Fabrication of silicon particles with graphene-like coatings and their application in lithium-ion battery anodes

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Abstract: In this contribution we present two different innovations: (i) a plasma-based method to synthesize silicon nanoparticles with a controlled nanoscale size (5-50 nm), tight particle size distribution (within 10% of the average size) and high purity (oxygen content < 3 wt%) and (ii) a Chemical Vapor Deposition process to coat silicon nanoparticles with a graphitic carbon shell. The synthesized composite works as a simple "drop-in" additive in graphite lithium-ion battery anodes and enables an increase of the storage capacity up to 50%.

Keywords: Nanoparticles, silicon, carbon, graphene, additive, lithium-ion battery, anode.

1. Introduction

Over the last decade, the research community engaged in significant efforts to investigate novel anode materials to substitute graphite in commercial lithium-ion -Li-ion- batteries with the goal of increasing the storage capacity of these devices.[1] Graphite reversibly intercalates the lithium ions in between its planes during the battery discharge/charge process and grants an overall maximum gravimetric capacity of 300-372 mA h g^{-1} and volumetric capacity of 756 mA h cm^{-3}. [2] Among the several candidates that have being actively investigated for the replacement of this carbonaceous compound, silicon -Si- is widely considered as the most promising choice due to its Earth abundancy, low toxicity and highest theoretical gravimetric and volumetric storage capacities, i.e. 3579 mAh g^{-1} and 2190 mAh cm^{-3} respectively. [2] These benefits are, however, encompassed by severe technical challenges as the material displays very large volume swelling upon lithiation (up to 300%) that causes electrode rupturing and a corresponding rapid capacity fade upon cycling. Marked progresses were achieved in addressing the described limitations and lead to identify the use of Si materials with tailored nanoscale size and encapsulated with graphitic carbon -C- coatings as the most promising strategy to achieve stable cycling performance from Si-based anodes. The small size of the Si nanostructures, below the so-called critical size for crack propagation, tackles the volume swelling upon lithiation and increases the lithium-ion diffusion in the material. The carbonaceous coatings, on the other hand, improve the electrical conductivity of the composite and prevent the direct interaction of Si with the electrolyte which in turn enhances the stability of the solid electrolyte interphase. [3] Although a wide range of Si-C nanocomposites have been investigated over time, these structures are often produced with complex methods characterized by questionable scalability hence hindering an immediate introduction of this technology into industrial manufacturing. In this contribution, we describe a facile, cost-effective and scalable-by-design route for the fabrication of Si-core graphite-shell nanoparticles -NPs. The approach comprises two distinct material synthesis innovations: (i) a non-thermal plasma system for the production of a battery-grade silicon nanopowder and (ii) a Chemical Vapor Deposition -CVD- system to coat Si NPs with highly graphitic C coatings. Both the setups have been purposely designed to enable a low-cost, large-volume synthesis and a straightforward future scale-up.

2. The silicon NPs synthesis method

The production of Si NPs with battery-grade quality notoriously represents a challenging endeavour for established commercial suppliers of Si nanomaterials.[4]

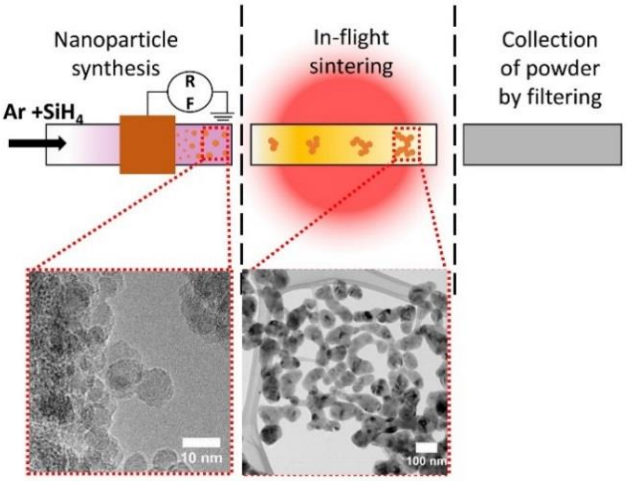

Fig. 1. Schematic of Si NPs synthesis setup. The TEM images in the lower part of the picture show the Si NPs in the two stages of the reactor.

