The perspectives on fluoride phosphates cathode materials for metal-ion batteries

Evgeny Antipov

Department of Chemistry, Moscow State University
Outline

- Introduction
- Main types of cathode materials for LIB
- AMPO4F and A$_2$MPO$_4$F fluoride-phosphates
- Concluding remarks

1995: «Advances in battery research are always restricted by chemistry»

R. E. Powers (N.Y. Times)
Energy storage systems

Increase of Energy and Power

Stationary energy storage

HEV, EV

Consumer electronics

up to 250 Wh/kg
Perspectives for Li-ion batteries

"Battery technology is one of the most important subjects affecting the technological future of man"

Charlie Munger
Vice Chairman of Berkshire

(Yunil HWANG, A. D. Little Korea, Korea, “Nano-enhanced Market Perspectives in Solar & Li-ion Battery” OECD workshop on “Nanotechnology for sustainable energy options”, 2010)

<table>
<thead>
<tr>
<th>Year</th>
<th>Robot Share ('19)</th>
<th>CAGR ('09-'19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'19</td>
<td>17.6%</td>
<td>52.4%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>Storage Share ('19)</th>
<th>CAGR ('09-'19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'19</td>
<td>18.5%</td>
<td>18.2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>EV Share ('19)</th>
<th>CAGR ('09-'19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'19</td>
<td>40.5%</td>
<td>79.8%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>IT Share ('19)</th>
<th>CAGR ('09-'19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'19</td>
<td>23.3%</td>
<td>9.1%</td>
</tr>
</tbody>
</table>
Safety problem

**Batteries at the Heart of the Crisis**

- Electrolyte fluid in the batteries can be highly flammable if it leaks and is also corrosive.
- US safety watchdogs say that if the faults are not corrected it ‘could result in damage to critical systems and structures, and the potential for fire in the electrical compartment’.

**Flying Power Plant**

- The Dreamliner uses about five times more electrical power than other aircraft.
- It generates power using two lithium ion battery packs – the main one near the front and a second one in the rear (above).
- Electric power is used to start the engines, run the cabin pressurisation and air conditioning, melt ice on the wings, and operate the brakes.

- A lithium battery fire can burn at up to 1000°C – three times hotter than the melting point of the Dreamliner’s revolutionary carbon-fibre skin at 343°C.

Daily Mail, 20.01.2013
Impact of crystallography

Design of new structures:
- crystal chemistry concepts
- data mining
- *ab initio* structure predictions

Crystallographic aspects of electrochemical reactions:
- *in situ* and *ex situ* X-ray and neutron diffraction studies
- spectroscopic methods (EXAFS, XPS, XANES etc)
- microstructure evolution

Electrochemical processes on atomic scale:
- *ex situ* electron diffraction (PED) studies, atomic resolution TEM imaging and spectroscopy
- *in situ* TEM

J. Hadermann et al., Chem. Mat. 23 (2011) 3540
Main discovery

0025-5408/80/060783-07$02.00/0 Copyright (c) 1980 Pergamon Press Ltd.

$\text{Li}_x\text{CoO}_2 (0 < x < 1)$: A NEW CATHODE MATERIAL FOR BATTERIES OF HIGH ENERGY DENSITY

K. Mizushima, P.C. Jones, P.J. Wiseman and J.B. Goodenough
Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR

The synthetic route requires use of a starting high-temperature material that allows low-temperature extraction of lithium. The resultant phase need not necessarily be thermodynamically stable.

Examination of the known Li$^+$-ion solid
**Li-ion battery**

**Concept (1980) - Commercialization: Sony (1990)**

$$\text{C}_6 + \text{LiCoO}_2 \xleftarrow{charge} \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \quad x \approx 0.5-0.6 \text{ e}^-$$

**Voltage: 3.6 V**

$$E^0 (\text{cathodic}) - E^0 (\text{anodic}) = E^0 (\text{cell})$$

**Electrolyte**
- salts: LiPF$_6$, LiBF$_4$, LiClO$_4$, LiAsF$_6$, LiCF$_3$SO$_3$
- solvents: EC, PC, DMC, DEC

1M LiPF$_6$ in EC/DEC/DMC

$$E_g (\text{gravimetric}) = C_g (\text{charge transferred between two electrodes per unit weight}) \times E^0 (\text{cell})$$
Why Li?

