Low temperature ionothermal synthesis of $LiFeSO_4F$ cathode material for lithium-ion battery

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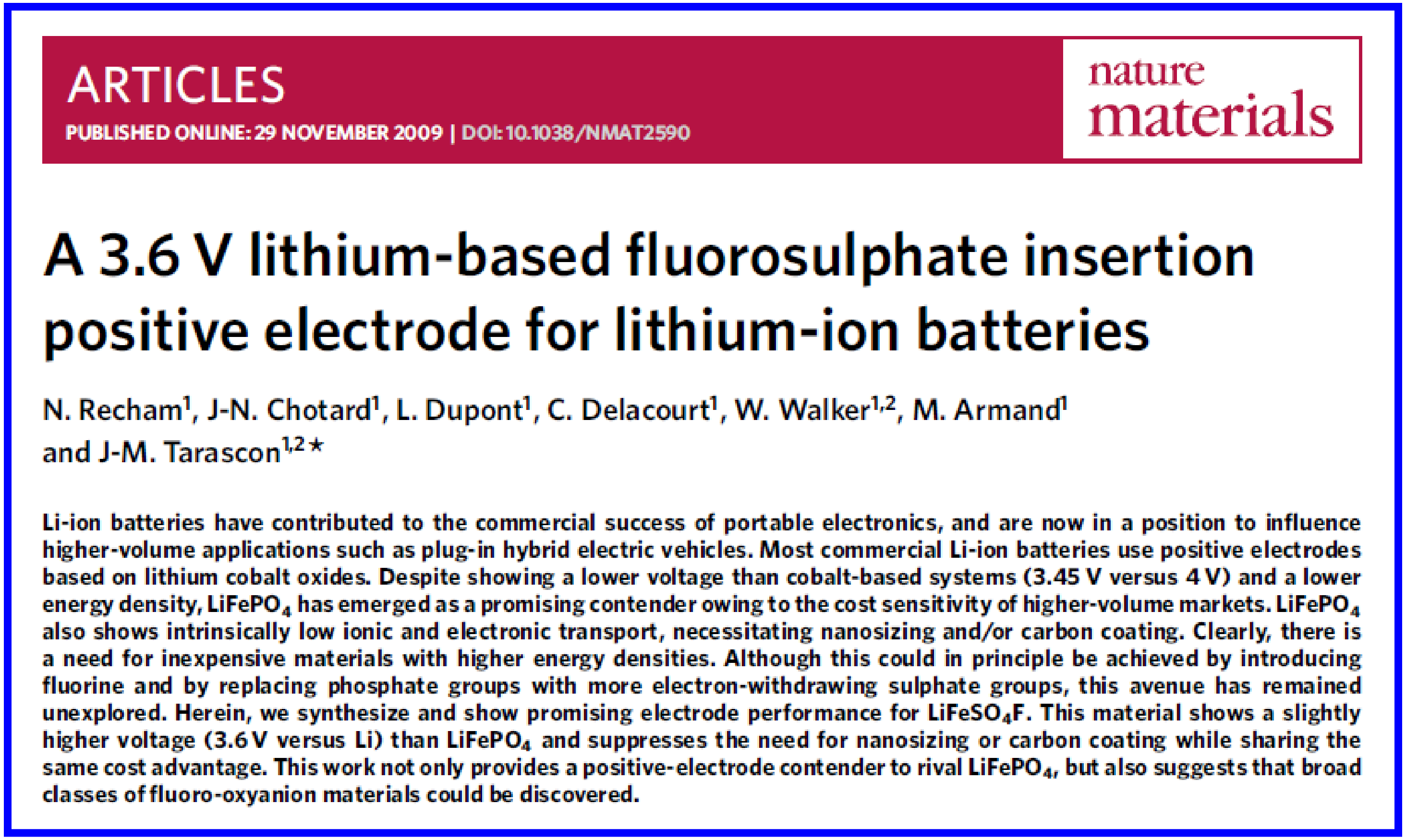
Outline

- Background
- Introduction
  - Material ($LiFeSO_4F$)
  - Methodology (Ionothermal)
- Experimental procedure
- Results and discussion
- Conclusions
- Acknowledgements

History........$LiFeSO_4F$ (2009-2010)



ARTICLES

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

N. Recham[1], J-N. Chotard[1], L. Dupont[1], C. Delacourt[1], W. Walker[1,2], M. Armand[1] and J-M. Tarascon[1,2]★

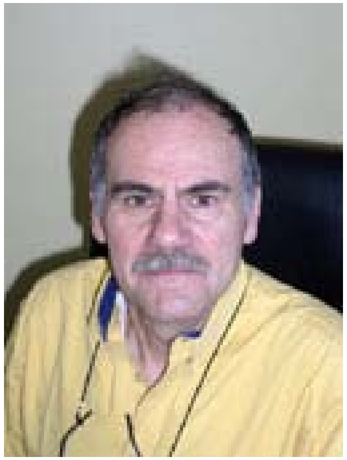
Li-ion batteries have contributed to the commercial success of portable electronics, and are now in a position to influence higher-volume applications such as plug-in hybrid electric vehicles. Most commercial Li-ion batteries use positive electrodes based on lithium cobalt oxides. Despite showing a lower voltage than cobalt-based systems (3.45 V versus 4 V) and a lower energy density, $LiFePO_4$ has emerged as a promising contender owing to the cost sensitivity of higher-volume markets. $LiFePO_4$ 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 $LiFeSO_4F$. This material shows a slightly higher voltage (3.6 V versus Li) than $LiFePO_4$ 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 $LiFePO_4$, 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

