Is doping of LiFePO$_4$ possible? Desirable?

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understand the electronic transport of LiFePO$_4$ (LFP) $d$-electrons responsible for e$^-$ transport AND magnetism
⇒ Both must be described self-consistently
In relation to the electronic structure
↓
Is doping possible (enough to make LFP “metallic”) ?
  Is it desirable ??
Crystallo-chemistry of LiFePO$_4$ (triphylite)

- orthorhombic olivine structure ($Pnma$)
- distorted hexagonal close-packed framework containing Fe$^{2+}$ ions
- layers of edge-sharing FeO$_6$ octahedra
- layers are separated by PO$_4$ tetrahedra.

**lattice parameters**

LiFePO$_4$ (*triphylite*)

$a=10.3375$ Å, $b=6.0112$ Å, $c=4.6950$ Å

FePO$_4$ (*heterosite*)

$a=9.7599$ Å, $b=5.7519$ Å, $c=4.7560$ Å.

Electronic structure

Zhou, F.; Cococcioni, M.; Kang, K.; Ceder, G.

\[
\text{LiFePO}_4 \\
U=4.3 \text{ eV}
\]

\[
\begin{align*}
\text{Density of states (eV}^{-1}\text{)}
\end{align*}
\]

\[
\begin{align*}
\text{E}_g=3.7 \text{ eV}
\end{align*}
\]

\[
\text{Fe}^{2+} \text{ in (eg}^{\uparrow})^2(tg^{\uparrow})^3tg^{\downarrow} \text{ spin } S=2
\]
Optical properties

\[ \Phi(R) = \frac{(1 - R)^2}{2R} \]

\[ [\Phi(R)h\nu]^n \propto h\nu \]

\( n = 2 \) (instead of 1/2)

The energy gap is HUGE: 3.84 eV

LFP is IONIC, not a semiconductor
Formation of small polaron

- Phonon
- Photon at optical gap

Final state: \( \text{Fe}^{3+} + e^- \)

Initial state: \( \text{Fe}^{2+} \)

Energy (au)

Configuration coordinate \( q \)

\( E_g \)
Electronic conductivity

$E_a = 0.6 \text{ eV}$

characteristics of Fe-phosphate glasses:

$xP_2O_5 - (1-x)FeO$

$(50-x)FeO - 50 P_2O_5 - xBaO$

$- xNa_2O$

$- xCaO$

Etc.


Solid State Ionics 2003, 157, 293 and references therein
Polaronic conductivity

Mott formula: \[
\sigma = c(1-c)\frac{e^2\nu_e}{RkT}\exp(-2\alpha R)\exp\left(-\frac{E_a}{kT}\right)
\]

wave function decay for iron ion is \(\alpha = 1.5 \text{ Å}^{-1}\)

Fe-Fe distance is \(R=3.87 \text{ Å}\).

electronic frequency is \(\nu_e = 10^{15} \text{ Hz}\)

\(E_a = 0.62 \text{ eV}\): barrier energy to overcome to jump on next site

\[c = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}+\text{Fe}^{3+}]} = 3.5 \times 10^{-3}\]
Magnetic properties

LiFePO$_4$

$\mu_{\text{eff}} = 4.98 \mu_B$

$\mu_{\text{eff}} = 5.36 \mu_B$

$T_N = 52$ K

Temperature (K)

H/M (mol Oe/emu)
(Magnetic) polaron in LiFePO$_4$
What does the Curie-Weiss law tell us at $T>T_N$?

\[ \mu_{\text{eff}} = g\mu_B \sqrt{S(S+1)} \]

« spin only value (quenched) »

Theoretical value for Fe$^{2+}$(S=2): $4.90\mu_B$

Magnetic polaron in LiFePO$_4$

\[ \mu_{\text{eff}}^2 = (1-c)[\mu(\text{Fe}^{2+})]^2 + c(\mu_{\text{pol}})^2 - 8c[\mu(\text{Fe}^{2+})]^2 \]

\[ \mu_{\text{eff}} = 5.36, \mu_{\text{pol}} = (8*2+5/2)*2 = 37 \]

\[ c = 3 \times 10^{-3} \]
Case of a semiconductor: EuO (ferromagnet, Tc=69 K)

- Gd$^{3+}$ ion or O vacancy
- Eu$^{2+}$ and Gd$^{3+}$ carry a spin S=7/2

Case of “doped” EuO

In the paramagnetic phase:
Formulation of a polaron

Case of “doped” EuO

In the ferromagnetic phase:
Classical donor
EuO

Mauger, A.; Godart, C.

