Experimental report

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Proposal: **1-04-101** **Council:** 4/2015

Title: SANS CHARACTERIZATION OF CORE-SHELL SILICON CARBON-COATED NANOPARTICLES USED AS ANODE MATERIALS FOR LITHIUM-ION BATTERIES

Research area: Materials

This proposal is a new proposal

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Samples: SiC

Instrument	Requested days	Allocated days	From	To
D33	0	1	25/11/2015	26/11/2015
D22	1	0		

Abstract:

We have successfully synthesized, by laser pyrolysis technique, new core-shell silicon carbon-coated nanoparticles (Si@C-NPs) used as anode materials for lithium-ion batteries. This technique allowed producing Si nanoparticles (Si-NPs) in a very versatile manner. Indeed, we have synthesized either Carbon coated or naked NPs of different size as well as crystalline or amorphous Si core. We observed that Si@C material exhibited a high and stable capacity whereas the bare Si material obtained from the same synthesis showed a rapid capacity fading. Furthermore, amorphous Si@C shows even better performances, particularly in terms of coulombic efficiency. These results clearly showed that both the surface state and the crystallinity of the Si-NPs govern the electrochemical behavior of the material. The aim of the present SANS proposal is to investigate the shape, size, core-shell structure evolution of such promising NPs according to the elaboration process, at different stages of lithiation.

SANS CHARACTERIZATION OF CORE-SHELL SILICON CARBON-COATED NANOPARTICLES USED AS ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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Due to their great success for portable electronic devices, lithium-based batteries are becoming increasingly important for powering (hybrid) electric vehicles. Yet, in order to achieve driving ranges comparable to those provided by combustion engines, substantial improvements regarding their energy density are required. Concerning the anode side, most commercial lithium-ion batteries use carbonaceous materials and silicon material seems promising due to its high theoretical specific capacity (up to 3580 mAh.g^{-1}) and its relatively low operational potential. However, the huge volume expansion of silicon alloys upon lithiation (up to 300%) leads to electrical contact loss and pulverization of the material, as well as a continuous consumption of lithium due to the decomposition of the electrolyte on the renewed fresh surface of Si exposed by the cracks of the particles volume expansion. Thus, it leads to poor cycling stability and rapid capacity fading. These effects can be partially counteracted by using nanometer sized Si particles (Si-NPs) that can better sustain the mechanical strains induced by the heterogeneous volume changes. In addition, the particle expansion could be limited by carbon shell coating onto the nanoparticles, which can enhance the electronic conductivity and stabilize the initially formed solid-electrolyte interphase (SEI).

We have combined these two advanced strategies and succeeded in developing a synthesis method based on the laser pyrolysis technique to produce Si-NPs in a very versatile manner. Indeed, we can synthesize either Carbon coated or naked NPs as well as crystalline or amorphous Si [1] [2]. **The aim of the present study was to investigate the shape and size evolution of such promising NPs according to the elaboration process, before and after the first lithiations.**

Electrodes with the various NPs samples (see table 1) were processed and tested in coin cell configuration versus lithium foil. Transmission electronic microscope images (TEM) of these samples are also reported in figure 1 right. The composite electrodes were composed of an active mass (i.e. Si or Si@C NPs with either amorphous or crystalline cores), conductive carbon additives (a mixture of carbon fibers (VGCF) from Showa Denka and carbon nanoparticles from Timcal, reference Super P C-65) and sodium carboxymethyl cellulose binder (CMC). The electrochemical behavior was monitored and it was shown that carbon coating leads to improved capacity upon cycling. The cells were cycled once (1C) and five times (5C) (see Fig. 1 left) then the silicon electrode was carefully separated from the rest of the battery components in an argon glovebox, washed with dimethyl carbonate (DMC) and sealed in a hermetic bag before characterization by SANS in Hellma cells (immersion in the various solvents in the ILL glovebox). Ex situ SANS measurements were carried out on D33 beamline using neutron wavelengths of λ=0.6 nm and λ=1.3 nm and two sample-detector distances of 2 and 13m in order to cover the range of momentum transfer $0.0014 < Q < 0.4$ ang^{-1} (doi:10.5291/ILL-DATA.1-04-101). The contrast variation method was also employed: hexane (C_6H_{14}), deuterated hexane (C_6D_{14}) and a mixture of 50/50 C_6H_{14}/C_6D_{14} were used in order to either match the core or shell structure of the NPs as well as some other components of the electrode. Data were merged, normalized by transmission measurements and corrected from the background contribution using the ILL program “LAMP”.

