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Fluidized Bed Chemical Vapor Deposition of Silicon on Carbon Nanotubes for Li-Ion Batteries

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Silicon was deposited on balls of entangled multi-walled carbon nanotubes (CNT) with a mean diameter of several hundred microns, by Fluidized Bed Chemical Vapor Deposition from silane (SiH₄). The weight total percentage of deposited silicon was between 30 and 70%, to test their efficacy in Li-ion battery anodes. TEM and SEM imaging revealed that silicon deposits were of the form of nanoparticles uniformly dispersed on the whole CNT surface. The diameter of these nanoparticles increases with the deposited silicon percentage from 18 to 36 nm whereas their density remains constant at 5 10^{22} nanoparticles/g of CNT. This indicates a low affinity of chemical species born from silane pyrolysis with the CNT surface for nucleation. The increase of the silicon nanoparticles diameter leads to the decrease of the Specific surface area and the porous volume of the balls, probably due to the filling of the pores of the CNT network by silicon. A slight increase of the mean diameter of the balls was observed for the two highest silicon percentages, certainly due to the ability of the CNT network to be deformed under the mechanical stress induced by the silicon nanoparticles growth.

Keywords: Fluidized Bed CVD, Multi-Walled Carbon Nanotubes, Silicon, Silane, Li-Ion.

1. INTRODUCTION

The wide implementation of electronic devices and increasing environmental concerns has led to a push for high performance rechargeable batteries, offering high energy and power densities, safe usage and long service life, with the lowest possible production costs. Great scientific interest is focused on the lithium-ion technology, specially about the anode material for which graphite could be replaced by silicon.^{1,2} The theoretical gravimetric specific capacity of $Li_{22}Si_5$ (maximum Li-containing alloy phase of Li–Si system) is of 4200 mAh/g, more than ten times higher than the graphite, but cycling a massive Si-based anode involves enormous volume changes and phase transitions during lithium alloying and dealloying. This leads to decrepitation of the particles composing the electrode, leading to rapid capacity decay until battery failure.

Si nanoparticles mixed with carbonaceous material,^{3,4} thin Si layer on carbon nanofibers,⁵ one-dimensional nanostructures like Si nanowires,^{6,7} C–Si core–shell nanowires⁸ and hybrid Si/carbon nanotubes (CNT) nanostructures⁹ have shown promising performances as anode materials.

Authors have obtained silicon with a conventional sputtering system or by Chemical Vapor Deposition on a plane substrate. Our work is based on the Fluidized Bed Chemical Vapor Deposition (FBCVD) process, which is particularly efficient to uniformly coat powders with various materials. In a previous study,¹⁰ silicon FBCVD on agglomerates of submicronic TiO₂ particles has been investigated, showing that using specific operating conditions, silicon can be uniformly deposited as nanoparticles on the whole powder surface. In this paper, multiwalled carbon nanotubes Graphistrength® were decorated with silicon nanoparticles in a mass-production method. After a description of the experimental FBCVD equipment allowing the deposition of silicon from silane SiH₄, the structural and morphological features of the decorated nanotubes will be presented and discussed.

2. EXPERIMENTAL DETAILS

The experimental equipment was presented previously.¹¹ 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



Fig. 1. MEB view (a) and TEM view (b) of Graphistrength® CNT balls.

distribution of the gas phase and its flange was watercooled 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 online acquisition of the differential pressure and FB temperatures. Electronic grade silane SiH₄ and N50 nitrogen (from Air Liquide) were supplied to the bottom of the bed through a ball rotameter (GT1355, Brooks Instrument) and a mass flow meter (FC7710CD, Aera), respectively.

Multi-walled carbon nanotubes Graphistrength[®] from Arkema (called CNT in the following), were used without any purification treatment. As can be seen in Figure 1, they are entangled in coarsely spherical balls of several hundred microns. Nanotubes walls are made of 10-15 concentric graphenes with a mean external diameter of 12 nm. The BET specific surface area of CNT balls is 233 m²/g and their BJH volume of pores is 1.29 cm3/g. The ability to fluidize of these CNT was first studied. Bed pressure drop measurement indicated that fluidization was achieved with a minimum fluidization velocity $U_{\rm mf}$ of 1.2 cm/s at 20 °C. 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 run durations. They were chosen in order to cover the 30-70 wt.% range of deposited silicon, according to literature results about C/Si anode materials.^{4, 8, 12} The runs are named Sii, ii representing the expected wt.% of deposited silicon.

The powder morphology was observed by (i) Scanning Electron Microscopy (SEM) on a Hitachi TM3000 on

which energy dispersive spectroscopy (EDS) was also performed, and (ii) Transmission Electron Microscopy (TEM) on a Philips CM30. The specific surface area was obtained by the Brunauer-Emmet-Teller (BET) method,¹³ and the porous volume was calculated by the Barret-Joyner-Halenda (BJH) method,¹⁴ using a physisorption analyzer Micromeritics ASAP2010, after 2 hours of degassing at 200 °C. Only the N₂ adsorption isotherms were considered. 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. Each measurement corresponds to an average value calculated over 5 runs. The mass of Si deposited was measured by bed weighing and by ICP-AES chemical analysis, on a Thermo-Fisher iCAP6300.

