Experimental report

13/02/2017

Proposal:	**1-04-106**	**Council:**	4/2016

Title: OPERANDO SANS OF LITHIUM-ION BATTERIES USING CARBON-COATED SILICON NANOPARTICLES ANODES

Research area: Materials

This proposal is a continuation of 1-04-101

Main proposer: **Coraline MILLOT**

Experimental team:
Guillaume LEFEVRE
Jean Francois COLIN
Sandrine LYONNARD
Hakima MENDIL JAKANI
Coraline MILLOT
Gerard GEBEL

Local contacts: Lionel PORCAR

Samples:
Si
Si@C

Instrument	Requested days	Allocated days	From	To
D22	4	4	08/12/2016	12/12/2016

Abstract:

The aim of the present proposal is to follow in situ/operando process of lithium insertion and de-insertion in a Silicon based lithium-ion battery along charge/discharge. We focus on new anodes prepared with core-shell silicon carbon-coated nanoparticles (Si@C-NPs) of typically 20-30 nm. We want to follow the evolution of the size, shape and composition of the NPs by SANS, taking advantage of the sensitivity of neutrons to lithium. We have shown in our previous ex situ experiments on these materials that SANS is well suited to characterize the evolution of the Si-NPs anodes during cycling. With this operando experiment we want to correlate the real time morphological changes to the battery performances.

OPERANDO SANS OF LITHIUM-ION BATTERIES USING CARBON-COATED SILICON NANOPARTICLES ANODES

Experimental team: MILLOT Coraline, COLIN Jean Francois, MENDIL JAKANI Hakima; LYONNARD Sandrine and PORCAR Lionel

The aim of the present study was to understand the impact of lithium insertion and de-insertion on the nanostructure of silicon-based anodes for Lithium ion batteries. We have selected anodes using crystalline silicon nanoparticles (Si-NPs) of typically 30 nm diameter and an optimized formulation (carbon, binder). Operando SANS was attempted to follow the real-time evolution of the NPs morphology during the charge/discharge of our home-made neutron-transparent battery cell. .

Preparation of samples

Based on our previous ex-situ study of silicon-based electrodes prepared at different stages of lithiation/delithiation (doi:10.5291/ILL-DATA.1-04-101), we have optimized the electrode formulation to enhance the SANS signal of the Si-NPs during cycling. Indeed, disentangling the various contributions to the scattering pattern is challenging, therefore we decided to i) simplify the formulation (no carbon particles) and ii) vary the contrasts by using deuterated binder. We prepared a series containing:

- Commercial vapor grown carbon fibers (VGCF) used as long-range electronic percolators.
- Polyacrylic acid as binder. The binder was either fully hydrogenated (h-PAA), either fully deuterated (d-PAA, synthesized at CEA) to match the carbon contribution and enhance the Si-NPs signal.
- Two types of Si particles were used as active matter: commercial crystalline Si-NPs (100 nm diameter, quite polydisperse) and crystalline nanometer sized silicon particles (Si-NPs) synthesized at CEA using the laser pyrolysis technique [1-2] yielding to low polydisperse NPs. The CEA-made particles were uncoated or coated with carbon.

The slurry of the active material was prepared with a (50/25/25) formulation of (active material/VGCF/binder). We coated 4*2 electrodes prior to the SANS experiment (e.g. commercial Si-NPS/h-PAA, commercial Si-NPs/d-PAA, CEA SI-NPs/h-PAA and CEA SI-NPs/d-PAA, doubled in case of problems). The slurry of carbon-coated particles for preparing other electrodes was also available.

Neutron-transparent battery cell

Our battery cells were designed to fulfill the specifications for both SANS (neutron transparency, scattering angle) and electrochemistry. The cell is made of three main parts as shown in Figure 1a. Two titanium bases are used for the cathode and the anode, respectively, separated by a PEEK linking body allowing a 1mm gap thickness between the electrodes. The Si-based anodes are coated on the Titanium part on one side. Li metal discs were used as counter electrode on the other side. The cells were assembled in glove-box (level C) at ILL prior to the measurements and filled with LiPF6- EC: DMC (1M- 1: 1) electrolyte. We have constructed 4 of these cells to be mounted on the specially-designed rack adapted to D22 spectrometer, and connected to a VPS potentiostat system, as shown on Figure 1b. During the SANS experiment, neutrons cross the two titanium parts and the electrochemical components (silicon anode, liquid electrolyte and lithium thin disc).

