



XPS/PES stability studies of iron silicate cathode materials for up-scaled Li-ion batteries

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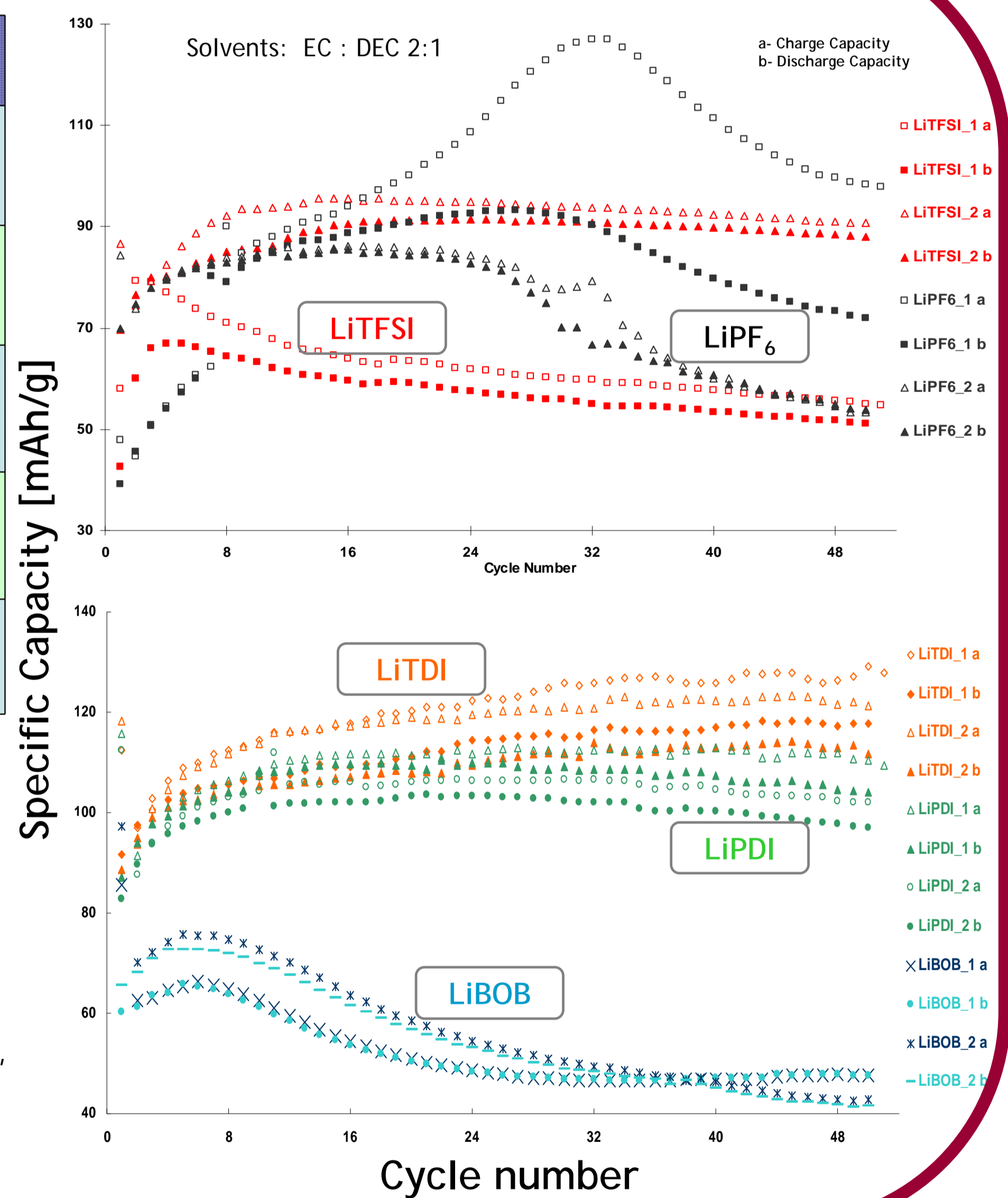
Global Climate & Energy Project

