

# Perspectives on Electrochemical Insertion of Lithium in Carbon Nanotubes

#### by Vito Sgobba and Dirk M. Guldi

arbon nanotubes (CNTs) are emerging materials with high potential in several disciplines, in particular electronics and photovoltaics. Moreover, the unique structural features, such as high aspect ratio, have established CNTs as novel materials in nanotechnology, especially in composites. Importantly, the structure of vehicles and hybrid electric vehicles. Owing to the successful development of carbon based anodes to be incorporated into lithium ion batteries,<sup>1</sup> lithium intercalation into, for example, different carbon nanostructured materials emerged as an interdisciplinary topic to improve the overall device performances. Additionally, the outstanding electrical conductivity, of specially designed sample holders and cells including a beryllium window allowing the transmission of X-rays and a magnet operated reservoir. Overall, such a cell configuration assists in attaining full control over the electrolyte level as a means to dope and/or dedope. Simultaneously, X-ray data accumulation is guaranteed.<sup>4</sup>

A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler, and R. E. Smalley, "Solid-State Electrochemistry of the Li Single Wall Carbon Nanotube System," *J. Electrochem. Soc.*, 147, 2845 (2000).

# 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

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a single walled nanotube (SWNT) can be conceived as wrapping a one-atom-thick layer of graphite, called graphene, into a seamless cylinder with diameters in the range of 1-2 nm and lengths of several hundreds micrometer. They form long crystalline bundles consisting of a few to thousands of individual SWNTs packed in triangular lattices. The interstitial channels with a size of 0.6 nm provide the necessary intercalation sites analogous to those found in the interlayer galleries in graphite or the tetrahedral/octahedral vacancies in fcc C<sub>60</sub>.

Lithium ion batteries are the main power source in today's portable electronic devices. These also bear the great potential to take over as power sources of electric the remarkable mechanical strength and the lasting chemical stability of carbon nanotubes, in general; and of single wall carbon nanotubes, in particular, triggered a run to test them as high capacity lithium storage anode materials.<sup>2</sup>

In this featured article,<sup>3</sup> for the first time the insertion of lithium into a purified and highly crystalline SWNT was performed. To this end, electrochemical cycling with lithium was pursued as the method of choice. The formation of the new SWNT/lithium systems were complementary monitored by *in situ* galvanostatic charge-discharge, cyclic voltammetry, X-ray diffraction, as well as resistivity measurements. Notably, the work necessitated the construction

In contrast to the aforementioned cell configuration, in situ resistivity measurements are required to contact SWNTs with Cu wires-two as current leads and two as voltage leads. Such SWNT assemblies were placed between ceramic plates screwed together to achieve optimum pressure contacts. While the current leads were connected to an ac constant current source, the two voltage leads were connected to a lockin amplifier to measure the voltage drop. Furthermore, one of the current leads was also connected to the potentiostat to polarize the SWNT films. The use of ac for resistance measurements and dc for electrochemical control eliminated interference due to, for instance, cross coupling between the two circuits. The breakthrough in this approach has lately been manifested through its wide applicability in fine-tuning the electronic structure of semiconducting SWNTs. Equally important are contemporary contributions toward thorough estimations of electron affinities and ionization potentials.<sup>5</sup>

This paper has received, since 2001, a steady number of citations averaging well over 18 per year. The number of citations to Ref. 3 is presented in Fig. 1 as a function of the publication year.

One of the major accomplishments of the work by Claye, *et al.* is the reversibly conducted electrochemical insertion of Li into SWNTs. Here, galvanostatic charge/ discharge cycles were run in half-cell configurations that implemented purified SWNT buckypaper, on one hand, and Li metal on the other hand. Determination of the total and irreversible specific capacities of these materials required the use of a 1 M LiPF<sub>6</sub> electrolyte in an ethylene carbonate/dimethylcarbonate solvent mixture (1:1 v/v).

Considering that buckypapers are mechanically self-supporting and electrically conductive, no need for a binder or carbon black evolved. This

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Fig. 1. The number of papers citing Ref. 2 as a function of the year the paper was published.

# **Prominent Contributions in Fullerenes and Carbon Nanotube Research** *by Prashant V. Kamat*

Carbon-based systems are quite familiar to electrochemists as they are an integral part of many modern day sensors, catalysts, and power sources. The recent emergence of carbon nanostructures offers challenges to explore new frontiers in electrochemistry. As a newcomer to the electrochemistry community, fullerenes and carbon nanotube research has made a significant impact. Five of the most cited papers (as of January 2010) published in *Journal of The Electrochemical Society* are listed as the five References below.

