Kinetics of alkali insertion in single wall carbon nanotubes: an electrochemical impedance spectroscopy study

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Abstract

Electrochemical impedance spectroscopy (EIS) was used to study the kinetics and insertion mechanism of alkali metals in single wall carbon nanotubes (SWNT). Three distinct processes with very different time constants were identified: charge transfer across the macroscopic electrolyte/electrode interface, diffusion through the mesoscale porosity of the SWNT electrode, and nanoscale diffusion in individual SWNT ropes. Electrode resistance and capacitance from EIS compare well with direct dc measurements. We propose that alkalis decorate the internal and external surfaces of the SWNT ropes.

1. Introduction

Single wall carbon nanotubes (SWNT) constitute the newest carbon guest–host system. van der Waals forces between adjacent nanotubes in a rope allow for the reversible insertion of electron donors and acceptors, similar to intercalated graphite and doped polyacetylene. Alkali insertion by vapor [1,2] or electrochemical doping [3,4] dramatically changes the electronic properties of SWNT. We recently showed that electrochemical doping with K increases the conductivity and spin susceptibility due to charge transfer between the alkalis and the carbon host [4]. While the electronic properties of the alkali-doped SWNT have been extensively studied, little is known about the insertion mechanism due to the doping-induced structural disorder in the host lattice [3–5]. The irreversible loss of crystallinity upon doping by either method makes standard structural tools such as X-ray diffraction of little utility.

Electrochemical impedance spectroscopy (EIS) measures the frequency-dependent complex impedance of an electrochemical cell as a function of cell potential, the latter being directly related to the dopant concentration. Using equivalent circuits to model the data, one obtains parameters relating to the kinetics and energetics of the doping process. EIS has been widely used to study the diffusion of alkali metals in graphite [6–8] and polyacetylene [9], and of bisulfate ions in graphite [10]. In this Letter, we used EIS to investigate the doping mechanism and the kinetics for Li and K insertion in SWNT.
2. Experimental

SWNT were synthesized at Rice University using the dual pulsed laser vaporization process [11]. Impurities such as catalyst particles, disordered carbons, graphite and C_{60} were removed using an HNO_{3} reflux, several cross flow filtrations, and a vacuum anneal at 1200°C [12]. The samples used in this work consisted of porous, self-supporting mats called buckypapers [12]. X-ray diffraction showed that these buckypapers are largely free of graphitic impurities, metal catalyst residues and amorphous carbon [12], and that the SWNT ropes lie preferentially in the plane of the buckypaper as a consequence of filter deposition from water/surfactant suspension [13]. There is, however, no alignment of the ropes within the plane. Uniaxial alignment can be achieved by filter deposition in a 25 T magnetic field, yielding samples about three times denser than regular buckypapers and up to 100 times denser than as-grown ‘felt’ [14].

EIS was performed on three-electrode cells, with \sim 0.5 mg of buckypaper as the working electrode and Li or K as the counter and reference electrodes. As buckypaper is mechanically self-standing and electrically conductive, no binder or carbon black was added. Li doping was performed using 1 M LiPF_{6} in a 50:50 mixture of ethylene carbonate and dimethyl carbonate as the electrolyte. K doping was performed using 1 M KCN in a 1 M solution of triethylborane in tetrahydrofuran. Electrical contacts were ensured with stainless steel current collectors and Ni wires passing through air-tight electrical feedthroughs. The Li/SWNT cell was pre-treated with 10 galvanostatic cycles between 3 and 0.15 V vs Li/Li^{‡} in order to stabilize the ‘solid–electrolyte interphase’ (SEI) [15], which forms on the surface of all carbon anodes during the first reduction in this electrolyte. EIS measurements were performed using an EG&G PAR 273A potentiostat coupled with a Solartron 1250 frequency response analyzer. SWNT were doped potentiostatically at 0.1 V intervals. The cell was equilibrated for several hours after each step, after which the complex impedance was measured using 5 mV rms amplitude at frequencies between 1 mHz and 64 KHz.