1) Larger “electrolyte window” → higher specific energy
2) Weak Li-O bonds → high Li-ion conductivity
3) Low size → mechanical stability

“electrolyte window”
Water – 1.23 V, for Li-electrolytes – up to 4 V

Cathode materials: importance

The energy density of a battery is the product of its capacity and its potential, and is mainly governed by the capacity of the positive electrode. Simple calculations show that an increase in cell energy density of 57 per cent can be achieved by doubling the capacity of the positive electrode, while one needs to increase the capacity of the negative electrode by a factor of 10 to get an overall cell energy density increase of 47 per cent (Tarascon 2002).

Tarascon, J.-M. 2002 Actualité Chimique 251, 130–137.

"Cost of Lithium‐Ion Batteries for Vehicles" – ANL Report

Li‐ion battery fabrication costs based on a LiCoO2‐type cathode:

Σ "Material": 76%

Component
- cathode 36%
- anode 14%
- separator 8%
- electrolyte 18%
- labor cost 12%
- overheads 12%
Selection of Electrode Material


H$_2$O – 1.23 V, Li-electrolyte – up to 4 V

Electrolyte window
(Oxidation and reduction of electrolyte outside the window)

How to reach this value?

To increase specific energy → to higher cathode potential and capacity

To increase power → to higher Li-ion diffusion rate
Cathode materials: characteristics and requirements

- Voltage
- Capacity
- Ionic mobility
- Electronic mobility
- Structural stability

M^{n+}/M^{(n+1)+} redox potential

\[ C_T (\text{A h g}^{-1}) = \frac{26.8 \times \Delta n}{M} \]

Energy = Voltage x Capacity

Molecular weight (g)

number of e⁻ or Li⁺
Cathode materials: characteristics and requirements

- **Energy**
  - Voltage
  - Capacity
- **Power**
  - Rate capability
    - Ionic mobility
    - Electronic mobility
    - Structural stability
- **Cyclability**

M\textsuperscript{n+}/M\textsuperscript{(n+1)+} redox potential

\[ C_T (\text{A h g}^{-1}) = \frac{26.8 \times \Delta n}{M} \]

*number of e\textsuperscript{-} or Li\textsuperscript{+}*

Molecular weight (g)

Energy = Voltage x Capacity

Increasing capacity (multi-valent systems)
Cathode materials: characteristics and requirements

Energy

- Voltage
- Capacity

Rate capability

- Ionic mobility
- Electronic mobility
- Structural stability

Cyclability

Energy = Voltage x Capacity

\[
\text{Energy} = \text{Voltage} \times \text{Capacity}
\]

\[
C_T (\text{A h g}^{-1}) = \frac{26.8 \times \Delta n}{M}
\]

\(\text{M}^{n+}/\text{M}^{(n+1)+}\) redox potential

\[\text{Molecular weight (g)}\]

\[\text{number of e}^- \text{ or Li}^+\]

\(\leq 4.8 \text{ V (vs. Li/Li}^+\)\)

\(V \times C\) enhancing potential

(Cathode materials: characteristics and requirements)
Selection of composition
Main Structure Types

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

**Main Structural Types**

- **Hexagonal close packing**
- **Cubic close packing**

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_t$ (mAh/g)</th>
<th>$E_g$ (Wh/kg)</th>
<th>$\sigma$ (S/cm)</th>
<th>$D$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>278 (0.5C$_t$)</td>
<td>556</td>
<td>$10^{-3}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>148</td>
<td>592</td>
<td>$10^{-5}$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>170</td>
<td>583</td>
<td>$10^{-9}$</td>
<td>$10^{-15}$</td>
</tr>
</tbody>
</table>
Polyanion cathodes

