.

Secret recipe of calculational parameters

	r_c (bohr)	Atomic basis
Fe		
PAW*	1.90	$3s, 4s, 3p, 4p, 3d, \epsilon d$
PWscf [†]	1.90	$3s, 4s, 3p, 4p, 3d, \epsilon d$
LAPW	1.95	$3s, \epsilon s, 3p, \epsilon p, \epsilon d$
O		
PAW*	1.41	$2s, \epsilon s, 2p, \epsilon p$
PWscf [†]	1.40	$2s, \epsilon s, 2p, \epsilon p$
LAPW	1.28	$2s, \epsilon s, \epsilon p$
P		
PAW*	1.51	$2s, 3s, 2p, 3p$
PWscf [†]	1.50	$3s, \epsilon s, 3p, \epsilon p, \epsilon d$
LAPW	1.38	$\epsilon s, 2p, \epsilon p$

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

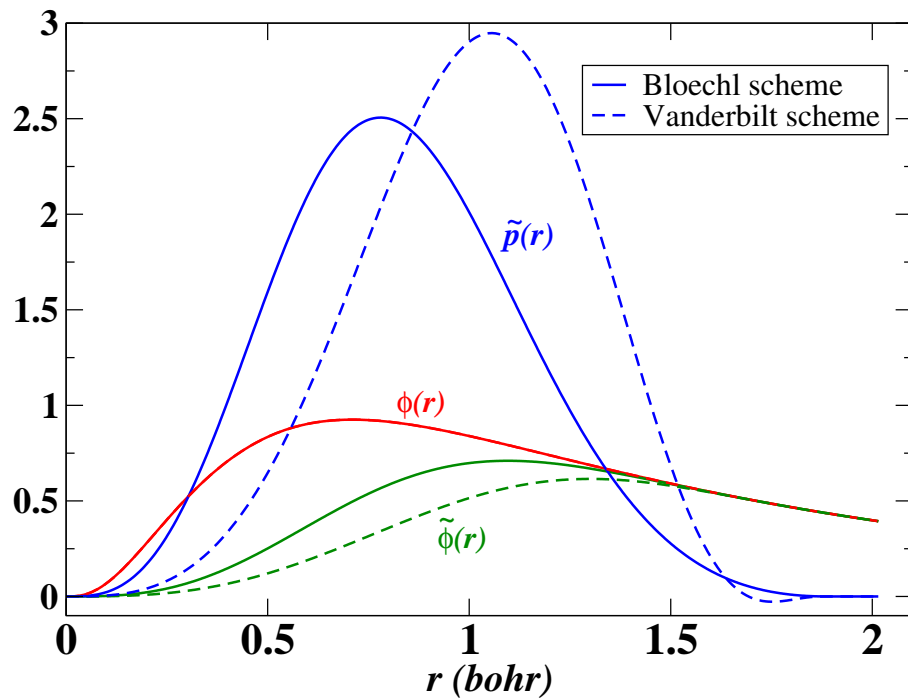
[†] Ultra-soft pseudopotentials generated by *uspp* code of David Vanderbilt.

Details on constructing the PAW basis and projector functions

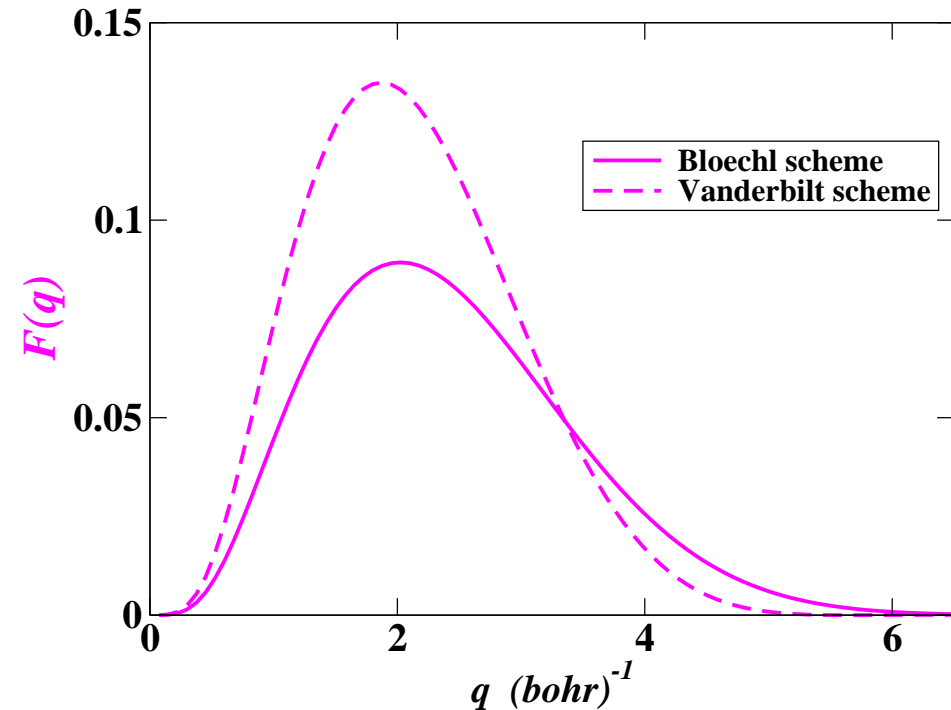
For each all-electron basis function $\phi_i(r)$, we need to construct corresponding pseudo-basis functions $\tilde{\phi}_i(r)$ and projector functions $\tilde{p}_i(r)$. Two slightly different variations:

