

# COUPLING SURFACE IMAGING, FIB, AND SPECTROSCOPIES TO UNDERSTAND SILICON ANODES LITHIATION AND AGEING MECHANISMS

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To follow growing energy demand of new devices, batteries energy density needs to be improved. Silicon-based anode is a serious option since it offers a specific capacity almost ten times higher than carbonaceous materials. Even so silicon anodes suffer from a drastic capacity fading making it unusable after few cycles. A fine understanding of the lithiation mechanism of silicon could participate to the elaboration of more robust architectures.

In this work, composite silicon electrodes have been electrochemically cycled vs Li. After a transfer from a glove box to a ToF-SIMS by using an air-tight vessel, chemical mapping of the inside of silicon grains can be done by achieving an *in-situ* FIB cut.

The first lithiation has been extensively studied. By stopping lithiation at different stages it is possible to follow the evolution of the core-shell structure (*ie* LiSi alloy shell and pure Si core) as shown in fig.1. This method also permits to observe the Si particles, considering their position within the depth of the electrode. To complete this study, cross analysis with Auger spectrometer and SEM have been performed, allowing to quantify Li presence in the  $\text{Li}_x\text{Si}$  alloy and better understand the pure Si core morphology. At the end, a complete mechanism for silicon micron-sized particles is proposed.

In a second time, Si electrodes have been observed after 3, 5 and 10 cycles (limited capacity of  $1000 \text{ mAh.g}^{-1}$ ) in both lithiated and delithiated states. After three cycles the core-shell structure is still visible in lithiated state. After 10 cycles the presence of Si particles containing lithium at the end of the charge are observed and associated to particle getting out of the conductive grid and trapping lithium. This phenomena is detrimental to battery lifespan.

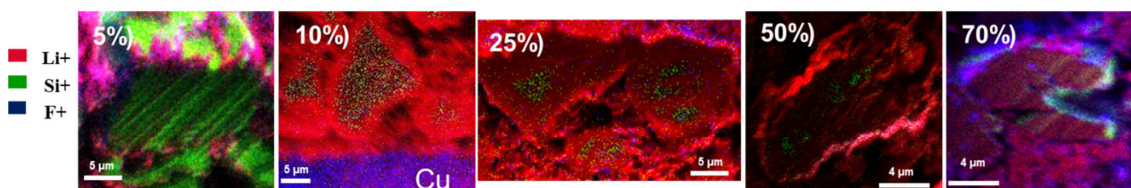


Figure 1: Evolution of the core-shell structure upon first lithiation