3. Results and discussion

Fig. 1 presents the EIS data plotted as imaginary (capacitive) vs real (resistive) components of

![Graph](image-url)
the complex impedance, at four different potentials covering the range from pristine SWNT (cell voltage 2.9 V, curves A) to nearly fully doped SWNT (0.3 V, curves D). The independent variable which generates each curve is the frequency, labelled in Hz at representative points on each curve. The top panel (a) covers the entire frequency range but emphasizes the lowest frequencies. The response is largely capacitive but with a slope less than 90°. Note that $Z_{\text{im}}$ decreases with decreasing potential at fixed frequency (e.g., 1 mHz), indicating that the working electrode is taking up Li as explained below. The middle panel (b) zooms in on the 0.1–10 Hz range, revealing a slope change in the range 10–100 mHz, and a semi-circle (the signature of a one-stage RC filter) for frequencies > 1 Hz. The further expanded bottom panel (c) shows that the height and width of the semi-circle vary with Li concentration. To summarize: each spectrum is composed of three distinct frequency-delimited regimes; the complex impedance depends not only on the frequency but also on the state of charge of the SWNT electrode; and the diameter of the high frequency semi-circle decreases continuously with decreasing potential while the low frequency capacitive tail becomes shorter at low potential.

We previously interpreted this data in terms of an empirically motivated Randles equivalent circuit [3], which explained reasonably well the impedance response and its variation with potential, in particular the ~45° slope at intermediate frequencies (Fig. 1b). However, this model did not reproduce the near-vertical low frequency behavior, yielding instead a purely capacitive tail at the lowest frequencies, Fig. 1a. Furthermore, since one of the elements of a Randles circuit is purely ad hoc, this model gives no insight about the intrinsic physical properties of the electrode or the insertion mechanism. Here we take a more general approach by using transmission lines (TL) rather than the empirical ‘Warburg’ element of the Randles model. A TL model has been applied successfully to analyze the diffusion of H\textsuperscript{+} during the overcharging of graphite bisulfates, in which the resistance of the TL was demonstrated to be equal to the ionic resistance of the intercalated H\textsubscript{2}SO\textsubscript{4} layer [10], thus providing an alternate description of the graphite–bisulfate intercalation compound as a nanoscale supercapacitor.

We modelled the EIS spectra of Fig. 1 using the equivalent circuit represented in Fig. 2. The two TL in parallel represent the external and internal surfaces of an average SWNT rope. $R_{\text{ext}}$ is the ionic resistance for Li ions to diffuse through the meso-scale porosity of the buckypaper to reach the external surface of a rope and $C_{\text{ext}}$ is the capacitance associated with this surface, while $R_{\text{int}}$ is the resistance for Li\textsuperscript{+} to diffuse inside a SWNT rope and $C_{\text{int}}$ is the internal capacitance of the rope. Finally, $C_{\text{dl}}$ is the double layer capacitance at the macroscopic electrode/electrolyte interface, and the sum of $R_{\text{cti}}$ and $R_{\text{cte}}$ behaves like an apparent charge transfer resistance for ions and electrons to interact at that interface. The model is sensitive only to the sum of $R_{\text{cti}}$ and $R_{\text{cte}}$ in series, thus the inferred charge transfer resistance is both ionic and electronic. The two TL complex impedances were computed by numerical integration using 100 circuit elements. Least-squares fits were performed on the absolute values of the impedance, hence overweighting the large impedance values at low frequencies. There is considerable statistical uncertainty in the fitted parameters, especially those which govern the time constants appropriate to the three frequency regimes, so the derived time constants are only approximate.

![Equivalent circuit used to model EIS data.](image-url)
The fitting results for the EIS spectra of Fig. 1 are presented in Table 1, and the calculated impedance response (solid curve) is compared with the experimental data at 1.2 V vs Li/Li$^+$ in Fig. 3. The model reproduces very well the three frequency regimes of the data, and the transitions between these regimes. At high frequency the impedance reflects charge transfer across the macroscopic interface, which results in a semi-circle in the complex plane. The semi-circle in the experimental data is depressed below the real axis, which is frequently observed in porous and rough electrodes [9]; this effect was ignored in our model. At intermediate frequencies, the linear behavior is dominated by Li diffusion through the porosity of the buckypaper. Finally, at the lowest experimental frequencies, the impedance is due to Li diffusion into the SWNT ropes. A fourth regime consisting of a vertical line is predicted by extrapolating the model to frequencies below 1 mHz, here data accumulation is extremely slow and parasitic capacitances become important.

