Li-Fe-Silicates as Cathode Materials for Up-scaled Li-ion Batteries: Experimental

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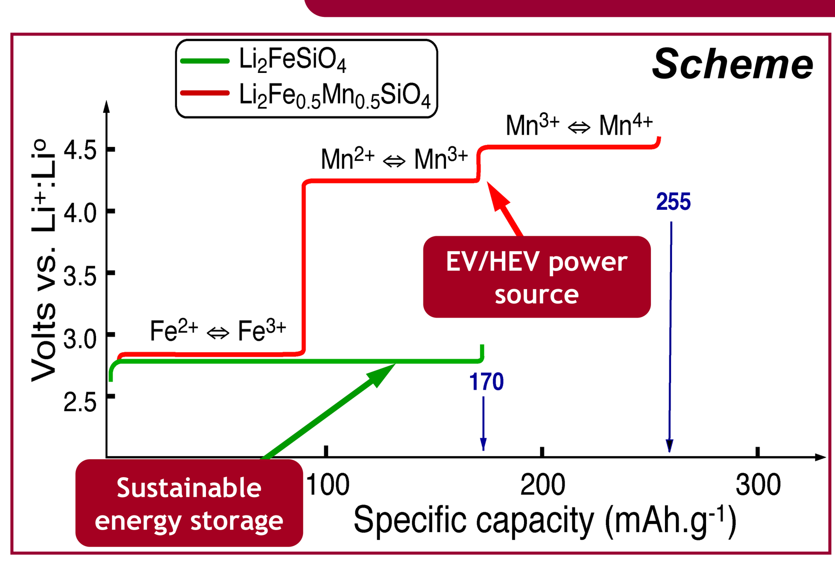
Global Climate & Energy Project

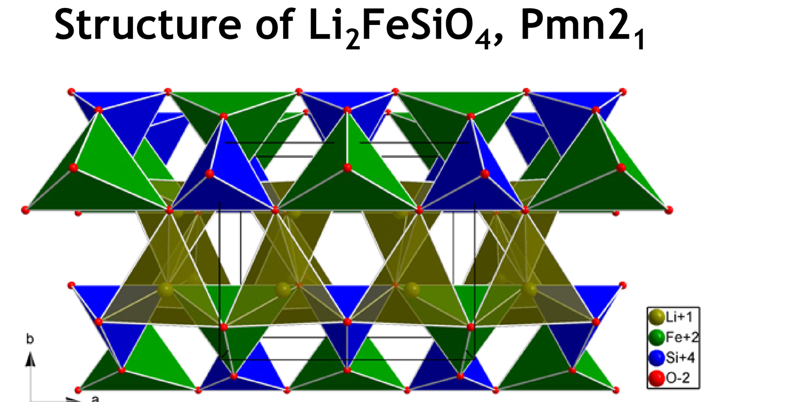
Introduction

- There has been tremendous interest in recent years in developing new cathode materials suitable for high performance Hybrid and Plug-in Hybrid Electric Vehicles (HEVs and PHEVs).
- Li_2FeSiO_4 holds great promise because of its:
  - low cost, high abundance and non-toxicity
  - excellent stability
  - $>1e^-$ per 3d-metal in a mixed-ion system
- Our goal is to examine the feasibility of using iron silicates in large-scale and high power systems