Jean-Marie Tarascon

Michel Armand



Introduction to $LiFeSO_4F$ cathode materials

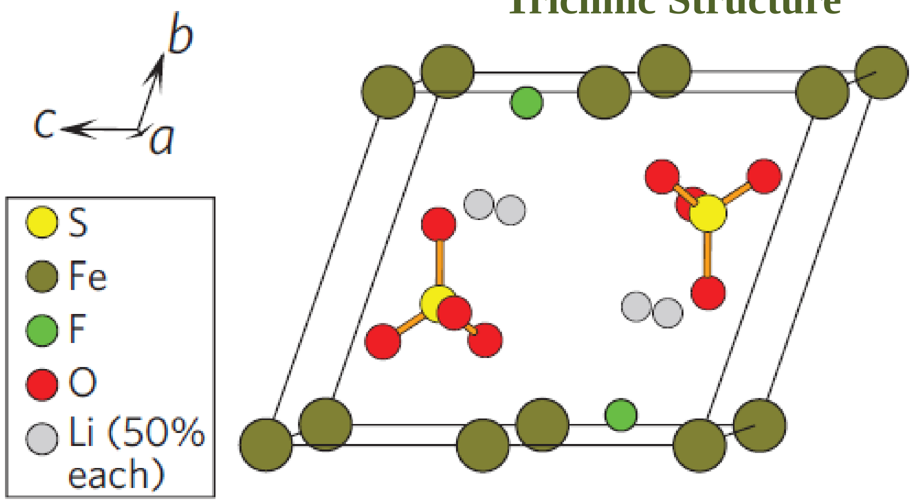
Pros of $LiFeSO_4F$

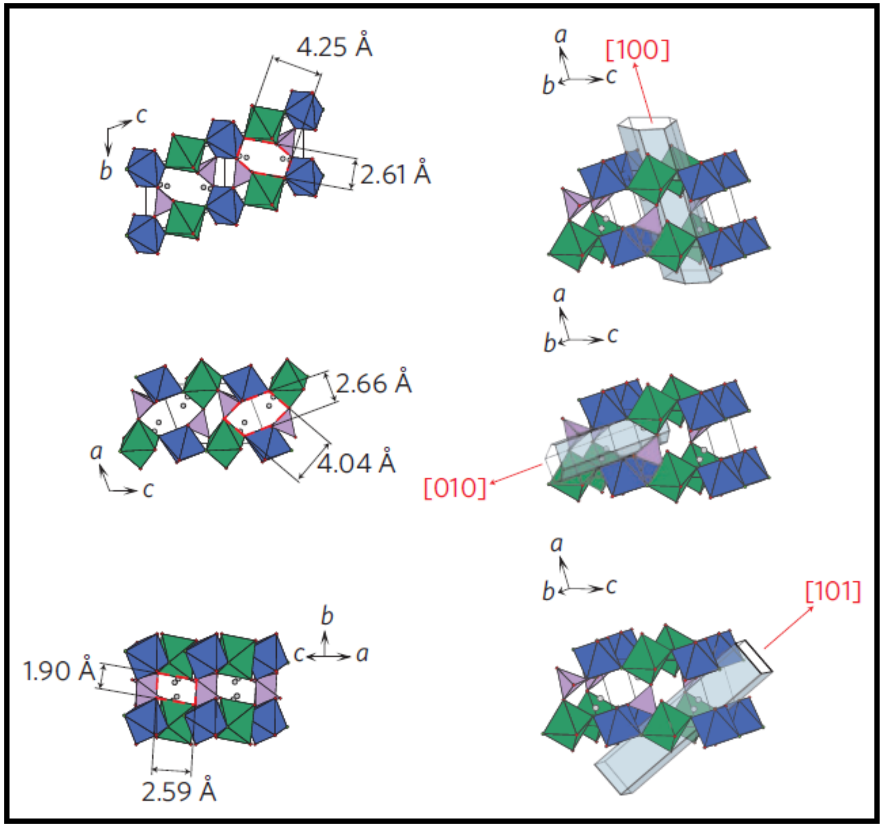
- Slightly higher voltage (3.6 V versus Li)
- Tavorite structure (3D channels for Li migration)
- Low temperature synthesis (~300^{o}C)
- Better ionic and electronic property
- Lower packing density
- Low cost

Cons of $LiFeSO_4F$

- Low capacity (~151 mAh/g)
- Not stable in water ($LiFeSO_4F \rightarrow FeOOH + LiF$)

Triclinic Structure





Source: *J-M. Tarascon et al., Nat. Mater., 2010, 9, 68.*

Michael Faraday
(1791-1867), England

Charles-Augustin de Coulomb
(1736-1806), France

demonstrated the relation between **electricity** and **chemical bonding**,

Capacity (mAh/g) = [(F × n_{Li}) / (M × 3600)] × 1000

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

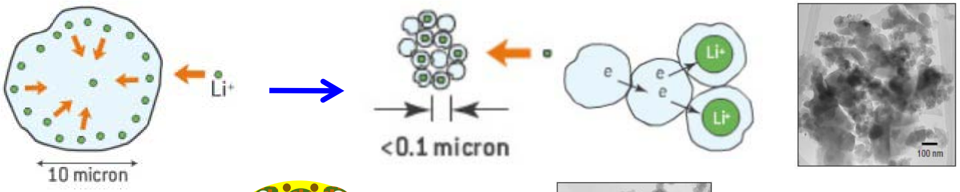
$$Cathode: \quad LiFeSO_4F + e^- \rightarrow Li + FeSO_4F$$

$$LiFeSO_4F = \frac{96500 \times 1}{177.85 \times 3600} \times 1000 = 151 \quad mAh/g$$

