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## Solid-State Electrochemistry of the Li Single Wall Carbon Nanotube System

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Reversible insertion of lithium into purified single wall carbon nanotubes was achieved electrochemically. Nanotubes exhibited reversible capacities on the order of 460 mAh/g, corresponding to a stoichiometry of  $Li_{1.23}C_6$ . The material also presented very high irreversible capacities (1200 mAh/g) which we ascribe to the large specific surface area (350 m<sup>2</sup>/g). Galvanostatic charge-discharge and cyclic voltammetry indicated that there is no well-defined redox potential for lithium insertion or removal in the nanotube lattice, ruling out the hypothesis of a staging mechanism via well-defined interstitial sites. *In situ* X-ray diffraction revealed an irreversible loss of crystallinity, suggesting that doping disrupts the intertube binding, analogous to exfoliation in layer hosts. *In situ* resistance measurements showed a 20-fold decrease upon doping, consistent with charge transfer between lithium and carbon. Electrochemical impedance spectra were interpreted in terms of a Randles-type equivalent circuit. The data showed a continuous decrease in charge transfer resistance upon doping, consistent with the decrease in electronic resistivity of the electrode. It also showed that the high lithium capacities are not due to double layer capacitance effects, but to an actual ion insertion/extraction process in the bulk material.

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Electrochemistry has proven to be very useful for the study of guest-host systems, particularly, carbon intercalation compounds. Not only does electrochemistry provide essential information about the thermodynamics and kinetics of these systems, but it also offers accurate control of guest stoichiometry which is difficult to achieve by other doping methods. Therefore, electrochemical doping has been used extensively to study the properties of carbon guest-host systems. *In situ* X-ray diffraction and electrochemical doping were used to study the phase diagram of  $\text{Li}_x C_6$  graphite,<sup>1</sup> phase transitions in Li-doped polyacetylene<sup>2</sup> and the structure of Li-doped solid  $C_{60}$ . <sup>3</sup> *In situ* resistivity measurements were used to study the electronic transport properties of K- and Na-doped polyacetylene.<sup>4,5</sup> In this work, electrochemistry was used to study a new carbon guest-host system: Li/carbon nanotubes.

Two types of carbon nanotubes can be distinguished according to their structural properties: multiwall (MWNT) and single wall (SWNT).<sup>6</sup> MWNT consist of graphitic sheets rolled into closed concentric cylinders, with a structure similar to that of Russian dolls. The concentric tubes are separated by Van der Waals gaps of  $\sim$ 3.4 Å, a typical interlayer spacing in turbostratically disordered graphite. External diameters can be as large as 50 nm, and lengths are of micrometer scale. SWNT can be envisioned as a single graphene sheet rolled into a cylinder, with diameters in the range 1-2 nm and lengths of several micrometer. SWNT of nearly uniform diameters self-organize into long crystalline "ropes" in which parallel nanotubes are bound by Van der Waals forces.<sup>7</sup> The diameter of a rope is typically 10-50 nm corresponding to 30-600 tubes per rope. Ropes containing as few as 2-3 tubes or as many as several thousand are occasionally found.

Figure 1 presents a high resolution transmission electron microscope (HRTEM) image of purified and annealed SWNT, in which several entangled ropes with different diameters can be observed. The parallel fringes within each rope are due to the constructive scattering from the parallel planes of SWNT. The fact that the fringe spacings differ among ropes does not arise from a wide distribution in nanotube diameters, but rather from the different orientation of each rope zone axis with respect to the electron beam. Figure 2 shows an X-ray profile from purified and annealed SWNT. The welldefined reflections at 6.3, 10.5, 16.5, and  $22^{\circ}$  can be indexed on a 2-D triangular lattice<sup>7</sup> represented in the inset of Fig. 2. For a tube diam of 13.6 Å, the Van der Waals spacing between adjacent tubes is 3.2 Å, such that the lattice parameter is 16.8 Å. The Van der Waals spacings and triangular symmetry create large interstitial channels between the tubes, with a diam around 6 Å. Both MWNT and SWNT often contain impurities and defects which vary with synthesis conditions. Impurities generally consist of catalyst particles, graphite, and disordered carbons, most of which can be removed by purification. Defects such as dangling bonds, sidewall holes, and open ends can generally be healed by high temperature annealing.