- 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

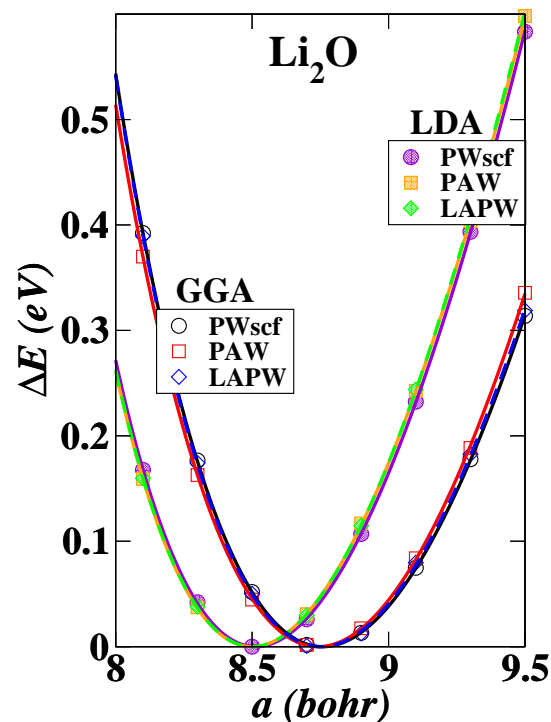


$$F(q) \equiv \tilde{p}(q)\tilde{\phi}(q)q^2$$

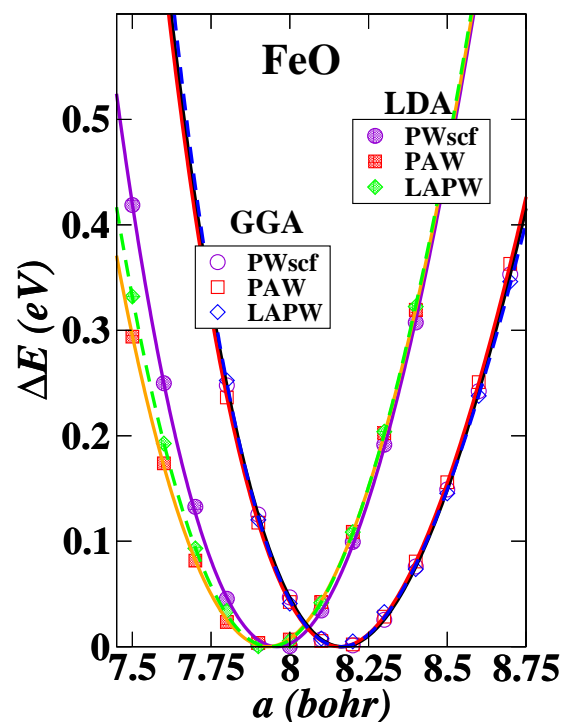
Other computational details

- Spin polarized calculations performed assuming full crystal symmetry (“ferromagnetic” spin configuration).
- Exchange-correlation functionals –
LDA: J. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992)
GGA: J. Perdew, K. Burke, and M. Ernzerhof, *PRL* **77**, 3865 (1996)

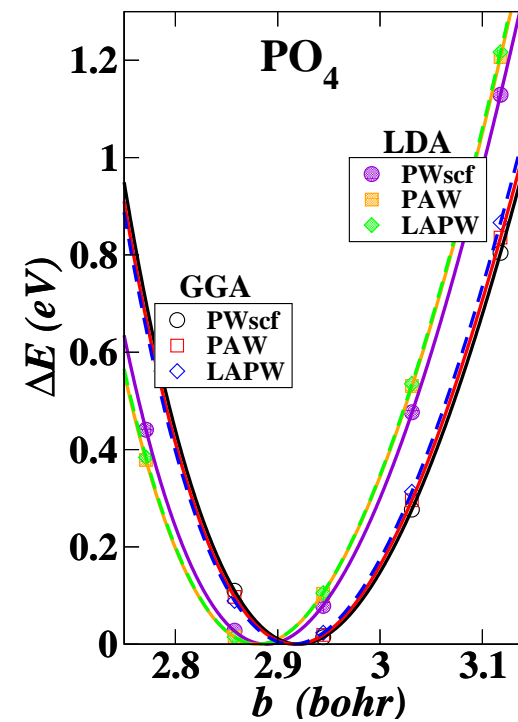
Test results for simple oxides



Fluorite structure



NaCl structure



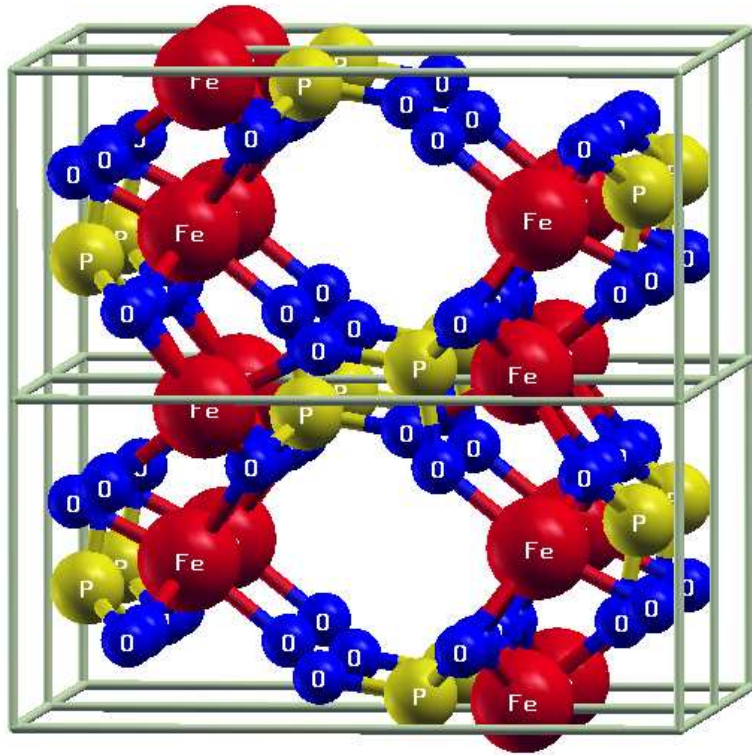
Tetrahedral molecule

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

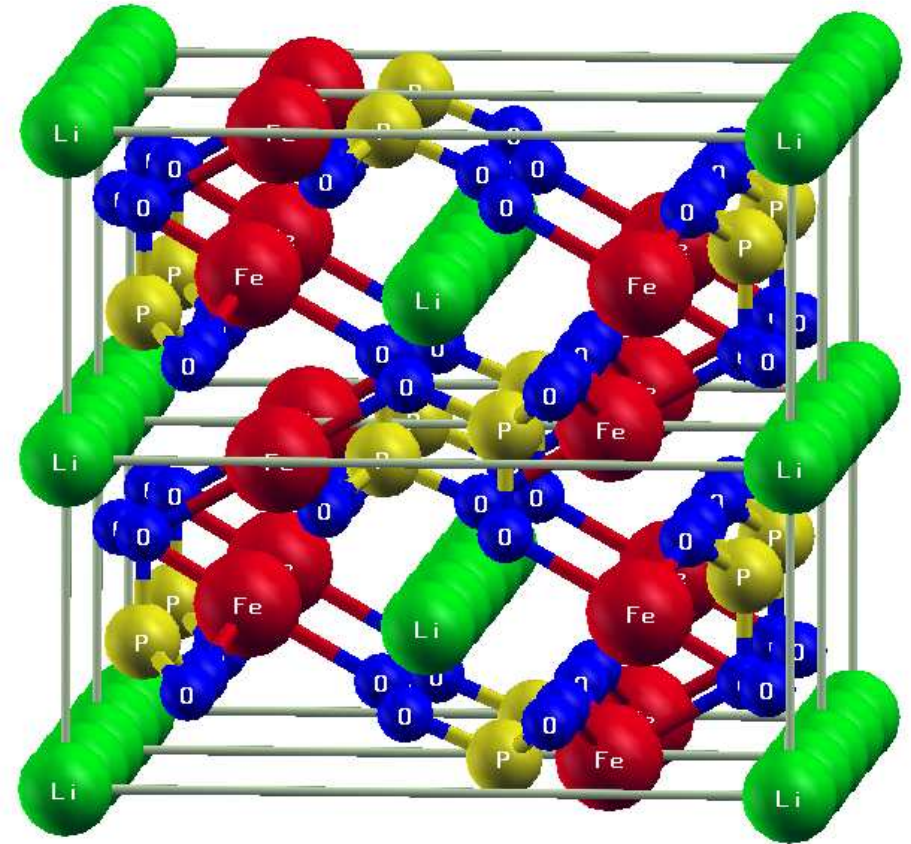
Introduction to general features of the electronic structures of the electrochemically active forms of LiFePO_4 and FePO_4

