In-situ study on the structural changes of a lithium ion battery with LiFePO4.VOx as the cathode materials by neutron and synchrotron radiations

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**Table. The comparison of various lithium ion batteries**

<table>
<thead>
<tr>
<th>Cathode materials</th>
<th>LiCoO$_2$</th>
<th>LiNiO$_2$</th>
<th>LiMn$_2$O$_4$</th>
<th>LiFePO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted capacities (mAh/g)</td>
<td>130~150</td>
<td>170~200</td>
<td>100~120</td>
<td>140~170</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>good</td>
<td>good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>&gt;500</td>
<td>-</td>
<td>&gt;500</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Mineral resources</td>
<td>few</td>
<td>medium</td>
<td>rich</td>
<td>Rich</td>
</tr>
<tr>
<td>Main applications</td>
<td>Cell phone, notebooks</td>
<td>Cell phone, notebooks</td>
<td>High power batteries, Car batteries</td>
<td>High power batteries, Car batteries</td>
</tr>
</tbody>
</table>

**Advantages of LiFePO$_4$**
- Environmentally friendly nature (less toxic).
- Higher safety
- Long lifetime
- Low cost
DSC (Differential Scanning Calorimetry)

Properties of Lithium Iron Phosphate

- Environmental friendliness, low price, non-toxicity, and exceptional stability.
- Orthorhombic -Pnma space group
- Fe$^{3+}$/Fe$^{2+}$ redox reaction in Li$_x$FePO$_4$ generates 3.4 V versus Li/Li$^+$
- Theoretical capacity = 170mAh/g
- **Major Limitation**: Poor rate performance
**Properties of LiFePO$_4$**

Environmental friendliness, low price, non-toxicity, and exceptional stability.

* Slow kinetics of lithium ion diffusion through the LiFePO$_4$/FePO$_4$ interface.

**Improvement**

- Minimize particle size
- Sol-Gel Co-precipitation
- Hydrothermal Solvothermal Spray Paralysis etc.

*Low electronic conductivity.*

**Improvement**

- Enhance electronic conductivity
- Supervalent cation doping (Li$_{1-x}$M$_x$FePO$_4$, M=Mg$^{3+}$, Zr$^{4+}$)
- Added conductive agent Metals (Ag, Cu)
- Carbon coating

Performance Enhancement of LFP-NCO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electroconductivity $\sigma$(S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO$_4$</td>
<td>$10^{-9}$-$10^{-10}$*</td>
</tr>
<tr>
<td>LiFePO$_4$ (/C)</td>
<td>$4.75 \times 10^{-4}$</td>
</tr>
<tr>
<td>LiFePO$_4$·zVO$_x$ (/C)</td>
<td>$1.9 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

LFP-NCO cathode material increases the electronic conductivity of LFP by a factor of $\sim 10^8$.

The specific capacity of LFP-NCO is enhanced by 33% compared to that of LiFePO$_4$.

Typical charge/discharge curves of the LiFePO$_4$ and LiFePO$_4$·zVO$_x$ cells at low current density (0.1C).

**APPLICATIONS**

- Real time: Single shot (kinetic) measurements
- Real time: Stroboscopic (cyclic, periodic) measurements (reversible)
- Small sample volumes
- Magnetic studies at “long” wavelengths (2.36 Å and 4 Å)
IN SITU NEUTRON DIFFRACTION ON A COMMERCIAL AVAILABLE LIFEPO4 BATTERY (7 MM THICK, 10 LAYERS)

Graphite + LiC₆  
LiFePO₄ + FePO₄  
Cu  
High Harmonic

Scan numbers

Two Theta (degrees)
THE in-situ neutron DIFFRACTION PATTERN OF Li$_x$C$_6$ (002)—FOR ANODE

The (002) peak corresponding to the average layer spacing shifts smoothly as Li$^+$ is added in lithiation graphite.

Fig. Neutron intensity vs scattering angle for the (002) region of Li$_x$C$_6$ in each stage phase measured by in-situ diffraction at room temperature.
Fig. (a) The second electrochemical cycle for charge and discharge of a Li$_x$C$_6$/LiFePO$_4$ commercial battery using a current corresponding to 0.1 C-rate at room temperature. (b)(c) These plateaus correspond to the coexistence range: dilute stage-1, stage-4, stage-3, stage-2, and stage-1.
Stage formation during electrochemical lithiation graphite. A: schematic constant current charge curve. B: schematic voltammetric curve.

LiC₆, space group P6/mmm with a=4.305 Å, and c=3.706 Å; LiC₁₂, space group P6/mmm with a=4.288 Å and c=7.063 Å.