Introduction

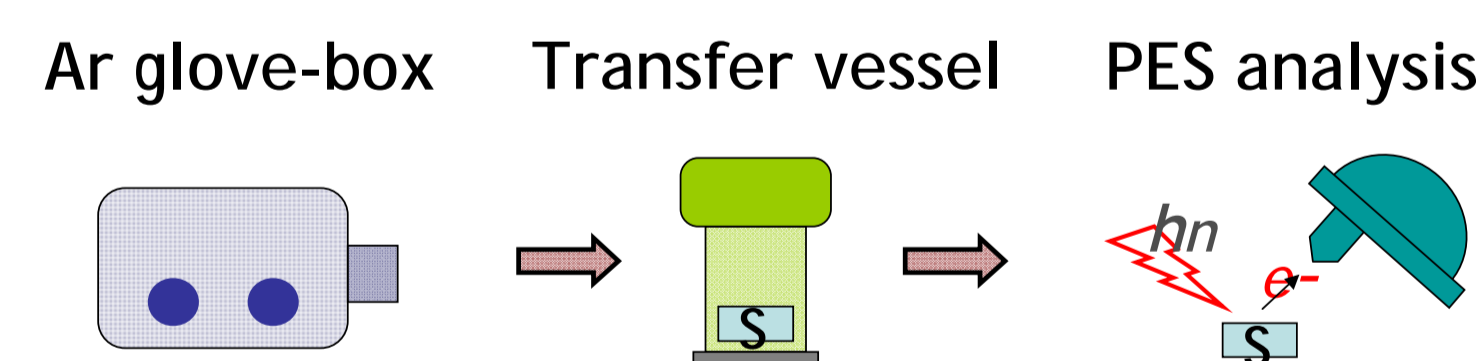
- $\text{Li}_2\text{FeSiO}_4$ is a recent addition to the group of interesting and potentially cheap cathode materials for large-scale lithium-ion battery applications. [1,2]
- The correlation between cycling performance and the chemical composition of the SEI formed on the electrode has been probed by a combination of XPS and electrochemical measurements.
- Differences in solvent- and salt-stability have been observed for different electrolyte systems. An example of a comparative XPS study for LiTFSI- and LiPF₆-based electrolytes is shown here.

Overview of salt systems studied and cycling performance

Salt	Structure	Cut-off voltage [V]	Conc.	Name
LiTFSI		2.0 - 3.7	1 M	Lithium bis(trifluoromethanesulfonyl)imide
LiPF ₆		2.0 - 3.7	1 M	lithium hexafluorophosphate
LiTDI		2.0 - 4.0	1 M	Lithium trifluoromethyl dicyanoimidazole
LiPDI		2.0 - 4.0	1 M	Lithium pentafluoroethyl dicyanoimidazole
LiBOB		2.0 - 4.2	0.8 M	Lithium bis-oxalato borate