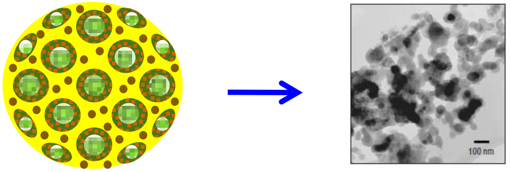
$LiFeSO_4F$ V.S. $LiFePO_4$

Material	$LiFePO_4$	$LiFeSO_4F$
Average working voltage (V)	3.4	3.6
Density (g/cm^3)	3.5	3.23
Structure	1-D, Olivine	3-D, Tavorite
Theoretic specific capacity (mAh/g)	170	151
Practical specific capacity (mAh/g)	140-155	130-140
Energy Density (kWh/L)	1.9	1.6
Conductivity (S/cm)	$\sim 10^{-9}$	$\sim 10^{-6}$
Li ion diffusivity (cm^2/s)	$\sim 10^{-14}$	…
Cycle life	> 1000 cycle	…
Safety	superior	…
Cost	low	lower

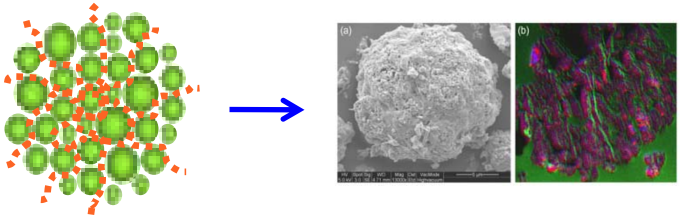
- downsizing the particle size



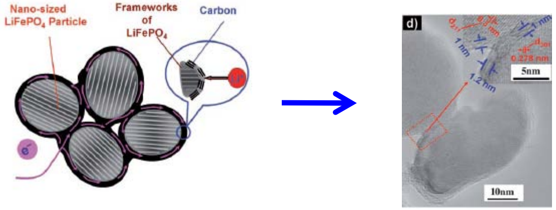
- dopants



- Nano carbon conducting network

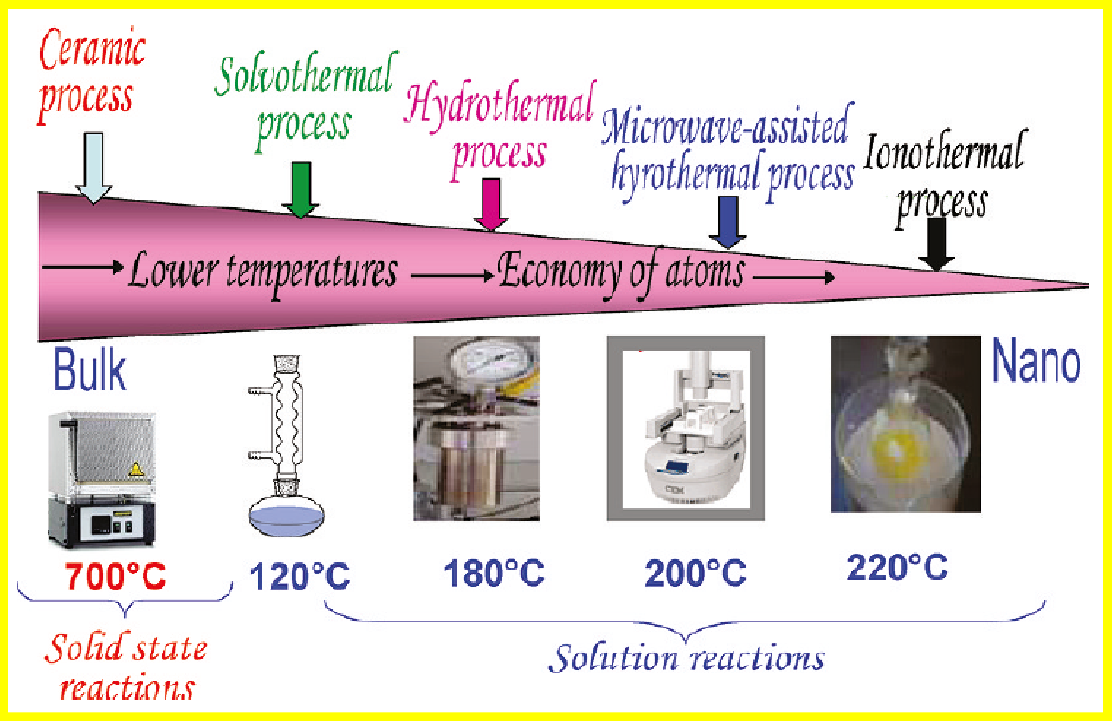


- Carbon nanocoating



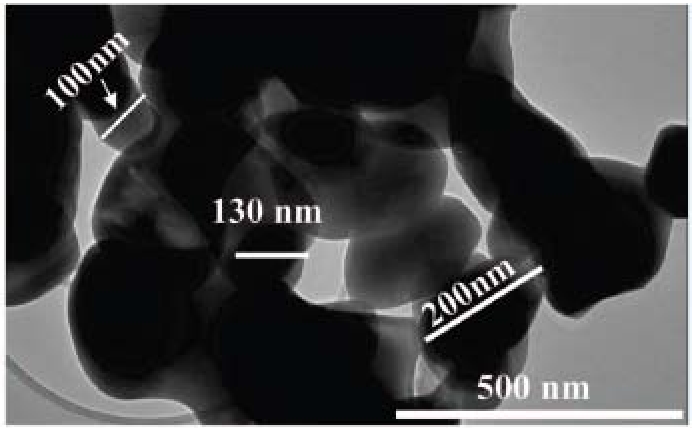
However, for $LiFeSO_4F$???