Ref: “Electronic structures of FePO_4 , LiFePO_4 , and related materials”, Ping Tang and N. A. W. Holzwarth, *Phys. Rev. B* **68**, 165107 (2003)

FePO_4 and LiFePO_4 in olivine (Pnma) structure

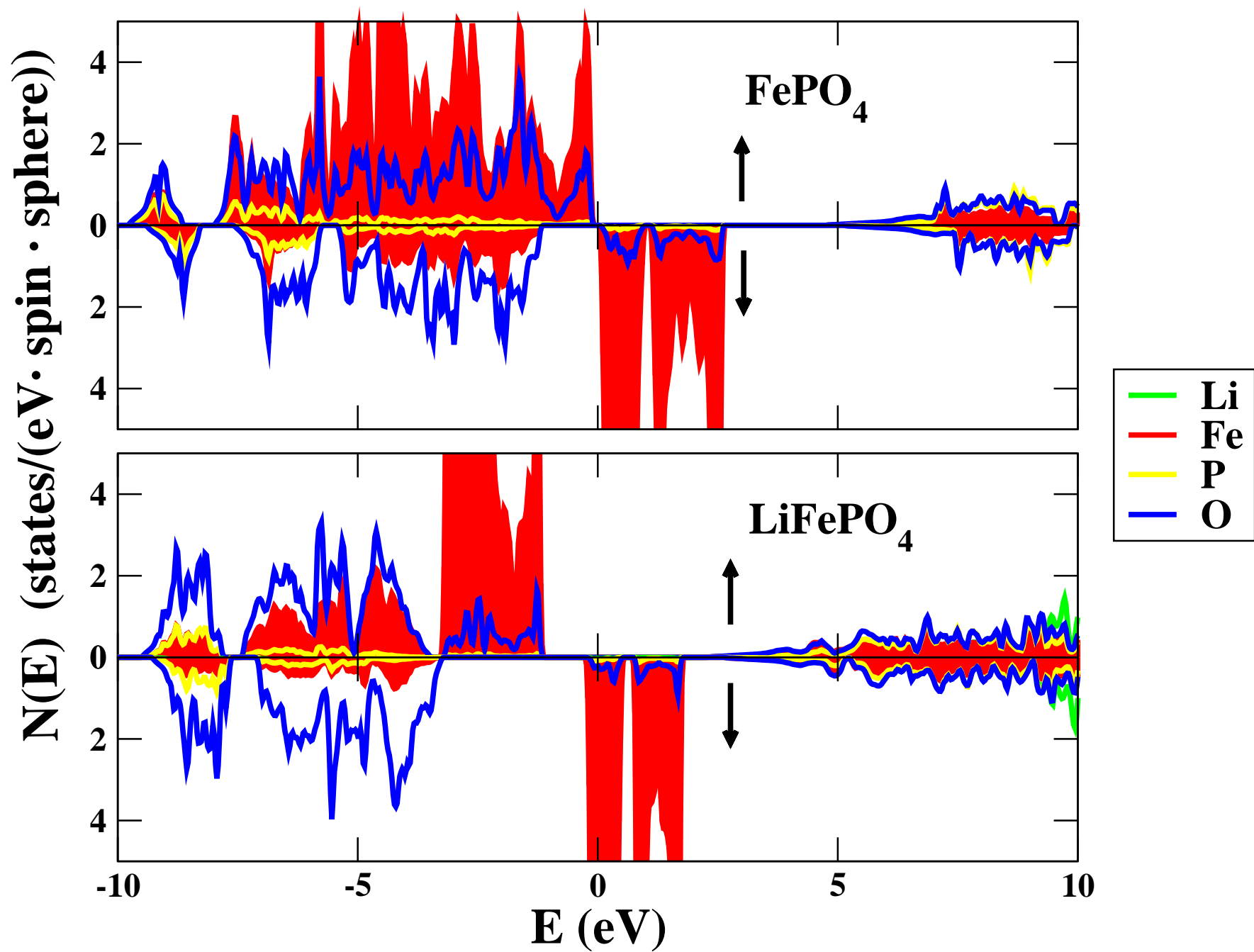


FePO_4

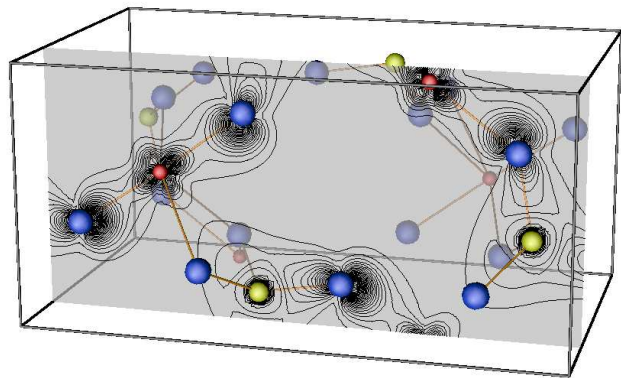
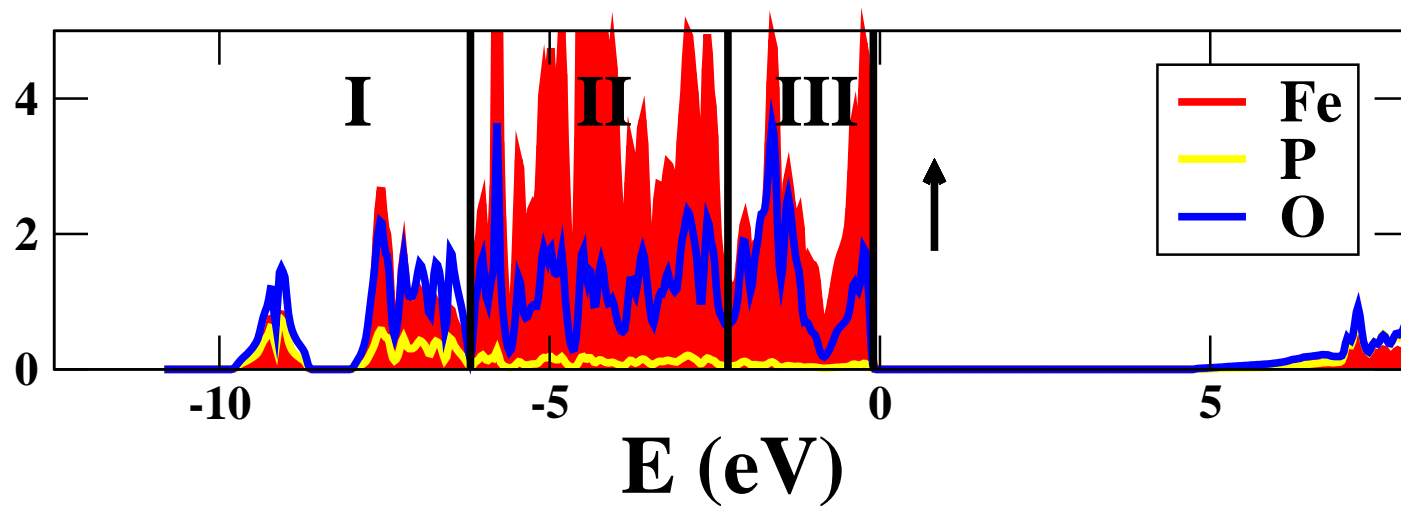