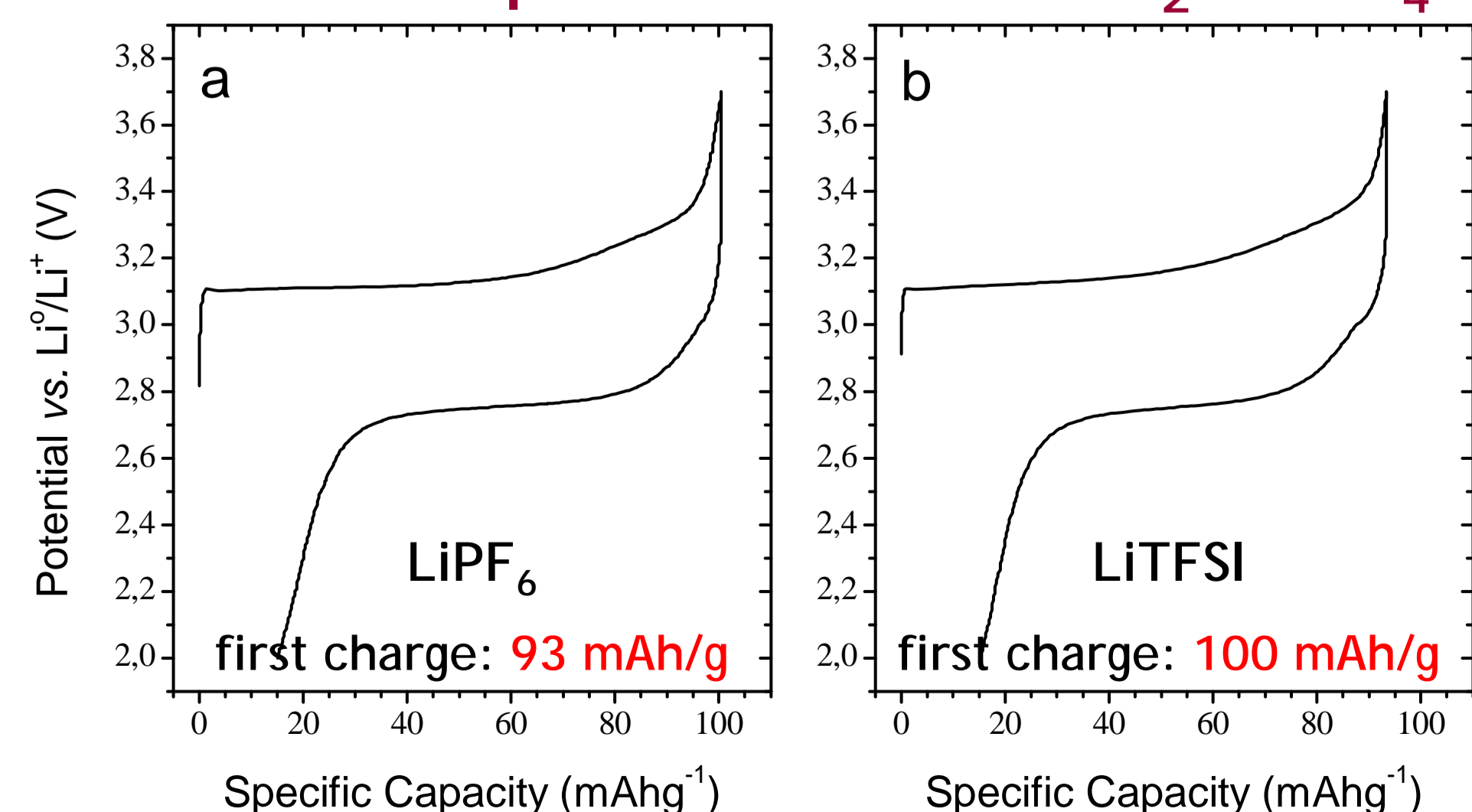


Safe transfer from cell to XPS analysis



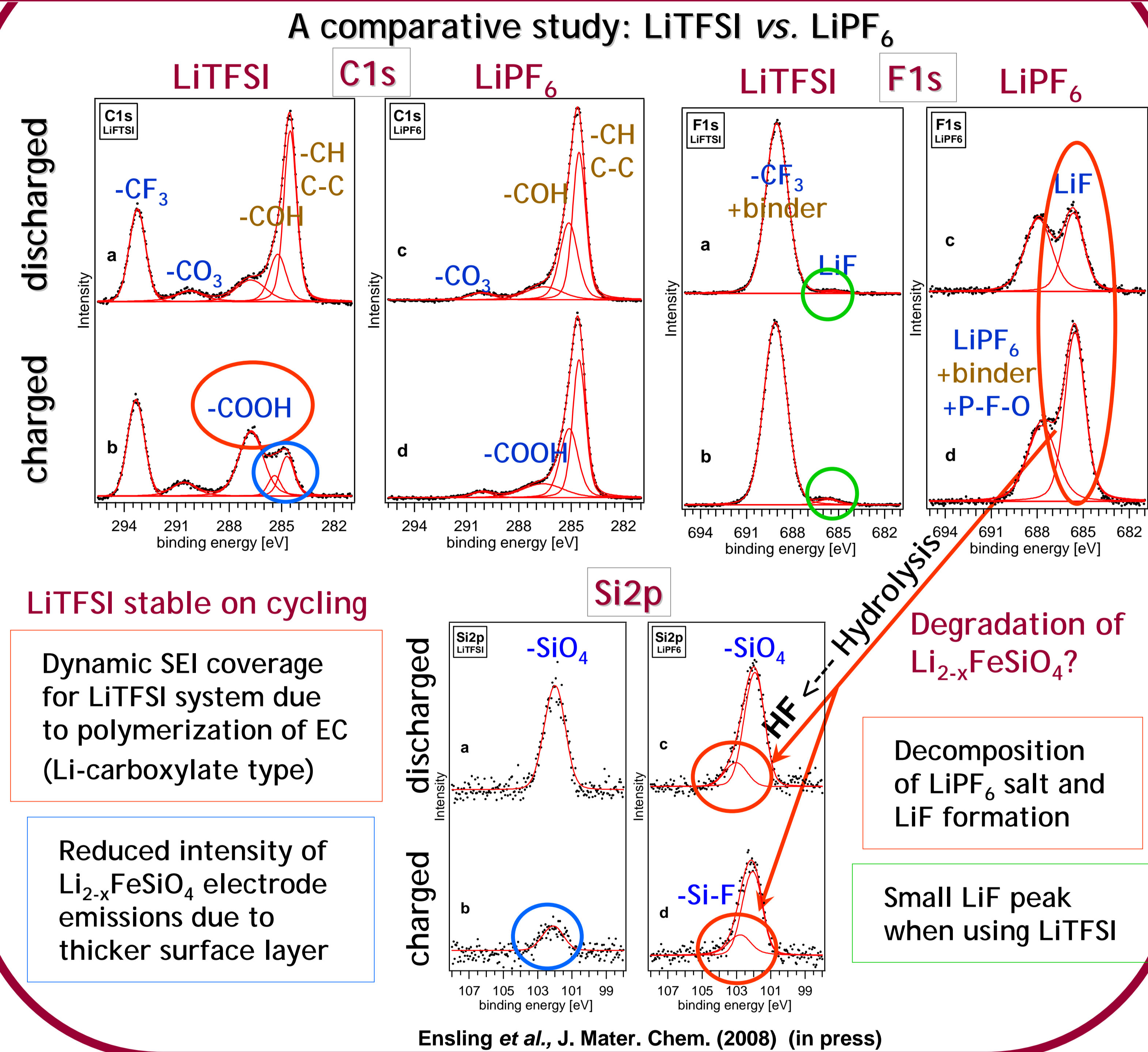
References: [1] A. Nyten, A. Abouimrane, M. Armand, T. Gustafsson and J.O. Thomas, *Electrochem. Comm.*, 7 (2005) 156.
[2] A. Nyten, S. Kamali, L. Häggström, T. Gustafsson and J.O. Thomas, *J. Mater. Chem.* 16 (2006) 2266.

Electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ electrodes



First-cycle charge and discharge of $\text{Li}_2\text{FeSiO}_4/\text{C}$ electrodes (55°C, C/20) in: a) LiTFSI EC:PC (1:1) and b) LiPF₆ EC:PC (1:1)

XPS surface analysis of cycled $\text{Li}_2\text{FeSiO}_4/\text{C}$ electrodes



LiTFSI stable on cycling

Dynamic SEI coverage for LiTFSI system due to polymerization of EC (Li-carboxylate type)

