

Si anode failure mechanism in full Li-ion cells using advanced characterization tools

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The behavior of silicon electrode in half cell set-up (i.e. cycled vs lithium metal) is now well understood and methods to optimize its performance have been extensively described. In this configuration, the lithium supply is not limited, therefore failure mechanisms can be completely different from those obtained in full cell (Li-ion) set-up. As of today, a much faster aging of silicon anode in full cell has been observed but the failure mechanism has not been understood. In this work, silicon electrodes are cycled in full cell set-up *versus* $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as the positive electrode that initially contains the cyclable lithium. A combination of techniques, such as ^7Li , ^{19}F MAS NMR, XPS, TOF-SIMS and STEM-EELS, provides an in-depth characterization of the SEI forming on the surface of silicon particles as well as its evolution upon cycling.

Upon cycling, heterogeneous thick patches of LiF and carbonates appear at the surface of the Si particles. The development of the inorganic part of the SEI mostly occurs during the early stages of cycling, while an incessant degradation of the organic solvents of the electrolyte occurs continuously. After extended cycling, all the lithium from the positive electrode is consumed either trapped in an intermediate part of the SEI or in the electrolyte. While the cell cannot function properly anymore, degradation of the organic electrolyte solvents goes on, leading to the formation of Li-free organic degradation products thickening the SEI. Such comprehensive work allows for a better study of the failure mechanisms of Si-based composite electrodes for Li-ion batteries cycled in a Li-ion configuration.

From these multiprobe and multiscale characterization results, the mechanism of SEI formation will be described, and our comprehension of the origin of the much faster aging of silicon anode in full cell *versus* half cell will be disclosed.