Low temperature ionothermal synthesis of LiFeSO$_4$F cathode material for lithium-ion battery

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A 3.6 V lithium-based fluorosulphate insertion positive electrode for lithium-ion batteries

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Li-ion batteries have contributed to the commercial success of portable electronics, and are now in a position to influence higher-volume applications such as plug-in hybrid electric vehicles. Most commercial Li-ion batteries use positive electrodes based on lithium cobalt oxides. Despite showing a lower voltage than cobalt-based systems (3.45 V versus 4 V) and a lower energy density, LiFePO₄ has emerged as a promising contender owing to the cost sensitivity of higher-volume markets. LiFePO₄ also shows intrinsically low ionic and electronic transport, necessitating nanosizing and/or carbon coating. Clearly, there is a need for inexpensive materials with higher energy densities. Although this could in principle be achieved by introducing fluorine and by replacing phosphate groups with more electron-withdrawing sulphate groups, this avenue has remained unexplored. Herein, we synthesize and show promising electrode performance for LiFeSO₄F. This material shows a slightly higher voltage (3.6 V versus Li) than LiFePO₄ and suppresses the need for nanosizing or carbon coating while sharing the same cost advantage. This work not only provides a positive-electrode contender to rival LiFePO₄, but also suggests that broad classes of fluoro-oxyanion materials could be discovered.

Source: NATURE MATERIALS VOL 9 JANUARY 2010.

Laboratory of Reactivity and Chemistry of Solids, University of Picardie Jules Verne, France
Introduction to LiFeSO₄F cathode materials

Pros of LiFeSO₄F
- Slightly higher voltage (3.6 V versus Li)
- Tavorite structure (3D channels for Li migration)
- Low temperature synthesis (~300°C)
- Better ionic and electronic property
- Lower packing density
- Low cost

Cons of LiFeSO₄F
- Low capacity (~151 mAh/g)
- Not stable in water
(LiFeSO₄F → FeOOH + LiF)

Source: J-M. Tarascon et al., Nat. Mater., 2010, 9, 68.
demonstrated the relation between electricity and chemical bonding,

\[
\text{Capacity (mAh/g)} = \left[ \frac{F \times n_{\text{Li}}}{M \times 3600} \right] \times 1000
\]

Where, 
- \(F\) = Faraday’s constant (96,500 coulombs per gm equivalent)
- \(n_{\text{Li}}\) = Number of Li per formula unit of the electrode material
- \(M\) = Molecular mass of the electrode material

\[
\text{Cathode: } \text{LiFeSO}_4 F + e^- \rightarrow \text{Li} + \text{FeSO}_4 F
\]

\[
\text{LiFeSO}_4 F = \frac{96500 \times 1}{177.85 \times 3600} \times 1000 = 151 \text{ mAh/g}
\]
<table>
<thead>
<tr>
<th>Material</th>
<th>LiFePO₄</th>
<th>LiFeSO₄F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average working voltage (V)</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.5</td>
<td>3.23</td>
</tr>
<tr>
<td>Structure</td>
<td>1-D, Olivine</td>
<td>3-D, Tavorite</td>
</tr>
<tr>
<td>Theoretic specific capacity (mAh/g)</td>
<td>170</td>
<td>151</td>
</tr>
<tr>
<td>Practical specific capacity (mAh/g)</td>
<td>140-155</td>
<td>130-140</td>
</tr>
<tr>
<td>Energy Density (kWh/L)</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td>Conductivity (S/cm)</td>
<td>~10⁻⁹</td>
<td>~10⁻⁶</td>
</tr>
<tr>
<td>Li ion diffusivity (cm²/s)</td>
<td>~10⁻¹⁴</td>
<td>…</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&gt; 1000 cycle</td>
<td>…</td>
</tr>
<tr>
<td>Safety</td>
<td>superior</td>
<td>…</td>
</tr>
<tr>
<td>Cost</td>
<td>low</td>
<td>lower</td>
</tr>
</tbody>
</table>

- downsizing the particle size
- dopants
- Nano carbon conducting network
- Carbon nanocoating

However, for LiFeSO₄F ???
Summary of synthesis approaches toward the electrode materials

The experiment were carried out at 250 °C in glassware containers using EMI-TFSI as ionic liquid and LiH₂PO₄, FeC₂O₄·2H₂O precursors with concentration of $2.5 \times 10^{-3}$ mol/L.