Advantages:
- greater chemical and thermal stability, which provides reliable long-term electrochemical cycling and allows them to be used in large-sized batteries
- a rich variety of crystal structures – larger playground for various substitutions
- the inductive effect, leading to a significant increase of the redox potential $M^{n+}/M^{(n-1)+}$

Drawbacks:
- Larger molecular weight – smaller capacity
- More sophisticated synthesis
The inductive effect

$A_xM M'(PO_4)_3$
LiFePO$_4$ - olivine

c_t = 170 mAh/g; E ~ 3.5 V

**Advantages:**
- stable material (3D structure + PO$_4$)
  \[ \text{LiFePO}_4 \leftrightarrow \text{FePO}_4 + \text{Li}^+ + \text{e}^- \]
- ecologically friendly
- cheap

**Disadvantages:**
- low electronic conductivity $\sim 10^{-9}$ S/cm
- low $D \sim 10^{-15}$ cm$^2$/s (t $\approx r^2/D$)
  - 2-phase mechanism
- low density
- medium potential
  (for phases with Mn = 4.2 V, Co = 4.9 V)

Li-ion diffusion pathway


BVS mapping with 3DBVSMAPPER program

\[
BVS = \sum_{j=1}^{N} \left[ \exp\left( \frac{R_o - d_j}{b} \right) \right] d_j \quad \text{bond distance,}\n\]

\[
R_o, b \quad \text{tabular constants}\n\]

Li$_{1-x}$Fe$_{1-y}$Mn$_y$PO$_4$: influence of cation substitutions

LiMPO$_4$:C:PVDF = 75:15:10, 1M LiPF6 in EC:DMC = 1:1

Increasing electrochemical capacity at high discharge rates (10C, 20C) with increasing Mn content
In situ XRPD

a) For \( \text{Li}_{1-x}\text{FePO}_4 \), almost whole process of is two-phase (LFP and FP)

b) For \( \text{Li}_{1-x}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{PO}_4 \), Li-deficient phase exhibits solid solution region \( \text{LxFMP} \) for \( \Delta x \) appr. 0.2-0.3 per f.u.

c) For \( \text{Li}_{1-x}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4 \), charge:

(two-phase region between LFMP and LxFMP) \( \rightarrow \) (solid solution LxFMP) \( \rightarrow \) (two-phase region between LxFMP and FMP).

discharge:

similar picture, but noticeable increase in the extent of the single-phase region is detected

Na-based olivines

$E_a$ for NaFePO$_4$ (maricite) 2.11 eV

Fedotov S.S. et al. submitted SSI
Crystallochemical tools in search for cathode materials of rechargeable Na-ion batteries and analysis of their transport properties