The double layer capacitance $C_{dl}$ for the SWNT electrode was found to be on the order of 5 μF (Table 1). The double layer capacitance for carbon electrodes in organic electrolytes is about 10 μF/cm², so our $C_{dl}$ corresponds to a surface area of 0.5 cm², consistent with the macroscopic surface area of the buckypaper strip (0.2 cm²). This suggests that only the macroscopic surface area of the electrode takes part in the apparent charge transfer mechanism, i.e., the internal porosity of the buckypaper cannot be accessed at the high frequencies which determine $C_{dl}$. The charge transfer resistance $R_{ct}$ (the sum of $R_{cti}$ and $R_{cte}$) was found to decrease monotonically with decreasing potential. In Fig. 4 we plot $R_{ct}$ as a function of potential, and compare it with the bulk electronic

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Table 1
Fitting results obtained from the Fig. 2 model for the SWNT/Li cell at various potentials

The fitting results for the EIS spectra of Fig. 1 are presented in Table 1, and the calculated impedance response (solid curve) is compared with the experimental data at 1.2 V vs Li/Li$^+$ in Fig. 3. The model reproduces very well the three frequency regimes of the data, and the transitions between these regimes. At high frequency the impedance reflects charge transfer across the macroscopic interface, which results in a semi-circle in the complex plane. The semi-circle in the experimental data is depressed below the real axis, which is frequently observed in porous and rough electrodes [9]; this effect was ignored in our model. At intermediate frequencies, the linear behavior is dominated by Li diffusion through the porosity of the buckypaper. Finally, at the lowest experimental frequencies, the impedance is due to Li diffusion into the SWNT ropes. A fourth regime consisting of a vertical line is predicted by extrapolating the model to frequencies below 1 mHz, here data accumulation is extremely slow and parasitic capacitances become important.

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**Fig. 3.** Experimental and fitted EIS data for SWNT at 1.2 V vs Li/Li$^+$: Top panel (a) presents the whole frequency range between 64 kHz and 1 mHz. Middle panel (b) shows the intermediate frequency region. Bottom panel (c) emphasizes the high frequency response. Symbols are the data and the solid curve is the fit.
The variations in $R_{ct}$ closely mirror those of the electronic resistance, suggesting a significant electronic contribution to the charge transfer resistance. The difference in absolute values for $R_{ct}$ and four-probe resistance can be partly explained by the different geometries of the SWNT in the two experiments: the resistance is measured in the plane of the buckypaper, while $R_{ct}$ is measured normal to it. Furthermore, since there is some preferential alignment of the SWNT ropes in the plane of the buckypaper, we expect the in-plane resistivity to be lower.

Fig. 4. (a) Charge transfer resistance $R_{ct}$ vs potential (filled triangles) for the Li/SWNT cell, compared with bulk electronic resistance of the electrode measured in situ using four-probe resistivity (solid curve) [3]. (b) SWNT capacitance as a function of cell potential in EC:DMC LiPF$_6$. Filled triangles are the EIS results ($C_{ext} + C_{int}$) while the solid curve was derived from galvanostatic measurements using the relation $C = dQ/dE$.

Fig. 5. Experimental (symbols) and fitted (solid curve) EIS spectra for SWNT at 0.9 V vs K/K$^+$. Top panel (a) presents the whole frequency range between 64 kHz and 1 mHz. Middle panel (b) shows the high and intermediate frequency region. Bottom panel (c) shows the SWNT capacitance as a function of cell potential in 1 M KCN THF/triethylborane. Filled triangles represent the EIS results ($C_{ext} + C_{int}$) while the solid curve was obtained from galvanostatic measurements using the relation $C = dQ/dE$. 
lower than that normal to it. Similar results were observed in the K/(CH)_x system [9]. The values of C_{ext} and C_{int} were found to increase monotonically with decreasing potential, as shown by the shorter low frequency tails at low potentials in Fig. 1. In Fig. 5 we plot the total capacitance of SWNT (C_{ext} + C_{int}) as a function of potential, and compare it with the ‘static’ capacitance calculated from previous galvanostatic measurements [3] using the relation C = dQ/dE. We find good qualitative agreement between EIS and galvanostatic data, confirming that the low frequency part of the spectrum mirrors the charging of the SWNT. We hence propose that the storage mechanism for Li ions consists of charging the external and internal surfaces of SWNT ropes.