Figure 1. HRTEM image of purified and annealed SWNT. Several entangled ropes with different diameters can be observed. The parallel fringes within each rope arise from constructive scattering from the parallel planes of SWNT. Scale bar: 20 nm.

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**Figure 2.** X-ray profile for purified and annealed SWNT. Reflections can be indexed in terms of a 2-D triangular lattice represented in the inset (intensity maxima do not correspond exactly to Bragg positions due to the unusual behavior of the X-ray form factor.<sup>7</sup>) The interstitial channels between individual tubes are 6 Å in diam.

MWNT and SWNT can be doped with alkali metals<sup>8,9</sup> and therefore, can be considered as guest-host systems. In the case of MWNT, dopants are believed to intercalate into the intertube spacings through defects, which destroy the structural integrity of the nanotubes.<sup>8</sup> In the case of SWNT, little is known about the exact location of the dopants. For an isolated SWNT, possible binding sites are limited to the external surface of the tube through physi- or chemisorption, and to the interior of the tube if its ends are open. However, unless etched in concentrated acid, the ends of SWNT are rarely open, which limits the possibilities for dopants to diffuse inside the tube. In a SWNT rope, the 6 Å diam channels between tubes provide additional intercalation sites analogous to the interlayer galleries in graphite or to the tetrahedral and octahedral vacancies in face-centered cubic (fcc) C<sub>60</sub>. These channels are large enough to accommodate the insertion of Li or K without any lattice dilation, and therefore are considered as the most likely intercalation sites for dopants in SWNT ropes.

The insertion of Li into carbon nanotubes has recently attracted much attention, due to their potential application as anodes in Li-ion batteries. Previous experiments described very high Li concentrations in MWNT reacted in molten Li at high pressure.<sup>10</sup> More recently, two groups investigated the properties of MWNT upon elec-trochemical doping with Li. <sup>11,12</sup> They reported Li reversible capacities in the range of 80-640 mAh/g (corresponding to stoichiometries of Li<sub>0.2</sub>C<sub>6</sub> and Li<sub>1.7</sub>C<sub>6</sub>, respectively), depending on the synthesis conditions. Both groups showed that the Li capacity increases with structural disorder, suggesting that Li insertion in MWNT is correlated with defects. We decided to focus our attention on SWNT because the channels in the rope structure allow for insertion without defects. We recently showed that Li can be reversibly inserted electrochemically in SWNT samples comprised initially of mostly ropes.<sup>13,14</sup> Similar materials were reversibly doped with Li to compositions of LiC<sub>6</sub> by chemical redox reactions with solutions of radical anions.<sup>15</sup> Subsequent studies showed that the reversible electrochemical capacity of SWNT can be increased from 600 mAh/g (Li<sub>1.6</sub>C<sub>6</sub>) to 1000 mAh/g Li<sub>2.7</sub>C<sub>6</sub> after introducing defects by ballmilling.<sup>16</sup> The focus of this paper is the behavior of purified, highly crystalline SWNT bulk material upon electrochemical cycling with Li. We chose to use purified and annealed SWNT in order to avoid the possible reaction of Li with impurities or defects. Here we present the electrochemical performance of this new guest-host system, and describe the effect of doping on structural and electronic transport properties using in situ methods.

#### Experimental

SWNT synthesis and purification.—SWNT were synthesized using the dual pulsed laser vaporization developed by the Smalley group and described in detail elsewhere.<sup>7</sup> This method consists of the double laser ablation of a graphite rod containing 0.6 atom % each of Ni and Co as catalysts. Impurities such as catalyst particles, disordered carbon, graphite, and C<sub>60</sub> were removed using a recently developed purification treatment<sup>17</sup> involving a reflux in HNO<sub>3</sub>, several filtrations, and a vacuum anneal at 1200°C. HRTEM indicated that although the acid treatment creates defects in the molecular structure, most of these are healed during the 1200°C anneal.<sup>18</sup> The heat-treatment is, therefore, an essential step of the purification process that minimizes the density of defects and increases the crystallinity of the ropes.<sup>17</sup> The samples used in this work were in the form of self-supporting foils called buckypaper.<sup>17</sup>