Summary of synthesis approaches toward the electrode materials



Source: *Jean-Marie Tarascon et al., Chem. Mater. 2010, 22(3), 724.*

Ionothermal Synthesis for $LiFePO_4$

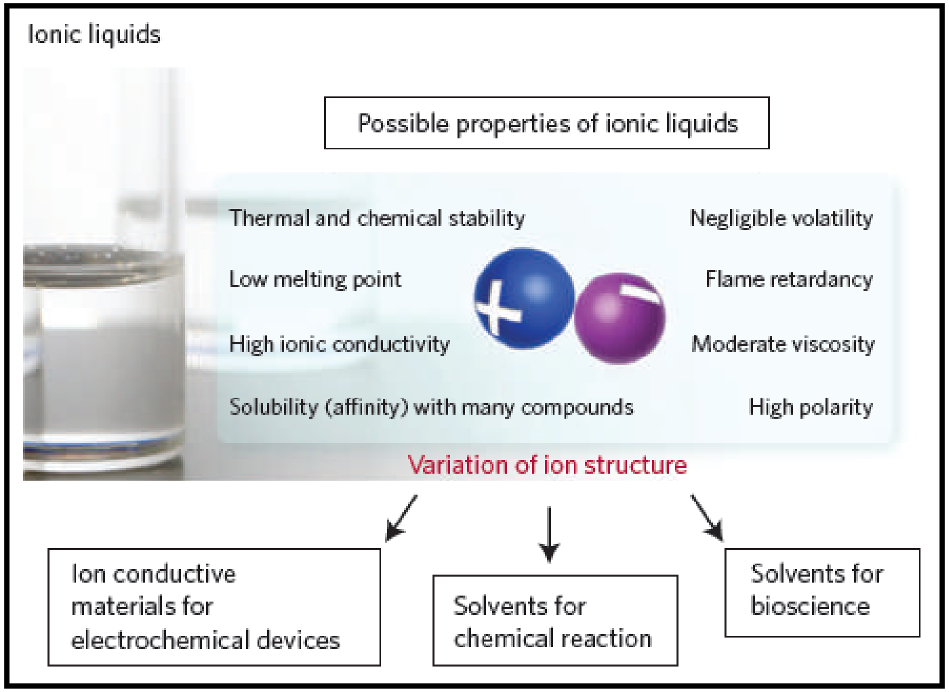


The experiment were carried out at 250 °C in glassware containers using EMI-TFSI as ionic liquid and LiH_2PO_4, $FeC_2O_4 \cdot 2H_2O$ precursors with concentration of 2.5×10^{-3} mol/L.

Source: *N. Recham et al.,Chem. Mater. 2009, 21, 1096.*

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

Properties and applications of ionic-liquids



Ionic liquids

Possible properties of ionic liquids

Thermal and chemical stability

Low melting point

High ionic conductivity

Solubility (affinity) with many compounds

Negligible volatility

Flame retardancy

Moderate viscosity

High polarity

Variation of ion structure

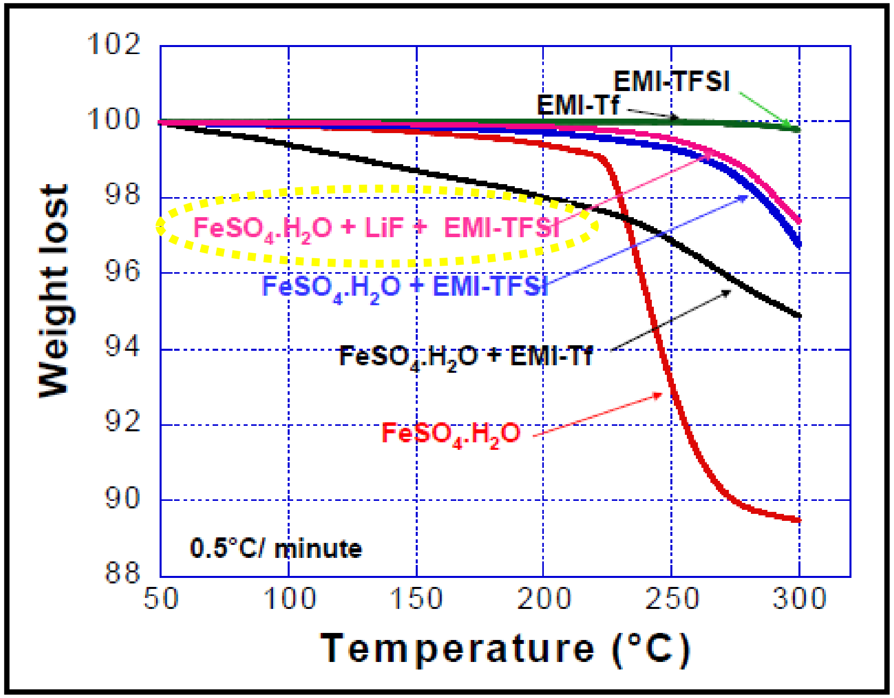
Ion conductive materials for electrochemical devices