In Table 1 we list the time constants obtained from the RC products for the three different processes. The time constant obtained for charge transfer t_1 increases slightly with doping. The time constant t_2 for diffusion through the porous buckypaper increases continuously with doping by about a factor of 10, reflecting the continuous increase in C_{ext}. On the other hand t_3, which we assign to diffusion inside a rope, does not vary systematically with potential, and is of order 1500 s. From t_3 we estimate a diffusion coefficient for Li in a rope using the relation D = L^2/T, where L is the diffusion length. Assuming that Li diffuses mainly parallel to the tube axes and enters from both ends of a rope, we take L as half the average length of a rope (0.5 μm), to obtain D = 1.5 × 10^{-12} cm^2/s. This is close to the value reported for 1-D Li diffusion in polyacethylene fibrils [9] which have similar nanoscale structures. On the other hand it is much lower than the values reported for 2-D Li diffusion between adjacent graphene monolayers in bulk graphite [7]. This value is an upper bound since no doubt some Li enters the ropes through defects in the rope lattice or short tubes on the rope surface, either of which would produce a smaller average value for L. In contrast to t_1 and t_3, the concentration dependence of t_2 implies that diffusion through the porosity slows down as more Li is added to the system. Taking the electrode thickness as the characteristic length for diffusion through the porosity, D decreases from 4.7 × 10^{-6} at 2.9 V to 3.5 × 10^{-7} at 0.3 V. This range of D’s is consistent with a value reported for alkali diffusion in a porous (CH)_x film [16].

Very similar results were obtained for K-doped SWNT. In Fig. 6, we present the experimental and fitted EIS spectra for the K/SWNT cell at 0.9 V vs K/K^+. The experimental spectrum is again comprised of three frequency-delimited regimes. The high-frequency semi-circle is attributed to charge transfer across the electrolyte/electrode interface, the 45° line at intermediate frequencies to K diffusion through the porosity of the buckypaper, and the capacitive tail at low frequencies is attributed to diffusion of ions inside the ropes. The complex impedance was fitted as before; the fit in Fig. 6 reproduces the experimental data very well on the three frequency regimes. Table 2 lists the fit parameters at various potentials. The double layer capacitance C_{dl} is on the order of 1 μF, independent of potential, again consistent with the macroscopic surface area of the electrode. C_{ext} and C_{int} were again found to increase monotonically with decreasing potential. In Fig. 7 we plot the total capacitance of SWNT (C_{ext} + C_{int}) as a function of potential (vs K/K^+), and compare it with the ‘static’ capacitance calculated from previous galvanostatic measurements using the relation C = dQ/dE. We find excellent agreement between EIS and the galvanostatic data, confirming that the low frequency

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*Electrode dimensions were 8 × 8 × 0.02 mm^3, mass = 0.44 mg.*
part of the spectrum mirrors the charging of the SWNT. We therefore propose that both alkalis studied in this work decorate the internal and external surfaces of SWNT ropes.

Table 2 lists the RC time constants obtained for the three different processes at various potentials. The time constant $t_3$ for diffusion in a rope was again found to be constant with potential, on the order of 2500 s, again yielding a diffusion coefficient $\sim 10^{-12}$ cm$^2$/s. Diffusion of K ions through the porosity is again faster than in a rope of order of $10^{-7}$ cm$^2$/s, consistent with K diffusion in the pores of a (CH)$_n$ film [14].

4. Conclusion

We have successfully modelled the ac impedance of Li/SWNT and K/SWNT cells using an equivalent circuit including TL previously developed for graphite intercalation compounds. We identified three processes with three different time constants: apparent charge transfer across the electrode/electrolyte interface, diffusion through the porosity of the buckypaper, and diffusion inside a SWNT rope. The diffusion coefficient for alkali metals inside a rope was found to be of order $10^{-12}$ cm$^2$/s, similar to Li diffusion in polyacetylene fibrils. We believe that the overall doping process consists of decorating internal and external rope surfaces with Li or K ions. Since rope crystallinity is not a prerequisite, our interpretation of the EIS results is consistent with the observation that alkali doping generally leads to the loss of rope Bragg peaks in X-ray diffraction [3–5]. The EIS results are also be consistent with a recently proposed model of inhomogeneous doping in non-crystalline rope bundles [4]. It would be interesting to repeat the EIS experiments on SWNT electrodes with known and controllable microstructure and porosity.

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References