Supporting information for

'Multi-probe study of the SEI on silicon based electrode in full cell configuration'

N. Dupré[1,*], P. Moreau[1], E. De Vito[2], L. Quazuguel[1], M. Boniface[3], A. Bordes[2,4], C. Rudisch[1], P. Bayle-Guillemaud[3], D. Guyomard[1]

[1] : Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

[2]: CEA, LITEN, Minatec Campus, 17 rue des Martyrs, F-38054 Grenoble, France. Univ. Grenoble Alpes, F-38000, Grenoble, France.

[3] Université Grenoble Alpes, INAC-SP2M, F-38000, Grenoble, France. CEA, INAC-SP2M, F-38054 Grenoble, France.

[4] Groupe de Physico-Chimie des Surfaces, Institut de Recherche de Chimie Paris, CNRS-Chimie ParisTech, 75005 Paris, France.

Author to whom correspondence should be addressed: N. Dupré, Nicolas.dupre@cnrs-imn.fr

Table of contents:

Electrochemical cycling in half cells (*vs* Li)

Half cells (*vs* Li) have been cycled in carbonate electrolyte using a VMP cycling/data recording system, in a galvanostatic mode, starting with a 12h rest for a good electrolyte impregnation:

- For the silicon electrode: between 1 and 0.005 V *vs* Li^+/Li with limited discharge capacity of 1200 mAh g^{-1} of silicon at a rate of 1Li in 2h in discharge and charge, corresponding to a current density of 480 mA g^{-1} of silicon. The active mass loading of silicon is around 0.8 mg cm^{-2}.
- For the NMC and NCA electrode: in galvanostatic mode, between 4.2 and 2.8 V *vs* Li^+/Li with a formation cycle at 1Li in 10h then 1Li in 2h for the following cycles.

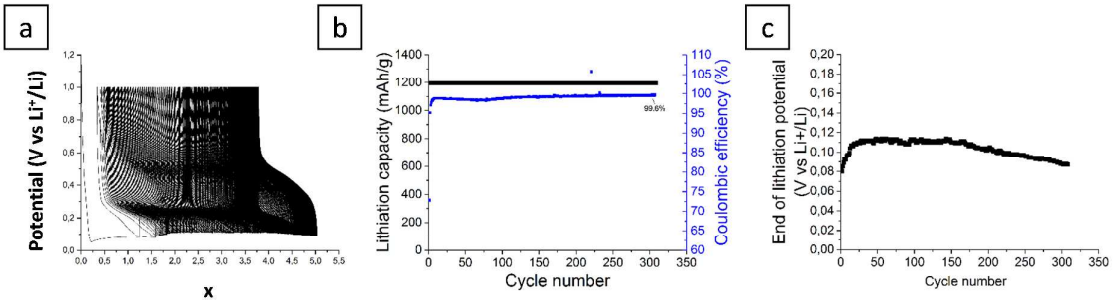

Figure S1: (a) Electrochemical cycling of Si vs Li in carbonate electrolyte, (b) Capacity of the Si electrode according to the number of cycles and (c) the end of lithiation potential vs Cycle number

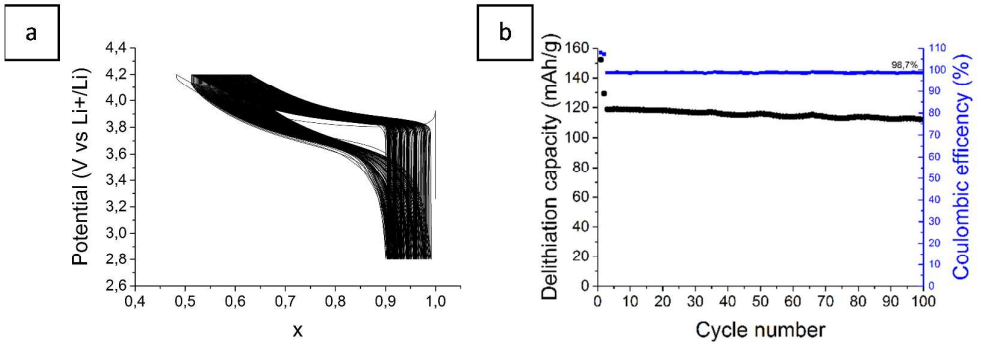

Figure S2: (a) Electrochemical cycling of NMC vs Li in carbonate electrolyte, (b) Capacity of the NMC electrode according to the number of cycles

Pristine silicon powder characterization

The silicon power bought from Nanostructured & Amorphous Materials (NAM) was taken as-is, dispersed in water and deposited onto a copper mesh grid for TEM analysis in an FEI Titan SuperTwin microscope operated at 200kV. We observe a bimodal distribution of nanoparticle sizes, with smaller (10 - 40 nm) polycrystalline ones that are fused together in long chains and larger (70 – 150 nm) mostly monocrystalline ones.

