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Decorated carbon nanotubes by silicon deposition in fluidized bed for Li-ion battery anodes

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\textbf{A B S T R A C T}

Multi-walled carbon nanotubes Graphistrength\textsuperscript{a} were decorated with silicon by Fluidized Bed Chemical Vapor Deposition. The ability to fluidize of these nanotubes forming ball-shaped jumbles of several hundreds of microns in diameter and that of the final CNT-Si balls was first studied. These balls reveal to fluidize with characteristics of Geldart’s group A particles, i.e. without bubbles and with high bed expansion. Coating experiments from silane SiH\textsubscript{4} were performed at 500 °C in the 30-60 wt.% range of silicon deposited. SEM and TEM imaging reveals that the nanotubes are coated by silicon nanoparticles uniformly distributed from the periphery to the center of the balls for the whole conditions tested. On-line acquisition of key process parameters evolution shows that the material remains fluidizable, even for large proportions of silicon deposited. The Sauter diameter and the tapped, untapped and skeleton densities of balls increase with the percentage of silicon deposited, whereas their specific surface area decreases due to the progressive filling of the pores by the deposit. This composite material is a promising candidate as anode to replace graphite in lithium-ion batteries.

\textbf{Keywords:} CVD; Fluidization; Carbon nanotubes; Silicon; Silane; Li-ion

1. Introduction

In the context of high demand for energy in mobile devices, numerous studies concern the lithium-ion cell technology. Lithiated cobalt oxide and graphite respectively used as cathode and anode material could be replaced by nanostructured composites, in order to improve safety, power density and energy density, for always lower cost (Armand and Tarascon, 2008). Considering the poor energy density of graphite as anode material, silicon is a good candidate with a theoretical capacity ten times higher, but it has to face two major problems: a rapid fading of the capacity and an increased polarization at higher current rate (Obrovac and Christensen, 2004; Kasavajjula et al., 2007). Vertically aligned or randomly networked carbon nanotubes or nanofibers have been explored as a support for silicon (Chen et al., 2011; Cui et al., 2009, 2010; Wang and Kumta, 2010). Authors often use sputtering or conventional CVD (Chemical Vapor Deposition) to coat the carbon support by silicon.

Our work is based on the Fluidized Bed CVD (FBCVD) process, which is particularly efficient to uniformly coat powders by various materials. Yu et al. (2006) have shown that carbon nanotubes can be fluidized under the form of agglomerates and that their fluidization was smooth and highly expanded, thus presenting characteristics of Geldart’s group A particles. Such group A particles correspond to small size and low densities powders. They exhibit a non-bubbling fluidization regime with high fluidized bed expansion (Geldart, 1973).

In a previous study of our group, silicon FBCVD on agglomerates of submicron TiO\textsubscript{2} particles has been investigated, showing that using specific operating conditions, silicon can be uniformly deposited as nanodots on the whole powder surface (Cadoret et al., 2010). These conditions have been recently applied to deposit silicon nanoparticles on the whole surface of multi-walled carbon nanotubes agglomerates. Detailed SEM (Scanning Electronic Microscopy) and TEM ( Transmission Electronic Microscopy) analyses of the morphology, diameter and number of the deposited silicon nanoparticles have already

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been presented elsewhere (Coppey et al., 2011). The present article focuses on the fluidization ability and physical characteristics of these agglomerates of nanotubes before and after CVD treatment and on the FBCVD process behavior. The experimental FBCVD equipment allowing the deposition of silicon from SiH₄ is first described. Then the characteristics of the carbon nanotubes and the methods of characterization employed are detailed. The results obtained are finally presented and discussed.

2. Experimental

The experimental equipment is presented in Fig. 1. It consisted first in a vertical cylindrical stainless steel column (referenced ¹ in Fig. 1), 0.083 m ID and 1 m high. At the bottom of the column, a perforated steel plate ² provided a homogeneous gas distribution and its flange was cooled by water to avoid any silane premature decomposition. At the exit, a high performance HEPA13 filtration cartridge ³ allowed collecting the elutriated particles. The reactor was externally heated by a two-zone electrical furnace ⁴ 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 ⁵ to monitor the axial profile of temperature. Experiments were performed at atmospheric pressure. Electronic grade silane SiH₄ and N₂O nitrogen (from Air Liquide) were supplied ⁶ to the bottom of the bed through respectively a ball rotameter (GT1355, Brooks Instrument) and a mass flow meter (FC7710CD, Aera). Uncertainties of ±5% could affect the silane flow rate measured and then the amounts of injected silane. A differential fast response pressure sensor (LPX5480, Druck) measured the total pressure drop across the bed. An absolute pressure sensor allowed monitoring the total pressure below the distributor. A DasyLab ⁷ system enabled the on-line acquisition of the differential pressure and FB temperatures. Hydrodynamic measurements at ambient temperature were performed in a glass column 5 cm ID equipped with the same differential pressure sensor and filtering cartridge.