LiFePO_4

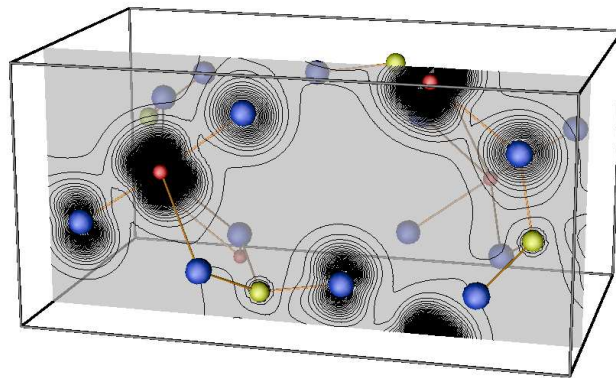
LSDA partial densities of states for olivine materials



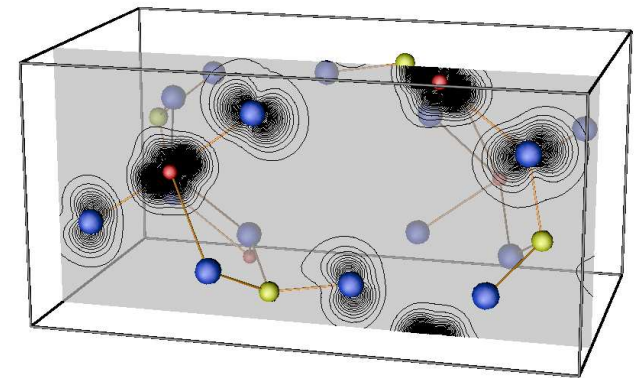
Partial densities for majority spin FePO_4 states



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

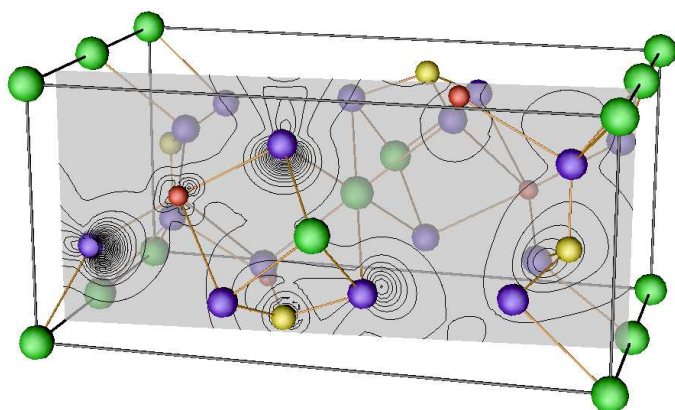
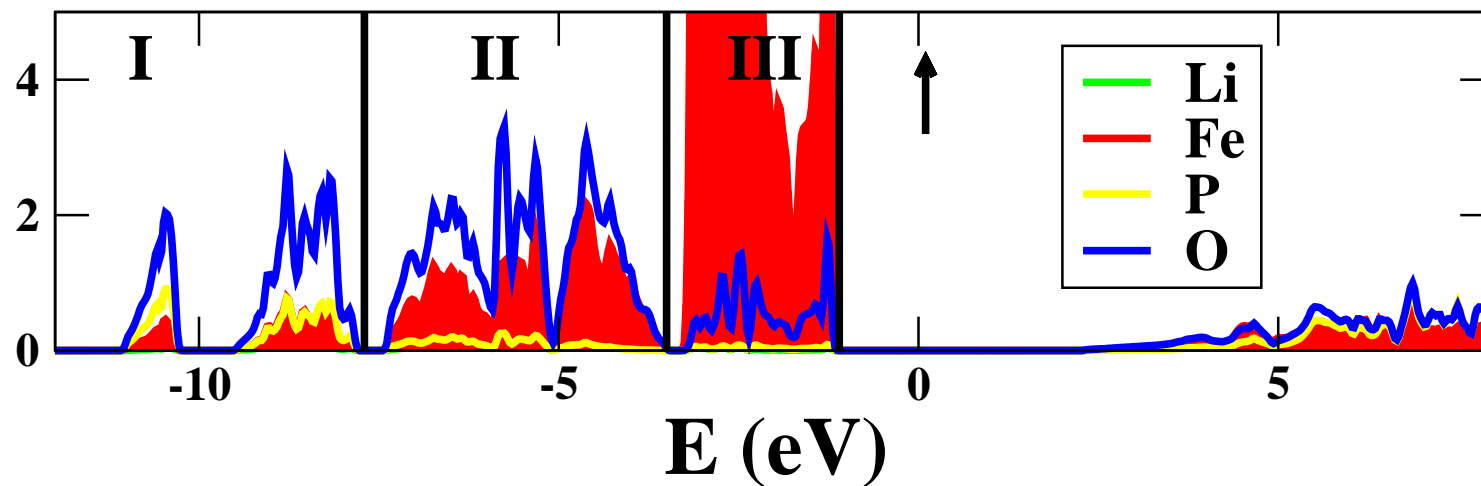