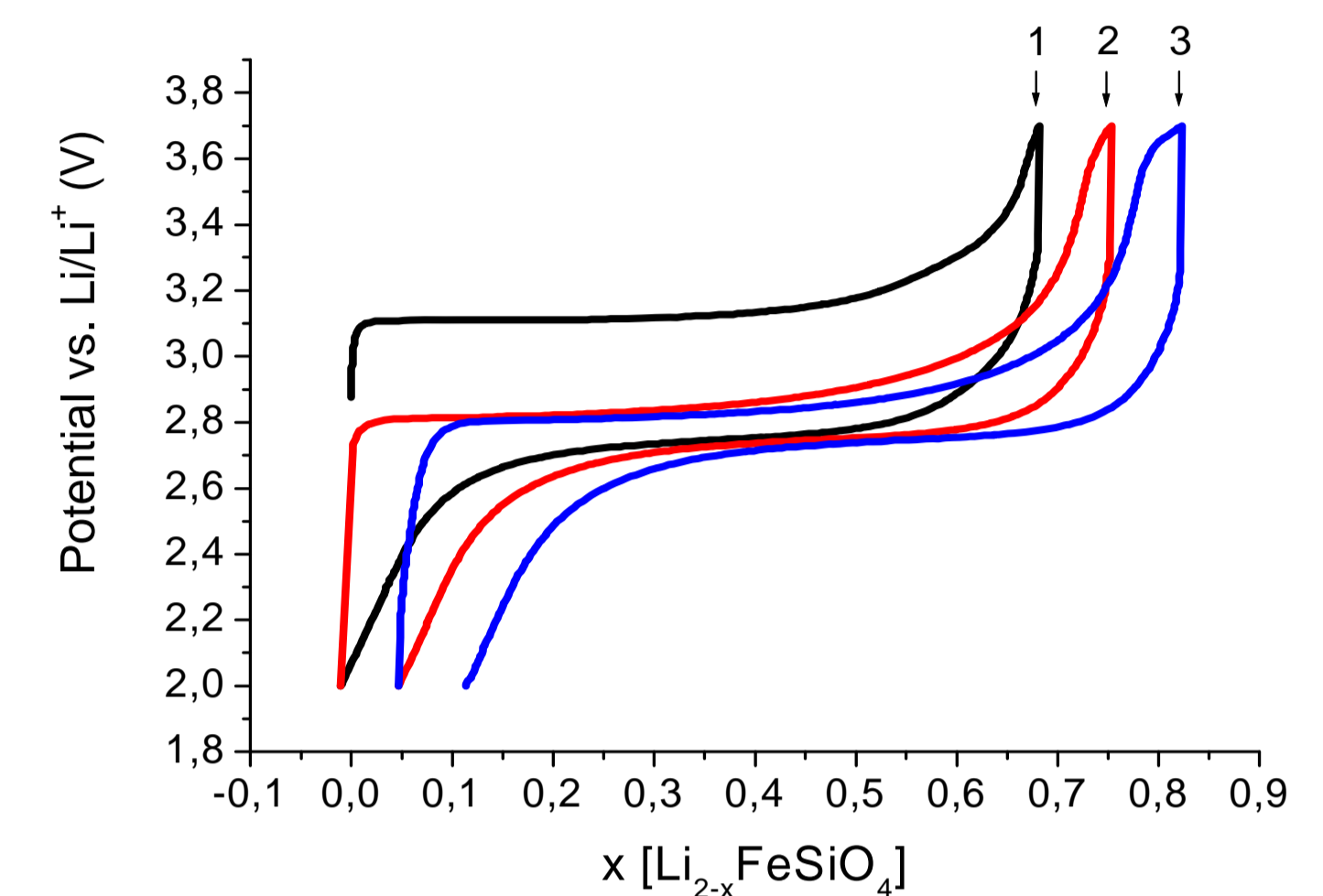
Reduced intensity of $\text{Li}_{2-x}\text{FeSiO}_4$ electrode emissions due to thicker surface layer