The hydrodynamic behavior of powders in the fluidization column was analyzed by classically measuring (i) the pressure drop of the gas crossing the bed and (ii) the bed expansion, as a function of gas velocity (Kunii and Levenspiel, 1991).

Multi-walled carbon nanotubes Graphistrength® from Arkema (called CNT in the following), were used without any purification treatment. Their average external diameter is close to 12 nm and some iron catalyst nanoparticles are present, as can be seen in Fig. 2. They are agglomerated under the form of roughly spherical balls as shown in Fig. 2a. The Sauter diameter of these CNT balls is of 340 μm and their skeletal density is equal to 1980 kg/m³. Their specific surface area is close to 230 m²/g, as measured by BET method. Their Hausner ratio is equal to 1.1, indicating a low cohesivity.

For the hydrodynamic study, 35 g of CNT were used leading to a fixed bed height of 24 cm. Each FBCVD experiment was performed with 100 g of CNT, which corresponds to a fixed bed height of 18.4 cm. As previously studied by Cadoret et al. (2010), the inlet molar fraction of silane and the bed temperature were chosen in order to work in conditions of high chemical limitation, i.e., in conditions for which the heterogeneous reaction rate is low in comparison with the gaseous species transport, in order to exalt gaseous species diffusion through the porosity of the CNT balls. Our aim was clearly to obtain uniform deposits on the entire CNT surface, from the periphery to the center of the CNT balls. For all experiments, we chose to keep constant the reactor temperature at 500 °C, the fluidization ratio U_P/U_mg at 4 and the inlet SiH₄ concentration at 7.5 vol.%. The mass of deposited silicon was then controlled by run duration. We selected them in order to cover the 30–60 wt.% range of silicon deposited, according to literature results on CNT/Si anode materials (Si et al., 2010).

The CNT balls before and after CVD were analyzed as follows:

- the mass of Si deposited was measured by bed weighing and by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) chemical analysis, on a Thermo-Fisher iCAP6300,
- the powder morphology was observed by (i) Scanning Electron Microscopy (SEM) on a Hitachi TM3000 on which energy dispersive X-ray spectroscopy (EDS) was also performed, (ii) Field Effect Gun SEM (FEG-SEM) using a Jeol 6700S, and (iii) Transmission Electron Microscopy (TEM) on a Philips CM30, LaB₆ gun, operated at 150 kV to minimize damaging irradiation effects,
- 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 BET surface area was measured by a physisorption analyzer Micromeritics ASAP2010, after 2 h of degassing at 200 °C;
- the skeleton density of balls was measured by helium pycnometry on a Micromeritics Accupyc1330,
- tapped and untapped densities were determined on a powder tester FT-E Hosokawa Micron, with a 100 cm³ cylindrical vial tapped 50 times by minute during 4 min. Each measurement corresponds to an average value calculated over 3 runs.

3. Results and discussion

3.1. Hydrodynamic study of the fluidization of CNT and of CNT-Si composites

In a first step, the ability of the untreated CNT to fluidize was studied in the glass column using N₂ as fluidization gas. The bed expansion and the bed pressure drop were measured at decreasing gas velocity, because of the possible existence of a pressure over shoot at increasing gas velocity due to particle side wall friction and particle cohesion forces which can affect the transition between fixed bed and fluidized bed (Weber and Hrenya, 2007).

The results are reported in Fig. 3. \( \Delta P^* \) is the normalized pressure drop corresponding to the measured bed pressure drop divided by the theoretical one (i.e. the weight of particles per unit surface area of column) and \( H^* \) is the dimensionless expansion, corresponding to the ratio between the expanded bed height and the fixed bed height.

The pressure drop curve clearly shows that the fluidization of CNT was achieved. Indeed, the fluidization plateau at \( \Delta P^* = 1 \) can be drawn easily and the minimum fluidization velocity \( U_{mf} \) was determined as equal to 1.2 cm/s, at the intersection between the plateau and the fixed bed zone, according to the method of Davidson and Harrison (1963).