II: $-6.2 \leq E \leq -2.3$ eV

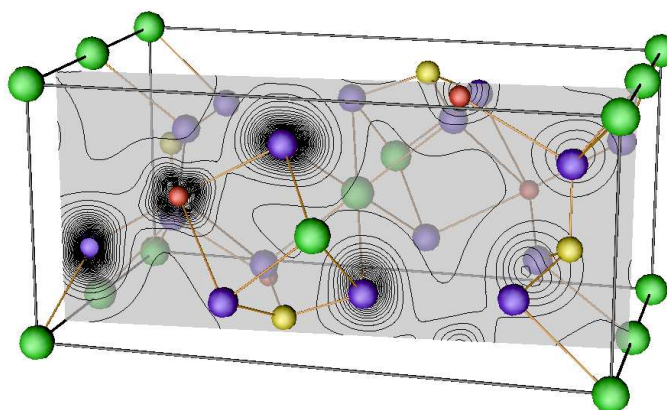


III: $-2.3 \leq E \leq -0.1$ eV

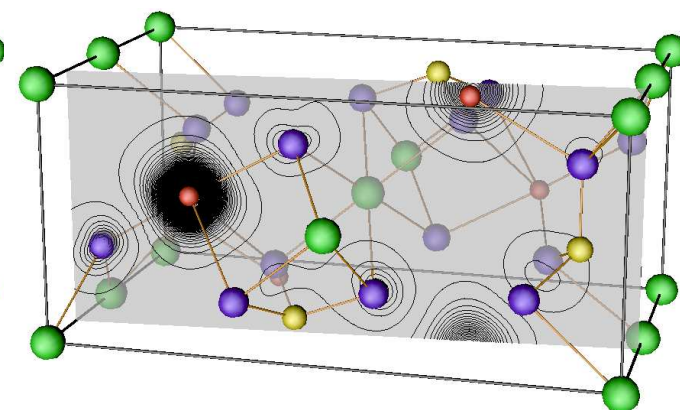
Partial densities for majority spin LiFePO_4 states



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

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

$\text{LiFePO}_4 - \text{Fe}^{+2} \iff \text{Fe } 3d_{\uparrow}^5 d_{\downarrow}^1$; 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

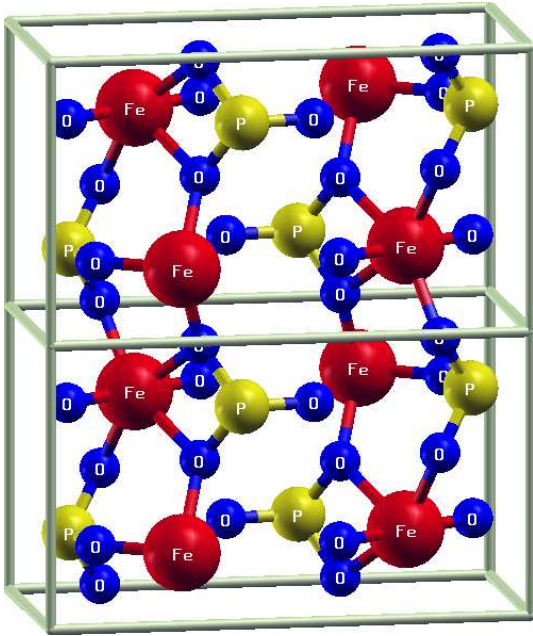
Summary of experimental situation:

- 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 $\approx 600^\circ\text{C}$.
- 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 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

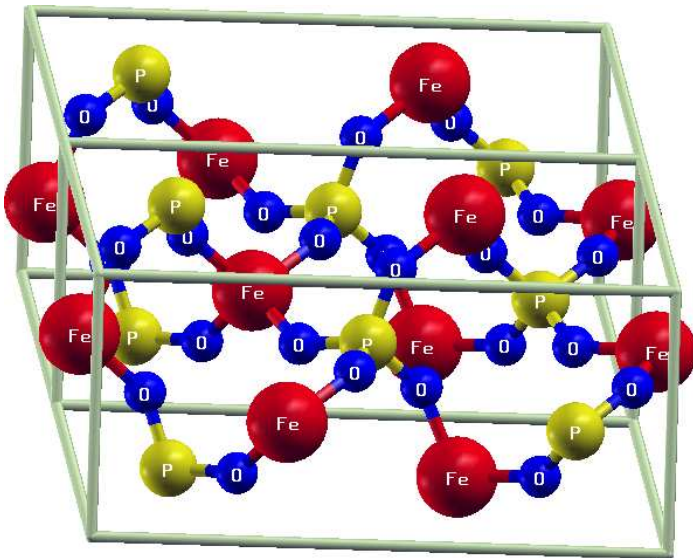


“Olivine”

Space group: Pnma

Mineral names: olivine, heterosite

Properties: Li ion cathode (LiFePO_4)



“Quartz”

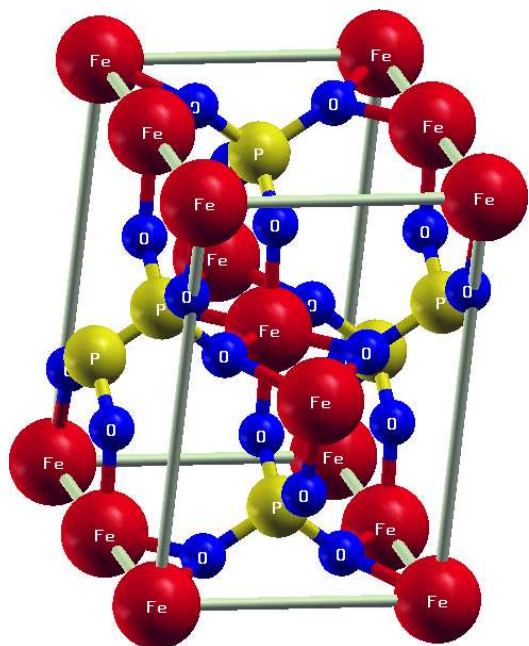
Space group: $P3_121$

Mineral names: α -quartz, berlinite

Properties: Catalyst, electrochemically inactive

Forms at 600°C from olivine phase

Crystal structures – continued



“CrVO₄-type”

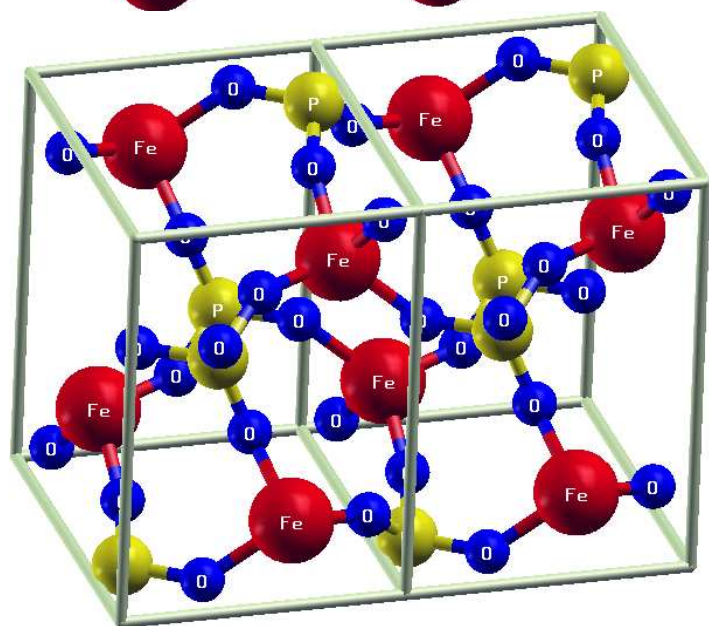
Space group: Cmc₂m

Synthesized at high pressure from quartz form

Properties: Electrochemically inactive

Arroyo-de Dompablo, Gallardo-Amores, Amador,

Electrochem. Solid-State Lett. **8**, A564 (2005)



