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The Electrochemical Properties of Bundles of Single-Walled Nanotubes

Thomas A. Zawodzinski Jr.*, Prathap Haridoss and Francisco A. Uribe

Abstract

This is the final report of a Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). We studied electrochemical properties of single-walled fullerene nanotube bundles. The materials exhibited a highly anisotropic conductivity. Electrochemical cycling in solutions of alkyl ammonium salts in propylene carbonate revealed that the nanotubes are stable to at least ±1.5 V and have a fairly high accessible surface area. Double-layer charging currents of approximately 30 farads per gram were observed. This is on the same order of magnitude, though somewhat lower, than state-of-the-art values for ultra-capacitor materials. Electrochemical insertion of lithium was attempted. Though several features were observed in a slow cyclic voltammetric scan, these features were not reversible, indicating little reversible insertion. Several possible reasons for this behavior are discussed.

Background and Research Objectives

Smalley and his co-discoverers of fullerenes recently won the Nobel Prize in Chemistry for their work on fullerenes. Recently, the Smalley group at Rice announced the production of long bundles of single-walled carbon nanotubes with a fullerene structure, which they termed "bucky ropes" [1]. The bundles form spontaneously in the presence of certain additives to the buckyball synthetic mix and are quite stable structures. Quite long (up to a micron) ropes can be formed. These tubes have a further interesting property: they are electronically conducting. This has been shown by contacting the bucky rope at two ends of a scanning-tunneling microscope (STM) tip and doing a dc conductivity measurement.

Various forms of carbon are under investigation for a range of applications, including active materials for batteries and ultra-capacitors and catalyst supports for electrochemical devices. The high electronic conductivity observed by Smalley and co-workers, as well as their expected high internal surface area, suggests that these carbons could be very attractive for electrochemical applications. Our work sought to investigate the properties of bucky ropes for electrochemical applications.

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There is presently a worldwide research effort aimed at finding improved carbons for lithium batteries. This stems from the extensively studied electrochemical intercalation of lithium into graphite. Lithium can be electrochemically inserted into graphite at voltages close to the reversible voltage for lithium metal deposition, a desirable property for high energy density batteries. However, in graphite, a stoichiometry of 1 lithium atom per 6 carbons is achieved. This is a limitation on the quantity of charge stored per unit weight, the capacity, of a battery. This corresponds to 372 mAh/g of carbon. There are reports of differently structured carbons in which insertion of more than 372 mAh/g is achieved. However, in many cases not all of this capacity is reversibly used. Capacity is lost due to parasitic processes, such that a series of charge/discharge cycles of the battery will yield progressively lower capacity.

Though the bucky ropes are likely to be too expensive as electrode materials, their unique structure could provide critical clues to improved 'designer carbons' for facile intercalation/de-intercalation processes. In particular, the intercalation into the ropes of alkali metal cations, such as lithium, is of interest. Important properties required of carbon used for this purpose include high stability under both oxidizing and reducing conditions, the ability to reversibly take up significant amounts of lithium, high diffusion coefficients of intercalated lithium, and suitable surface properties for compatibility with other components of a composite electrode that allows mixed ionic and electronic conduction. The bucky ropes have potential for such applications. The bundles have a structure which could lead to much higher capacity of lithium than the canonical 1 lithium atom per 6 carbons typically found for graphite. This is because the ropes pack into bundles with paired graphene-like sheets facing each other. The separation between graphene planes reported by Smalley et al. is nearly optimal for insertion of lithium with minimal structural perturbation. Other alkali metal cations could also be studied.

Another possible application of these carbons is as active materials for carbon-based double layer ultra-capacitors. In this case, electrochemical charging of the double layer is the physical process underlying the application. Key requirements for this application include stability of the material over a wide range of voltage, good electronic conductivity of the active material, and a very high surface area accessible on the millisecond time scale. The bucky ropes offered some potential in this regard since each rope is composed of individual single-walled tubes approximately 1.2-1.4 nm (1) in diameter.

We set out to study the electrochemical properties of nanotube bundles. We focused on the potential application of these materials as carbon components of a composite electrode. For this short duration project, our objectives were:

(1) Bulk conductivity measurements.

(2) Preliminary exploration of the use of nanoropes as an electrode in various solvents, focusing on the redox window of these materials. If the materials have a high accessible surface area, they could be promising as materials for double-layer ultra-capacitors.

(3) Assessment of the ability to reversibly insert various alkali metal cations into the carbon, starting with lithium. Key issues here are the insertion process itself--achievable capacity and the size of the cation that can be inserted; the stability of the carbon upon insertion; and the tendency of the carbon to reactively form passivation layers during cycling. These latter issues are important to the potential use of these carbons as battery materials.