Solvents for chemical reaction

Solvents for bioscience

Source: *Michel Armand et al., Nat. Mater., 2009, 8, 621.*

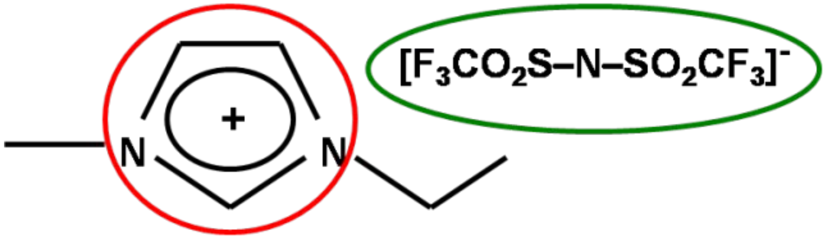
Role of the ionic liquid



TGA measurements conducted in the presence of either $FeSO_4 \cdot H_2O$ + ionic liquid, or $FeSO_4 \cdot H_2O$ + ionic liquid + LiF are compared to those done with only ionic liquid or $FeSO_4 \cdot H_2O$. Note that EMI-TFSI postpones the release of H_2O 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 $LiFeSO_4F$.

Source: *Jean-Marie Tarascon et al., Chem. Mater. 2010, 22(3), 724.*

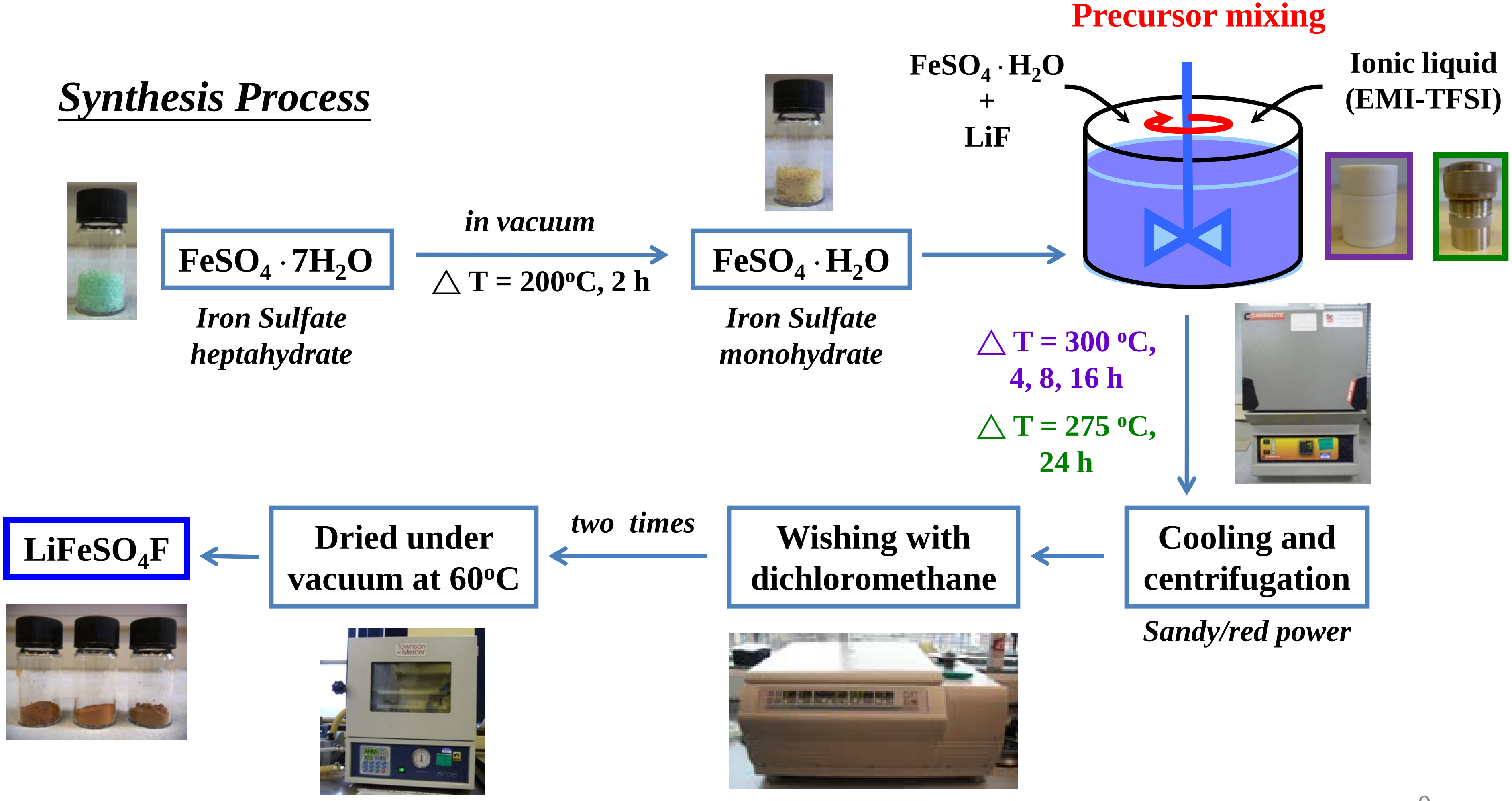
EMI-TFSI: cation-anion pair



Flow chart of the $LiFeSO_4F$ synthesis as a cathode material

Reaction: $FeSO_4 \cdot H_2O + LiF \rightarrow LiFeSO_4F + H_2O$

Synthesis Process



$FeSO_4 \cdot 7H_2O$

Iron Sulfate heptahydrate

in vacuum

$\triangle$ T = 200°C, 2 h

$FeSO_4 \cdot H_2O$

Iron Sulfate monohydrate

Precursor mixing

$FeSO_4 \cdot H_2O$ + LiF

Ionic liquid (EMI-TFSI)