“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 $\text{\AA}^3/\text{FePO}_4$)

Crystal	LDA	GGA	Exp
Olivine			67.9
(LAPW)	67.5	74.5	
(PAW)		74.5	
(PWscf)	68.1	74.0	
Quartz			82.4
(LAPW)	79.9	91.9	
(PAW)		91.9	
(PWscf)	79.8	91.3	
CrVO ₄ -type			64.2
(LAPW)	62.3		
(PWscf)	62.8	68.6	
Monoclinic			82.1
(LAPW)	81.3	91.4	
(PWscf)	81.9	88.4	

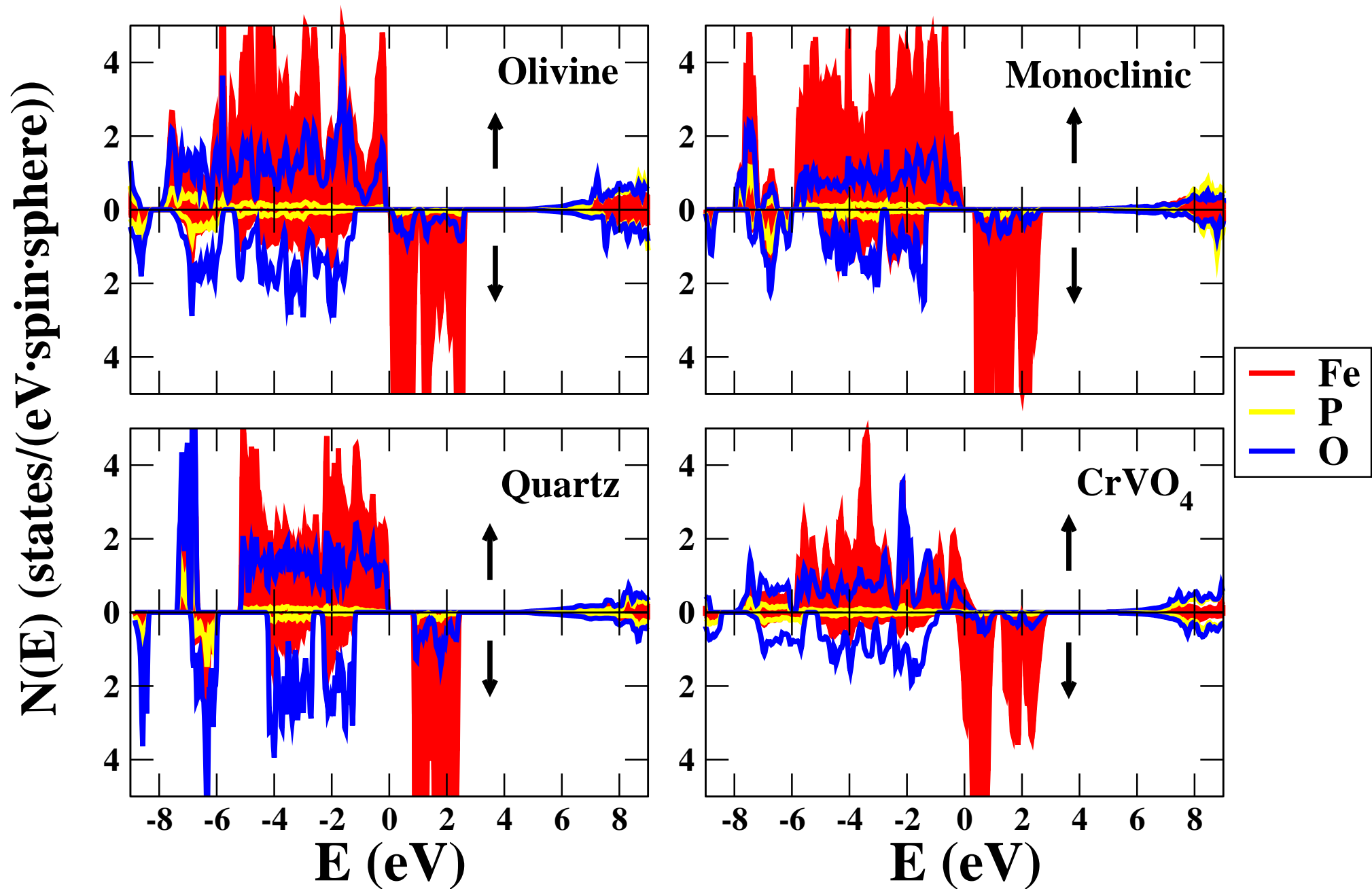
Internal Energy Differences

(in units of eV/FePO₄)

Crystal	LDA	GGA	Exp
Olivine	0.00	0.00	0.00
Quartz			0.12*
(LAPW)	0.09	-0.35	
(PAW)	0.05	-0.27	
(PW _{scf})	0.09	-0.25	
CrVO ₄ -type			
(LAPW)	-0.10		
(PAW)	-0.11	0.07	
(PW _{scf})	-0.07	0.07	
Monoclinic			
(LAPW)	0.02	-0.19	
(PAW)	-0.01	-0.16	
(PW _{scf})	-0.02	-0.17	

*Iyer, Delacourt, Masquelier, Tarascon, and Navrotsky,
Electrochemical and Solid-State Letters **9**, A46 (2006).

LDSA partial densities of states for FePO_4



LSDA band gaps and widths for FePO₄ crystals

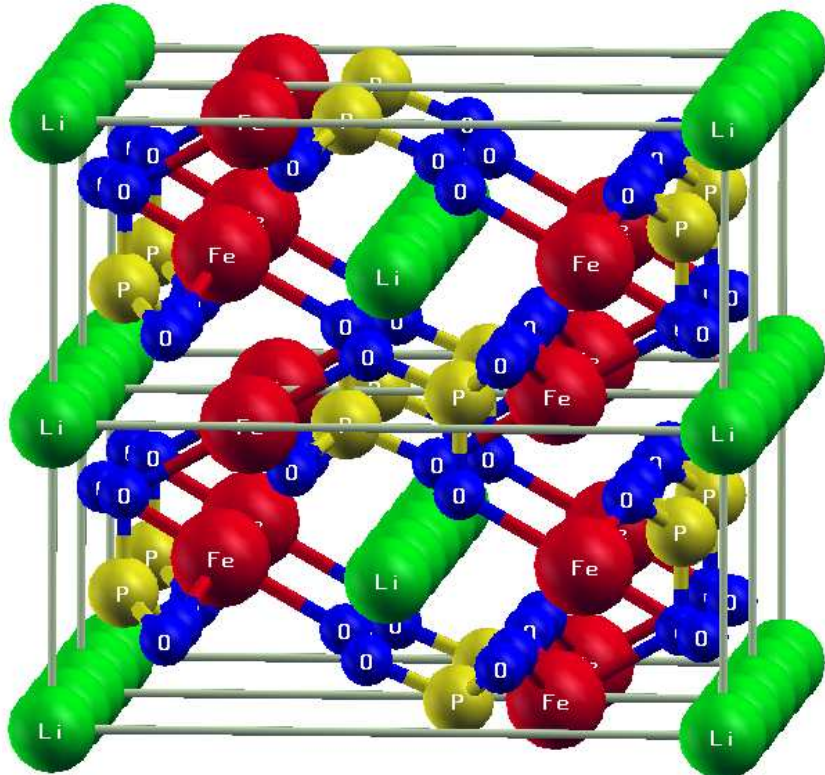
(Band widths refer to Fe 3*d* majority spin states)