Issues with battery cycling due to glove bow contamination

Our plan was to cycle 4 cells simultaneously (namely commercial Si-NPS/h-PAA, commercial Si-NPs/d-PAA, CEA SI-NPs/h-PAA and CEA SI-NPs/d-PAA) and acquire SANS data at regular intervals by moving from cell 1 to 2, 3 and 4, and doing this in series for the first 3 cycles. In fact, it is expected that major changes in electrode structure are happening in the first charges/discharges of the battery. The comparison of h-PAA/d-PAA systems on one hand, and Commercial vs CEA-made on the other hand, was planned to allow for quantitative analysis of the data in terms of size, shape and composition of the core-shell NPs along cycling (during lithiation, the silicon core is progressively amorphized). However, we were unable to measure all our batteries during the D22 run because of issues with the sample manipulation inside the ILL Level C Glove box. We noticed the presence of dust/impurities as well H_2O and $O_2 > 20$ ppm. Hence, we were not in the position to realize a good quality battery and unfortunately, most of our cells could not start cycling due to extremely poor contacts induced by pollution. It has to be mentioned that all our cells were checked carefully at CEA before the SANS experiment, and cycled perfectly whatever the Si electrode formulation tested.

After all our efforts to prepare new coatings, mount and dismount the cells three times each, only one operando cell could start. We were able to test it during the first cycle before it crashed (see Figure 1c showing the unusual degraded state of lithium, note the presence of holes).

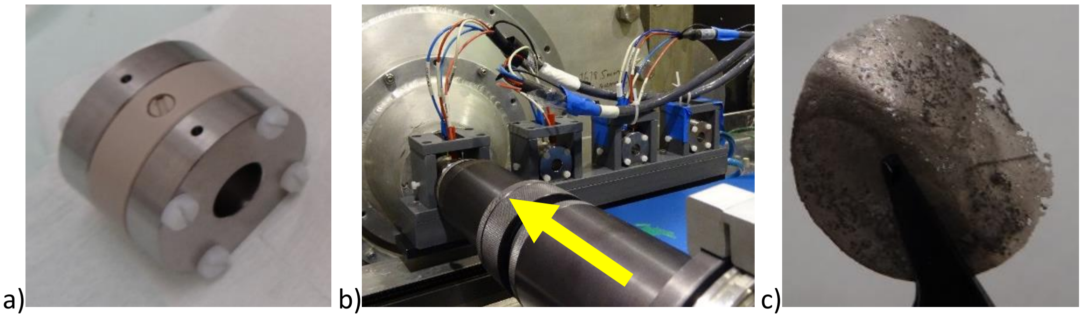

Figure 1: a) Operando cell in SANS configuration b) Set-up on D22 beamline with 3 cells connected via a GPC potentiostat. c) State of the lithium after dismounting the dead cell: abnormal presence of holes

Operando SANS: raw data and first qualitative insights into mechanisms

Electrochemical cycling was performed by galvanostatic charge/discharge of the operando cell in the range of 1 mV to 1.5 V vs Li+/Li, monitored by a VSP system (Biologic), at a C/20 rate. Records of voltage were made every 5 mV and are reported in Figure 2. Operando SANS measurements were carried out on D22 beamline using neutron wavelength of λ=6 Ang and two sample-detector distances of 2.8m and 17.6m in order to cover the range of momentum transfer 0.002 < Q < 0.34 Ang-1 (doi: 10.5291/ILL-DATA.1-04-106). SANS patterns were taken every 15 minutes during the first charge/discharge (see red dots in Figure 2a). Data were normalized by transmission measurements and corrected from the cell background contribution using the ILL program “GRASP”. Data were merged and analyzed using NIST macro on Igor Pro.