$\triangle$ T = 300 °C, 4, 8, 16 h

$\triangle$ T = 275 °C, 24 h

Cooling and centrifugation

Sandy/red power

Wishing with dichloromethane

two times

Dried under vacuum at 60°C

$LiFeSO_4F$

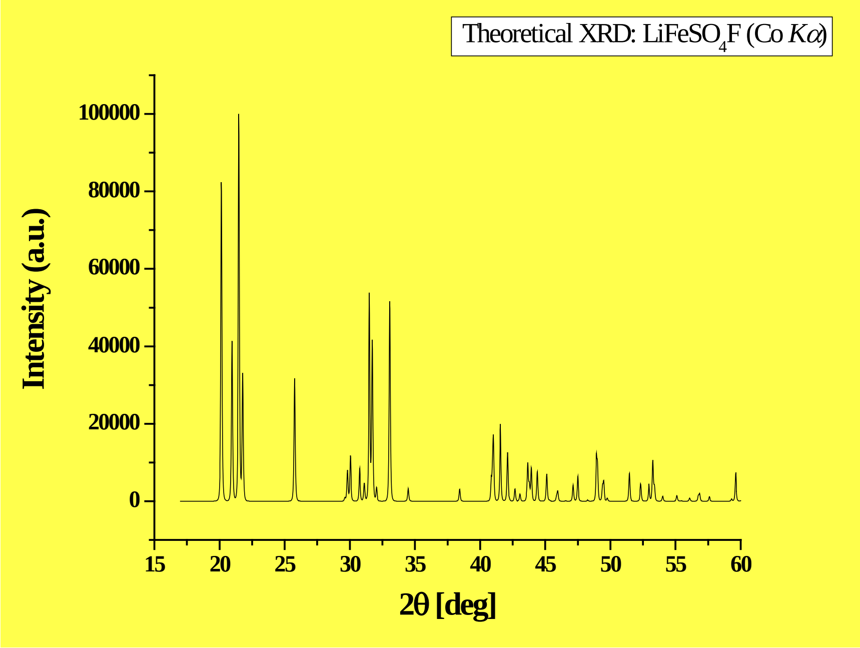
Source: *Inorganic Materials Laboratory (Room I5), Department of Engineering Materials, The University of Sheffield.*

Experimental characterization of $LiFeSO_4F$

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

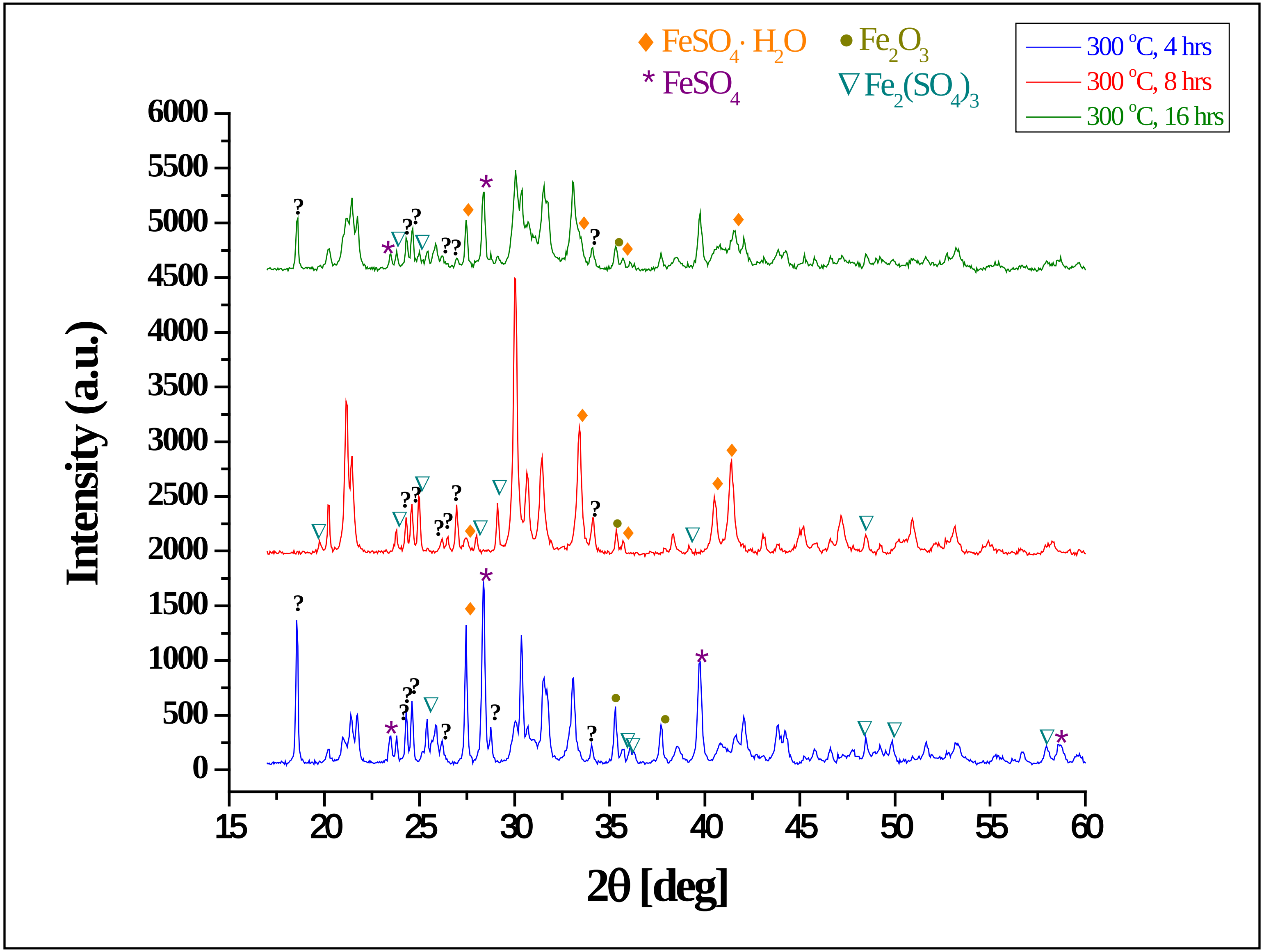
Source: *Ceramics and composites Laboratory (Room I6), Department of Engineering Materials, The University of Sheffield.*