Common issues of these products are represented by broad particle size distributions, feedstock quality variation and high level of oxygen contamination that overall negatively affect the performance of the anodes fabricated with these raw materials. With the goal overcoming the above described limitations we recently developed an "in-house" Si NP synthesis system. A schematic of the prototype setup is depicted in Fig. 1. The system comprises two stages (more details are reported in the publication of A. A. Barragan et al [3]). The first stage is a non-thermal RF plasma reactor (13.56 MHZ) that produces small sized silicon NPs (5 nm in size) from the dissociation of silane - SiH_4. [5] The method has been developed at the University of Minnesota, demonstrating high-rate material production of monodisperse and high-purity nanocrystals. The silicon NPs are then seeded into a tube furnace, the second stage of the setup, that allows for their controlled in-flight coalescence into larger structures.

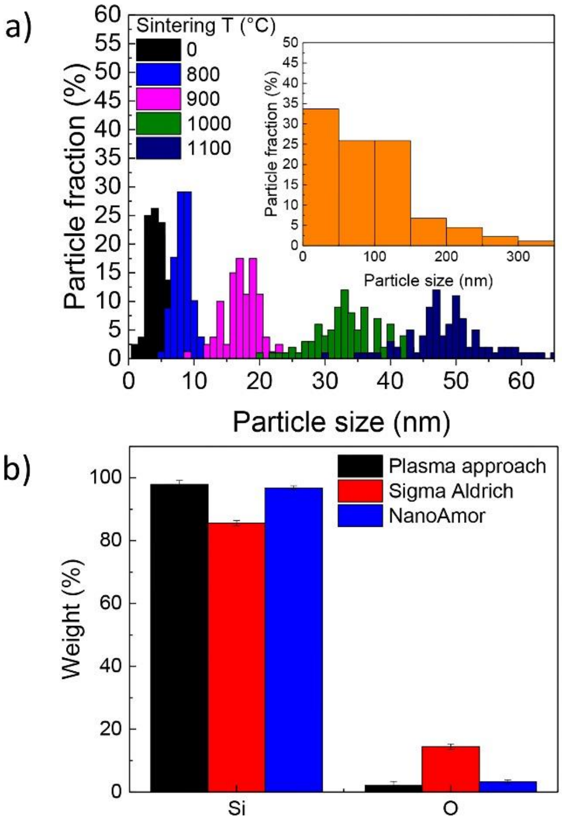

Fig. 2. (a) Particle size distribution as a function of the temperature of the annealing stage (measured by TEM analysis). The inset displays the typical particle size distribution of a commercial silicon powder (average size 100 nm). (b) SEM/EDS chemical analysis of two commercial powders and the 50 nm powder produced with our novel approach (in black).

This add-on to the plasma process enables tailoring the primary structure size in a broader range of values, i.e. from 5 nm to 50 nm, while maintaining a size distribution within 10% of the average value, a markedly better control with respect to commercial powders. The size is tuned by simply chancing the temperature of the thermal step in the range 800°C-1000°C (see Fig. 2a) and the synthesized materials exhibit very low oxygen content (below 3 wt%; see Fig. 2b). The presented setup reaches a high production-rate of 1-2 g h^{-1} with a 1.5% mixture of SiH_4 in argon- Ar. The electrochemical performance of the 50 nm Si powder produced with this approach was tested in 2032 half-cell Li-ion batteries (cathode: lithium foil; current: 0.1 C; electrolyte: LiPF6 in 1:1 v/v ethylene carbonate/diethyl carbonate + 10 wt% FEC) and compared with NPs from industrial manufacturers. The Si powders were coated with a thin C layer carbon through a simple CVD method to increase their electrical conductivity. [3] The electrodes preparation procedure was analogous to the one used in established industrial Li-ion battery manufacturing and comprised dispersing the particles into a slurry (85 wt% silicon-based material, 15 wt% CMC), coating a copper substrate with a Meyer rod and drying the electrode under vacuum at 90 °C for 12h. The solvent-binder combination selected for the anode production was an eco-friendly water-CMC. [6]