Electrochemical measurements.—The electrochemical insertion of Li into SWNT was investigated by galvanostatic charge-discharge and cyclic voltammetry experiments on Li/SWNT half-cells. Airtight screw-in electrochemical cells were assembled inside an Ar filled glove box. Li metal (Aldrich) was used as the counter and reference electrode. The working electrode consisted of a thin disk of buckypaper with a mass on the order of 1 mg, previously dried at 150°C under vacuum for 2 h. Because buckypaper is mechanically self-supporting and electrically conductive, no binder or carbon black was added. A microporous polypropylene separator was placed between the two electrodes to prevent electrical shorting, while allowing ionic conduction. The electrolyte used was mainly the industry standard, battery grade 1 M LiPF<sub>6</sub> in a 1:1 volume ratio of dimethyl carbonate (DMC) and ethylene carbonate (EC) (Merck Selectipur). Its moisture content was found to be 3 ppm using Karl Fisher titration. A few experiments were carried out with LiPF<sub>6</sub> in tetrahydrofuran (THF) for comparison. Galvanostatic experiments were conducted between 3 and 0.010 V using a Macpile multichannel galvanostat/ potentiostat. Cyclic voltammetry (CV) was performed between 3 and 0 V at a 0.1 mV/s rate using an EG&G PAR 273A potentiostat/galvanostat.

*X-ray diffraction.*—X-ray diffraction was performed using an Inel powder diffractometer equipped with a sealed Cu tube operating at 1 kW, a flat HOPG monochromator, and a curved "linear" detector covering  $120^{\circ}$  in  $2\theta$  with a 4096 channel multichannel analyzer. Samples consisted of 1 cm diameter disks of buckypaper, and were mounted freestanding and at grazing angle. For *in situ* experiments,



**Figure 3.** Electrochemical cell used for *in situ* X-ray diffraction. The cell is shown in the configuration for galvanostatic charge/discharge. For X-ray measurements the magnetic piston is raised such that the electrolyte falls into the reservoir and the sample is exposed to X-rays through the Be cylinder.

an electrochemical cell was specially designed. Figure 3 presents the main features of the cell: a beryllium window allowing the transmission of X-rays at the sample position, a magnet operated reservoir allowing removal of the electrolyte from the X-ray path during spectrum acquisition, and airtight electrical feedthroughs made of stainless steel Swagelok fittings with pierced Teflon plugs. SWNT were doped under galvanostatic charge (20 mA/g) for a finite time, after which the circuit was opened and the system relaxed for 30 min. The electrolyte was then transferred into the reservoir by raising the magnetic piston, and an X-ray spectrum was accumulated for 1 h. After completion of the acquisition, the electrolyte was transferred back into the cell, and the galvanostatic charge was continued. This process was repeated many times during the doping and undoping cycles, in order to study the progressive structural changes of SWNT upon cycling with Li.

In situ resistivity.-In situ resistivity measurements were made in a specially designed cell in which a SWNT sample was held against four Cu wires, i.e., two voltage leads and two current leads. The assembly was placed between two ceramic plates screwed together to insure good pressure contacts. A Ni mesh welded to a Ni wire and coated with metallic Li was used as the counter and reference electrode. The cell was then filled with electrolyte. The cell assembly as well as the in situ resistivity measurements were conducted inside an Ar filled glove box. The two current leads were connected to an ac constant current source, while the two voltage leads were connected to a lock-in amplifier. The galvanostat was placed between the Li counter electrode and one of the current leads. The use of ac for resistance and dc for electrochemical control eliminated cross talk between the two independent circuits. The sample was cycled under galvanostatic charge-discharge (20 mA/g), and the resistivity was measured continuously as a function of the doping level.