One of the early challenges in understanding properties of fullerenes and their derivatives was the characterization of the reduction and oxidation states. Up to six reversible reductions of  $C_{60}$  were established using cyclic voltammetry. The spectroelectrochemical experiment by Parkinson and coworkers<sup>1</sup> provided the first spectral fingerprint (IR absorption band of  $C_{60}$ ) and this landmark paper has served to establish many interesting redox properties of fullerenes.

The other area of interest is in the utilization of carbon nanotubes in storage batteries, fuel cells, and supercapacitors. Early work of Smalley and coworkers<sup>2</sup> in the electrochemical insertion of lithium ions into purified single wall carbon nanotubes demonstrated reversible capacities on the

order of 460 mAh/g, corresponding to a stoichiometry of  $\text{Li}_{1.23}\text{C}_6$ . Their studies demonstrated that the high lithium capacities in carbon nanotubes were not due to double layer capacitance effects, but to an actual ion insertion/extraction process in the bulk material.

Wu, *et al.*<sup>3</sup> also observed that the structures of carbon nanotubes play major roles in both specific capacity and cycle life. A nanocomposite electrode single-walled carbon nanotube of (SWNT) and polypyrrole (Ppy) exhibited improved specific capacitance of the supercapacitor properties.4 Shao, et. al5 report on the durability of multiwalled carbon nanotubes supported Pt (Pt/CNTs) catalysts highlighted potential application of carbon nanostructures in polymer electrolyte membrane fuel cells. Carbon nanostructures will continue to play an important role in designing next generation energy conversion and storage devices.

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#### References

- D. R. Lawson, D. L. Feldheim, C. A. Foss, et al., "Near-IR Absorption-Spectra for the Buckminsterfullerene Anions. An Experimental and Theoretical Study," J. Electrochem. Soc., 139, L68 (1992); cited 112 times.
- S. Claye, J. E. Fischer, C. B. Huffman, et al., "Solid-State Electrochemistry of the Li Single Wall Carbon Nanotube System, J. Electrochem. Soc., 147, 2845 (2000); cited 160 times.
- 3. G. T. Wu, C. S. Wang, X. B. Zhang, *et al.*, "Structure and Lithium Insertion Properties of Carbon Nanotubes," *J. Electrochem. Soc.*, **146**, 1696 (1999); cited 108 times.
- K. H. An, K. K. Jeon, J. K. Heo, et al., "High-Capacitance Supercapacitor Using a Nanocomposite Electrode of Single-walled Carbon Nanotube and Polypyrrole," J. Electrochem. Soc., 149, A1058 (2002); cited 90 times.
- Y. Y. Shao, G. P. Yin, and Y. Z. Gao, "Durability study of Pt/C and Pt/CNTs Catalysts under Simulated PEM Fuel Cell Conditions," *J. Electrochem. Soc.*, 153, A1093 (2006); cited 80 times.

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approach is, in fact, so appealing and so unique that buckypapers as (1) free standing films and (2) in all-solid-state configurations paved the way to the first investigations focusing on *in situ* CNT visible/near-infrared and Raman spectroelectrochemistry.<sup>6,7</sup>

These pioneering investigations have unambiguously demonstrated that SWNTs give rise to reversible capacities outperforming those theoretically predicted for graphite, that is, 460 versus 372 mAh/g, which is equivalent to a Li<sub>1.23</sub>C<sub>6</sub> stoichiometry. A setback is that initially a large irreversible capacity of 1200 mAh/g evolved. In fact, the latter decrease up to 15% in the subsequently performed cycles. Implicit is that a significant amount of Li could not be recovered as the number of cycles increased. A likely rationale for this setback lies in the posttreatment procedure of SWNT, namely heat treatment at 1200°C. At 1200°C the SWNT caps/ends are presumed to be still intact, which prevents the efficient diffusion of Li inside the SWNTs. Reassuring is that in a followup study, which emphasized the use of opened SWNT, the specific Li storage capacity increased up to an impressive 1000 mAh/g.<sup>8</sup> The corresponding  $LiC_3$ stoichiometry corroborates the notion that Li is not anymore hampered to diffuse into the inside of SWNTs.

