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SILICON NANOPARTICLE/CARBON NANOTUBE COMPOSITES FOR LI-ION BATTERY ANODES

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Introduction

In the context of high demand for energy in mobile devices, many studies deal with the lithium-ion cell technology. Because of its larger uptake ability of Li, silicon was suggested for being used (combined with a conductive material) instead of graphite, currently the most frequently used anode material for combining good electrical conductivity and the ability to host Li as intercalated ions between the graphenes [1,2]. However, charge/discharge cycles induce fatal structural damages to bulk Si, as a consequence of successive swellings and shrinkings of the Si lattice [3]. Hence bulk graphite and/or Si anode materials could be replaced by nanostructured composites combining mechanical strength, electrical conductivity, and high charge capacity. Carbon nanotubes mixed with silicon nanoparticles appear as a promising material [4-6]. Here, multi-walled carbon nanotubes Graphistrength® were used as substrate for the Fluidized Bed Chemical Vapour Deposition (FBCVD) of silicon from silane (SiH₄). The paper describes the synthesis and characterisation of the nanostructured composite material obtained, as well as the results of the electrochemical tests (involving charge-discharge cycles) carried out to analyze their behavior as Li-ion cell anodes.

Experimental

The experimental equipment was presented previously [7]. It consisted first in a vertical cylindrical stainless steel column, 0.083 m ID and 1 m high. At the bottom of the column, a perforated steel plate provided a homogeneous distribution of the gas phase and its flange was water-cooled to avoid any premature decomposition of silane. At the exhaust, an HEPA13 cartridge allowed capturing the elutriated particles. The reactor was externally heated by a two-zone electrical furnace and its wall temperatures were controlled by two thermocouples connected to PID regulators. Several thermocouples were also placed into a vertical tube of 6 mm in diameter inside the reactor to monitor the axial profile of temperature. Experiments were performed at atmospheric pressure. A differential fast response pressure sensor (LPX5480, DRUCK) measured the total pressure drop across the bed. A DasyLab® system enabled the on-line acquisition of the differential pressure and FB temperatures. N₂ electronic grade silane SiH₄ and Alpha1 high purity nitrogen (from AIR LIQUIDE) were supplied to the bottom of the bed through a ball rotameter (GT1355, BROOKS INSTRUMENTS) and a mass flow meter (FC7710CD, AERA), respectively.

The laser scattering size analyses of CNT balls after air-dispersion under an over pressure of 0.1 bar were performed with a Malvern MasterSizer2000 setup. The specific surface area of the CNT was obtained by the Brunauer-Emmet-Teller (BET) method, using a physisorption analyser MICROMERITICS ASAP2010, after 2 hours of degassing at 200 °C. The mass of Si deposited was measured by bed weighing and by ICP-AES chemical analysis, on a THERMO-FISHER iCAP6300. The powder morphology was observed by Transmission Electron Microscopy (TEM) on a PHILIPS CM30 on which X-photon energy dispersive spectroscopy (EDAX), with a 150 kV accelerating voltage, was also performed. Raman spectra were recorded at room temperature using the MicroRaman instrument from RENISHAW INC. The scattered light was collected in backscattering geometry using a microscope objective x100 to focus the laser beam (514 nm) on the sample. X-ray photoelectron spectroscopy was performed on a KRATOS Axis Ultra 165, with aluminium X-ray source.

Electrochemical tests were conducted with a prototype half-cell using a 15 cm² PTFE bescher filled with 5 cm³ of electrolyte, closed with a lid supporting working and counter electrodes plunged into the electrolyte. A copper mesh was folded to receive the as-synthesized CNT-Si balls and was connected to the working electrode plot. The counter electrode was a 1 cm² lithium foil, and 1 M LiPF₆ in ethylene carbonate (EC) / diethyl carbonate (DEC) (1:1 vol. ratio) was employed as the electrolyte. The cell was assembled and tested in an argon-filled glovebox (Compact 21, MBRAUN,[H₂O])
Constant-current charge-discharge cycles were conducted with a potentiostat RADIOMETER ANALYTICAL at C/10 rate, considering the theoretical specific capacity of silicon (pure silicon: 3579 mAh/g), between 1.2 and 0.05 V vs Li⁺/Li.