Fedotov S.S.. et al. submitted SSI

<table>
<thead>
<tr>
<th>Material</th>
<th>CC</th>
<th>Theoretical capacity, mAh/g</th>
<th>BVS mismatch (BVSMM), ±eV, u.</th>
<th>Activation energy, $E_a$ (BVEL), eV</th>
<th>Migration map dimensionality</th>
<th>VDP</th>
<th>BV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaFePO$_4$ maricite*</td>
<td>85671</td>
<td>154</td>
<td>1.32</td>
<td>8.94</td>
<td>-</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>NaFePO$_4$ olivine</td>
<td>169118</td>
<td>154</td>
<td>0.35</td>
<td>1.25</td>
<td>1D</td>
<td>1D</td>
<td></td>
</tr>
<tr>
<td>NaMnPO$_4$ olivine</td>
<td>36249</td>
<td>155</td>
<td>0.30</td>
<td>1.30</td>
<td>1D</td>
<td>1D</td>
<td></td>
</tr>
<tr>
<td>NaMnAsO$_4$ olivine</td>
<td>95087</td>
<td>124</td>
<td>0.22</td>
<td>1.22</td>
<td>1D</td>
<td>1D</td>
<td></td>
</tr>
<tr>
<td>NaFeSO$_4$F*</td>
<td>290051</td>
<td>138</td>
<td>0.92</td>
<td>5.14</td>
<td>-</td>
<td>1D</td>
<td></td>
</tr>
<tr>
<td>O3-Na$_{0.92}$CoO$_2$*</td>
<td>155498</td>
<td>218</td>
<td>0.67</td>
<td>3.76</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>P2-NaCoO$_2$</td>
<td>246585</td>
<td>237</td>
<td>0.29</td>
<td>0.72</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>O3-Na$<em>{0.60}$Mn$</em>{0.30}$Fe$_{0.30}$O$_2$*</td>
<td>420380</td>
<td>162</td>
<td>0.47</td>
<td>2.90</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>P2-Na$<em>{0.67}$Mn$</em>{0.33}$Fe$_{0.10}$O$_2$</td>
<td>194731</td>
<td>162</td>
<td>0.11</td>
<td>0.50</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>NaNiAsO$_4$</td>
<td>63353</td>
<td>122</td>
<td>0.08</td>
<td>0.50</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>Na$_2$FeVF$_7$</td>
<td>401862</td>
<td>188</td>
<td>0.06 (1D)</td>
<td>0.70 (1D)</td>
<td>2D</td>
<td>1D/2D</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.19 (2D)</td>
<td>1.07 (2D)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaFeF$_3$</td>
<td>68981</td>
<td>197</td>
<td>0.77</td>
<td>3.99</td>
<td>3D</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>Na$_2$NiZr(PO$_4$)$_3$</td>
<td>172807</td>
<td>158</td>
<td>0.23</td>
<td>1.16</td>
<td>3D</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>Na$_2$NiP$_2$O$_7$F$_2$</td>
<td>251666</td>
<td>148</td>
<td>0.13 (1D)</td>
<td>0.59 (1D)</td>
<td>3D</td>
<td>1D/2D</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.15 (2D)</td>
<td>0.80 (2D)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31 (3D)</td>
<td>0.85 (3D)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$V$_2$(PO$_4$)$_3$</td>
<td>248140</td>
<td>198</td>
<td>0.32</td>
<td>1.25</td>
<td>3D</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>Na$<em>2$Fe$</em>{2.5}$(SO$_4$)$_3$</td>
<td>252402</td>
<td>189</td>
<td>0.16</td>
<td>1.46</td>
<td>1D</td>
<td>1D</td>
<td></td>
</tr>
<tr>
<td>Na$_2$V$_2$(PO$_4$)$_3$</td>
<td>188671</td>
<td>145</td>
<td>0.17</td>
<td>1.35</td>
<td>3D</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O·11Al$_2$O$_3$*</td>
<td>67545</td>
<td>–</td>
<td>0.08</td>
<td>0.24</td>
<td>2D</td>
<td>2D</td>
<td></td>
</tr>
</tbody>
</table>

* - reference materials chosen for comparison

Table 4. Calculated BVS mismatch values and activation energies for some selected and reference materials.
Search for new cathode materials: + Fluoride anion

Ionicity of the M-L bond

Inductive effect: LiFePO$_4$ (J. Goodenough 1997)*

Compounds with polyanions $(XO_m)^{n-}$: $(BO_3)^{3-}$, $(SiO_4)^{4-}$, $(PO_4)^{3-}$, $(SO_4)^{2-}$

Inductive effect + higher ionicity of the M-F bond → high energy density

Difference in formal charges → faster Li$^+$ transport → high power density

$r$(O$^{2-}$) = 1.21Å  ≈  $r$(F$^-$) = 1.15Å

Search for new cathode materials: + Fluoride anion

inductive effect: $\text{LiFePO}_4$ (J. Goodenough 1997)*

compounds with polyanions $(\text{XO}_m)^{n-}$: $(\text{BO}_3)^{3-}$, $(\text{SiO}_4)^{4-}$, $(\text{PO}_4)^{3-}$, $(\text{SO}_4)^{2-}$

$r(\text{O}^-) = 1.21\text{Å} \approx r(\text{F}^-) = 1.15\text{Å}$

inductive effect + higher ionicity of the M–F bond → high energy density

difference in formal charges → faster Li$^+$ transport → high power density

Compounds with two anions: $(\text{XO}_m)^{n-}$ and F$^-$

$(\text{SO}_4)^{2-}$ and F$^-$

LiMSO$_4$F**

$(\text{PO}_4)^{3-}$ and F$^-$

LiMPO$_4$F, Li$_2$MPO$_4$F

Fluoride-sulphates: LiFeSO$_4$F

FeSO$_4$ * H$_2$O + LiF $\xrightarrow{300^\circ C, IL}$ LiFeSO$_4$F + H$_2$O
tavorite