Ionic liquid: 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imide (EMI-TFSI)

**Properties and applications of ionic-liquids**

- Thermal and chemical stability
- Negligible volatility
- Low melting point
- Flame retardancy
- High ionic conductivity
- Moderate viscosity
- Solubility (affinity) with many compounds
- High polarity

**Role of the ionic liquid**

TGA measurements conducted in the presence of either FeSO₄ · H₂O + ionic liquid, or FeSO₄ · H₂O + ionic liquid + LiF are compared to those done with only ionic liquid or FeSO₄ · H₂O. Note that EMI-TFSI postpones the release of H₂O until temperatures greater than 280°C, temperatures at which the double ion exchange reaction (H⁺ for Li⁺ and OH⁻ for F⁻) can proceed leading to the formation of LiFeSO₄F.


**EMI-TFSI: cation-anion pair**

Source: Michel Armand et al., Nat. Mater., 2009, 8, 621.
Flow chart of the LiFeSO$_4$F synthesis as a cathode material

Reaction: $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{LiF} \rightarrow \text{LiFeSO}_4\text{F} + \text{H}_2\text{O}$

Synthesis Process

FeSO$_4$ $\cdot$ 7H$_2$O → FeSO$_4$ $\cdot$ H$_2$O → FeSO$_4$ $\cdot$ H$_2$O

in vacuum

$\triangle T = 200^\circ\text{C}, 2\ h$

FeSO$_4$ $\cdot$ H$_2$O
Iron Sulfate heptahydrate

FeSO$_4$ $\cdot$ H$_2$O
Iron Sulfate monohydrate

$\triangle T = 300^\circ\text{C}, 4, 8, 16\ h$

$\triangle T = 275^\circ\text{C}, 24\ h$

LiFeSO$_4$F
Sandy/red power

Dried under vacuum at 60$^\circ$C

Wishing with dichloromethane

Precursor mixing

Ionic liquid (EMI-TFSI)

Cooling and centrifugation

Source: Inorganic Materials Laboratory (Room 15), Department of Engineering Materials, The University of Sheffield.
Experimental characterization of LiFeSO₄F

X-ray diffraction (XRD): to analyze phase composition of materials

The theoretical X-ray power diffraction pattern ($\lambda_{Co}$) of LiFeSO₄F was drawn using XRD software (STOE WinXPOW) following lattice parameters, cell volumes and atomic coordinates for LiFeSO₄F.

Source: Ceramics and composites Laboratory (Room 16), Department of Engineering Materials, The University of Sheffield.

Source: Supplementary information, Nat. Mater., 2010, 9, 68
XRD results of LiFeSO₄F

Intensity (a.u.)

2θ [deg]

FeSO₄·H₂O  Fe₂O₃  FeSO₄  Fe₂(SO₄)₃

300 °C, 4 hrs
300 °C, 8 hrs
300 °C, 16 hrs
XRD results of LiFeSO₄F

- FeSO₄·H₂O
- Fe₂O₃
- FeSO₄
- FeSO₄·H₂O

275 °C, 24 hrs
280 °C, 48 hrs

Intensity (a.u.)

2θ [deg]
Latent difficulties to synthesize single phase LiFeSO₄F:
1. The reaction paths of ionothermal synthesis and mechanism of ion-exchange for phase stabilization of LiFeSO₄F is hard to understand because of experimental temperature, pressure, composition and reaction time.
2. Too many Li⁺ perhaps solve into ionic liquid due to the existence of FeSO₄ · H₂O phase in produced material.
3. It is difficult to keep the monohydrated precursor free of Fe(III) (Iron oxidation: Fe²⁺ → Fe³⁺)
Conclusions

- The ionothermal synthesis of LiFeSO₄F cathode is quite straightforward. However, more studies need to be done to understand thermodynamic and kinetic stabilities of the ionic liquids with respect to the electrode materials.

- Ionic liquids can introduce kinetic lags in material dehydration (FeSO₄·H₂O → FeSO₄). Therefore, a greater effort into determining the solubility temperature dependence of the precursors need to be done because ionic liquid is active in the growing process of the newly born phases.

- To minimise the iron oxidation changed from Fe²⁺ to Fe³⁺ (Fe₂O₃ and Fe₂(SO₄)₃), ionothermal synthesis for LiFeSO₄F could be operated under an argon or a nitrogen atmosphere.
Acknowledgements

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