The third set of issues mentioned above deserves some additional backgound discussion. Reversible insertion of lithium into carbon is a critical research area in the lithium battery world. This is an important technological issue because 'breaking in' a battery by cycling to a steady-state condition is a costly problem with present-day lithium ion batteries. Our expectation with the nanotube bundles was that insertion could be facile since the spacing between graphene layers is ‘pre-set’ to allow insertion with little structural change, and thus little energy penalty. In graphite, the insertion process can cause exfoliation of outer planes due to solvent insertion. The severity of this problem is highly solvent dependent. A second source of irreversibility in the insertion/de-insertion cycle is the formation of a passivating solid-electrolyte interphase (SEI) layer on the carbon in a composite electrode. At the outset of this work, our hope was that the nanotubes will have few if any nucleation sites for the formation of this layer and thus the SEI formation by parasitic reactions with deposited lithium will be minimal.

Importance to LANL's Science and Technology Base and National R&D Needs

This work helps to meet an important research need in the United States, namely the study of novel materials for electrochemical energy storage processes. Because of applications of advanced batteries based on carbon materials in consumer electronics and, potentially, electric vehicles, there is strong national interest in this type of work. Furthermore, this problem represents a good example of the use of national laboratory facilities to foster the introduction of research developed in university laboratories to a more applied setting. We are leveraging experience gained in studying battery materials for electric vehicle applications in our work. Finally, the collaboration with a member of the

Smalley group represents a possible high profile activity at the Laboratory because of Smalley's accomplishments.

Scientific Approach and Accomplishments

We obtained a sample of a circular mat of the bucky ropes from Hongjie Dai of the Smalley group. The mat was prepared by collection on a filter after purification.

Preliminary Characterization

As preliminary steps in our study of the nanoropes, we carried out Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and conductivity measurements on portions of the sample provided by Dai. The SEM photo in Figure 1 shows rod-like features stacked and oriented randomly in the plane. Conspicuously absent are 'end-on' circular structures. The XRD scan, shown in Figure 2, which provides structural information on the material and a basis for the study of structural effects of lithium insertion into the carbon, had two peaks: a high-intensity, sharp peak corresponding to a spacing of 3.36 Å and a smaller peak at 2.04 Å. These are two typical peaks found in graphite and indicate that the material has features that are graphite-like. The spacings likely correspond to the spacing between graphene planes of adjacent tubes in the ropes and across the six-membered rings of the bucky tube structure.

The conductivity measurement was carried out using two different methods corresponding to different directions of electronic conduction. These are schematically shown in Figure 3. Dramatically different conductivities were observed in the two directions. This is in accord with similar observations made by the Smalley group. The phenomenon is most likely an outgrowth of the directional conductivity of the individual tubes in the rope, combined with the rigidity of the tubes. From this and the SEM results showing few ends in the plane, we conclude that the mat is formed from a 'pile' of individual ropes that deposit much as a collection of uncooked spaghetti noodles would. Thus, conduction along the surface of the mat occurs primarily along the tubes (intra-bundle) while conduction through the mat takes place primarily by relatively poor inter-bundle electron transfer. For our purposes, the most important conclusion is that, at least in one direction, the conductivity is quite high and thus electrodes can be prepared directly from the nanorope mat.

Electrochemical Stability and Double Layer Capacitance of Bucky Ropes

Our approach to assessing the electrochemical stability of the nanoropes was to prepare an electrode and then electrochemically cycle it in an electrolyte that was known to have a high voltage range of stability, often referred to as its 'electrochemical window.' The first step in this work was electrode preparation. We prepared an electrode by cutting out a small rectangular piece of the mat of about 0.2 cm^2. Contact was made by inserting one end of the piece in a loop of gold wire.

The electrochemical response of the nanorope electrode to a cyclic linear potential scan is shown in Figure 4. The electrode is immersed in a solution of tetraethylammonium tetrafluoroborate in an ehtylene carbonate/propoylene carbonate (EC/PC) mixture. This response is largely featureless. The features at ±1.5 V are the limit of the electrochemical stability of the nanoropes or the solution. We can conclude that the material is stable over at least this voltage range, comparable to other types of carbon electrode. The current that flows during the cycling corresponds to charging the electotrode electrical double layer. A similar scan in the same electrolyte on a typical carbon electrode (glassy carbon) of low surface roughness has roughly 4 orders of magnitude lower charging current. This excited our interest in this material as a potential ultra-capacitor active material. Determination of the total charge upon cycling by integration over the useable voltage range of the current from this voltammogram indicates a capacitance of roughly 30 farads/g for this material over a 3-volt range. The capacitance is somewhat low for practical purposes. Niu et. al. [2] have reported specific capacitances of the same order magnitude for carbon nanotubes electrodes in aqueous H_2SO_4.