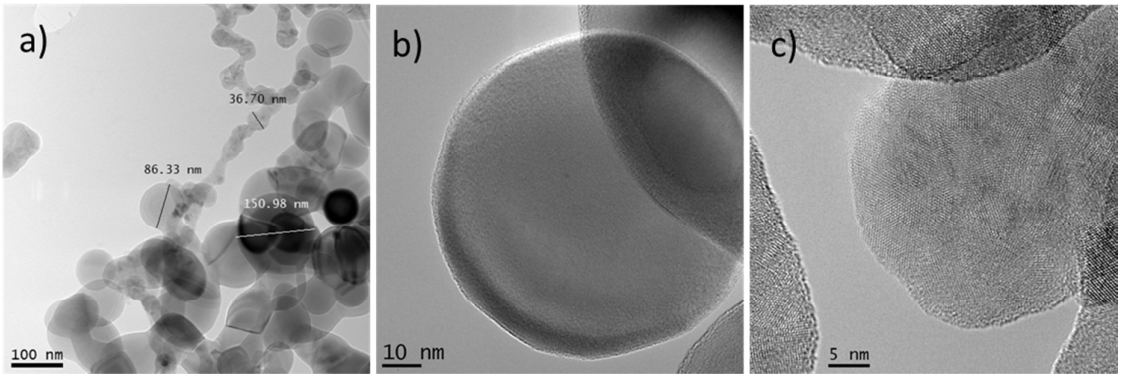

Figure S3: TEM images of a) a large area showing the nanoparticle populations. b) of monocrystalline nanoparticles of 82 nm diameter c) Polycrystalline nanoparticle of 35 nm diameter.

Post mortem ^{7}Li MAS NMR on silicon electrodes after 100 cycles in complete Si/NMC Li-ion cell configuration

^{7}Li MAS NMR spectra recorded after 100 cycles at 0.2 V (end of "lithiation") and at 1.0 V (end of delithiation) display one broad resonance centered at 0 ppm with a very similar integrated intensity (Figure 12), suggesting that after 100 cycles the majority of lithium is trapped in the SEI and no lithium can be inserted or extracted from the electrode, in agreement with the electrochemistry data. Since the ^{7}Li NMR shift for Li_xSi_y is strongly overlapping with the signals of surface Li, it is not possible to completely rule out the presence of a small amount of such alloy. Its quantity is however small and cannot account for the main Li loss phenomenon.

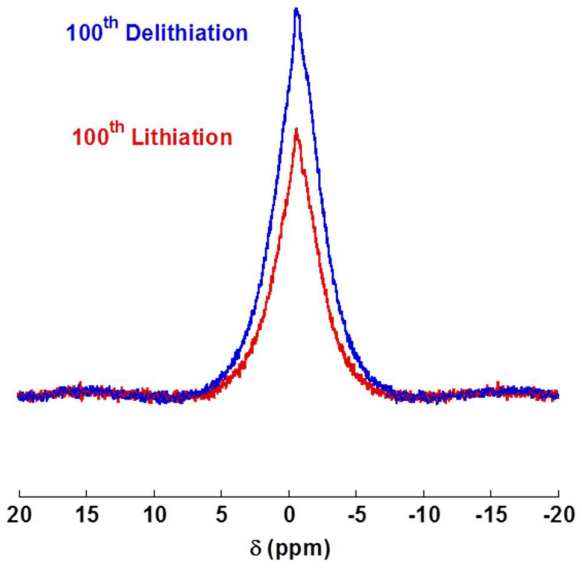

Figure S4: Normalized ^{7}Li MAS NMR spectra after 100 cycles, at the end of lithiation and delithiation. NMR data have been normalized with respect to the mass of sample and number of scans and the spectra are given in absolute intensity.