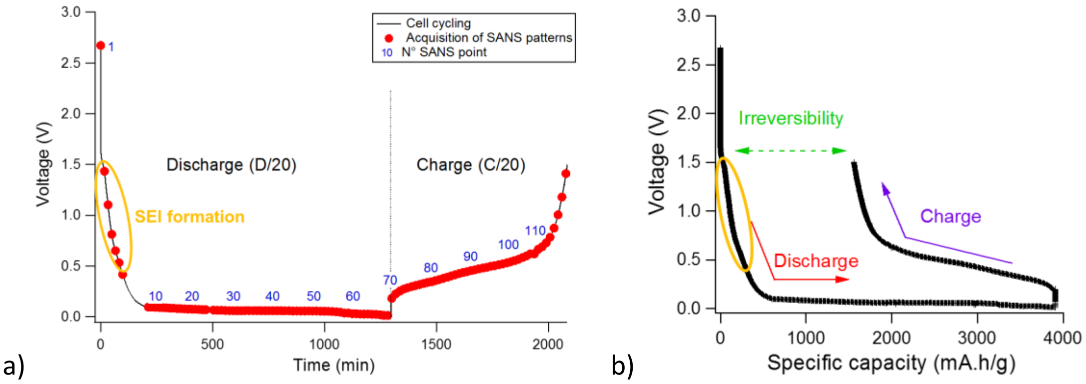

Figure 2: a) Evolution of the voltage during galvanostatic cycling as a function of time upon discharge and charge. The acquisition of SANS patterns is indicated by red dots; b) Specific capacity of the cell during the first cycle.

The SANS spectra are reported on Figure 3. We observe a continuous evolution upon lithiation (Figure 3a) and delithiation (Figure 3b). The profiles are characterized by a low-Q and high-Q Porod’s behavior, with an intermediate region related to the shape and size of the particles. The analysis of the intensity variations in terms of form factor of the NPs is not straightforward, because of polydispersity and aggregation. However, we can already notice very interesting qualitative features on these data. The increase of intensity in the Q-range typically around 0.02 A-1 during the charge is related to the growth of the core-shell NPs due to Li alloying, while the decrease of intensity during the discharge relates to the shrinking phase associated to de-lithiation. This phenomenon is not fully reversible, as seen on Figure 3b (the last data (purple) do not superimpose to the pristine state, black curve). This irreversibility is, in part, responsible for the capacity fading along battery cycling and subsequent loss of performance, which is the main issue for Si-based anodes.

We can go one step further by integrating the scattered intensity in selected Q-regions, namely at low angles (LA, q=[0.003-0.0045 Ang^{-1}]) and medium angles (MA, q=[0.005-0.03 Ang^{-1}). The LA and MA integrated intensities are represented in function of time, e.g. during the cycling, on Figure 4a. There is a direct correlation between the SANS data and the electrochemistry, as highlighted also in Figure 4b where we show the relation between voltage and integrated intensity. In fact, we first observe the formation of the Solid

Electrolyte Interphase (SEI, layer formed at the electrode-electrolyte interface due to electrolyte degradation), and then the growth of the silicon particles.