The theoretical X-ray power diffraction pattern (λ_{Co}) of $LiFeSO_4F$ of was drawn using XRD software (STOE WinX^{POW}) following lattice parameters, cell volumes and atomic coordinates for $LiFeSO_4F$.



Source: *Supplementary information, Nat. Mater., 2010, 9, 68*

XRD results of $LiFeSO_4F$



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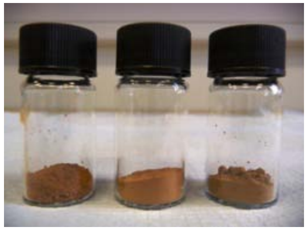
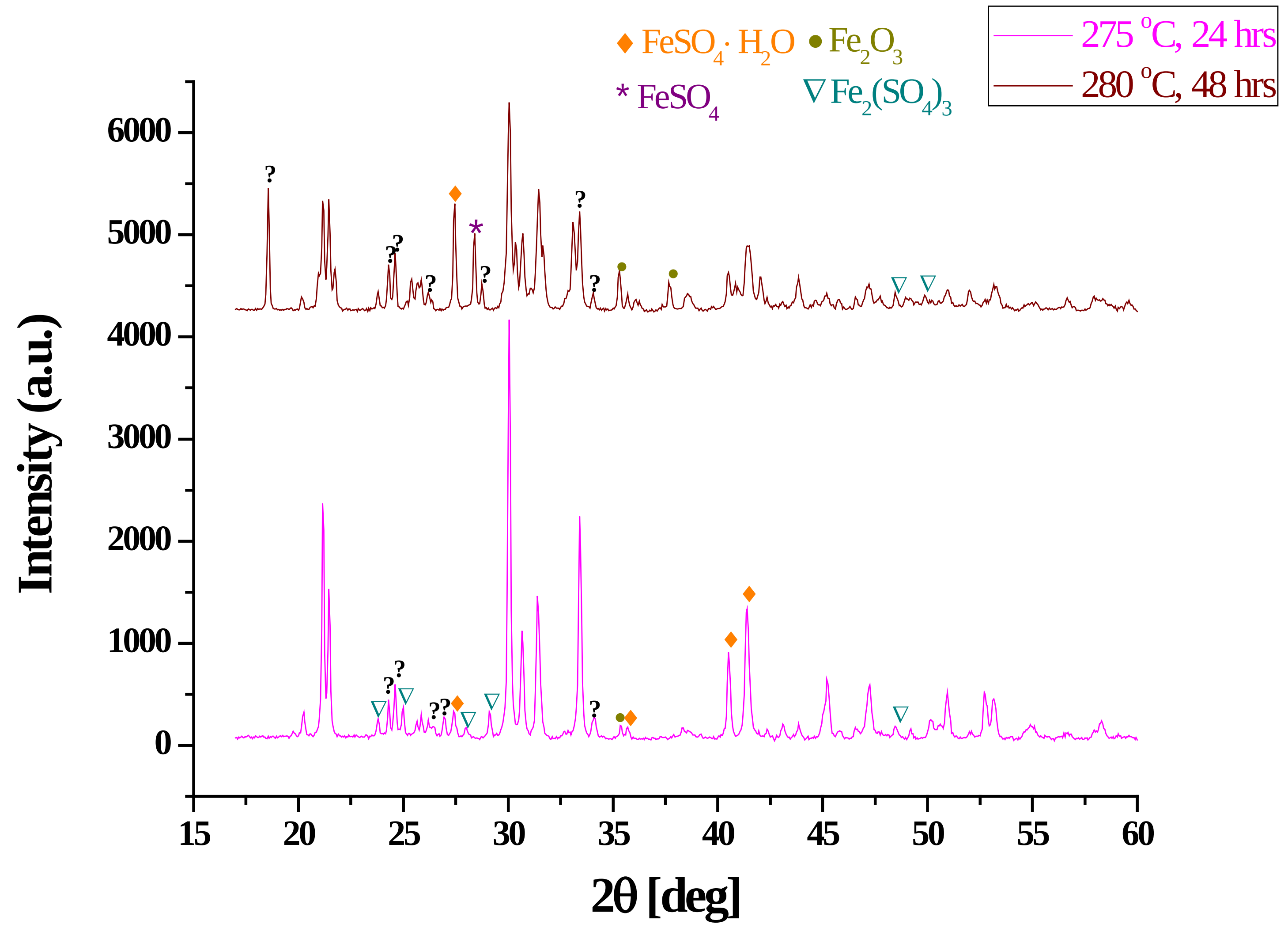