Si2p

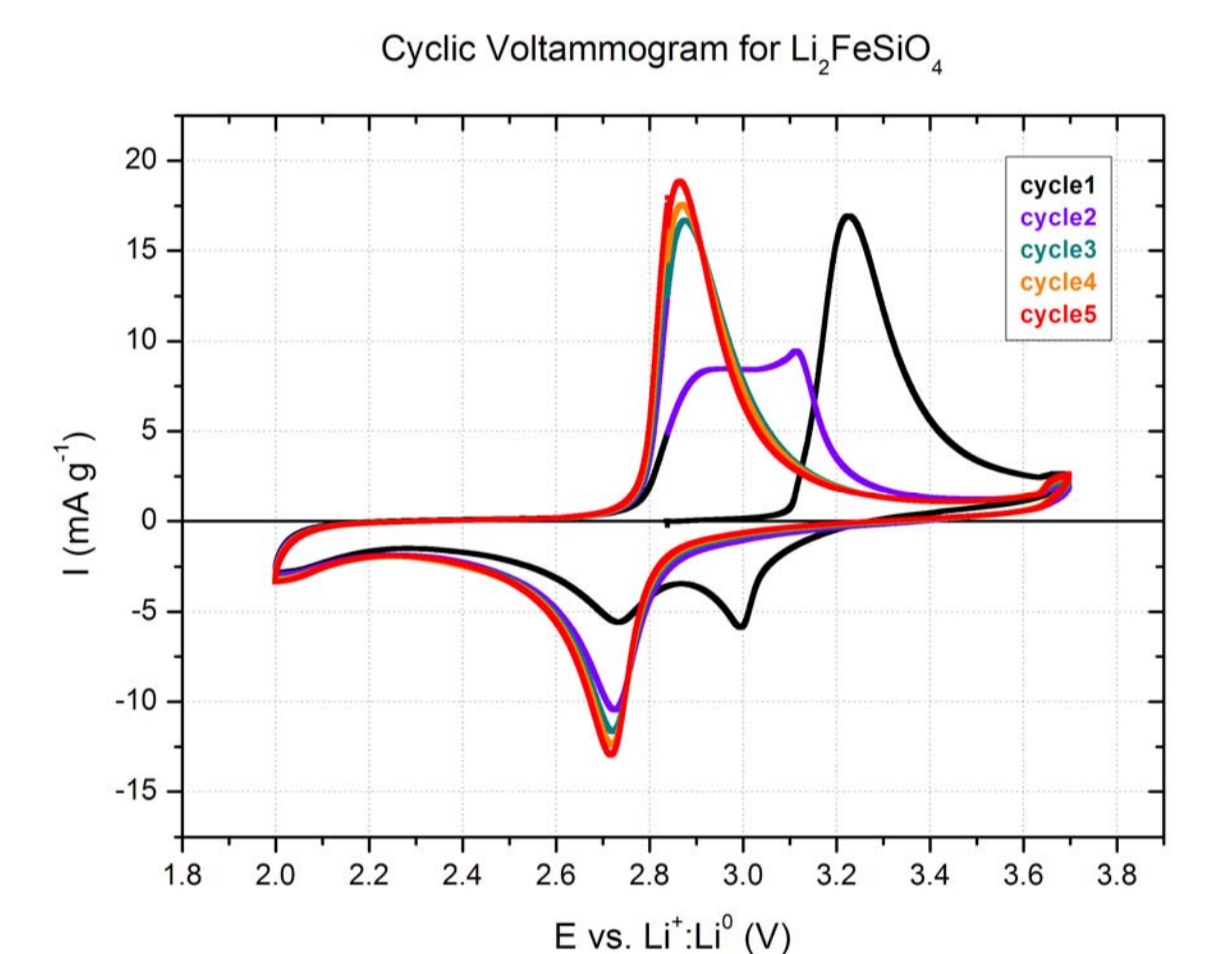
Degradation of $\text{Li}_{2-x}\text{FeSiO}_4$?
Decomposition of LiPF₆ salt and LiF formation

Small LiF peak when using LiTFSI

Ensling et al., *J. Mater. Chem.* (2008) (in press)



Discharge curves for the first three cycles of $\text{Li}_2\text{FeSiO}_4/\text{C}$ (55°C, C/25) in LiTFSI EC:PC 1:1. Minimal irreversible capacity observed during the first cycles.



Cyclic voltammetry of the first five cycles of $\text{Li}_2\text{FeSiO}_4/\text{C}$ (55°C, C/25) in LiTFSI EC:PC 1:1. The undoped $\text{Li}_2\text{FeSiO}_4$ material undergoes a transition during the first cycles. The system stabilizes after the 3rd cycle.

Conclusions

LiPF₆-based electrolyte

- forms thin surface layer with small amounts of carbon-based reaction products
- LiPF₆ salt is unstable - decomposing to Li_xPF_y , $\text{Li}_x\text{PO}_y\text{F}_z$ and LiF
- indications of $\text{Li}_2\text{FeSiO}_4$ degradation through reaction with HF (formed in hydrolysis of LiPF₆)

LiTFSI-based electrolyte

- polymerisation of the EC/DEC solvents; the salt is stable
- dynamic - even reversible - SEI coverage depending on state-of-charge (SOC)