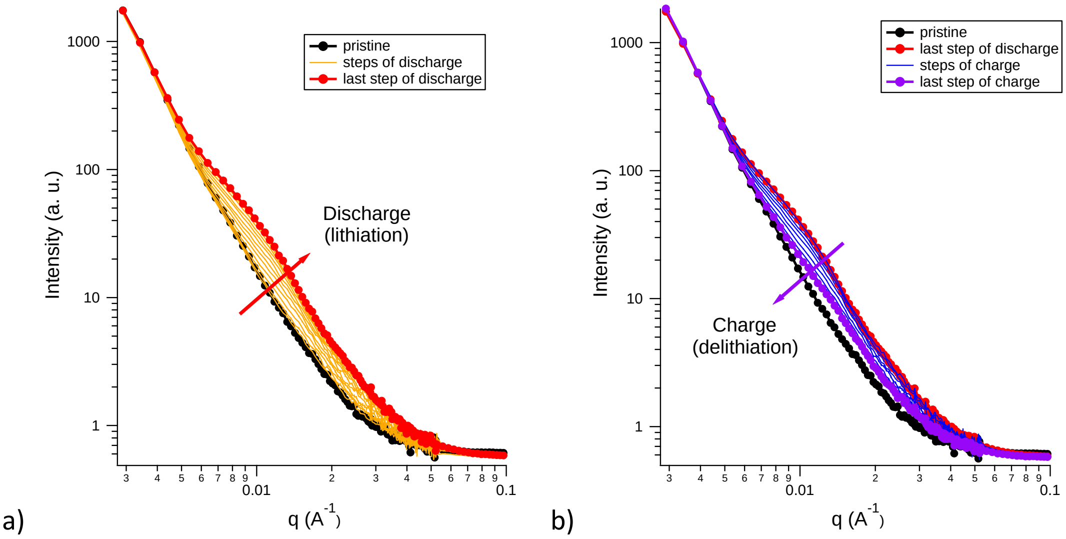

Figure 3: SANS profiles of CEA Si-NPs during a) discharge (lithiation effect) and b) charge (delithiation effect)

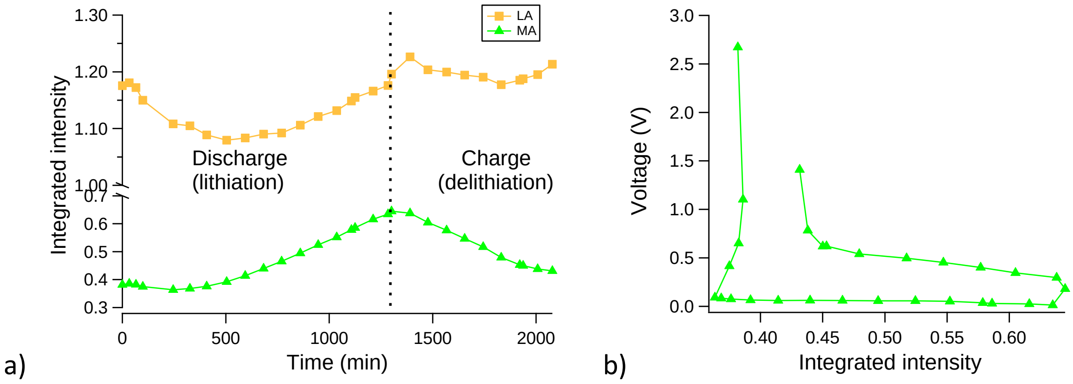

Figure 4: Variation of integrated intensity as a function of a) time and b) in relation with voltage for MA curve, showing the initial formation of SEI (no core-shell formation) and subsequent growth of the lithiated particles.

Conclusions

We have successfully performed the first operando SANS experiment on silicon-based nanostructured anodes in the course of battery cycling. We have shown the feasibility and suitability of SANS to bring real-time information on the structural evolution of the NPs, in relation to the electrochemical behavior of the cell. A qualitative analysis supports the core-shell formation of lithiated particles, corresponding to the penetration of lithium ions into the crystalline Si-NPs leading to the amorphization of the shell containing Li_xSi_y alloys [3-4]. At the end of the full discharge, fully lithiated particles are expected ($Li_{15}Si_4$). A more quantitative analysis using core-shell form factors is needed, but we have only one contrast condition (d-PAA), therefore is it complicated to establish the possible variations in NPs composition. Also, it would be very important to reach at least 3 full cycles to complete this set of data.

What is remained to do: Due to the glove box contamination, we could only perform a small part of our research program. However, we have realized the technical conditions for a complete study: our neutron battery cell is validated, as well as the concept of operando SANS to monitor nanostructured anodes modifications upon lithiation and delithiation. We want to perform the full operando SANS investigations that were planned initially, e.g. varying the physical parameters of interest (carbon coating, crystalline vs amorphous core) of the Si-NPs and the contrast conditions.

References

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