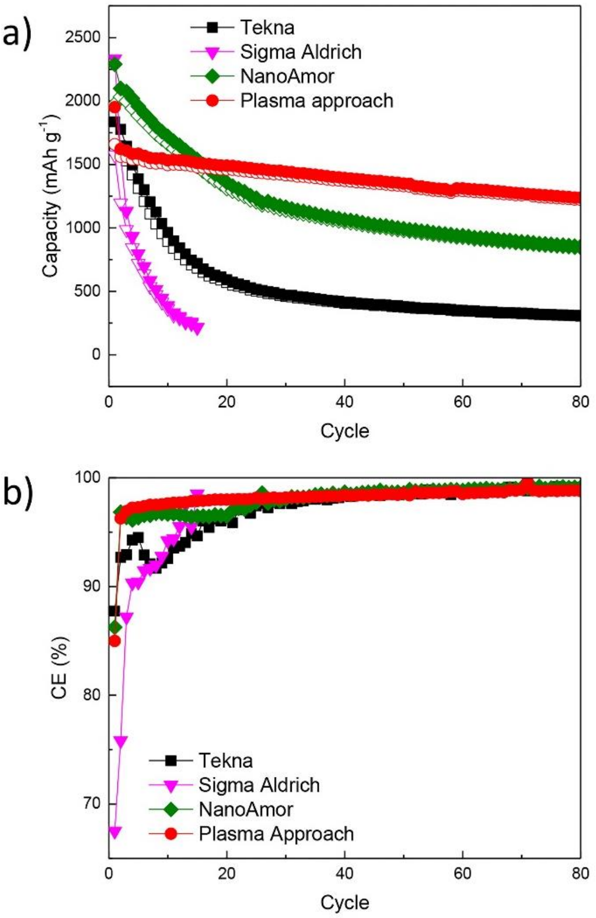

Fig. 3. (a) Cycling performance in half-cell of Si NPs from three different commercial suppliers (Tekna, Sigma Aldrich and Nanostructured and Amorphous Materials) and the 50 nm Si NPs produced with our method (in red). (b) Corresponding CE.

Fig. 3 details the performance of the fabricated electrodes. Our novel silicon powder exhibits the best cycling stability and a CE that, starting from 85%, rapidly increases above 98% in the first 8 cycles. This improved performance with respect to commercial powders is attributed to a combination of the better size control and the lower level of oxygen impurity enabled by our novel synthesis method. [3]

3. The CVD coating method

The second innovation presented in this contribution is a two-step CVD system. Through an in-depth study of the coating process, we have successfully developed a protocol to grow highly graphitized carbon shells directly onto the surface of silicon NPs, without the need of any oxide protection layer and without the formation of a carbide interface (both of which would negatively affect functionality). [3, 7]

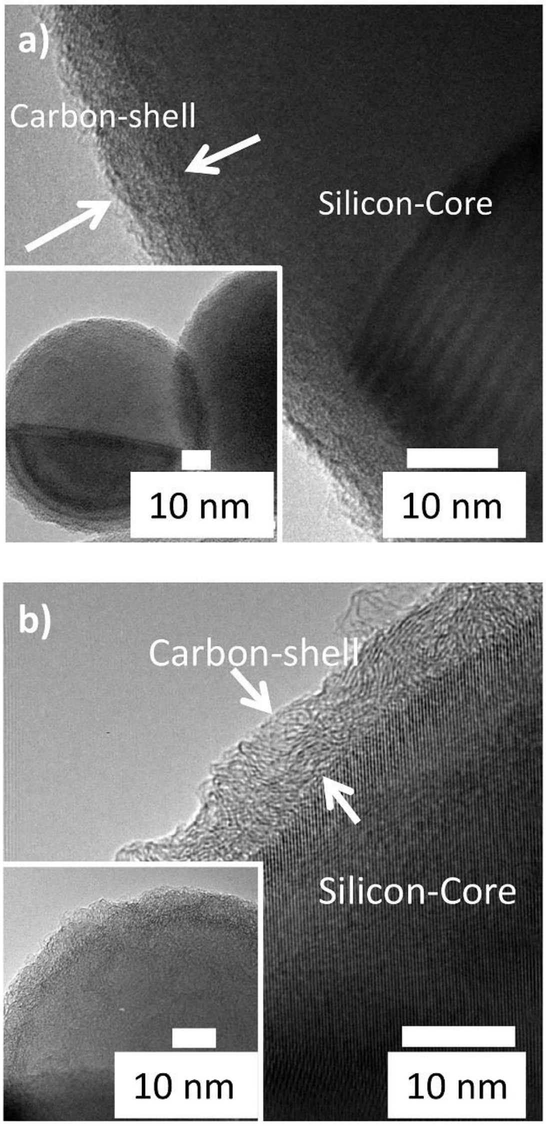

Fig. 4. TEM micrographs of Si NPs with (a) amorphous C coating and (b) graphitic C coating. The low-resolution insets display the highly conformal C coating wrapping a single NP.