The scan is of a rate (100 mV/sec) such that it is in the desirable range for discharge or charge of an ultra-capacitor. Since we expect that the internal surface area of the nanorope bundle is very high, it is likely to be the case that the total surface area of the nanoropes is not accessible during such a scan. This was taken into account in the work shown below related to lithium insertion. It should also be pointed out that this rather preliminary screening was not obtained with an electrolyte optimized for use with the nanoropes but rather with a typical electrolyte. It may still be possible, for example by using somewhat smaller anions and cations, to access more of the internal surface of the nanoropes at practically reasonable scan rates. Finally, the voltage window obtained is probably a reflection of the electrolyte used--i.e. the limiting processes are probably electrochemical decomposition of electrolyte components. This could possibly be improved by a suitable alternative choice of electrolyte.

Electrochemical Insertion of Lithium into Bucky Ropes

The main goal of this work was investigation of the nanoropes as lithium-battery negative-electrode materials. To this end, we carried out slow electrochemical cycles of the electrodes in an electrolyte containing a lithium salt. Our object was to look for the electrochemical signatures of lithium insertion. Lithium intercalates between graphite sheets as atoms or ions participating in charge transfer complexes with the graphitic host. The overall electrochemical process involves electron transfer concomitant with or followed by diffusion of lithium into the host. Since the diffusion process is expected to be slow based on similar properties in graphite, studying the electrochemical insertion of lithium into carbon hosts typically involves scan rates of a few microvolts per second. Thus, since the voltage range is several volts, it takes some weeks to acquire data for a single charging cycle of the material. We constructed a special measurement system specifically for these scans as part of this project.

Results are shown in Figure 5. The voltammogram is quite complicated. The most interesting observations from this work are the onset of current flow at 0.6 V vs. Li, the fact that no reverse current is observed and the peculiar redox behavior at higher voltages vs. Li. We are unsure of the origin of the latter. The onset of current from 0.6 V onward is roughly consistent with observations of the onset of intercalation of lithium into graphite, which occurs through a series of 'stages.' In graphite, insertion occurs between more closely spaced planes as the voltage approaches that of lithium metal. In a voltammogram, this appears as a series of steps in the voltammogram. Such a series is completely absent in Figure 5. Only the first step seems to appear. Furthermore, assuming the current observed corresponds to insertion of lithium, there is no corresponding reverse current from release of lithium upon reversal of the scan direction. The charge associated with lithium insertion into the ropes amounts to roughly 40 mAh/g, roughly 10% of that observed for insertion into graphite.

There are at least two possible explanations for this: (1) the insertion process is completely irreversible; all lithium is reduced to metal and ensuing parasitic reactions with solvent or impurities in the carbon consume the plated lithium; or (2) the insertion occurs in a steady-state mode under complete diffusion control, similar to that observed on a microelectrode. Thus, diffusion to a reactive surface is the rate-limiting process. This may be plausible because of the nature of the insertion process in this material. Insertion must occur through the circular end of the rope. Given the aspect ratio of the ropes (small circular face, very long), this is likely to be a somewhat slow process. This suggests that using shorter lengths of nanoropes is a likely means of improving the lithium insertion process. This may also help increase the accessible surface area for ultra-capacitor applications.

Summary and Prognosis

The short duration of this project (approximately 5 months) could not do justice to the type of work needed to realize the potential of these materials for electrochemical devices. At this stage, we cannot claim to have anything approaching a reasonable understanding of the electrochemical behavior of these materials. Nonetheless, several features discussed above are interesting or encouraging and further study is warranted. In particular, the possibility of increasing accessible surface area by controlling the typical rope length may be worth following up. The conclusions drawn from such work could indeed be quite illuminating regarding insertion processes in technologically important carbons.

References

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2. Nui C.M., Sichel E.K., Moy D., and Tennent H. *Appl. Phys . Lett.* **70**, 1480 (1997).

