Supporting Information

Improved performances of nano-silicon electrodes using the salt LiFSI – A photoelectron spectroscopy study

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Figure S1: (a) Discharge capacity *vs.* cycle number of Li//Si cells (cycling between 0.12V and 0.9V with a rate of 150 mA/g of Si) using LiFSI. (b) Potential vs. capacity curves of the 1^{st} , 5^{th} and 10^{th} cycles (Precycling is not shown).

The discharge capacity increase observed in **Figure S1a** can be explained by the evolution of potential vs. capacity curves shown in **Figure S1b**. The capacity increase is not due to a modification of the curve in the high voltage region (> 0.4V, capacity < 100mAh/g). It is thus not due to an increased decomposition of the electrolyte (SEI formation), since solvent molecules are expected to be reduced before lithium insertion into silicon. Actually

Figure S1b clearly shows that it is due to an increase of the 0.3-0.2V voltage plateau corresponding to the formation of Li-Si alloys. This suggests that more and more silicon is converted into Li-Si alloy at each cycle. One explanation for this observation is that after the precycling step (which consists of an incomplete lithiation process to avoid huge volume changes), small particles of pristine silicon still remain present and upon further cycles. These particles are being lithiated upon the following cycles, resulting in an increase of the capacity.