Polaronic regime $E_a=0.6$ eV: energy to send the bound electron to the conduction band

Semicon. $E_a=\text{few mev}$

Metal
Cation doping

Doping by substitution of \( \text{Fe}^{2+} \) by \( M^{n+} \) (\( n \neq 2 \)) is not possible because LFP is too ionic: **HOPPING** transport, i.e. **not** driven by ionization of electrons of bound polarons.

\( \text{Nb}^5, \text{Zr}^4, \text{Ti}^4, \text{Cr}^{3+}, \text{V}^5 \ldots \)
combined neutron and X-ray diffraction studies locate the supervalent-cation dopants (Zr,Nb,Cr) on Li, and charge compensation assumed by Li vacancies:
M. Wagemaker, B.L. Ellis, D. Lützenkirchen-Hecht, F.M. Mulder, L. Nazar,

Any other claim results from artifacts (metal Nb, Zr,… impurities at the surface)
Doping is not to be confused with surface modifications

- Surface coating by conductive carbon is the best solution since 2001. Alternative: conductive polymer

- Since the limit of solution of “dopant” such as Nb, Zr, Cr, Ti, V etc is small (3%), the excess may form a metal coat at the surface (uncontrolled + massy; should be avoided).

- Coating with Fe$_2$P: efficient only on a short term basis: Fe$_2$P dissolves into the electrolyte: reduces the calendar life: PROHIBITED!!
Doping with Mg ??

- If Mg is in substitution to Fe: isovalent (2+): **no doping** in any other case, the channels are blocked:
- If Mg in substitution on Li (J. Song, Y. Zhang, G. Shao, J. Nanomat. (2013) Article ID 687501): damageable
- Ab initio calculations: antisite (Mg on Li site + Li on Fe site) H. Zhang et al. Appl. Phys. A 104 (2011) 529

\[ \text{hopless} \]
Doping by deviation from stoichiometry?

- Li-rich: \( \text{LiFePO}_4 + x \text{Li}_3\text{PO}_4 \rightarrow \) does not work
- Li-poor: \( \text{Li}_{1-2x}\text{Fe}_x\text{FePO}_4 \), i.e. \( \text{Fe}^{\bullet}\text{Li} + 2\text{V}^{'\text{Li}} \rightarrow \) does not work


Such a doping is impossible
Anion Doping

• F⁻₁ doping
  X.Z. Liao, Y.S. He, Z.F. Ma, X.M. Zhang, L. Wang, J. Power Sources 174 (2007) 720 assume that 3(F⁻) substitute for (PO₄)³⁻, very unlikely: computations suggest that O tends to be replaced by Cl⁻ [M.E. Arroyo de Dompablo, U. Amador, J.M. Tarascon, J. Power Sources 174 (2007) 1251]... the results are not as good as “undoped” C-LiFePO₄.

• Cl⁻ doping
  Cl⁻ doped C-LFP has a capacity 90 mAh/g at rate 20C but tests on few cycles only, and concentration of Cl⁻ is unknown! [C.S. Sun, Y. Zhang, X.J. Zhang, Z. Zhou, J. Power Sources 195 (2010) 3680].

In any case it means a deformation of the PO₄³⁻ ions
(confirmed by the changes in P-O distances by Cl-doping)
What if the PO$_4$ phosphate is de-stabilized by anion doping so that the material reduces to a simple transition metal oxide???

Two major consequences

- Lost of thermal stability
- Tendency to loose oxygen that will migrate to the carbon electrode, and C+O$_2$ --> CO$_2$ exothermic reaction: thermal runaway: we have lost SAFETY
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160 (2013) A3001
Do you really want an unsafe battery?

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Conclusion

• Self-consistent quantitative analysis of both electronic and magnetic properties show that LiFePO$_4$ is a truly ionic material.

• The small polaron is a new kind of magnetic polaron that must be distinguished from the other kinds of magnetic polarons investigated before in magnetic (not so ionic) semiconductors.

• Consequence: cation doping is not possible.
• Doping by deviation from stoichiometry is not possible
• Anion doping is possible, BUT not desirable: no evident improvement vs. un-doped C-LFP, plus risks to loose thermal stability, and loss of safety (check equilibrium pressure of oxygen !!)