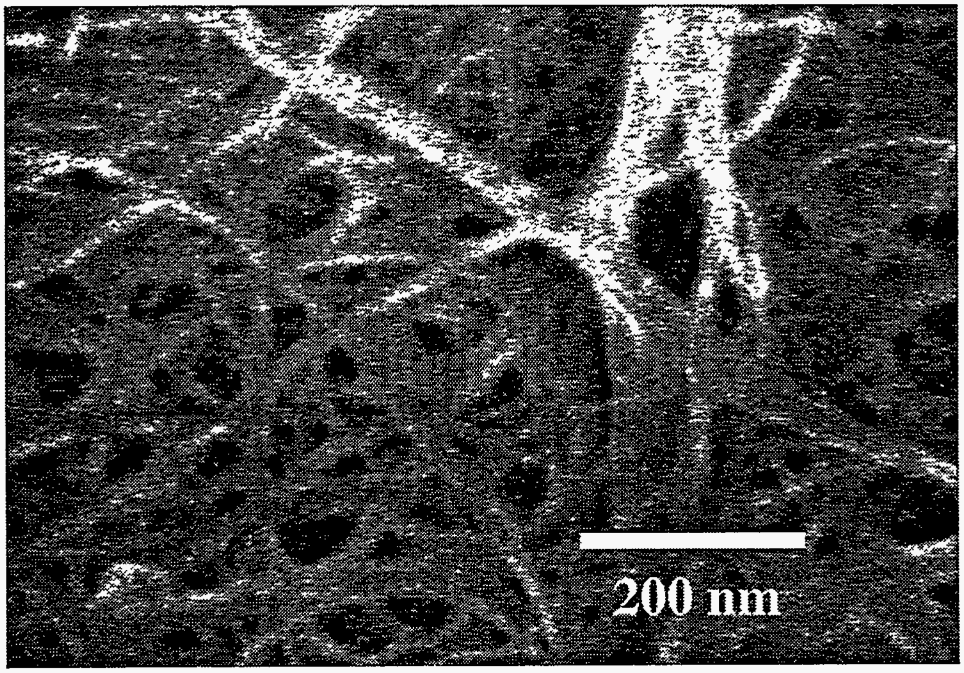


Figure 1. SEM of carbon nanorope mat.

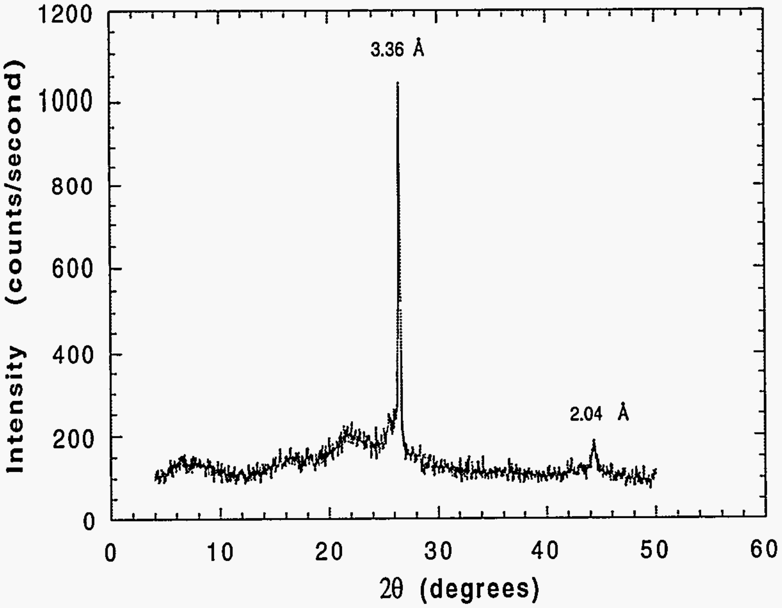
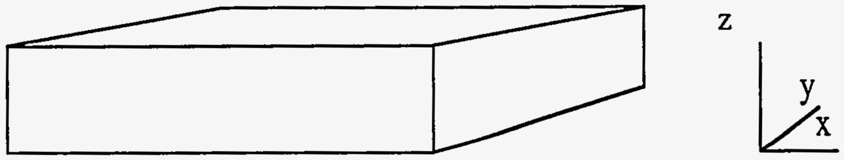


Figure 2. XRD scan of carbon nanorope.



**** Conductivity in the xy plane: 200 Ω^{-1} cm^{-1}

**** Conductivity in the z direction: 0.06 Ω^{-1} cm^{-1}

Figure 3. Schematic illustration of directional dependence of conductivity measurements.