Overview



Structure of Li_2FeSiO_4, $Pmn2_1$

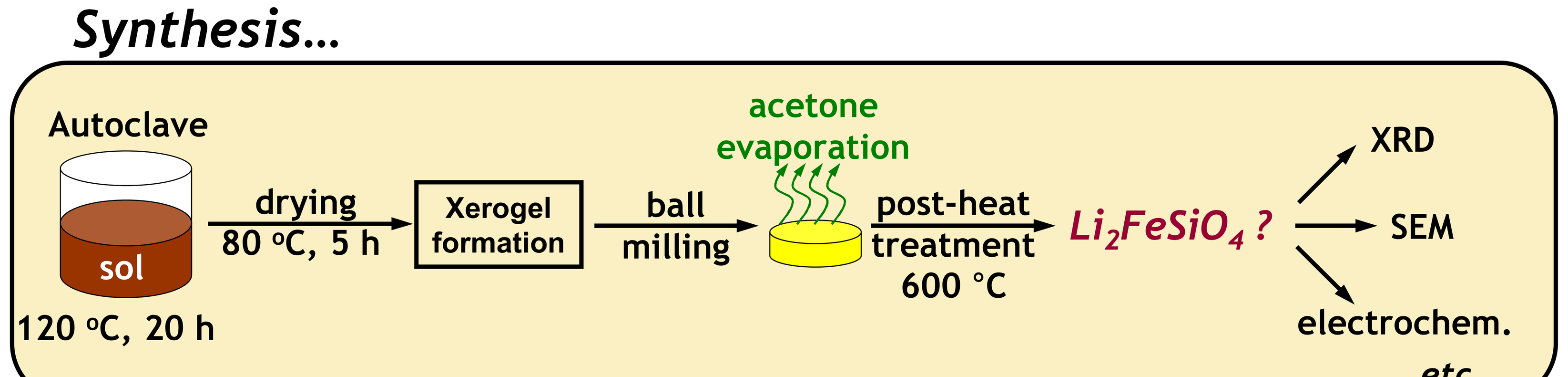


Nytén *et al.*, *Electrochem. Commun.* 7 (2005) 156.

$$Li^+_2(Fe^{2+}_{1-x}Mn^{2+}_x)SiO_4 \Rightarrow Li^+_{1-x}(Fe^{3+}_{1-x}Mn^{4+}_x)SiO_4 + (1+x)Li^+ + (1+x)e^-$$

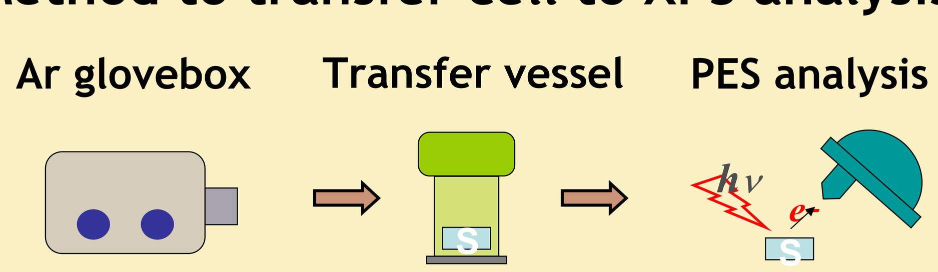
Experimental approach to the Li_2FeSiO_4 system

Synthesis…



Surface Studies…

Method to transfer cell to XPS analysis



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Synthesis and Properties

Solid-state synthesis involves heating the starting materials at 700 °C in CO/CO_2 for 18h.