The expansion curve indicates a linear increase of the expanded bed height with gas velocity, reaching high values (>1.3) for gas velocities higher than 6 \( U_{mf} \). The bed was found to expand even for \( U_g < U_{mf} \). This behavior has already been observed by previous authors (Wang et al., 2007; Zhu et al., 2005), and is believed to be a distinct feature of nanoparticle agglomerates fluidization. Visually, the fluidization occurred homogeneously, i.e. without gas bubbles, for fluidization ratios \( U_g/U_{mf} \) lower than 8. So, as found by Yu et al. (2006), these results indicate that the fluidization of these CNT balls present characteristics of Geldart’s group A powders. From \( U_g/U_{mf} \) equal to 8 and beyond, slugging occurred with higher fluctuations of the bed height, certainly due to wall effects induced by the relatively low column diameter (Kunii and Levenspiel, 1991).

It is worth noting that the determination of \( U_{mf} \) was also attempted from measurements of the standard deviations of bed height fluctuations vs. decreasing gas velocities, but no result was obtained because of low values of height fluctuations due to the absence of bubbles.

Fig. 2 – (a) SEM view, (b) FEG-SEM view and (c) TEM view of Graphistrength® CNT balls.

Fig. 3 – Normalized (a) pressure drop diagram and (b) expansion of the CNT bed vs. gas velocity.
In a second step, the ability to fluidize of the CNT-Si composite balls was also studied in the glass column, after each CVD experiment. The pressure drop curves (not shown) indicate that all the CNT-Si composite balls were fully fluidized with a clear horizontal plateau at $\Delta P^* = 1$. The minimum fluidization velocities $U_{mf}$ of the composites S30–S60 are given in Table 1 below. A progressive increase of $U_{mf}$ was observed from run S40, which can be explained by an increase of the mean diameter and density of the balls due to silicon deposition, as detailed in the next section. A bed expansion at gas velocities lower than $U_{mf}$ was still observed, indicating that the CNT-Si balls also behave as nanoparticle agglomerates. Only for the S60 composite, the presence of bubbles was observed for fluidization ratios higher than 2, leading to higher fluctuations of the expanded bed height. Such behavior is characteristic of Geldart’s group B particles.

It is worth noting that the morphology and mean diameter of the balls was unchanged after their fluidization suggesting that they are not subject to attrition, probably thanks to their entangled structure (Fig. 2b) and to the high mechanical resistance of CNT.

The hydrodynamic behavior of these CNT and CNT-Si balls in a fluidized bed column is then convenient, even with silicon deposited up to 50 wt.%. Therefore, thermal and mass transfers during silicon FBCVD experiments should be high enough to ensure reproducible and uniform deposits.

### Table 1 – Main characteristics of CNT-Si balls.

<table>
<thead>
<tr>
<th></th>
<th>Si wt.% from</th>
<th>Si wt.% from</th>
<th>Final $U_{mf}$</th>
<th>Final fluidization ratio $U/U_{mf}$</th>
<th>Untapped density (kg/m$^3$)</th>
<th>Tapped density (kg/m$^3$)</th>
<th>Hausner ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
<td>4</td>
<td>90</td>
<td>100</td>
<td>1.1</td>
</tr>
<tr>
<td>S30</td>
<td>29</td>
<td>27</td>
<td>1.2</td>
<td>4</td>
<td>154</td>
<td>163</td>
<td>1.1</td>
</tr>
<tr>
<td>S40</td>
<td>38</td>
<td>36</td>
<td>1.3</td>
<td>3.7</td>
<td>185</td>
<td>194</td>
<td>1.0</td>
</tr>
<tr>
<td>S50</td>
<td>47</td>
<td>42</td>
<td>1.5</td>
<td>3.2</td>
<td>217</td>
<td>224</td>
<td>1.0</td>
</tr>
<tr>
<td>S60</td>
<td>57</td>
<td>55</td>
<td>1.8</td>
<td>2.7</td>
<td>274</td>
<td>284</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.2. Fluidized Bed CVD of silicon on CNT

The temporal evolution of bed temperatures and bed pressure drop during FBCVD experiments was similar for each run. A characteristic example, corresponding to run S60 of Table 1 below, is shown in Fig. 4.

Thanks to PID regulators, the bed temperatures were maintained close to 500 °C during the coating step. Before silane injection, the bed of CNT was isothermal (differences between T1 and T2 lower than 2 °C), proving that fluidization was achieved. During CVD, a thermal gradient (max. value of 10 °C) appeared into the bed proportional to run duration. This behavior is probably due to a progressive increase of the minimum fluidization velocity $U_{mf}$ of the CNT-Si balls, as previously detailed. Since we worked at constant inlet gas flow rate, this led to a progressive decrease of the fluidization ratios $U/U_{mf}$ as calculated in Table 1, and then probably to a less isothermal bed. The T3 temperature corresponds to a thermocouple located above the bed. It increased during deposition because the furnace had to provide more energy to the reactor due to the lower fluidization quality and to the bed weight increase. Fig. 4 also shows that the bed pressure drop (normalized with the initial bed weight) increased proportionally to the weight of deposited silicon, confirming that the bed was fully fluidized all along run duration. As a consequence, the weight of deposited silicon was deduced from the bed pressure drop measurements. A mean error of 5% was found between these values and those deduced from bed weighing.