A close analysis of the resulting galvanostatic charge/discharge features prompt to substantial losses due to irreversibility. It is very likely that the reduction of the electrolyte, which is further augmented by the formation of a solid electrolyte interphase right at the surface of a SWNT, is the inception for such effects. Well in line with such an assumption is the fact that the intercalation and/or de-intercalation potentials were spread over a fairly wide range. Moreover, the high divergence between the potentials at which either insertion or extraction occurs, is the basis for a notable hysteresis. Recently, the original hypothesis, that is, formation of key intermediate such as C-H-Li, C-O-Li, etc. was unmistakably confirmed.9,10 The lack of well-defined potentials for the Li insertion or removal were also seen in the cyclic voltammograms.

A real asset of the work is the correlation between the 3D crystallographic structure, surface chemistry, and the electrochemical behavior of these materials, which have been elegantly performed by comparing and contrasting *in situ* X-ray diffraction and high resolution transmission electron microscopy. Here, the important conclusion is that an irreversible disorganization of the packing within the bundles dominates rather that a simple disassembling.

With regard to the change in resistance, as occurred during the doping and dedoping processes, use of an electrolyte that is known to not to interfere—1M LiPF<sub>6</sub> in THF—helped to decisively substantiate charge transfer processes between Li and C.<sup>11</sup> Here, a nearly 20-fold resistivity decrease was observed upon doping.

Finally, the Nyquist plots should be mentioned, which were derived from electrochemical impedance spectroscopy at various potentials and modeled within the frame of Randles-type equivalent circuits. The most far reaching conclusion is that the charge transfer resistance has significant electronic contributions. Since the double layer capacitance was found to be much lower than that expected for a SWNT Brunauer-Emmett-Teller surface area of 350 m<sup>2</sup>/g, double layer charging is ruled out as an origin of the large Li capacity. Instead, a closer inspection of the lower frequency EIS portion confirms that the large Li capacity of the SWCT is due to an actual ion insertion/extraction. Lately, these Nyquist plots were utilized as valuable standards to assess the quality of similar samples.<sup>12,13</sup>

## Conclusions

The Claye, et al. contribution is ground breaking. In fact, this innovative and visionary work comprises cutting-edge developments in the renewable energy sector and has over the last decade led to a comprehensive, scientific understanding of electrochemically intercalating ions in general into CNT buckypaper. This has shaped the scientific community's view on technological advances in the emerging fields of energy storage devices focusing on Li-ion secondary batteries, supercapacitors, hydrogen storage, etc. It also unveils the impact on contemporary advances and innovations in, for example, electrochemical doping of the Fermi level of CNT for photonic and nanoelectronic applications.

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### References

- 1. Y. Nishi, H. Azuma, and A. Omaru, U.S. Patent, 4959281 (1990).
- Z. W. Zhao, Z. P. Guo, H. K. Liu, and S. X. Dou, ECS Transactions, 6(25), 205 (2008).
- 3. A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler, and R.E. Smalley, J. Electrochem. Soc., **147**, 2845 (2000).
- 4. J. E. Fischer, Acc. Chem. Res., **35**, 1079 (2002).
- S. Kazaoui, N. Minami, N. Matsuda, H. Kataura, and Y. Achiba, *Appl. Phys. Lett.*, **78**, 3433 (2001).
- L. Kavan, P. Rapta, L. Dunsch, M. J. Bronikowski, P. Willis, and R. E. Smalley J. Phys. Chem. B, 105, 10764 (2001).
- 7. L. Kavan and L. Dunsch *Chem. Phys. Chem.*, **8**, 974 (2007).
- 8. H. Shimoda, B. Gao, X. P. Tang, A. Kleinhammes, L. Fleming, Y. Wu, and O. Zhou, *Phys. Rev. Lett.*, **88**, 015502 (2002).
- 9. J. Y. Eom, D. Y. Kim, and H. S. Kwon, *J. Power Sources*, **157**, 507 (2006).
- 10. S. Yang, J. Huo, H. Song, and X. Chen, *Electrochim. Acta*, **53**, 2238 (2008).
- L. W. Shacklette, J. E. Toth, N. S. Murthy, and R. H. Baughman, J. Electrochem. Soc., **132**, 1529 (1985).
- 12. S. H. Ng, J. Wang, Z. P. Guo, G. X. Wang, and H. K. Liu, *Electrochim. Acta*, **51**, 23 (2005).
- S. Venkatachalam, H. Zhu, C. Masarapu, K. Hung, Z. Liu, K. Suenaga, and B. Wei, ACS Nano, 3, 2177 (2009).