### Results and Discussion

In previous studies [7], silicon revealed to be deposited as nanoparticles (NPs), uniformly distributed inside the CNT balls. The nucleation occurred randomly with a possible preference for the morphological defects of the tubes. NPs are mostly individualized, suggesting that the reactivity of gaseous precursors is low with respect to nucleation. Moreover, the mean NP diameter tends to increase from 11 to 36 nm with the mass of deposited Si within the 10–70 wt.% range.

From high-resolution transmission electron microscopy (HRTEM), no crystalline structure could be observed for the Si NPs (Fig. 1). This result was wished because amorphous silicon could reduce the event of irreversible loss that usually occurs at the first lithiation-delithiation cycle for crystalline silicon [8]. It can be explained by the quite low deposition temperature used (500 °C).

**Figure 1:** HRTEM image of the silicon – carbon nanotube composite material

**Figure 2:** X-EDS line scan spectra of a 40 nm-large Si nanoparticle. The pseudo-Gaussian shape of the concentration curves reflects the progression of the ~10 nm large probe across the ~45 nm large NP.

*105 < 0.5 ppm.* From X-photon energy dispersive spectroscopy (X-EDS) line scan spectra of a Si NP (Fig. 2), the O signal follows the Si signal, indicating that the whole volume of the NP is affected by an oxidation event. The bulk O/Si atomic ratio is estimated at XXXX. Oxygen atoms come from the contact with ambient and they have diffused until the centre of the NP. A carbon signal is also detected, however with a contribution from the surrounding nanotubes with an extent which cannot be quantified. Raman spectroscopy (at 514 nm wavelength) results seem to confirm that Si NPs are slightly oxidized, and indicate the presence of hydrogen due to the silane pyrolysis generated C-H or Si-H bonds, as revealed by a strong luminescence (results not shown).

From X-ray photoelectron spectroscopy (XPS), silicon appeared in 3 different chemical environments (Fig. 3): mostly in Si° with 2p⁷/² and 2p⁹/² peaks at 99.4 eV and 100.0 eV respectively, and SiO₂ at 103.5 eV and 104.2 eV. Chemical C-Si bonds, scanned at 101.2 eV and 102.0 eV, were also found, probably between the surface of the Si NPs and that of the CNTs, respectively. Within the surface layer analysed by XPS – depth penetration is about 2 nm in such a material – the Si/O atomic ratio is estimated at ~0.9 by integrating the peak areas. This possible surface enrichment in O could not be seen by X-EDS because of the electron probe size used (~10 nm).

**Figure 3:** XPS binding energy
The formation of an irreversible capacity, added to the first discharge reversible capacity (total of 3187 mAh/g). From the charging voltage profile, a modulation in slope around 0.5 V vs Li+/Li can be attributed to the delithiation reaction of amorphous LiSiₙ.

From the charge-discharge characteristics (Fig. 5), a mean capacity loss of 2% per cycle is observed from the 2nd to 26th cycle, which could be attributed to the mechanical destruction of Si NPs due to the huge volume change during lithiation, in spite they are not crystalline.

A sample loaded with 70 wt. % of silicon was also tested without any significant result at this time. The formation of an unstable SEI layer was suspected to block the diffusion of Li⁺ ions into the Si NPs.

### Conclusions

Thanks to their amorphous structure and their individualized, nanosized morphology, the Si nanoparticles deposited by Fluidized Bed CVD on the multi-walled CNTs from CNT balls are able to be loaded with lithium with excellent specific capacity on the very first charge-discharge cycles. Si/CNT composite balls, used as-synthesized in Cu mesh-pack electrode, ensure good diffusion and uptake of Li⁺ and simple but efficient electrical contact. However, further studies are needed – actually in progress – to fix the problem of the degradation of the electrode, probably due to the formation of an unstable SEI and the mechanical instability of the NPs, by adjusting the composition of the electrolyte and the current density.

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