LiMn$_{0.05}$Fe$_{0.95}$SO$_4$F - triplite

N. Recham et al, Nature Mater. 9 (2010) 68
P. Barpanda et al, Nature Mater. 10 (2011) 772
Fluoride-phosphates $A_2MPO_4F$

- different conjugation of $(MO_4F_2)$ octahedra
- different transition metal

$(NaLi)_2FePO_4F$ – 2D

$Na_2MnPO_4F$ – 3D

$Li_2MPO_4F$ (M=Ni, Co) – 3D

$C_T \sim 140$ mAh/g for $M^{2+}/M^{3+}$

$C_T \sim 280$ mAh/g for $M^{2+}/M^{4+}$

1. B.L.Ellis et al., Nature Mat. 6 (2007) 749
3. M. Dutreilh et al., JSSC 142 (1999) 1
3D-Li$_2$CoPO$_4$F: crystal structure

S.G.: Pnma

- Li1 (8d) $+0.77$ +
- Li2 (4c) $+0.98$ ?
- Li3 (4c) $+1.22$ –

BVS mapping

• 3D structure (thermal and electrochemical stability)
• 1D Li-ion diffusion pathway
• 3 independent Li-positions, Li-ion mobility: Li1 > Li2 > Li3

N.R. Khasanova et al., J. of Power Sources 196 (2011) 355
### Activation Energies and Migration Path Lengths in Li$_2$ CoPO$_4$ F According to DFT-NEB

<table>
<thead>
<tr>
<th>N</th>
<th>path length, Å</th>
<th>transition type</th>
<th>$E_a$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.677</td>
<td>Li$_1$ $\rightarrow$ Li$_2$</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>3.330</td>
<td>Li$_1$ $\rightarrow$ Li$_1$</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>3.130</td>
<td>Li$_3$ $\rightarrow$ Li$_1$</td>
<td>0.43</td>
</tr>
<tr>
<td>4</td>
<td>3.110</td>
<td>Li$_3$ $\rightarrow$ Li$_1$</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>3.167</td>
<td>Li$_1$ $\rightarrow$ Li$_1$</td>
<td>0.41</td>
</tr>
<tr>
<td>6</td>
<td>2.416</td>
<td>Li$_1$ $\rightarrow$ Li$_2$</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Li-ion transport by DFT-NEB
$\text{Li}_2\text{CoPO}_4\text{F}$ vs $\text{LiCoO}_2$

<table>
<thead>
<tr>
<th>Crystal structure, dimensionality of polyhedral framework</th>
<th>LiCoO$_2$</th>
<th>Li$_2$CoPO$_4$F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td><img src="LiCoO2_2D.png" alt="Image" /></td>
<td><img src="Li2CoPO4F_3D.png" alt="Image" /></td>
</tr>
<tr>
<td>3D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Average exp. potential vs Li/Li$^+$, V                     | 3.9       | ~ 5              |
| Theo. capacity/specific energy, mAh·g$^{-1}$/mWh·g$^{-1}$  | 274 / 1068| 143 / 715 (1ē)   |
|                                                           |           | 215 / 1075 (1.5ē)|
| Exp. capacity/specific energy, mAh·g$^{-1}$/mWh·g$^{-1}$  | 140 / 545 | 140 / > 650      |
| Diffusion barrier, eV                                     | 0.52      | 0.12 – 0.42      |

More facile diffusion is anticipated for $\text{Li}_2\text{CoPO}_4\text{F}$

*S.Fedotov et al., Phys.Chem. C 121 (2017) 3194*
Li$_2$CoPO$_4$F: electrochemical properties

**high-voltage electrolytes**

- solid-solution mechanism of Li$^+$ de/intercalation
- discharge capacity of ~ 140 mAh$^{-1}$ (~1.0 Li$^+$)

N.R. Khasanova et al., *Beilstein Journal of Nanotechnology* (2013) 4, 860
J.Schoiber et al., Cryst.Growth Des. (2016), DOI: 10.1021/acs.cgd.6b00573
Li$_2$CoPO$_4$F: electrochemical properties

- Calculated voltage profile (DFT)

Involving of Li$_2$(Li$_3$) in diffusion: extraction of 1.5 Li$^+$ per f.u. At 5.8 V

High-voltage electrolyte! Adjusting the working potential!