Electrochemical impedance spectroscopy (EIS).—EIS was carried out on a three-electrode cell containing Li metal as the reference and counter electrodes, and purified SWNT as the working electrode. The SWNT sample consisted of a  $4 \times 5$  mm strip of buckypaper 60  $\mu$ m thick, of mass 0.43 mg. The cell was pretreated with 10 galvanostatic cycles between 3 and 0.15 V in order to stabilize the solid electolyte interphase (SEI). Measurements were performed inside an Ar filled glove box using an EG&G PAR 273A potentiostat coupled with a Solartron 1250 frequency response analyzer. SWNT were doped in potentiostatic mode using 100 mV increments. At each potential step, the cell was equilibrated for several hours, after which the complex impedance was measured using frequencies between 65 kHz and 10 mHz, with 5 mV modulation.

#### **Results and Discussion**

*Electrochemical testing.*—Figure 4 presents the results of galvanostatic charge-discharge on purified SWNT. During the first reduction, a very large capacity of 1660 mAh/g was observed, while a reversible capacity of 460 mAh/g was obtained from the first oxidation. The large irreversible capacity (1200 mAh/g) is attributed to electrolyte reduction and formation of a SEI on the carbon surface, as evidenced by the long plateau at 0.9 V in the first discharge. Since SEI formation in carbon anodes has been correlated with surface area<sup>19</sup> we believe the same factor is responsible for large irreversible capacity of SWNT. For our material the Brunauer-Emmett-Teller (BET) specific surface area was measured as 350 m<sup>2</sup>/g, much larger than that of graphite. Irreversible capacity also increased slightly through subsequent cycles, as indicated by the poor overlap of the charge-discharge curves in Fig. 4.

The reversible capacity upon first oxidation (460 mAh/g) is 23% larger than the theoretical value for graphite (372 mAh/g) and corresponds to a stoichiometry of  $Li_{1.23}C_6$ . The origin of this large capacity is not known. Assuming that Li ions decorate every second neighbor hexagon on the external surface of the rolled graphene sheet, the limiting stoichiometry would be the same as in graphite, *i.e.*, LiC<sub>6</sub>. The Li uptake could in principle be twice that of graphite if the internal surfaces were accessible. However, because our SWNT have



Figure 4. Galvanostatic charge/discharge (20 mA/g) for a SWNT/Li cell. The first 3 cycles are represented.

been heat-treated at 1200°C, we believe that most ends are closed, and that Li cannot diffuse inside the tubes.

The large Li density of SWNT could be interesting for Li-ion battery applications. Furthermore, the reversible capacity decreased only slightly when the electrochemical cell was cycled at much higher rates. At current densities of 186 mA/g (C/2 in battery terminology), the reversible capacity reached 405 mAh/g, while that of graphite was reported to be as low as 70 mAh/g for 44 µm particles.<sup>20</sup> The highrate capacity of SWNT is therefore much better than that of graphite. This can be partly explained by the large difference in particle size between the two materials. In graphite, the particle size is on the order of 1-50 µm, while the diameter of a SWNT rope is typically 10-50 nm. If we assume that the high rate performance is limited by bulk Li diffusion, it is reasonable that materials with the smallest particle size should perform best. Finally, we observed a continuous decrease in reversible capacity upon cycling. SWNT generally lost 15% of their initial reversible capacity after five cycles, independent of the cycling rate. Better cycling behavior should be obtained in coin cells, as opposed to the flooded cells used in the present study.

The voltage profiles in Fig. 4 are very different from those of Li intercalation into graphite. No voltage plateau was observed in the charge-discharge curves, indicating the absence of a staging mechanism via well-defined interstitial sites traditionally observed for alkali metal doping of graphite or polyacetylene.<sup>1,2,5</sup> There is no well-defined intercalation or deintercalation potential for Li into SWNT ropes; rather, insertion and removal proceed over a wide range of potentials, leading to steep voltage profiles similar to those of electrochemical capacitors. A large hysteresis was observed between charge and discharge; most of the Li was inserted below 0.25 V, while it was removed almost uniformly between 0 and 3 V. Such a large hysteresis was previously reported for ballmilled graphite,<sup>19</sup> balledmilled sugars,<sup>21</sup> and soft carbons containing substantial hydrogen.<sup>22</sup> It is generally attributed to bonding changes in the host, or activated processes such as the formation of Li-C-H<sup>22,23</sup> or C-O-Li <sup>24</sup> species. Since our purified material has been annealed at 1200°C, the density of dangling bonds and functional groups (C-H, C-OOH, or C-OH) must be very low. In situ annealing and TEM observations have confirmed that most defects in acid-treated SWNT heal when heated above 900°C.<sup>25</sup> Therefore, we believe that the large voltage hysteresis and the large reversible capacities cannot be attributed to functional groups in the material. The origin of this hysteresis in SWNT is not understood.