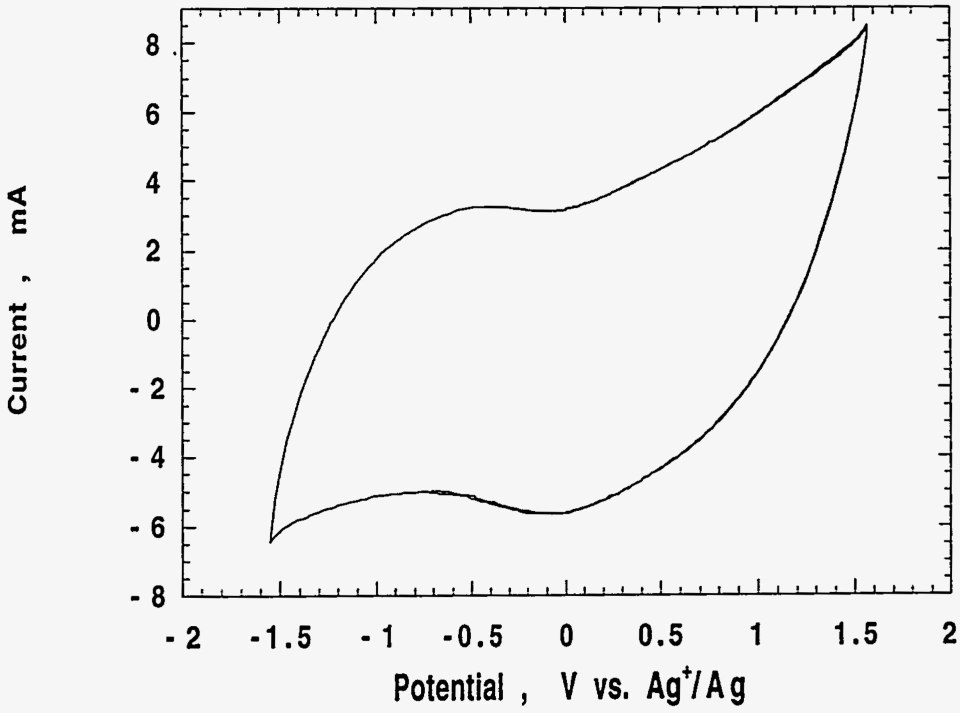


Figure 4. CV plot for a carbon nanorope electrode (0.2 cm^2, 1.6 mg) in 0.2 M Et_4NBF_4 in 1:1 EC/PC. Scan rate: 100 mV/s.

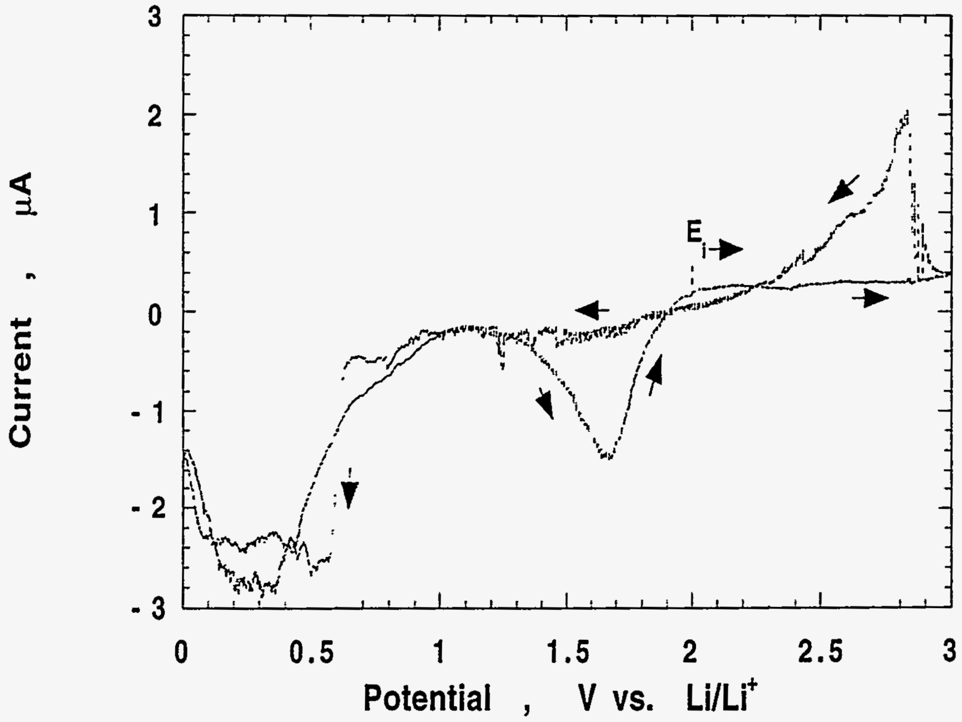


Figure 5. Cyclic voltammogram of a carbon nanorope electrode (0.2 cm^2) in 1 M $LiN(CF_3SO_2)_2$ in EC/PC(1:1). Cycle: 2V-3V-0V-2V at 5 μV/s.