S. Fedotov et al., Phys. Chem. C 121 (2017) 3194
Li$_2$MPO$_4$F system: substitution on metal sites

- **Alkali-metal site**
  - Li
  - Na

- **TM site**
  - Mn$^{2+}$
  - Fe$^{2+}$
  - Co$^{2+}$
  - Ni$^{2+}$

- \[ r, \text{Å} \]
  - \( 0.83 \)
  - \( 0.78 \)
  - \( 0.74 \)
  - \( 0.69 \)

- \[ E^*(M^{2+}/M^{3+}), \text{V} \]
  - \( 4.1 \)
  - \( 3.45 \)
  - \( > 4.8 \)
  - \( > 5.2 \)

- **Unit cell parameters of Li$_2$(Co$_{1-x}$Fe$_x$)PO$_4$F**
  - \( x \leq 0.3 \)

- **Unit cell parameters of Li$_2$(Co$_{1-x}$Mn$_x$)PO$_4$F**
  - \( x \leq 0.1 \)

- **“framework elasticity”**

- **Narrow range of solid solutions!**
NaLiFePO$_4$F: electrochemical performance

**Simulation**

6th cycle

formation of 3D- Li$_2$FePO$_4$F

**Li$_2$FePO$_4$F: ex-situ structure refinement after cycling at 75° C**

electron diffraction tomography

difference Fourier map:
complete Li/Fe ordering
antisite Li/Fe disorder

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Occupancy</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U$_{iso}$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>8d</td>
<td>0.908(7)Li</td>
<td>0.748(1)</td>
<td>0.960(2)</td>
<td>0.652(1)</td>
<td>0.0200(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.098(7)Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2</td>
<td>4c</td>
<td>0.64(1)Li</td>
<td>0.9726(8)</td>
<td>3/4</td>
<td>0.7156(7)</td>
<td>0.0200(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36(1)Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li3</td>
<td>4c</td>
<td>0.88(1)Li</td>
<td>0.282(1)</td>
<td>1/4</td>
<td>0.575(1)</td>
<td>0.0200(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.12(1)Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1</td>
<td>4a</td>
<td>0.71(2)Fe</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0200(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.29(2)Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe2</td>
<td>4b</td>
<td>0.61(1)Fe</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>0.0200(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39(1)Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

O. Karakulina et al. Chemistry of Materials 28 (2016) 7578
Li$_2$FePO$_4$F: antisite disorder

Heavily underbonded after Li1 deintercalation
Li$_2$FePO$_4$F: antisite disorder
Comparison: Li$_2$MPO$_4$F vs. LiFePO$_4$

solid solution  
D$_{\text{chem}}$ ≈ 10$^{-10}$ cm$^2$/s

2-phase mechanism  
≈ 10$^{-15}$ cm$^2$/s

Co        Fe
Volume change (%)  ~ 4.5 %  1.7%  6.7%
E$_g$ for 1Li (Wh/kg)  730  496  583
E$_g$ for 1.5 Li (Wh/kg)  1095  744  -

Possibility of Fe$^{2+}$/Fe$^{4+}$?  
Ab initio study for Li$_2$FePO$_4$F: Fe$^{3+}$/Fe$^{4+}$ possible at potentials ~ 5.1 V vs. Li/Li$^+$