Crystal	Band gap (eV)	Band width (eV)
Olivine	0.1	8.1
Quartz	0.8	5.2
CrVO ₄ -type	0.0	8.9
Monoclinic	0.4	6.0

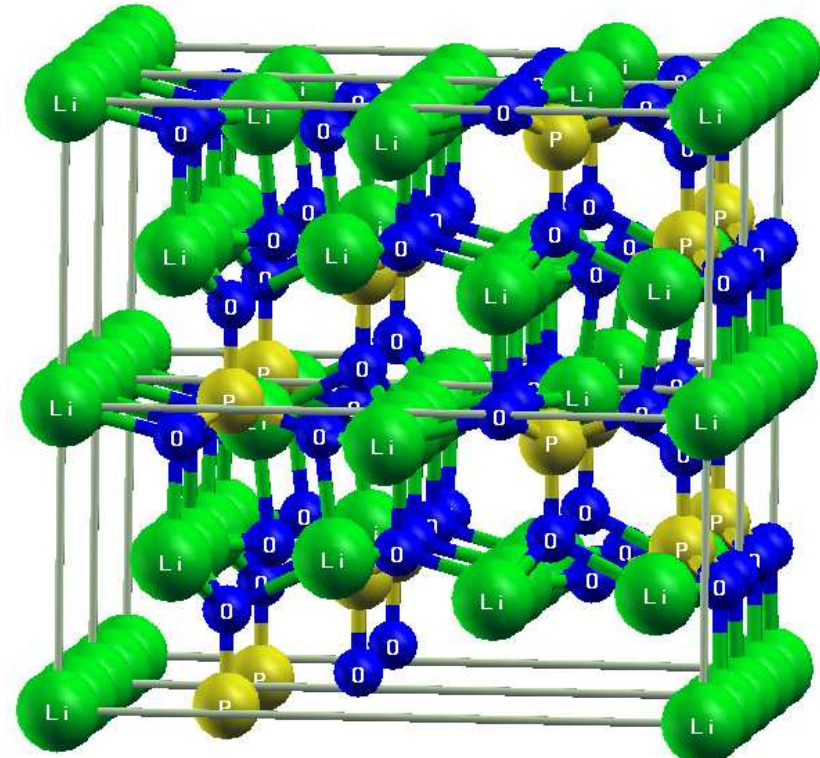
Results so far for FePO₄

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 Li_3PO_4



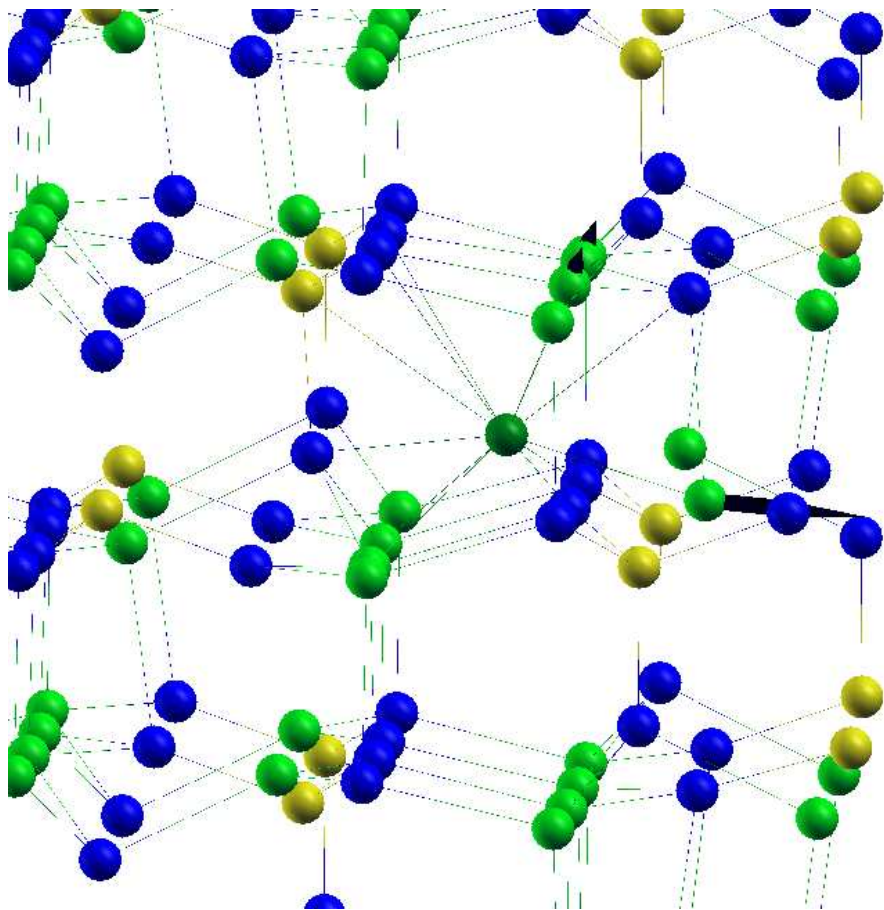
LiFePO_4
(cathode)



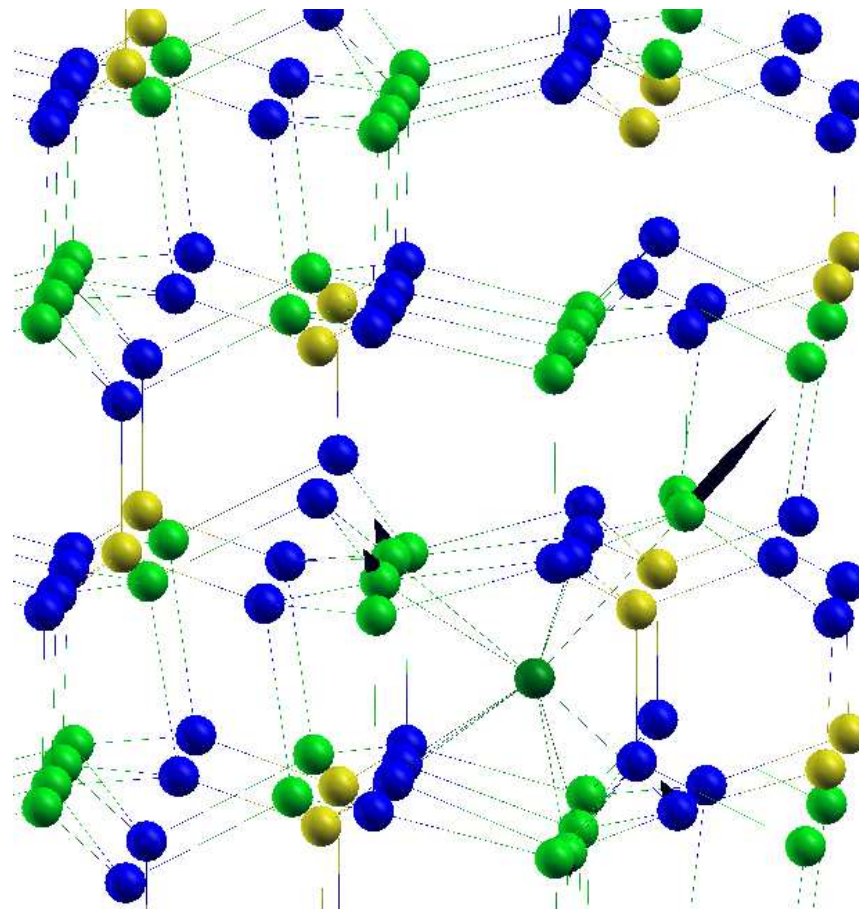
$\gamma\text{-Li}_3\text{PO}_4$
(electrolyte)

