

Probing the degradation mechanisms of silicon anodes in Li-ion batteries by STEM-EELS mapping

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Silicon represents one of the most promising anode materials for next generation lithium-ion batteries. However its colossal volume expansion (up to 300%) upon electrochemical reaction with lithium repeatedly exposes fresh surfaces and leads to continuous solid electrolyte interface (SEI) formation in which lithium is irreversibly consummated. This leads to very high irreversible capacities, compounded by the fact that parts of the silicon-based electrodes are progressively disconnected from both electrical and ionic transport networks.

In this characterization work, part of the European BACCARA project, we demonstrate the possibility to map major SEI components such as lithium carbonate (Li_2CO_3) and lithium fluoride (LiF) as well as quantifying lithium-silicon alloy compositions and Si crystallinity by combining scanning transmission electron microscopy and low-dose electron energy loss spectroscopy (STEM-EELS). Novel methods for careful dose control and rigorous sample preparation proved mandatory to preserve the integrity of the species of interest during measurements. Results on electrodes disassembled from full cells at their 1st, 10th and 100th charge at 1200 mAh/g indicate an early formation of patch-like LiF followed by continuous carbonate layer (fig 1.a). We observed a thicker SEI with increasing cycle number (fig 1.b-c), which is linked to poor cyclability of full cells. Observations of pristine c-Si as well as delithiated shells of a-Si at the end of the 10th and 100th charge (fig 1.d) also indicate disconnection of active material with cycling, which leads to over-lithiation of the remaining active material. Inhomogeneities in lithium content are present even at the single particle scale (fig 1.e), which highlights how critical both ionic and electronic transport are in Si anodes.

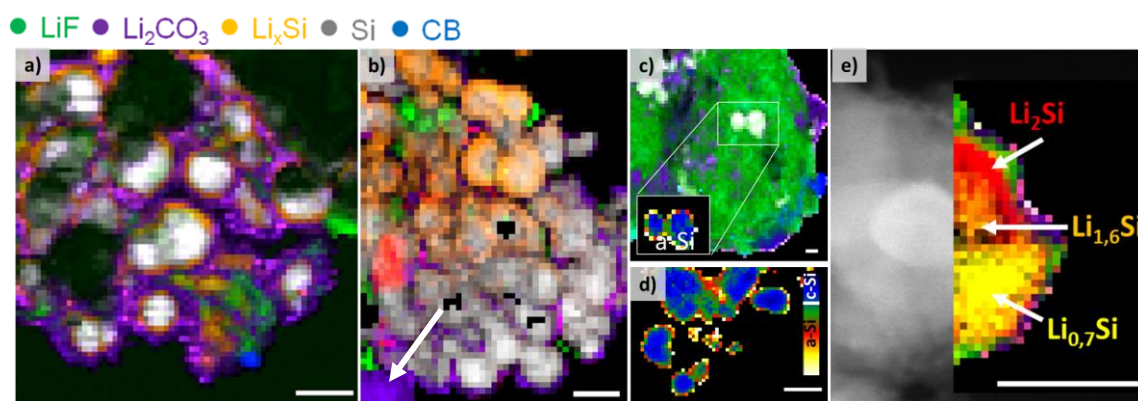


Figure 1: STEM-EELS maps representing: a) Li_xSi shells, Si cores and LiF/carbonate SEI after the 1st charge. b) Inhomogeneous lithiation and carbonate buildup after the 10th charge. c) Thick LiF buildup isolating formerly active Si after the 100th charge. d) c-Si/a-Si delithiated core-shell nanoparticles after the 100th charge. e) Inhomogeneous lithiation of a single SiNP after the 10th charge. All scale bars are 100 nm.

Reference: J. Danet et al., PCCP, 2010, 12-1, 220-6