The CV results for the third cycle on a SWNT/Li half-cell are presented in Fig. 5. Integration of the curves gave Li capacities consistent with the galvanostatic results. The absence of well-defined redox peaks confirms that there is no well-defined potential for Li insertion or removal, consistent with the galvanostatic data. These



Figure 5. Cyclic voltammogram (0.1 mV/s) for a SWNT/Li cell. Third cycle is represented.

results rule out the possibility of staging and suggest that the Li insertion mechanism is very different from that in graphite, polyacetylene, and solid  $C_{60}$ , all of which exhibit well-defined reduction and oxidation waves in the CV. <sup>24,26,27</sup> The fact that no significant peak was observed at the well-known redox potentials for Li intercalation in graphite suggests that graphitic impurities contribute negligibly to the total capacity of the SWNT samples.

In situ X-ray diffraction.—Figure 6 presents the in situ X-ray data obtained as a function of (a) doping and (b) dedoping. The results are separated in two intervals, *i.e.*, 3 to 14° and 24 to 33° (see below). An X-ray pattern before mounting in the electrochemical cell is included at the bottom of Fig. 6a for reference. In this spectrum the usual reflections of the SWNT 2-D triangular lattice appear, as well as a sharp peak at 26.4° corresponding to the (002) reflection of graphitic impurities. Since the structural changes of graphite upon doping with Li are well known, these impurities serve as an internal standard to confirm the proper functioning of the cell. Upon doping between 2.74 and 0.94 V, we observed a gradual loss of the SWNT first order peak at 6.3° and second order peak at 10.5°, both of which eventually disappeared. The third and fourth order peaks could not be observed due to a broad diffuse peak centered at 22° which we attribute to permanent wetting of the porous sample by the organic solvents. At a potential of 0.010 V, we observed a partial shift of the graphite (002) reflection to a value of 25.5° corresponding to the (001) of LiC<sub>6</sub>. This shows that some graphitic impurities were intercalated. The fact that part of the graphite peak remained unchanged while part was shifted can be explained by the presence of different types of layered impurities in the sample, some which can be doped with Li (such as graphite or disordered carbons), and some which cannot be doped (such as onions or other nested fullerenes). Upon dedoping to 0.57 V (Fig. 6b), the graphite peak recovered its original position, indicating the deintercalation of the graphitic impurities and thereby confirming the proper functioning of the cell.

Conversely, no recovery of the SWNT peaks was observed upon dedoping to 3 V, suggesting an irreversible loss of the triangular lattice. A 1 h vacuum anneal at 1200°C was sufficient to restore crystallinity (as indicated by X-ray diffraction, not shown), suggesting that the tubes were not destroyed, but only the rope crystallinity was



Figure 6. In situ X-ray data on SWNT as a function of electrochemical (a) doping and (b) undoping. Included at the bottom of a is a reference profile of a dry sample outside the cell.

disrupted. HRTEM observations indicated that nanotubes did not disassemble from the ropes but rather, their packing within the ropes became disorganized. A similar phenomenon was previously reported during intercalation of K, Cs, <sup>28</sup> and HNO<sub>3</sub> <sup>29</sup> in SWNT. This suggests that the dopants invade the channels between tubes and disrupt the intertube binding, analogous to exfoliation in layered hosts. The driving force for this structural disorganization remains unclear, considering that the channels between nanotubes are large enough to accommodate Li ions.