3. RESULTS AND DISCUSSION

Si-coated CNTs were observed by TEM at various magnifications up to lattice fringe imaging. Views of runs S40



Fig. 2. TEM views of CNT-Si balls after run S40 (a, b, c) and run S70 (d, e, f).

Run	wt.% of Si	Mean Si NP diameter (nm)	Mean Si NP number per gram of CNT	BET surface area (m²/g)	BJH volume of pores (cm ³ /g)	Mean diameter d ₅₀ of CNT balls (µm)
S 30	29	18	6 10 ²²	142	0.90	372
S40	38	22	5 10 ²²	121	0.67	370
S50	47	24	6 10 ²²	98	0.60	346
S60	57	29	5 1022	80	0.44	422
S70	67	36	4 10 ²²	47	0.31	439

Table I. Characteristics of Si NPs and CNT-Si balls.

and S70 are reported in Figure 2. Images (a) and (d) illustrate the overall dispersion of the Si nanoparticles (NPs) over the CNT network. No obvious difference is seen between both runs in spite of the difference in Si proportion. Images (b) and (e) make a close-up on Si-coated CNTs from both runs. The main difference between the two runs is the larger average NP size in (e) compared to (b), as detailed below in Table I. Lattice fringe images (c) and (f) provide two examples of NP/CNT relationship. Typically, the presence of the Si NPs is associated with a defective morphological feature of the CNT in both cases. In addition, the images illustrate the amorphous structure of the Si NPs, the concentric display of the graphenes making the CNT wall, and the rather good nanotexture quality of the latter (i.e., the overall low proportion of in-plane defects of the graphenes). It is worth noting the absence of a discriminated surface layer (e.g., originating from a surface oxidation effect). Whether oxidation has possibly affected the whole NP body is about to be investigated.

Numerous EDS mappings performed on CNT-Si balls embedded in epoxy resin and half-cut were also performed for all runs. They show that silicon nanoparticles (NPs) are uniformly distributed inside the CNT balls for all the conditions tested. A characteristic EDS result is presented in Figure 3(a) for run S60. White zones correspond to voids in the CNT ball (filled with resin), according to the high porosity of this macrostructure. Silicon is deposited anywhere carbon is present, uniformly from the periphery to the centre of the balls, as confirmed by the line profile in Figure 3(b). The profile is hashed because of the porosity of the ball. Therefore, as wished, the tested operating conditions have promoted the gas diffusion into the pores of CNT balls, where the deposition reaction was the limiting step of the process.

The differences between the wt. percentages of deposited silicon measured by ICP-AES and by weighing are lower than 5% for all runs. As detailed in Table I, they are close to the expected values, indicating a quasi complete silane conversion rate, probably due to the high specific surface area of CNT.

For each run, the mean diameter of the Si NPs was measured on at least one hundred particles, appearing on TEM views of the CNT-Si balls at 70000X scale, with ImageJ software. The NP density (in number of NPs per gram of CNT) has been calculated from this mean NP

diameter: by assuming the NPs spherical and using the density of silicon (2330 kg/m³), the mass of one NP has been calculated. By dividing the weight of deposited silicon by this mass, the number of NPs has been obtained, as reported in Table I. The mean NP diameter tends to increase with the wt.% of Si deposited from 18 to 36 nm, but their density remains unchanged at 5 10²² NPs/g of CNT for runs S30 to S60. This indicates that for the conditions tested, the deposition mostly occurs by the growth of already nucleated silicon NPs. This limitation of nucleation could be explained by the low affinity of the chemical species formed from silane pyrolysis at 500 °C with the CNT surface. It is then logical that the nucleation of silicon NPs seems to preferentially occur on the structural defects present on the CNT surface. For run S70, a slight decrease of the Si NP density is observed. It could be due to a beginning of Si NP coalescence. The increase of the NP diameter leads to the decrease of the specific surface



Fig. 3. Si mapping (dark contrast) by EDS of a half-cut ball embedded in epoxy resin (a) and corresponding line profile (b), after run S60.

area and of the porous volume of the balls, probably due to the filling of the pores of the CNT network by silicon. For use in Li-ion anodes, a compromise will have to be found between the weight of silicon deposited and the accessibility of silicon to the Li⁺ ions. A slight increase of the mean diameter of the balls is observed after runs S60 and S70, certainly due to the ability of the CNT balls to be deformed under the mechanical stress induced by the silicon NP growth.

4. CONCLUSION

A nanostructured hybrid Si/C material has been developed by decorating multi-walled carbon nanotubes (CNT) with silicon nanoparticles, by Fluidized Bed Chemical Vapor Deposition (FBCVD) from silane SiH₄. Only the run durations were varied to obtain silicon weight percentages between 30 and 70% for application in anodes of Li-ion batteries. The characterizations have shown that this material corresponds to a CNT network acting as a mechanical buffer, and to a cloud of finely divised Si nanoparticles potentially accessible to the Li⁺ ions, which could extend the service life of the electrode during the lithiation and delithiation cycles. Its application as anode of Li-ion batteries is now being tested and new runs aiming to preserve the specific surface area of the CNT-Si even at high percentage of deposited silicon are planned.

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