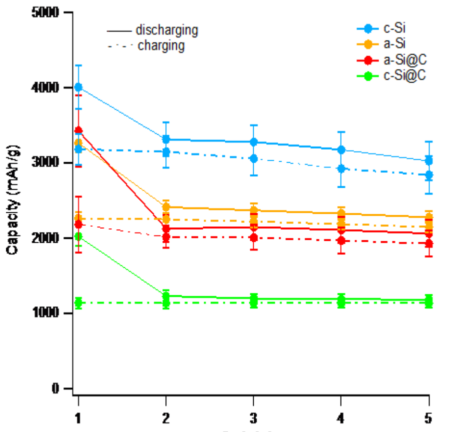
Name	State of Si-NPs	Diameter of the core (nm)	Thickness of the shell (nm)
a-Si	Amorphous	20	/
c-Si	Crystalline	30	/
a-Si@C	Amorphous	20	0.7
c-Si@C	Crystalline	30	2.5

Table 1: Morphology parameters of Si NPs [1] [2]

We could measure the SANS spectra of all our pristine and cycled electrodes. The SANS spectra show very interesting features, with modifications observed when comparing coated/uncoated particles, amorphous/ crystalline cores, and pristine/cycled electrodes.

1. Qualitative analysis: effect of composition.

On Figure 2, we show as an example the SANS spectra of pristine and 1C electrodes for the various anodes compositions in fully deuterated solvent. A qualitative inspection of these data allow to make the following observations:



Anode component	SLD (Ang-2)	Solvent	SLD (Ang-2)
Si	2,07^{E}-6	Hexane C6H14	-5,74^{E}-7
@C / Carbon NPs	6^{E}-6		
Super P	7,5^{E}-6	50/50	2,78^{E}-6
VGCF	6,67^{E}-6		
CMC	2,14^{E}-6	C6D14	6,14^{E}-6
Oxidation (SiO2)	3,63^{E}-3		

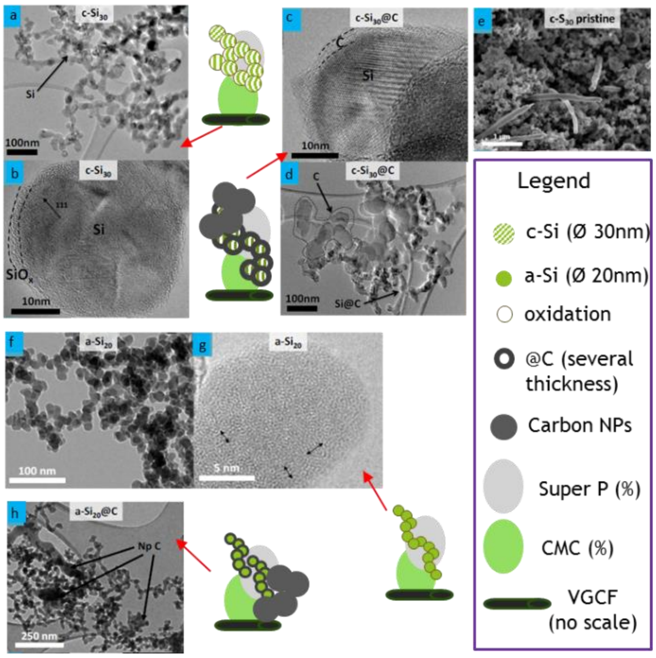


Figure 1: Left) Electrochemical behaviors of the different Si NPs anodes upon cycling. SLDs table of the anode components and solvents. Right) Bright-field TEM images of a) c-Si NPs, d) c-Si@C NPs, e) pristine of c-Si NPs, f) a-Si and h) aSi@C nanoparticles. Relative bright-field HRTEM image of b) one c-Si, c) one c-Si@C and g) one a-Si nanopartcile highlitghting SiO$_x$ oxide and C shell.

- **Effect of the Si-NP core.** After cycling, the SANS spectra of the crystalline Si core exhibit more detectable structural changes with respect to the amorphous core (Fig 2a) even in the presence of carbon coating (Fig. 2b). Changes in absolute intensities, as well as modifications of the observed slopes, are noticed, showing that the morphology of the NPs is modified after 1 cycle.

It can be explained by the fact that during the first lithiation, the crystalline core undergoes a process of amorphization. The state of the core (i.e. amorphous or crystalline) strongly impacts the electrochemical performance, which is also illustrated by the structural behavior.