As detailed in Table 1, they are themselves very close to the values obtained by ICP-AES analysis. The tapped and untapped densities logically increase with the percentage of deposited silicon. The Hausner ratio of the CNT-Si balls remains close to 1 for all samples, confirming their low cohesion and then their ability to fluidize.

Fig. 5 indicates that the Sauter diameter of the CNT-Si balls remains unchanged for 30 and 40 wt.% of Si, and tends to increase for higher values, probably because of an inflation of their flexible structure induced by the deposition. The flexible nature of the CNT-Si balls is a positive point for the Li-ion battery application, since the lithium insertion/extraction cycles can lead to mechanical failures of the electrodes (Obrovac and Christensen, 2004; Wu et al., 2012). The BET specific surface area linearly decreases when increasing the deposited Si.

![Fig. 4 – Temporal evolution of the reactor temperatures and normalized bed pressure drop for run S60 (T1: 6 cm above the distributor, T2: 22 cm, T3: 35 cm).](image1)

![Fig. 5 – Evolution of the Sauter diameter, BET surface area and skeleton density of CNT-Si balls with the weight percentage of deposited silicon.](image2)
weight, certainly due to a filling of the porous volume by the silicon deposit. For the application, a compromise will then have to be found between the weight of deposited silicon and the accessibility of silicon to the Li⁺ ions (Wu et al., 2012). The skeleton density increases proportionally with the percentage of deposited silicon. These values are in good agreement with theoretical ones calculated from the CNT and silicon individual skeleton densities for each Si percentage, confirming the validity of these latter.

Fig. 6a presents a FEG-SEM view of CNT-Si composites after run S60, these morphologies are typical of the whole samples obtained. The network of nanotubes appears but the CNT surface exhibits a rough aspect. This is due to silicon nanoparticles (NPs) homogeneously distributed on the surface of CNT. The presence of Si NPs is confirmed by the TEM view of Fig. 6b. Si NPs present a flattened spherical form, with a sharp size distribution around 30 nm. The NP diameter tends to increase with the Si percentage deposited. In order to evaluate the distribution of silicon into the balls, EDS mappings of silicon (Fig. 6c) were performed on polished cross sections of CNT-Si balls embedded in epoxy resin, as shown in Fig. 6d. Some parts of the balls are empty of CNT and then could not emit energy from the X-ray bombardment. On the Si map, this was confirmed by a white zone, without deposited Si. The main result is that a uniform silicon deposition was observed from the periphery to the center of the balls, meaning that the coating occurred on the whole surface developed by the CNT. This observation was repeated on numerous CNT-Si balls for all the Si percentages studied. This result proves that as wished for the operating conditions tested, the deposition reaction is the limiting step of the process, not the gas diffusion into the pores of the CNT balls.

4. Conclusion

Multi-walled carbon nanotubes (CNT) Graphistrength®, assembled in balls of several hundreds of microns, were decorated by Fluidized Bed Chemical Vapor Deposition (FB-CVD), without any purification treatment. Silicon was deposited within CNT balls from silane SiH₄ thermal decomposition. A hydrodynamic study showed a homogeneous fluidization of the untreated CNT bed with a high bed expansion, characteristic of Geldart’s group A powders. After CVD, the ability to fluidize of the CNT-Si balls was also demonstrated, with an increase of the minimum fluidization velocity due to Si deposition. For CVD experiments, various run durations were tested, leading to silicon contents in the 30–60 wt.% range. The inlet molar fraction of silane and the bed temperature were kept constant for all runs. They were chosen in order to work in conditions of high chemical limitation to favor silicon deposition on all CNT surface. During the runs involving deposited silicon weight percentages lower than 40%, the fluidized bed was isothermal, whereas a small thermal gradient appeared at higher Si percentages, due to a decrease of the fluidization ratio. Numerous EDS mapping images of cross-sectioned CNT-Si balls proved that the entire surface of CNT was uniformly coated by silicon nanoparticles from the periphery to the center of the balls. The Sauter diameter, tapped, untapped and skeleton densities of CNT-Si balls increase with the deposited silicon content, whereas their specific surface area decreases. Further works are in progress about (i) CNT pre-treatments, aiming to preserve the specific surface area of the CNT-Si balls even at high silicon percentages and (ii) electrochemical tests of this nano-structured composite material as anodes of Li-ion batteries.
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