Nazri G. A. et al., Lithium Battery: Science and Technology, 2009
The anode graphite charged
Intercalated, layers by layers
LiFePO₄ atom structure model

**Olivine structure**

- Space group: Pnmb
- \(a = 4.787\text{Å}, b = 10.086\text{Å}, c = 5.939\text{Å}\)
- \(\alpha = \beta = \gamma = 90^\circ\)

- Theoretic capacity: **170 mAh/g**
- Unmodified capacity: \(~110\text{ mAh/g}\)
- Conductivity: \(~10^{-9} \text{ S/cm}\)

Li-O length:
1. 2.0965Å (2) (coord.)
2. 2.1695Å (2)
3. 2.1943Å (2)
In situ X-ray diffraction

Asymmetry phase transition between LiFePO$_4$ and FePO$_4$ during charging/discharging process.
High Resolution Powder Diffractometer

APPLICATIONS
- Materials with complex crystal structures
- Subtle phase transitions
- Peak shape variation
  - strain, crystallite size, and defects
The lattice constant after doping with VOx did not change too much!
Did V atom really doped into LiFePO4?

V to replace Li is more probable. Create 3 Li vacancies.
Study of different charge rates by in-situ X-ray measurement at NSRRC

- 0.3 C Charging-Discharging
  - Asymmetry phase transition between LiFePO$_4$ and FePO$_4$ during charging/discharging process

- 2 C Charging-Discharging
  - Normal phase transition from LiFePO$_4$ to FePO$_4$ during charging
  - The phase cannot go back from FePO$_4$ to LiFePO$_4$ during discharging
Normal phase transition from LiFePO₄ to FePO₄ during charging.
The phase cannot go back from FePO₄ to LiFePO₄ during discharging.
Fourier transformation of the $k^3$-weighted EXAFS oscillations for 1% content sample: (a) V $K$-edge extend range and fitting curve, (b) simulated spectrum for V atom at Li octahedral site, (c) simulated spectrum for V atom at Fe octahedral site, and (d) Fe $K$-edge extend range and fitting curve.
Highly charge and discharge rate of LiFePO$_4$, resulting in the discharge very difficult (irreversible).

The asymmetry phase change is serious at high charge rate. V doped can alluviate part of this problem.
Experimental Results (XANES)

- **Fe K-edge**
  - [Graph showing Fe K-edge XANES with peaks and labels for Fe and Fe^3+ during Charge and Discharge processes.]

- **V K-edge**
  - [Graph showing V K-edge XANES with normalized absorption curves for Charge and Discharge processes.]
V to replace the Li site by seeing “the surrounding structure very similar to that of Li atoms”. V to be at site of Li and form a pillar-like support structure to allow Li atom more mobile?

Neel temperature is not change after adding V
DELAYED PHASE TRANSITION
NEUTRON POWDER DIFFRACTION
LiFePO$_4$/FePO$_4$ coexists
But, delay phase change might occur
Dope V change the “delay”.

The ratio between LiFePO$_4$/FePO$_4$ during the charge and discharge cycle reveals the kinetics results of Li diffusion mechanism. Doped with V, the phase change delay was not significant!
**DELAYED PHASE TRANSITION (LFPV-BASED)**

*In-situ* neutron powder diffraction: (Experiment at ANSTO)

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**non-delayed**

*In-situ* NPD patterns of triphylite (LFP:V) and heterosite (FP:V) during first (a) charging and (b) discharging cycle.
Delayed phase transition
Synchrotron XRD and XAS
-LFP-based-
Delay of phase transition
DEAD-LITHIUM (LFP-BASED)

![Graphs showing intensity vs. two theta for different cycles and conditions.](Image)

- **First cycle (0.5 C-1)**
  - Begin of charge
  - End of charge
- **Second cycle (0.5 C-2)**
  - Begin of charge
  - End of charge
- **Third cycle (1 C-1)**
  - Begin of discharge
  - End of discharge
- **Fourth cycle (1 C-2)**
  - Begin of discharge
  - End of discharge

Two theta (deg.) @ WV = 0.0953724 nm
The normalized in-situ Fe K-edge X-ray absorption near edge structure (XANES) spectra during first charge (a) and discharge (b) with contents of LiFePO₄ and FePO₄ calculation. The delayed phase transition of pristine-LFP was not observed. It seems like linear transition.
Phase delayed problem of LiFePO4:V:
Can be reduced by doping V by enhancing Li diffusion

Neutron powder diffraction show less delay full cell (graphite anode) and half cell (Li anode) small synchrotron beam -- non-uniform samples
X-ray absorption spectroscopy of Fe edge also show less delay some disordered structures
Summary

The delay of phase transition of LiFePO4 and FePO4 can be observed by in-situ neutron and X-ray diffraction. The delay of phase transition can be remedied partly by doping V atoms.

Observation of Fe+2 to Fe+3 during the charge and discharge cycle. The XANES of V shows no change of V valence state and the possibility of V replace the Li sites.

The structure of LiFePO4 cannot be recovered at very high charge and discharge rate.

The model of V to replace Li site might be V atoms acted as a supporting pillar to open the channel of Li diffusion.
Thank you for your attention!