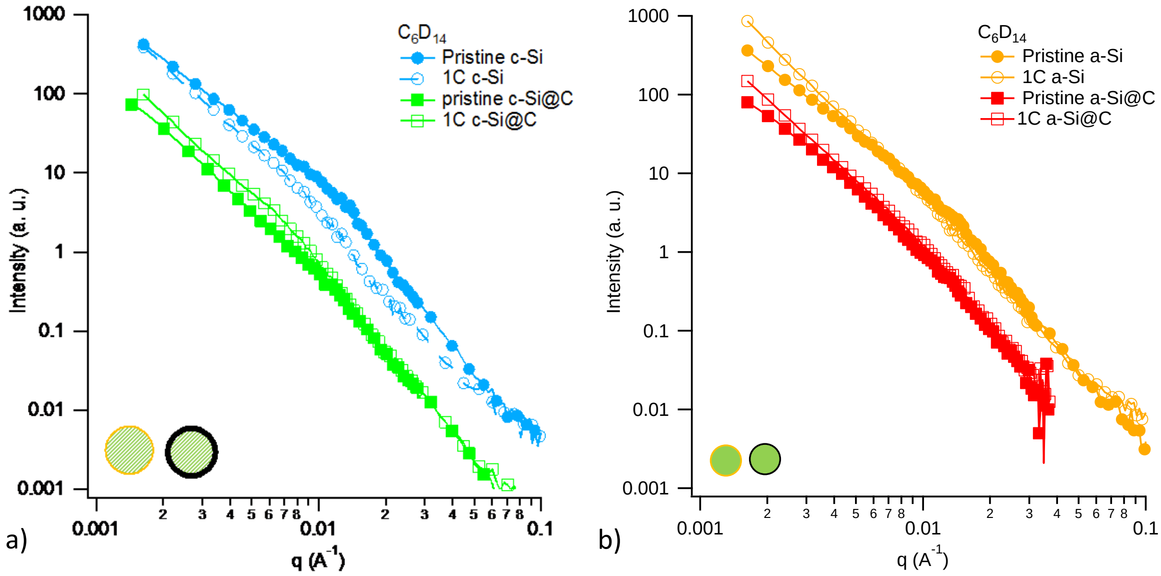


Figure 2 : SANS spectra in fully deuterated solvent for a) crystalline and b) amorphous core of Si NPs upon cycling (pristine and one cycle (1C)). Intensity has been shifted along the scale between the different NPs but not between pristine and 1C of the same NPs.

- **Effect of carbon coating.**

We have seen that cycling has an effect on the SANS spectra, in particular when the core is crystalline. Moreover, if we compare the coated and uncoated crystalline particles, we see that the difference between pristine and cycled electrodes is reduced when using carbon coating (green curves in fig x). This means that the carbon coating has an effect on the final morphology of the particles. The morphology is less modified, which is consistent with the enhanced electrochemical stability and behavior of the coated electrodes. This must be related to the beneficial impact of Carbon in limiting volume expansions and/or limiting internal stress and/or affecting the penetration of Lithium ions within the core.

- **Effect of cycling**

On figure 3 we report the SANS data for pristine, 1C and 5C electrodes. We observe peculiar cycling effects depending on the composition of the anodes. For instance, when particles are uncoated, and the core is crystalline, the more it is cycled, the more it is changed. But, in contrast, for carbon coated particles with a crystalline core, the shift of intensity varies upon cycling. This behavior is complex, and a quantitative analysis including the details of the various components is needed. Moreover, we have to stress that we investigate the final state of one electrode at the end of the charge and discharge process, therefore we are missing a number of phenomena taking place in the course of cycling.

