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Evaluation and Testing of Commercially-Available Carbon Nanotubes as Negative Electrodes for Lithium Ion Cells

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Abstract

Rechargeable lithium ion (Li-ion) battery technology offers significant performance advantages over the nickel-based technologies used for energy storage for the majority of NASA's missions. Specifically Li-ion technology offers a threefold to fourfold increase in gravimetric and volumetric energy densities and produces voltages in excess of three times the value of typical nickel-based battery systems. As part of the Advanced Battery Technology program at NASA Glenn Research Center (GRC), a program on the evaluation of anodes for Li-ion cells and batteries was conducted. This study focused on the feasibility of using carbon nanotubes as anodes in Li-Ion cells. Candidate materials from multiple sources were evaluated. Their performance was compared to a standard anode comprised of mesocarbon microbeads. In all cases, the standard MCMB electrode exhibited superior performance. The details and results of the study are presented.

Introduction

Lithium-ion cells employ a carbon/graphite anode (instead of metallic lithium) and a liquid organic electrolyte. The use of lithiated carbon-based materials in place of metallic lithium would significantly reduce the safety hazards associated with such systems (ref. 1). Li-ion cells have several advantages over the lithium metal such as long cycle life and higher charge rate capability over the lithium metal cells, wherein high rate charging might result in a non-uniform dendritic lithium deposition. These advantages would compensate the decrease in the specific energy resulting from the use of Li-intercalating anode in place of metallic lithium.

Cathodes

- High voltage cathodes, such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 are presently being used as candidate materials for Li-ion cells.

Anodes

- Typical anodes in Li-ion cells include carbon materials and graphite (refs. 2 and 3). Carbon has many advantages as an anode material (34: high storage capacity and a relatively flat potential profile near the redox potential of the Li/Li + couple during charge-discharge processes. However, the theoretical capacity of carbon is only 372 mAh/g, far below the 3670 mAh/g for the Li metal that it replaces. Much effort has been made to improve the capacity of the carbon-based anodes during these past few years.

As part of the Advanced Battery Technology program at NASA Glenn Research Center, a task addressing improvements to the anodes for Li-ion cells and batteries was conducted. One specific goal was to improve the specific energy of the Li-ion batteries by the use of carbon-based anodes. The program was initiated with the evaluation of different carbon materials such as mesocarbon microbeads (MCMB) and graphite materials from different vendors.

Carbon nanotubes (CNTs) have been the focus of intense interest since their discovery by Iijima (ref. 5). CNT's have been envisioned as promising materials for a variety of applications such as high

energy lithium batteries, super capacitors, and hydrogen storage (ref. 2). Their unique morphology is expected to be profitable for getting improved performance. CNTs are extremely small, thin, hollow cylinders structure formed by seamlessly rolling up a single layer of graphite. CNTs can be classified in two categories, e.g., multiwall carbon nanotubes (MWNTs) and single wall carbon nanotubes (SWNTs). These classes of CNTs are shown to undergo a reversible redox reaction with electron donors such as alkali metals resulting in a reduced electrical resistivity and electronic work function.

MWNTs consist of graphitic sheets rolled into closed concentric cylinders, in which the concentric tube is in a distance of $\sim 3.4 \text{ \AA}$. The MWNTs have external diameter that ranges from a few nanometers to tens of nanometers (ref. 6). The MWNTs can be of several micrometers long. SWNTs are cylindrical graphene sheet with a diameter of about 0.7 to 10.0 nm.

A growing list of carbon nanotubes were evaluated as different types of Commercial off the shelf (COTS) CNTs were procured evaluated and tested.

In this study, electrochemical applications of the different commercial-off- the-shelf (COTS) nanotubes from Rice University, Carbon Nanotechnologies, Inc. (CNI), Nanolab (NL), Materials and Electrochemical Research Corporation (MER) and SES Research (SES) were evaluated. A summary of the results will be critically discussed and compared. This paper reviews the performance of the anode materials for application in Li-ion batteries.

Experimental

Properties of Nanotubes Evaluated

The properties and characteristics of the nanotube materials evaluated as part of this study are summarized in table 1. Figure 1(a) shows the scanning electron micrographs of the COTS nanotubes and the MCMB graphite material used as the standard.

SWNT and MWNT can be selectively synthesized in various ways. The most common techniques used are: arc discharge, laser ablation, chemical vapour deposition, flame synthesis and gas-phase decomposition of CO (HiPCo) (ref. 7). In every method of CNT production, the impurities are always present. These impurities include fullerenes, carbon-coated metal and metal carbide nanoparticles, hydrocarbons, amorphous carbons, catalyst residues, and other graphitic debris. As a result, the CNTs must be purified. Removal of these impurities is never easy and has hindered the progress in testing the properties of CNTs. Several purification procedures have been reported (ref. 8). A limited amount of CNTs evaluated at NASA Glenn went through a purification procedure. Most of the CNTs were evaluated as received—some were purified by the suppliers and others were not.