The silicon NPs are positioned in an alumina combustion boat at the center of a tube furnace and the system is evacuated to a base pressure of 0.01 Torr. A flow of acetylene -C_2H_2, a cheap carbonaceous precursor is introduced into the furnace and the pressure is increase to 300-500 Torr using a needle valve positioned upstream of the pump. During the first CVD step, the silicon NPs are coated with a conformal layer of amorphous carbon that originates from the thermal decomposition of C_2H_2 at 650 °C, as depicted in the high resolution TEM micrograph in Fig. 4a. In the second CVD step, C_2H_2 is removed from the furnace, substituted by Ar and the temperature is rapidly increased up to 1000 °C.

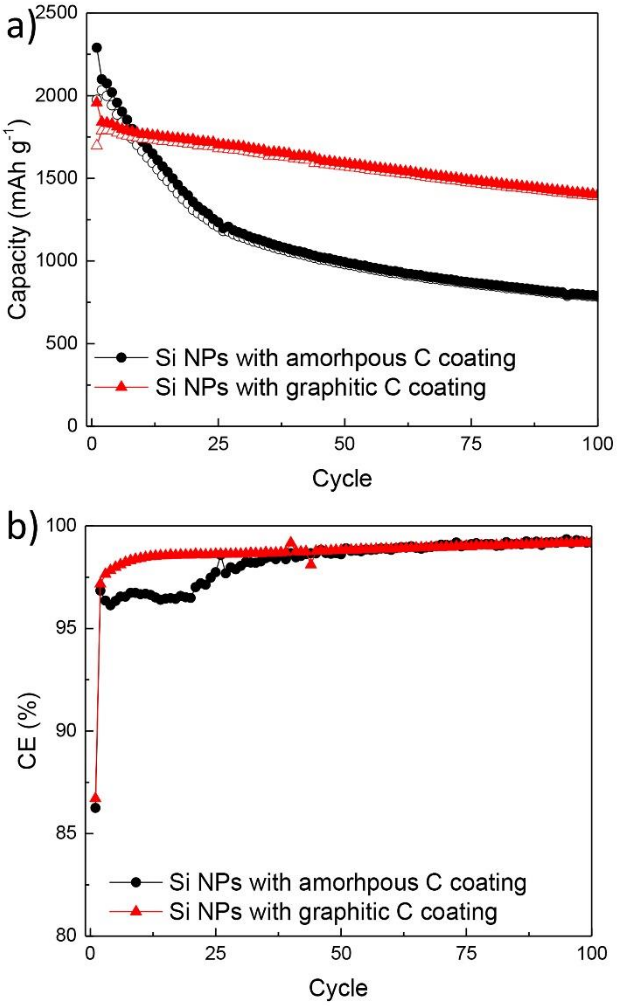

Fig. 5. (a) Cycling performance in half-cell of amorphous C coated and graphitic C coated silicon NPs. (b) corresponding CE.

The process leads to a controlled graphitization of the amorphous carbon shell, as highlighted by the appearance of graphene-like fringes in the corresponding TEM micrographs (see Fig. 4b), without changing the carbon layer thickness. The described process hence enables an independent control of the carbon shell thickness and degree of graphitization. The thickness of the carbonaceous coating is tuned by changing the duration of the dwell time of the first CVD step, [3] while the graphitic carbon content is governed by the temperature of the high-temperature thermal step. The setup achieves a high-production rate of 400 mg h^{-1} on a lab-scale. The electrochemical performance of these material was characterized in half-cell Li-ion battery assemblies (see Fig. 5) following the same methodology described in the previous paragraph. The Si NPs with an amorphous carbon coating deliver an initial storage capacity of 2200 mA h g^{-1} but show a fast capacity decay upon cycling and unstable CE value. A markedly superior electrochemical performance is displayed by the silicon NPs coated with highly graphitic carbon shells. The storage capacity starts from a value of 1800 m Ah g^{-1}, roughly 6 times higher than graphite, and remains above 1500 m Ah g^{-1} for more than 100 cycles, while the CE rapidly increase from 87% to values above 98% after the 6th cycle.