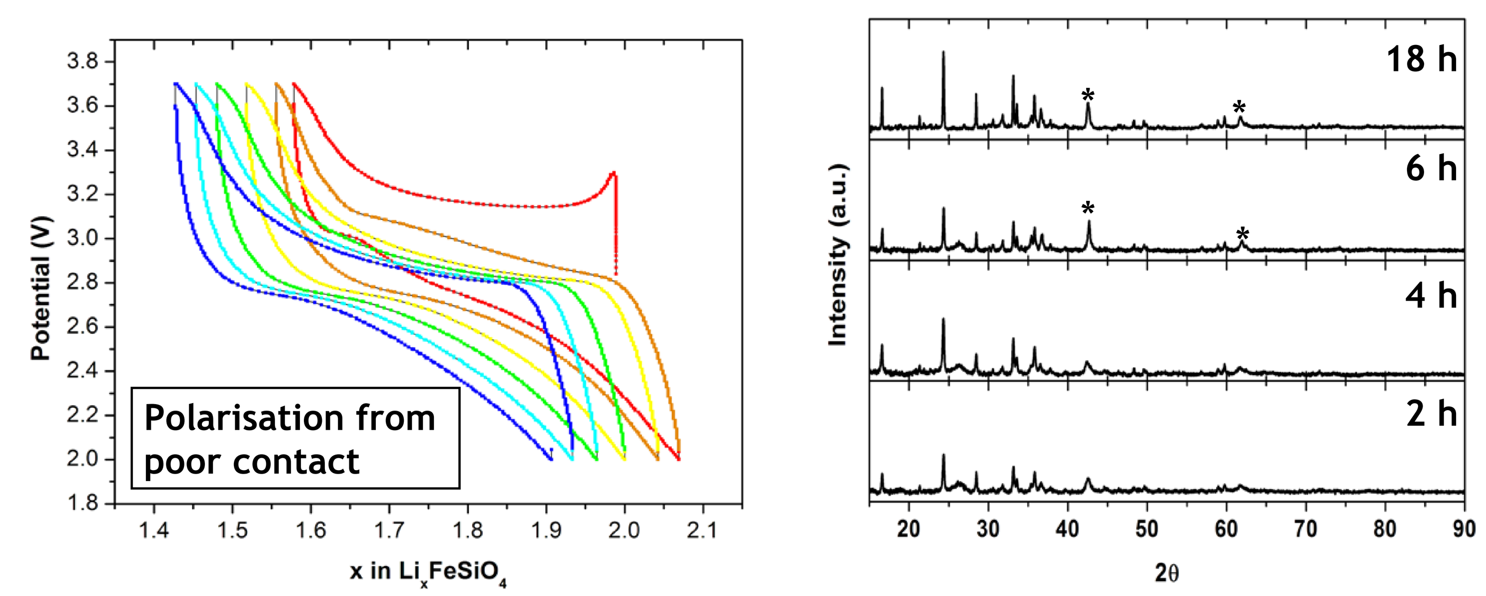
In solution-assisted synthesis (*e.g.*, citrate-assisted, solvothermal), conditions such as temperature and time can be varied.

Solution-assisted routes

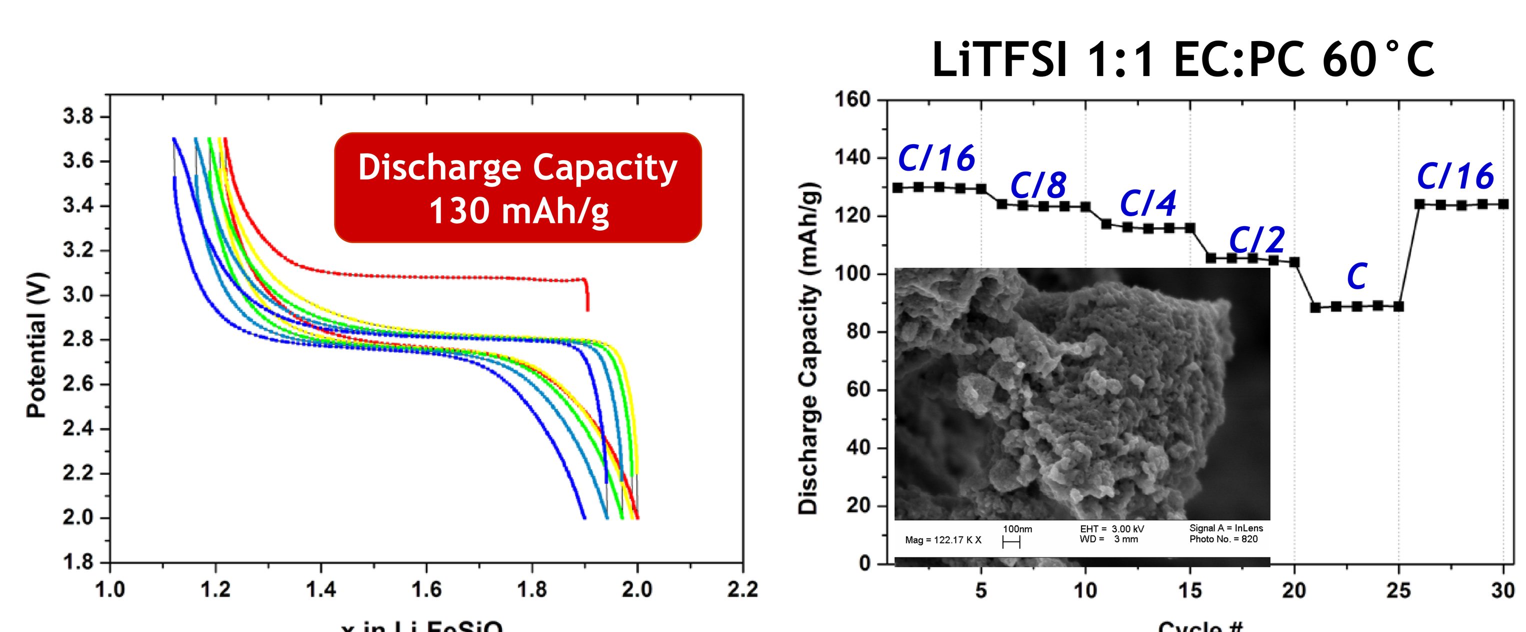
Advantages: Tuneable synthesis parameters (*e.g.*, heat-treatment time, temperature range), reactive precursors with good diffusion kinetics.