In situ resistance.—Figure 7 presents the in situ resistance of SWNT during five galvanostatic cycles in 1 M LiPF<sub>6</sub> EC:DMC. Part (a) represents the cell potential as a function of capacity, while part (b) represents the sample resistance as a function of capacity. Resistance values were normalized to that of the pristine sample. During the first reduction, we observed a 7-fold drop in resistance over a charge capacity of 50 mAh/g (or a stoichiometry of Li<sub>0.13</sub>C<sub>6</sub>), corresponding to a decrease in cell potential from 3 to 0.9 V. At 0.9 V, the SEI started forming, giving rise to a long reduction plateau between 50 and 700 mAh/g in the first charge of Fig. 7a. The growth of the SEI led to a steady increase of the sample resistance over the same range of capacities in Fig. 7b. This can be explained by the electrically insulating nature of the SEI, increasing the interrope contact resistance as it grows on the carbon surface. After the SEI was completly formed, the resistance decreased steadily upon further doping



**Figure 7.** *In situ* four-point resistance of SWNT during 5 galvanostatic cycles (20 mA/g) in EC:DMC 1 M LIPF<sub>6</sub>. Plot (a, top) represents the variation in cell potential, while plot (b, bottom) represents the changes in sample resistance.

between 0.7 and 0 V. Upon dedoping, the resistance increased continuously as we removed Li between 0 and 3 V on a discharge interval of 1480 to 1080 mAh/g. The resistance of the dedoped sample at 3 V was higher than that of the pristine sample because of the SEI which remained on the sample. During further cycling, no SEI effect was observed, such that the resistance reversibly decreased and increased upon doping and dedoping, respectively. The maximum change in resistance between the fully doped and dedoped state was a factor of 20 during the first discharge and the second charge. This factor decreased with cycling, as observed in Fig. 7b. The origin of this trend is not known. We suspect it might be related to the loss of reversible capacity with cycling. The decrease in reversible capacity and sample resistance at 3 V could mean that some additional Li remains inserted irreversibly after each cycle.

Another noticeable feature is that most of the resistance drop upon each charge took place at fairly dilute doping levels ( $\text{Li}_{0.1}\text{C}_6$ *i.e.*, less than 40 mAh/g) between 3 and 0.25 V. Upon discharge, the resistance increased more gradually over the whole capacity range, as seen in Fig. 7b. A hysteresis was, therefore, observed in the resistance between doping and undoping, similar to the voltage hysteresis in the electrochemical data. No hysteresis was observed if the resistance is plotted as a function of electrochemical potential, as illustrated in Fig. 8. The origin of the hysteresis in the charge-discharge and resistance data of Fig. 7 remains unknown.

In order to avoid the effects of surface passivation, we repeated the experiment using an electrolyte which is known to not create an SEI, namely, 1 M LiPF<sub>6</sub> in THF. <sup>30</sup> The *in situ* resistance of SWNT during one galvanostatic cycle is presented in Fig. 9. Part (a) represents the electrochemical potential as a function of capacity, while part (b) shows the sample resistance as a function of capacity. No SEI formation was observed in the first charge of Fig. 9a, such that the resistance continuously decreased during the first reduction in Fig. 9b. We attribute the large irreversible capacity in the first charge/ discharge of Fig. 9a to side reactions in the electrolyte due to the instability of the LiPF<sub>6</sub> salt in THF, <sup>31</sup> which corrupts the coulommetry. This phenomenon is however different from SEI formation since there is no well-defined reduction plateau in the first charge of Fig. 9a, and correspondingly no increase in resistance in Fig. 9b. These results confirm that the increase in resistance observed between 50 and 700 mAh/g in Fig. 7b is due to SEI formation. Conversely, using THF the resistance in Fig. 9b increased continuously as we removed Li between 0 and 3 V. The change in resistance between the fully doped and dedoped state was again a factor of 20. A hysteresis between doping and dedoping was seen, although less pronounced than that observed with the EC:DMC electrolyte.



Figure 8. In situ resistance of SWNT in EC:DMC LIPF<sub>6</sub>, plotted as a function of cell potential, for doping (solid line) and undoping (dashed line).