4. A "drop-in" additive for graphite anodes

Si-based technologies for Li-ion batteries often requires complex electrode fabrication methods, custom-made expensive equipment and aim at the complete replacement of the graphite anode. However, an approach introducing minimal or no changes to the established industrial fabrication methods and equipment would be more cost-effective and hence highly desirable to enable a straightforward and fast introduction these materials in industry. [3, 8]

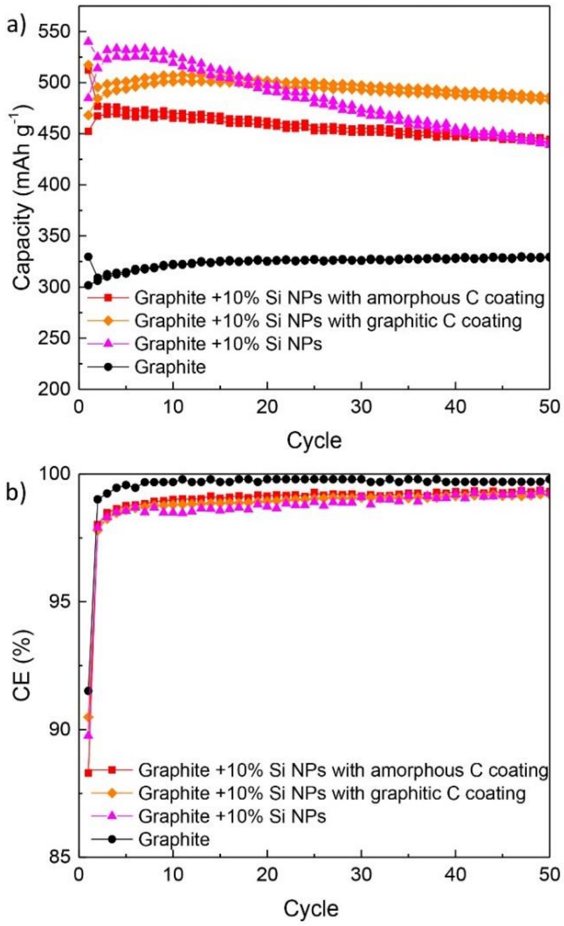

Fig. 6. (a) Cycling performance in half-cell and (b) corresponding CE of a graphite electrode and graphite electrodes containing: 10 wt% Si NPs with amorphous C coating, 10 wt% Si NPs with graphitic C and 10 wt% uncoated Si NPs. Testing is still ongoing.

We hence developed a simple "drop-in" protocol to use our silicon-based powder as a partial substitute of graphite in the electrode formulation. [9] We blended graphite, a small amount of our silicon-based powder, carbon black (a conductive additive) and CMC (a low cost binder) with weight ratio 81:9:6:4. The powder was then dispersed in water, mixed with a homogenizer for 3h to produce a slurry, coated onto a large area (7x7 cm^2) copper collector via Dr. Blade method and dried at 90°C in a vacuum oven for 12h. The procedure was performed using Si NPs with amorphous C coating, graphitic C coating and uncoated Si NPs with the goal of understanding the influence of the carbon layer quality on the anode properties. The electrochemical testing of the fabricated electrodes is displayed in Fig. 6. The Si NPs coated with the high-quality graphitic C layer show the best performance in terms of capacity, stability and CE. Notably, the storage capacity is 50% higher with respect to a pure graphite electrode, and the first cycle CE starts around 91%, a value compatible with application of the anode in full cell Li-ion batteries.

5. Conclusions

The synthesis approach described in this contribution represents a promising candidate for the large-scale and low-cost fabrication of high-quality Si-C composite materials for Li-ion battery anodes. Moreover, the method enables precise control over particle size, material purity, thickness and graphitic content of the conformal C coating wrapping the Si NPs. The presented R&D effort is currently focusing on the refinement of material properties through the optimization of the synthesis conditions and testing of the blended electrodes in full-cell Li-ion batteries deploying a commercial NMC cathode.

6. References

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