Disadvantages: Possible impurities, require fine control of homogeneity and good contact between particles.

Synthesis of Li_2FeSiO_4 (Un-optimized)

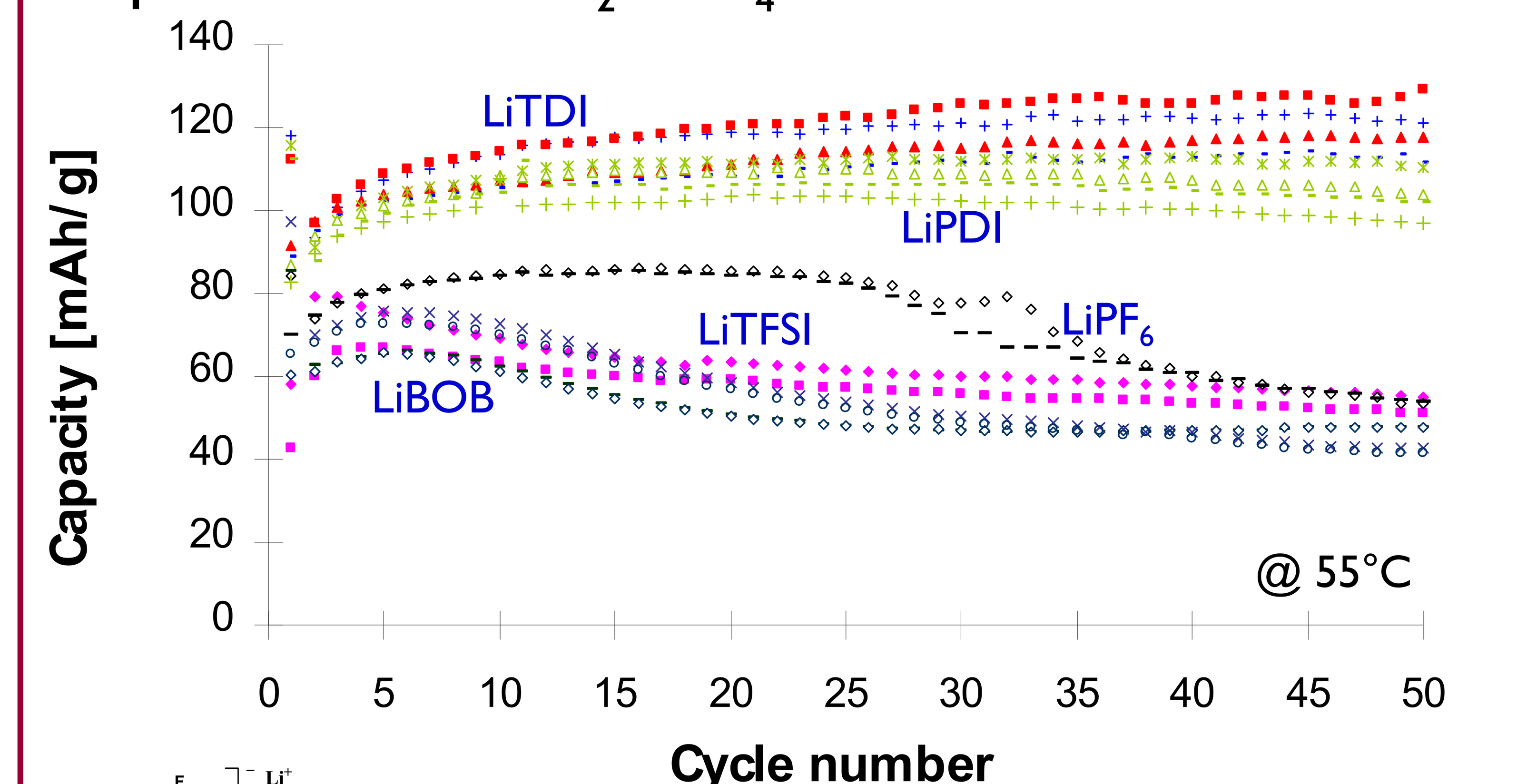


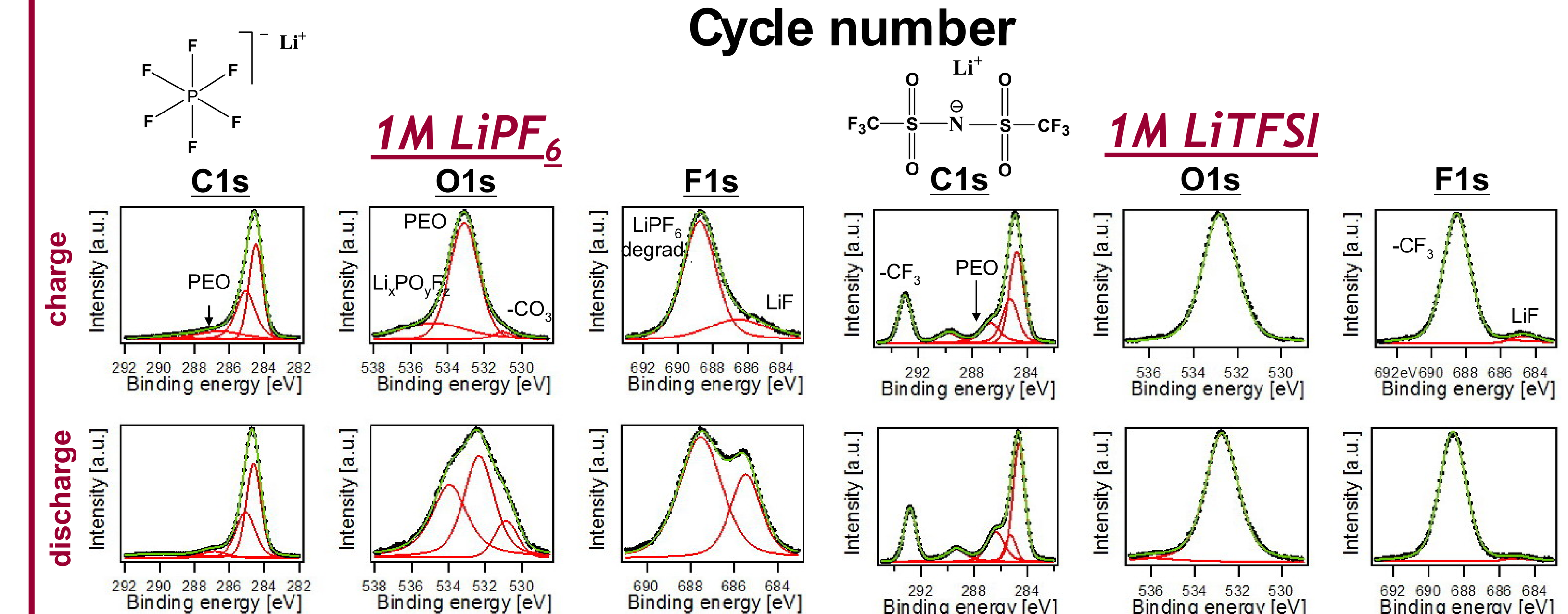
Optimized synthesis of Li_2FeSiO_4

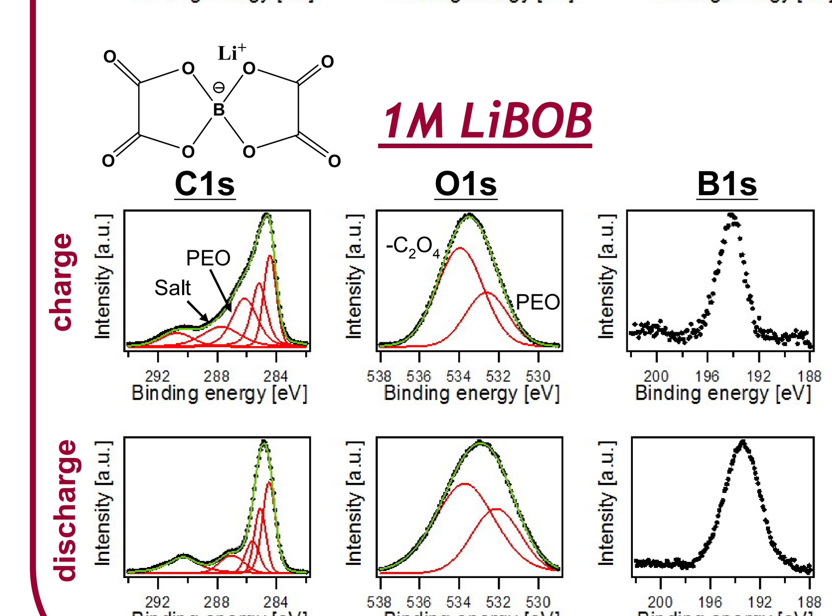


XPS Surface Analysis

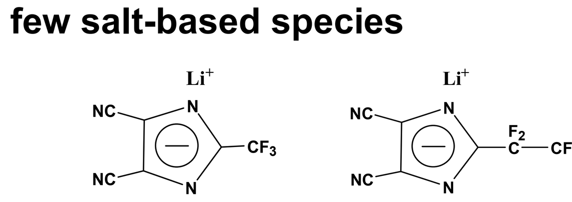
Comparison between Li_2FeSiO_4 for different salts in 2:1 EC:DEC







- $LiPF_6$: A dynamic SEI layer with various degradation products
- LiBOB: stable with no significant surface-layer formation
- LiTFSI: Surface-layer coverage with few salt-based species



- Other salts LiTDI and LiTDI: Dynamic and possibly reversible SEI layers are formed; solvent stability?

Conclusions

Synthesis via solution-assisted routes allows the formation of Li_2FeSiO_4 nanoparticles with excellent electrochemical performance.

- Synthesis conditions can be varied: Temperature range 600 – 700 °C and heat treatment period 2 – 18 h.
- Particle-size can be tuned: Particles prepared in the range 40 – 130 nm.
- Interparticle contact is important: Poor contacts can result in charge-discharge polarization and can also reduce the overall capacity.
- Good performance can be achieved: Up to 130 mAh/g; smaller particles allow good rate capability even at higher cycling rates.

XPS surface characterization provides detailed insights into the chemistry of the SEI layer and stability issues for different electrolyte systems.

- $LiPF_6$: Dynamic changes in the SEI layer are dependent on state-of-charge; indications of reactive behaviour (LiF). Small amounts of carbon-based reaction products.
- LiTFSI: Electrochemically stable salt; decomposition of solvent species.
- LiBOB: Good salt stability; indications of polymeric decomposition products of EC/DEC solvents.
- LiTDI/LiPDI: Good consistency between electrochemical performance and surface chemistry; dynamic changes dependent on state-of-charge.