QUANTIFYING THE “ELECTROLYTE DECOMPOSITION REACTION” CONTRIBUTION TO FALSELY HIGH OBSERVED CAPACITIES IN Li₂FeSiO₄ 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 (Li₂FeSiO₄) [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 Li₂FeSiO₄ 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 Fe³⁺/Fe⁴⁺ redox couple, and the possibility of cycling a 2nd 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 LiₓFe³⁺SiO₄/1MLiPF₆ EC:DEC (1:1)/LiₓFe³⁺SiO₄ (x = 1 and ≈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 ≈ 0 type symmetric cells. Almost 0.6Li of the lithium in LiₓFeSiO₄ (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 ~0.7 Li/f.u. can even be seen to “cycle” above 4.6V in x ≈ 0 type symmetric cells, despite the fact that neither of the FeSiO₄ electrodes themselves actually contains any intrinsic lithium!

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References: