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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 then 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. N50
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.

Multi-walled carbon nanotubes Graphistrength® from
ARKEMA (called CNTs in the following), were used without
any purification treatment. They are entangled in coarsely
spherical balls (CNT balls), with a Sauter diameter of 338
microns in the average, which could be fluidized
homogeneously, with excellent contact between the solid and
gas phases, according to preliminary experiments. Nanotubes
walls are made of 10-15 concentric tubes of graphene with a
mean external diameter of 12 nm. The BET specific surface
area of CNT balls is 233 m²/g. The deposition conditions were
chosen in order to exalt gaseous species diffusion through the
porosity of the CNT balls. 100 g of CNT were used per run.
For all experiments, we chose to keep constant the reactor
temperature at 500 °C, the total gas flow rate and the inlet
SiH₄ concentration at 10 vol. %; the mass of deposited silicon
was then controlled by the run durations. They were chosen in
order to cover the 10–70 wt. % range of deposited silicon,
according to literature results about C/Si anode materials [5,6].

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 cm³ 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) / diethyle 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])

105 < 0.5 ppm). 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.

110 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

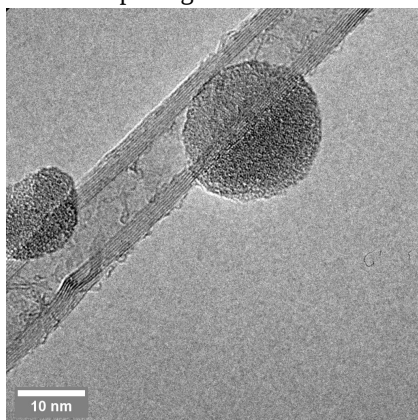


Figure 1: HRTEM image of the silicon – carbon nanotube composite material

115 mostly individualized, suggesting that the reactivity of gaseous precursors is low with respect to nucleation. 140 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.

120 From high-resolution transmission electron microscopy (HRTEM), no crystalline structure could be observed for the 145 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 125 silicon [8]. It can be explained by the quite low deposition temperature used (500 °C).

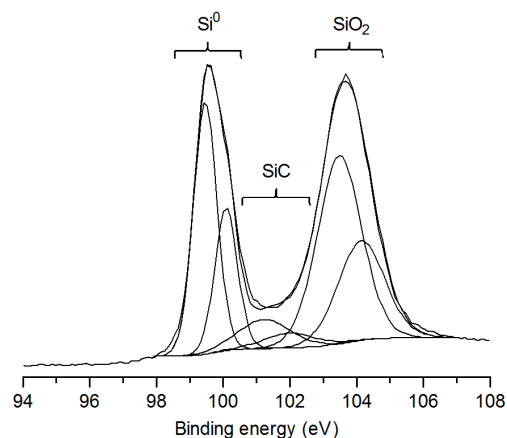


Figure 3: XPS binding energy

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 130 affected by an oxidation event. The bulk O/Si atomic ratio is estimated at xxxxx. 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 135 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 Si⁰ with 2p^{3/2} and 2p^{1/2} 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, 145 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 150 X-EDS because of the electron probe size used (~10 nm).

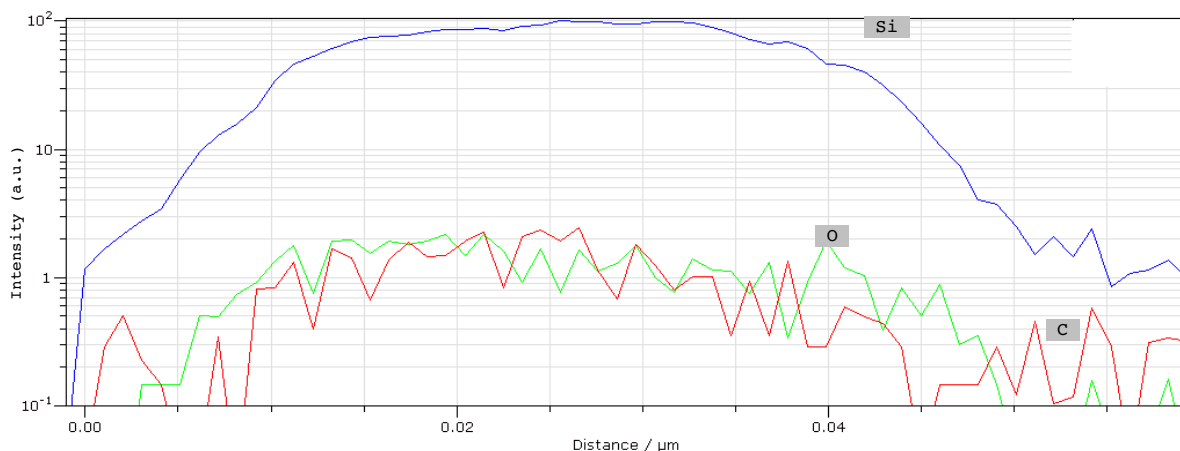


Figure 2: X-EDS line scan spectra of a 40 nm-large Si nanoparticle. The pseudo-Gaussian shape of the concentration curves reflects the progression of the ~10 nm large probe across the ~45 nm large NP.

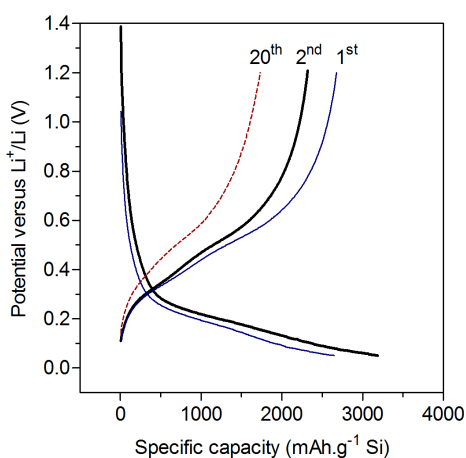


Figure 4: Voltage profile of a 30 wt % Si-containing sample, cycled at 20 mA/g current density. Specific capacity values are balanced with Si mass.

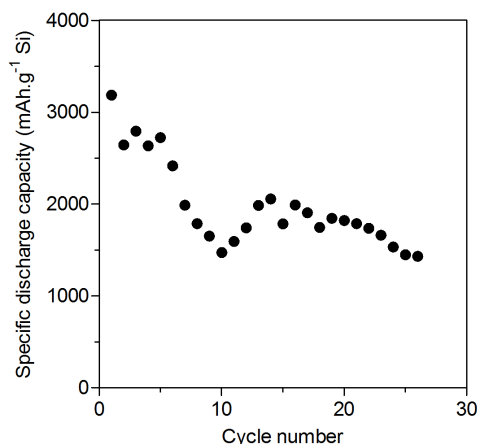


Figure 5: Charge-discharge characteristics of a 30 wt. % Si-containing sample, cycled at 20 mA/g current density.

The whole NP material can then be described as a $\text{Si}(\text{C}_x)\text{O}_y\text{H}_z$ amorphous material (with x , y , and $z \ll 1$).

Several identical CNT samples loaded with 30 wt. % of silicon were tested as Li-ion battery anode. Reproducible results were obtained. From the voltage profile (Fig. 4), a plateau beginning around 250 mV vs Li^+/Li can be observed, corresponding to the lithiation of amorphous silicon and, in the case of the first discharge, to the formation of a solid electrolyte interface (SEI) [9]. This phenomenon led to 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 LiSi_x .

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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