**Figure 9.** *In situ* four-point resistance of SWNT during 1 galvanostatic cycle (20 mA/g) in THF LIPF<sub>6</sub>. Plot (a, top) the variation in cell potential, plot (b, bottom) the changes in sample resistance.

The changes in resistance observed upon Li insertion and removal can be explained by charge transfer between Li and C, analogous to that in graphite intercalation compounds. Charge transfer was previously reported in SWNT doped with various electron donors and acceptors,<sup>32</sup> explaining the variations in conductivity upon doping. *In situ* Raman measurements during electrochemical doping in LiAsF<sub>6</sub> EC:DMC identified a charge transfer at potentials above that of SEI formation, after which the signal was attenuated and lost.<sup>33</sup> More data is needed to quantify the charge transfer between Li and C and its reversibility upon cycling.

*Electrochemical impedance spectroscopy.*—The EIS results for SWNT at various potentials are shown in Fig. 10a and b using the Nyquist representation. Part a presents the data for the full frequency range (65 kHz to 10 mHz), and part b emphasizes the high frequency portion. Each spectrum consists of a high frequency semicircle and a low frequency tail, and can be modeled by a Randles-type equivalent circuit represented in Fig. 11.  $R_S$  is the resistance of the electrolyte,  $C_{dl}$  and  $R_{ct}$  are the double layer capacitance and charge transfer resistance at the electrode/electrolyte interface, and  $Z_w$  is the Warburg impedance related to the diffusion of ions in the bulk electrode. In the ac response of a Randles circuit, the high frequency semicircle is attributed to charge transfer reactions, while the

low frequency tail is associated with diffusion processes.<sup>34</sup>  $R_{ct}$  can be directly determined from the diameter of the semicircle, while  $C_{dl}$ can be calculated at its maximum using the relation  $\omega(max) = 1/R_{ct}C_{dl}$ . Each of the high frequency semicircles in Fig. 10 appeared depressed below the real-axis, which is characteristic of porous samples.<sup>26</sup> The diameter of the semicircle varied with cell potential, suggesting a change in charge transfer resistance with doping. Figure 12 shows the plot of the value of  $R_{ct}$  for the SWNT electrode as a function of potential.  $R_{ct}$  decreased continuously upon doping (*i.e.*, with decreasing potential), similar to the electronic resistance measured directly *in situ* as shown in Fig. 8. The variations in  $R_{ct}$  closely mirrored those of the electronic resistance, suggesting a significant electronic contribution to the charge transfer resistance. The other contribution to  $R_{ct}$  is ionic in nature, and is due to the resistance to ion transfer across the electrolyte/electrode interface. The  $C_{dl}$  was found



**Figure 10.** Nyquist EIS spectra for SWNT at 2.9, 2, 1, and 0.1 V vs. Li. Part (a, top) presents the data on the full frequency range (65 kHz to 10 mHz); spectra are offseted horizontally for clarity. Part (b, bottom) emphasizes the high frequency response; spectra are superimposed for better comparison.



Figure 11. Randles equivalent circuit for an electrochemical system, in which  $R_s$  is the electrolyte resistance,  $R_{ct}$  is the charge transfer resistance,  $C_{dl}$  is the double layer capacitance, and  $Z_w$  is the Warburg impedance.

to be 4.3  $\mu$ F independent of potential. Assuming that a typical double layer capacitance for carbon electrodes in organic electrolytes is 10  $\mu$ F/cm<sup>2</sup> the measured double layer capacitance corresponds to a surface area of 0.43 cm<sup>2</sup>. This value is consistent with the macroscopic surface area of the sample (0.4 cm<sup>2</sup> but far smaller than the BET surface area of SWNT (350 m<sup>2</sup>/g, *i.e.*, 1505 cm<sup>2</sup> for a 0.43 mg sample). This suggests that at high frequencies, only the macroscopic surface of the bulk sample is accessed, and that porosity comes into play only at lower frequencies.