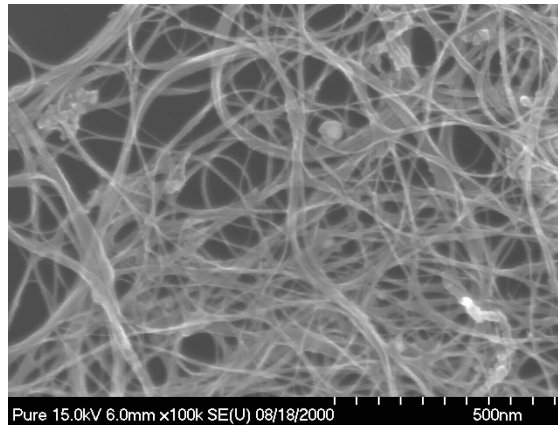
TABLE 1.—PROPERTIES OF COTS CARBON NANOTUBES VERSUS SOA GRAPHITE

| Source | Process | Particle Size | % CNT | Impurities |
|--------------|-------------------|--|-------|------------------------------|
| Tubes@Rice | Laser | D = 15 nm dia; L = 0.2-2 μm | 90 | Ni/Co catalyst particles |
| CNI | HiPCo | D = 50 nm dia L = 0.1-2 μm | 90 | <15 wt% ash |
| MER SWNT | Arc | D = 1.2-1.4 nm L = 10-50 μm | 12 | Fullerene, MWNT, amorphous C |
| MER MWNT | Arc | D = 140 \pm 30 nm L = 7 \pm 2 μm | 90 | Amorphous C |
| SES Research | Arc | D = 2-20 nm L = 5-550 μm | 75 | Amorphous C; Ash |
| NanoLab | CVD | L = 1-5 μm | 95 | Fe, Co, Ni |
| MCMB | 2800 heat treated | 25 μm grain size | NA | NA |

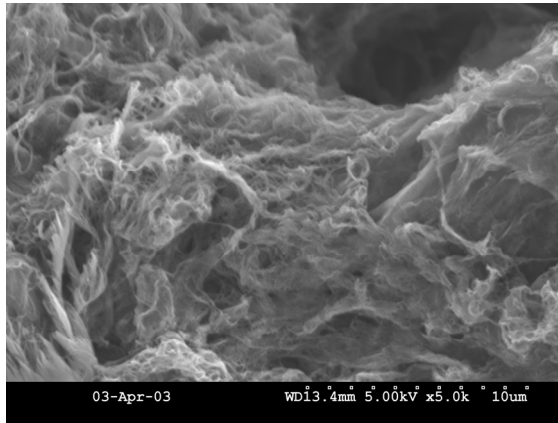
- 1) **Tubes @Rice**—The Tubes@Rice (Rice University) carbon nanotube was produced based on the pulsed laser vaporization of metal/carbon target in a furnace at 1100 °C which was first developed by Professor Smalley (ref. 9). The material consist of greater than 90 wt% SWNT with the principle impurity being nickel and cobalt catalyst particles, 3 to 15 nm diameter, over coated with a thin onion-like layer of graphitic carbon. To facilitate later processing, the SWNT was shipped as slurry in toluene. Toluene is advantageous because it produces a very porous SWNT mat upon configuration or filtration. The toluene is then rinsed off the slurry with methanol and water. The Scanning electron micrograph (SEM) of the SWNT after filtration is shown in figure 1(a).
- 2) **Carbon Nanotechnologies, Inc. (CNI)**—Rice University gave Houston-based Carbon Nanotechnologies, Inc. (CNI), whose SEM shown in figure 1(b), exclusive license to its carbon nanotube technology. CNI utilized the HiPCo (Shippensburg Pump Co., Inc.) process, a high pressure process using carbon monoxide, as feedstock, to create high purity Buckytubes (ref. 10), which are SWNTs that approach molecular perfection. These fullerene molecules are carbon cylinders with a diameter of only one billionth of a meter. They have the electrical conductivity of copper, thermal conductivity of diamond, and tensile strength 100 times that of steel.
- 3) **Materials and Electrochemical Research Corporation (MER)**—The MER materials shown in figure 1(c), were procured both as-produced SWNT and 95 percent pure catalytic MWNT. The as-produced SWNT, made by the Arc process (ref. 11), has about 12 wt% nanotube content. The powder is not pure and contains 25 wt% metal catalysts particles, ca. 10 wt% fullerenes (C60, C70, etc.) and ca. 10 wt% MWNT and other graphitic structures.
- 4) **SES Research**—As-produced SWNT and MWNT, purified opened end SWNT, and purified MWNT were procured from SES Research for this study. As produced SWNT are formed in a carbon arc in the presence of a metal catalyst/The SWNT physical properties ranges from 1.2 to 1.4 nm in diameter and 2 to 5 µm in length. The as-produced SWNT contain 20 percent nanotubes with the remaining material consisting of metal catalyst, carbon-coated metal nanoparticles, amorphous capon and other carbon nanoparticles. The purified opened end SWNT, as shown in figure 1(d), were treated to open the ends of the nanotubes, and remove the amorphous carbon and nanoparticles which produces up to 75 percent pure nanotubes and larger percentage of open end tubes.
- 5) **Nanolab**—Aligned multiwalled carbon nanotubes acquired from Nanolab, Inc were grown by dc hot-filament plasma Chemical Vapor Deposition (CVD) (ref. 9). These MWNTs come in two different structures—hollow and bamboo. NASA GRC procured both structures for this study but due to time constraint only the bamboo structure was evaluated (fig. 1(e)).
- 6) **Mesocarbon Microbeads**—Carbon-based negative electrodes (anodes) made from (MCMB) in Li-ion served as the standard for performance comparisons. The MCMB anodes have a stable lithium intercalation capacity of 325 mAh/g on high-rate charge-discharge cycling. The MCMB powder is derived from pitch and has been recognized as an excellent precursor to parts with high density and strength. MCMB is supplied by Osaka Gas Co., Japan and is graphitized at 2800 °C.