XRD results of $LiFeSO_4F$



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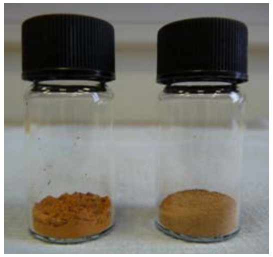
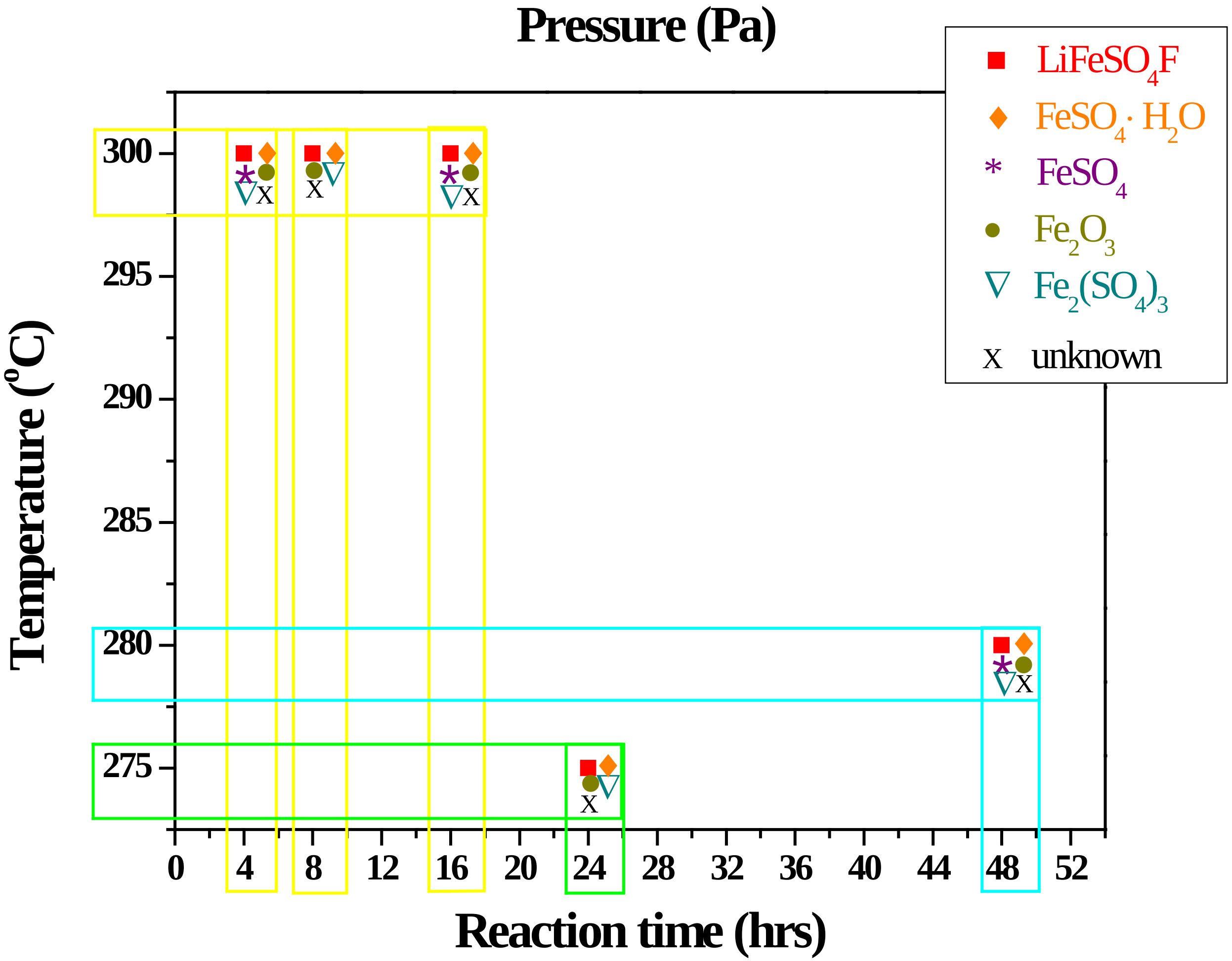


XRD discussion of $LiFeSO_4F$



Latent difficulties to synthesize single phase $LiFeSO_4F$:

1. **The reaction paths of ionothermal synthesis and mechanism of ion-exchange for phase stabilization of $LiFeSO_4F$ 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 $FeSO_4 \cdot H_2O$ phase in produced material .**
3. **It is difficult to keep the monohydrated precursor free of $Fe^{(III)}$ (Iron oxidation: $Fe^{2+} \rightarrow Fe^{3+}$)**

Conclusions

- The ionothermal synthesis of $LiFeSO_4F$ 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 ($FeSO_4 \cdot H_2O \rightarrow FeSO_4$). 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 Fe^{2+} to Fe^{3+} (Fe_2O_3 and $Fe_2(SO_4)_3$), ionothermal synthesis for $LiFeSO_4F$ could be operated under an argon or a nitrogen atmosphere.

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