

# QUANTIFYING THE “ELECTROLYTE DECOMPOSITION REACTION” CONTRIBUTION TO FALSELY HIGH OBSERVED CAPACITIES IN $\text{Li}_2\text{FeSiO}_4$ USING MÖSSBAUER SPECTROSCOPY

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Reversible cycling of two lithium ions (and two electrons) per transition-metal (TM) ion in a Li-ion battery is seen as a highly attractive way to increase the capacity of cathode materials to better match the higher capacities of today's anode materials – typically graphite. Such a process is suggestively more likely to occur in polyanionic cathode materials, since simple TM-oxides tend to be less stable [1]. Low-cost Fe- or Mn-based silicates, such as lithium iron silicate ( $\text{Li}_2\text{FeSiO}_4$ ) [2], are ideal candidate host materials in this context, provided they do not suffer from slow kinetics or structural volatility.

Highly reactive nano-composites of  $\text{Li}_2\text{FeSiO}_4$  and carbon, further enhanced by the presence of a glassy network to facilitate Li-ion conductivity [3], have here been studied to probe the controversy surrounding the  $\text{Fe}^{3+}/\text{Fe}^{4+}$  redox couple, and the possibility of cycling a 2<sup>nd</sup> Li-ion in this material. To this end, *in situ* Mössbauer spectroscopy has been used to monitor the oxidation state of the Fe-ions in symmetric  $\text{Li}_x\text{Fe}^{3+}\text{SiO}_4/1\text{MLiPF}_6$  EC:DEC (1:1)/ $\text{Li}_x\text{Fe}^{3+}\text{SiO}_4$  ( $x = 1$  and  $\approx 0$ ) cells cycled at RT and at low rate (C/20) over a wide voltage window. The de-intercalation reaction and electrolyte decomposition reaction(s) can be separated effectively by combining data from cycling these  $x = 1$  and  $x \approx 0$  type symmetric cells. Almost 0.6Li of the lithium in  $\text{Li}_x\text{FeSiO}_4$  ( $x = 1$ ) can be shown to cycle reversibly over 15 cycles, as seen from *in situ* Mössbauer spectra. However, electrolyte decomposition reaction(s) constitute a large fraction of the “cycled” Li above 4.6V. This explains the discrepancy between the cycled charge, as quantified from Mössbauer and electrochemical cycling data - and is further demonstrated with ultimate clarity when  $\sim 0.7$  Li/f.u. can even be seen to “cycle” above 4.6V in  $x \approx 0$  type symmetric cells, despite the fact that neither of the  $\text{FeSiO}_4$  electrodes themselves actually contains any intrinsic lithium!

*This work has been supported by the Swedish Energy Agency (VINNOVA) and the Swedish Science Research Council (VR).*

## References:

- [1] A.K. Padhi *et al.*, *J. Electrochem. Soc.*, 144 (1997) 1188- 1194.
- [2] A. Nyten *et al.*, *Electrochem. Commun.*, 7 (2005) 156-160.
- [3] J. Bai *et al.*, *J. Mater. Chem.*, 22 (2012) 12128-12132.