F. Yang et al., RSC Adv., 2014,4, 50195-50201
**Background:**
1) $\text{Li}_{1+x}\text{VPO}_4\text{F}$ (tavorite structure): 2-electron redox-transition:
   \[ \sim 4.2 \text{ V(vs. Li}^+/\text{Li)} \text{ (cathode)} \sim 1.8 \text{ V(vs. Li}^+/\text{Li)} \text{ (anode)} \]
   J.Barker et al. JES (2003)150, A1394

2) $\text{Li}_{1+x}\text{FePO}_4\text{F}$ (tavorite structure)
   \[ \sim 2.8 \text{ V(vs. Li}^+/\text{Li)} \]

3) $\text{LiFeSO}_4\text{F}$ (tavorite structure)
   \[ \sim 3.6 \text{ V (vs. Li}^+/\text{Li)} \]
   N. Recham et al, Nature Mater.9 (2010) 68

4) $\text{KFeSO}_4\text{F}$ (KTP structure)
   \[ \sim 3.7 \text{ V (vs. Li}^+/\text{Li)} \]

**AMPO$_4$F with KTP-type structure ???**
• **Synthesis** at 600° C, Ar-flow for 1h
  \[ \text{VPO}_4 + \text{KHF}_2 \rightarrow \text{KVPO}_4\text{F} \]

• **Structure**
  S.G. #33 *Pna2*$_1$, \(a = 12.8200(3) \text{ Å}, \ b = 6.3952(1) \text{ Å}, \ c = 10.6115(2) \text{ Å}\)

*Fedotov S.S. et al, Chem. Mater. 28 (2016) 411*
AVPO$_4$F (A = Li, K): cycling behaviour

A charge-discharge curve of Li$_x$K$_{0.15}$VPO$_4$F at C/5. The inset - the capacity retention and Coulomb efficiency in the cycling at 1C rate

C-rates capability upon cycling and discharge curves of Li$_x$K$_{0.15}$VPO$_4$F

A remarkable capacity retention at 40C maintaining more than 50% of theoretical (156 mAh/g) or 75% of initial specific capacity
Structural transformations: “depotassiated” and lithiated forms

Volume variation among all phases is less than 2.2% !!!
I. Low-voltage domain:

- Second Li$^+$?
- V$^{3+}$/V$^{2+}$?

Theo. capacity (2 Li$^+$) ~300 mAh/g!

The goal:
increasing both potential and capacity
AVPO$_4$F ($A = Li, K$): comparison of KTP and tavorite structures for LIB

- $E_g$: 624 Wh/kg
- $E_v$: ~2000 Wh/l
- $\Delta V$: ~2%
- Mechanism: Solid solution
- Perspective cathode material for high-power batteries
- Both materials can be used in symmetrical cell
KTP-type fluoride-sulfate framework


KFeSO₄F

Tarascon’s group

FeSO₄F

“Depotassiation”

Versatility of the KTP framework!
KVPO$_4$F against Li, Na and K

3-electrode cell configuration

Electrolyte: 1M APF6 or ACIO4 in EC/DEC

Counter electrodes: Li, Na or AgCl/Ag
Alkali ion diffusion

Bond Valence Energy Landscapes

From PITT: $D(\text{Li}) < D(\text{Na}) < D(\text{K}) \approx 10^{-13} - 4 \cdot 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$.
Fluoride-phosphates based Me-ion battery prototypes

$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3 / \text{Hard carbon}$

110 Wh/kg 18650 Na-ion battery


IBA-2016 meeting in Nantes, France:
RS2E announced a new 3.8 V LiVPO4F Li-ion battery prototype (outperforming LiFePO4 based Li-ion battery)

Fluoride phosphates are commercially viable cathode materials!
Na-ion batteries are coming on the market!!! KIB?
Acknowledgements

Nellie Khasanova
Oleg Drozhzhin
Viktoria Nikitina
Stanislav Fedotov
Alexander Samarin
Vasily Sumanov

Lomonosov Moscow State University

Skoltech Center for Electrochemical Energy Storage,
Skolkovo Institute of Science and Technology

Artem Abakumov, Keith Stevenson

EMAT, RUCA, Antwerp
Dmitry Batuk, Joke Hadermann, Olesya Karakulina

Samara University
Artem Kabanov, Vladislav Blatov