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Silicon core – carbon shell nanoparticles for Li-ion batteries anodes. Relationship between morphology and degradation mechanism studied by Impedance spectroscopy

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Performant electrochemical storage devices appear as one of the solution to face the challenge of energy transition and development of carbon-less energy processes. In this context, lithium-ion batteries are a well-developed technology because of their high energy density, their long life over cycling and their large field of applications, from microbatteries to stationary storage¹.

This work is focused on increasing the negative electrode's capacity by understanding the degradation mechanism occurring in the material. Graphitic carbon is commonly used as a negative electrode in commercial battery systems because of its stability, electronic conductivity, and its natural abundance. However, its maximum energy density remains too low to meet the requirements of demanding applications such as electric vehicles. Silicon is a promising alternative anode material to increase the capacity of the anode up to 3579 mAh/g, ten times higher than the 350 mAh/g of graphite². In silicon materials, lithiation and delithiation processes induce a 300 % volume change linked to the cleavage of the Si-Si bonds and the formation of a $\text{Li}_{15}\text{Si}_4$ alloy³. This dramatic structure change induces high mechanical stress⁴ which results in material fracture and rapid fading of performance.

Replacing bulk silicon material by nanometric particles is a well-known solution to alleviate this fracture problem⁵. An issue that becomes predominant at this scale size is the formation of an interphase between the electrolyte and the solid, and commonly named SEI. This SEI stability is fundamental to obtain stable performance of silicon electrodes.

Due to its ionic and electronic conductivity properties, the coating of the silicon surface by carbon has proved to protect the bare silicon surface and obtain a more stable SEI⁶.

In this work we synthesize core-shell carbon coated silicon nanoparticles (here designated Si@C) through double-stage laser pyrolysis. In the first reaction zone the laser induces decomposition of flowing silane in He to yield the silicon core. Amorphous (a-Si) and crystalline (c-Si) silicon core particles have been obtained (Figure 1a and 1b) and the crystallinity determined by nanodiffraction (inset of 1a and 1b). By adding a second stage where a carbon precursor (ethylene) is introduced into the flow of particles and subsequently decomposed by a second pass of the laser

carbon coated Si@C is formed. Carbon-coated amorphous (a-Si@C) and crystalline (c-Si@C) core-shell particles have been obtained (Figure 1c and 1d), and used as anode materials in the same coin cell configuration as the uncoated materials⁷.

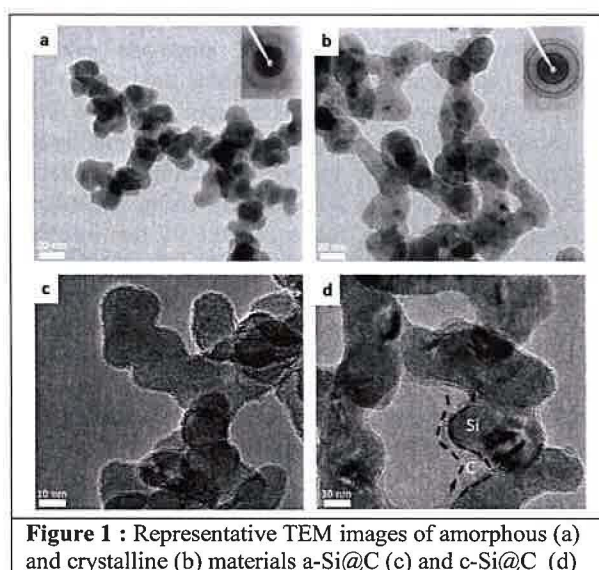
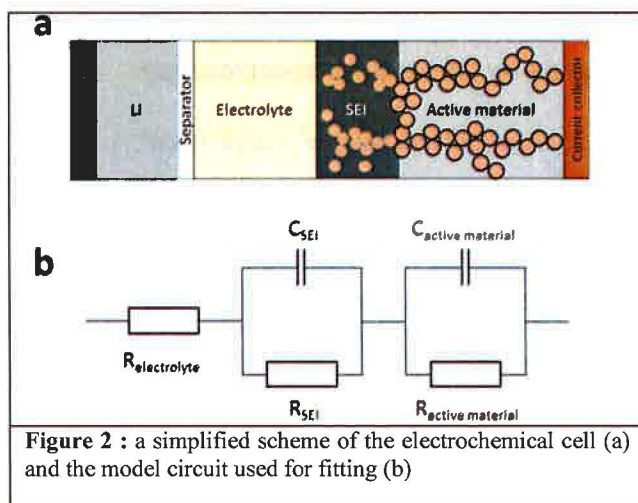


Figure 1 : Representative TEM images of amorphous (a) and crystalline (b) materials a-Si@C (c) and c-Si@C (d)

As shown in Figure 1, this synthesis results in particles of a “chain-like” morphology. Figure 1d shows evidences of a carbon shell presence, in good agreement with the results of chemical analysis, with a 6.7% for c-Si@C and 10% for a-Si@C. The comparison of electrochemical performances for coated and uncoated materials has been performed. The protective effect of the shell is demonstrated by a much higher specific capacity remains 300 cycles at C/5 for the coated material⁷. However, a large loss of capacity occurs during the first few cycles drastically reducing the lifetime performance of these electrochemical cells.

A powerful technique to probe such phenomena is Electrochemical Impedance spectroscopy (EIS).



Two mechanisms are suspected to reduce the capacity of the Si materials. First the volume change during cycling causes SEI expansion and cracking which exposes the underlying electrode material surface. This exposed surface enables continuous SEI creation with consumption of lithium followed by a rapid capacity fade. It is important to understand the SEI behavior in these first cycles and compare different materials. This can be achieved by using impedance spectroscopy to probe the evolution of the interface between different components of the electrochemical cells. The interfaces are shown in the simplified scheme of Figure 2.b. The SEI is at the interface between the active material and the electrolyte and EIS measures its electrical resistance. The behavior of the carbon shell can be extracted from the impedance comparison of a coated and an uncoated material.

High resolution EIS has been performed, meaning 50 EIS measurements were carried out during one lithiation or delithiation. This is used to investigate the changes during the SEI growth correlated to these structural modifications in the active material and in the carbon shell. An electrode of tested materials is assembled in a two electrode coin cell. In each battery, the first and the second cycles are compared. Then, the experiment is interrupted at the fiftieth cycles and the same number of EIS spectra are acquired in order to examine the ageing of the electrode. In a second experiment, three electrodes measurement have been acquired to remove the lithium contribution to the measured impedance.

the voltage for crystalline (a) and amorphous (b) materials.

The spectra obtained are then fitted to obtain the resistance values in the battery systems. The equivalent circuit used for modelling is shown in Figure 2.b. Figure 3 shows the resistances of active matter and SEI for amorphous and crystalline materials. Resistance values can be extracted and correlated to the degradation mechanisms. Amorphous materials have a better electrochemical behavior than crystalline materials. The results also confirm the protective effect of the carbon shell because the resistance increases less in the case of the Si@C materials compared to the Si materials.

Looking forward, we will perform EIS characterization of a wider range of materials to see the effect of the carbon shell thickness and silicon core size on the impedance properties in order to optimize synthesis conditions and resulting anode material.

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