The low frequency portion of the EIS spectra presented two regimes: a 45° line at intermediate frequencies and a quasi-vertical line at very low frequencies. Both regimes have been explained for Randles-type circuits; the 45° line is generally associated with diffusion kinetics, and the vertical tail is attributed to finite length effects.<sup>34</sup> At very low frequencies, the SWNT electrode behaves like a capacitor in series with a resistor, respectively, called  $C_{\rm L}$  and  $R_{\rm L}$ .  $C_{\rm L}$  was calculated using the lowest frequency data and the formula  $\overline{C_{\rm L}} = 1/\omega Z$ , and was found to decrease continuously with doping, as evidenced by the low frequency tail shortening at lower potentials in Fig. 10b. Values for  $C_{\rm L}$  varied between 9 F/g at 3 V and 460 F/g at 0.1 V. Considering a BET surface area of 350 m<sup>2</sup>/g for SWNT and a double layer capacitance of 10 µF/g for carbons in organic electrolytes, the maximum double layer capacitance for SWNT is on the order 35 F/g, which is much smaller than the measured value of  $C_{\rm L}$ . This suggests that the large Li capacity of SWNT is not due to double layer charging on the surface of the ropes, but to an actual ion insertion/extraction process in the nanotube ropes.



**Figure 12.** Charge transfer resistance  $R_{ct}$  vs. electrochemical potential of the SWNT electrode. The variations in  $R_{ct}$  closely mirror those of the electronic resistance shown in Fig. 8.

Diffusion coefficients for the guest species in the carbon host can generally be extracted from the low frequency EIS data using the relationship  $D = L^2/(3R_LC_L)$  where D is the diffusion coefficient and L is the diffusion length. Calculating a diffusion coefficient requires estimating L, which requires knowledge about the diffusion mechanism. In this context, estimating L is very difficult since nothing is known about the diffusion mechanism for Li in SWNT. If one assumes that the porosity does not play any role for Li diffusion in SWNT, then L is the sample thickness, *i.e.*, 60  $\mu$ m. This leads to a diffusion coefficient  $D = 4.2 \times 10^{-6} \text{ cm}^2/\text{s}$  at 2.9 V. If, on the contrary, one assumes that the porosity takes active part in Li diffusion, L should be taken as the bundle size. One might then wonder if diffusion takes place parallel to the bundle (in which case L is on the order of 1 µm) or normal to it (in which case L is about 20 nm, *i.e.*, the bundle radius). These two possibilities lead, respectively, to a diffusion coefficient  $D = 1.2 \times 10^{-9} \text{ cm}^2/\text{s}$  for diffusion along the bundle or  $D = 4.8 \times 10^{-13}$  cm<sup>2</sup>/s for diffusion across it. As the diffusion coefficient varies by several orders of magnitude depending on the assumed diffusion length L, more knowledge about the diffusion mechanism is required to quote a useful diffusion coefficient.

#### Conclusion

Reversible insertion of Li into SWNT was achieved electrochemically. SWNT exhibited reversible Li capacity on the order of 460 mAh/g, which is 23% larger than the theoretical value for graphite (372 mAh/g). The mechanism for Li insertion is not fully understood. Cyclic voltammetry and galvanometry have ruled out the hypothesis of a staging mechanism. In situ X-ray diffraction showed that Li doping induces irreversible structural disorder inside the rope lattice. This suggests that Li ions intercalate in the channels between nanotubes and disrupt the intertube binding, in contrast to the wellordered doping superlattices observed in graphite, polyacetylene, and C<sub>60</sub> hosts. In situ resistivity measurements presented a 20-fold decrease upon doping, similar to what is observed in graphite compounds. This can be explained by charge transfer between Li and C, again analogous to graphite intercalation compounds. EIS spectra were interpreted in terms of a Randles-type equivalent circuit. The data exhibited a continuous decrease in charge transfer resistance  $R_{ct}$ upon doping, consistent with the decrease in electronic resistance of the electrode. The double layer capacitance was found to be much lower than that expected for such a high surface area carbon, proving that the large Li capacity is not due to double layer charging. Further work remains to be done in order to identify the insertion mechanism.

The high reversible capacity and the high rate performance of SWNT suggest that they could offer some interest for Li-ion battery applications. The limiting factors so far are the large irreversible capacity and the large voltage hysteresis. We expect the former issue to be minimized by a better choice of electrolyte.

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