Li⁺ diffusion by possible interstitial mechanism in γ -Li₃PO₄

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.)



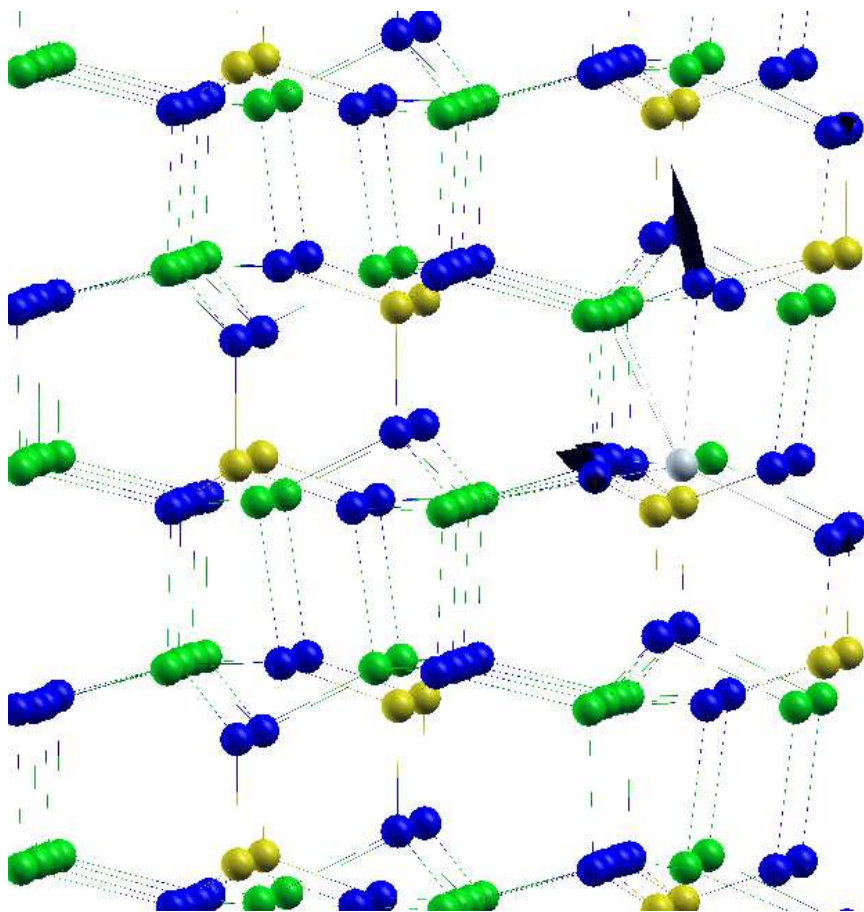
Site 1



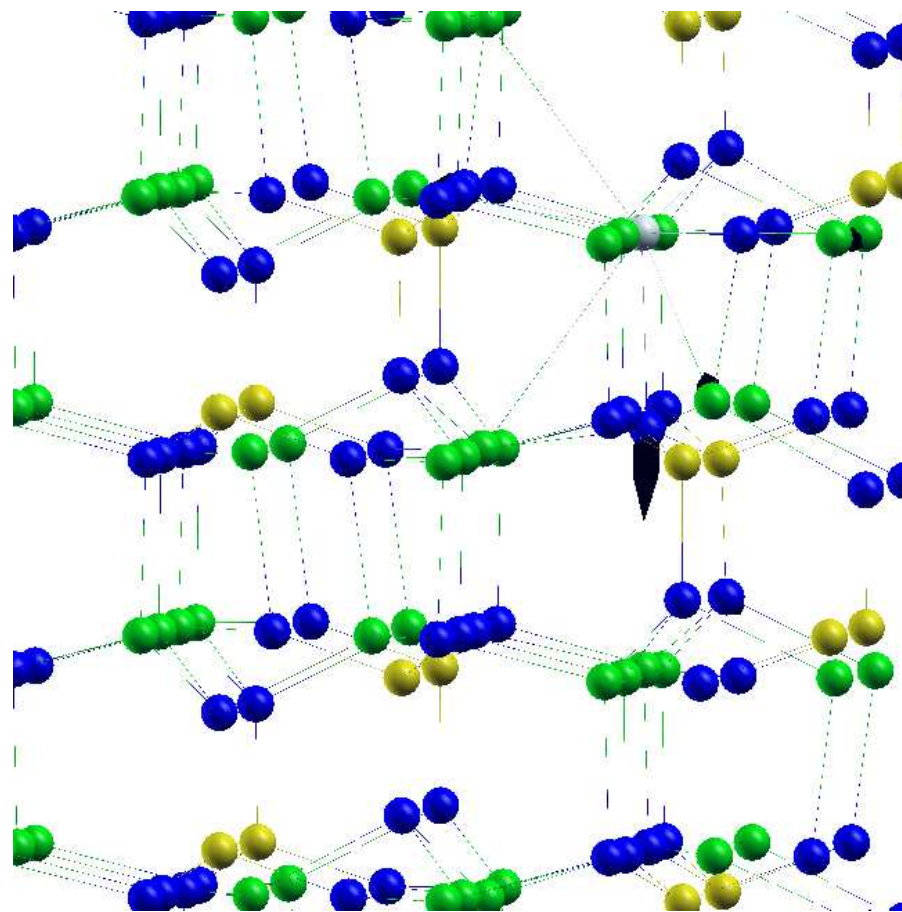
Site 2

Li⁺ diffusion by possible vacancy mechanism in γ -Li₃PO₄

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.)



Site 1



Site 2

Results so far for Li-ion diffusion mechanisms in γ -Li₃PO₄

- 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_3PO_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.)