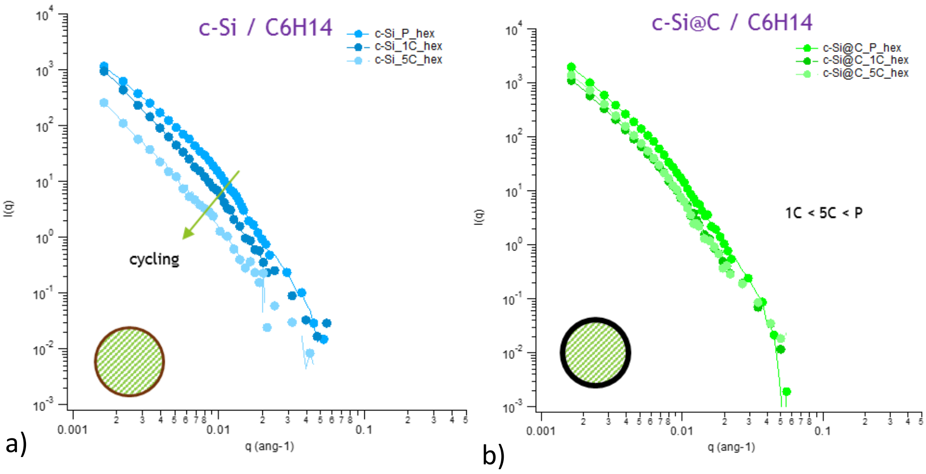


Figure 3: SANS spectra in hexane solvent for a) c-Si and b) c-Si@C NPs upon cycling (pristine, one cycle (1C) and five cycles (5C)).

2. Ongoing work: modeling.

We are currently proceeding to quantitative analysis using a fractal core-shell model to fit the spectra and monitor the various parameters: particle size, shell dimension, fractal correlation distance ξ, composition of core and shell. Indeed, the fractal core shell model seems to be appropriate as the TEM and HRTEM images show that Si NPs are organized into a branched network of self-similar objects (Fig. 1 right). Regarding pristines, SLD determinations are easily possible however regarding cycled electrodes, it is much harder to have access to SLD as some products have unknown density upon cycling. Thus, as our system is complex, it is of prime importance to optimize it for operando SANS characterization. One of the way is to replace the cellulose based polymer (CMC) binder by a deuterated version. Indeed, by this mean, the carbon-based moieties will be matched and it would avoid parasitic contributions to the Si NPs signal, as reported in Figure 4. In this purpose, we will use another binder (polyacrylic acid-PAA) that can be advantageously fully deuterated in contrast to CMC and whose SLD(d-PAA) is close to the one of d-CMC and much closer to the one of carbon NPs.

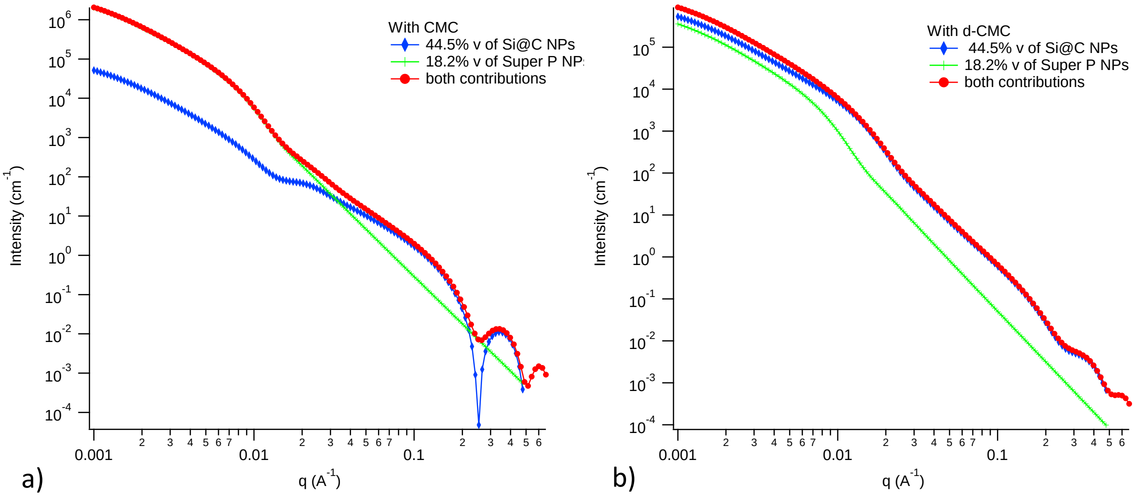


Figure 4: Simulations of Super P and Si NPs contributions with a) CMC and b) deuterated CMC binder. Fractal sphere model is used for Super P whereas fractal core shell model is used for Si@C NPs.

References [1] Sourice, J.; Quinsac, A.; Leconte, Y. ; Sublemontier, O. ; Porcher, W. ; Haon, C. ; Bordes, A. ; De Vito, E. ; Boulineau, A. ; Jouanneau Si Larbi, S. ; Herlin-Boine, N. ; Reynaud, C., *Appl. Mater. Interfaces*, **2015**, 7, 6637-6644.

[2] Sourice, J.; Chimie. University of Paris-Sud, 2015. (Thesis)