Electrode Fabrication

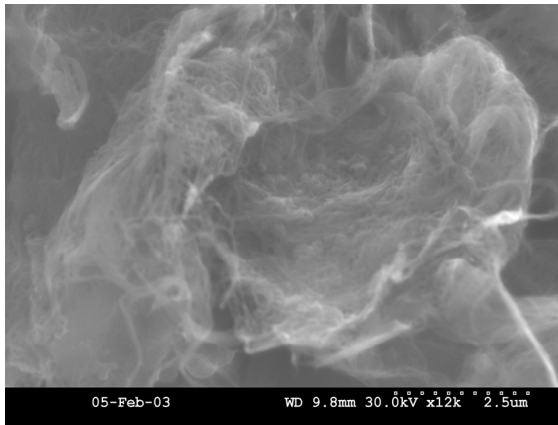
For electrochemical measurements, a typical working electrode was cast from CNT (80 to 95 wt%), and poly(vinylidene fluoride) (PVDF, Aldrich) binder (5 to 20 wt%). A solvent, 1-methyl-2-pyrrolidinone (Aldrich), was added to wet the mixture. No carbon black was added to the samples unless specified. A sonicator (Sonicator 3000, Misonix) was used to disperse the mixture to form uniform slurry which was cast on cleaned copper foil followed by drying at 150 °C in a vacuum oven for 24 hr.



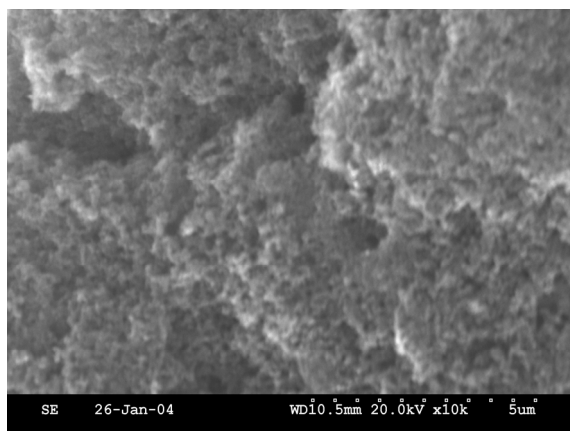
(a) SWNT from Rice University, 100K magnification.



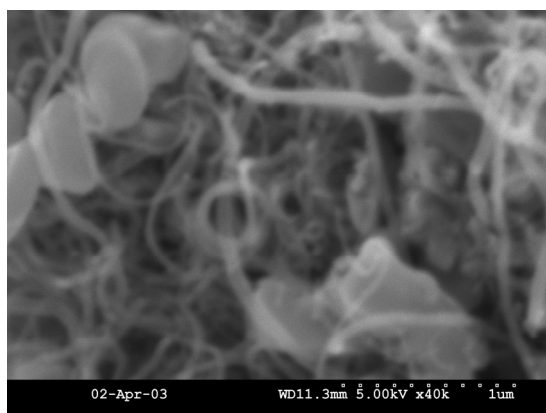
(b) CNI, 5K magnification.



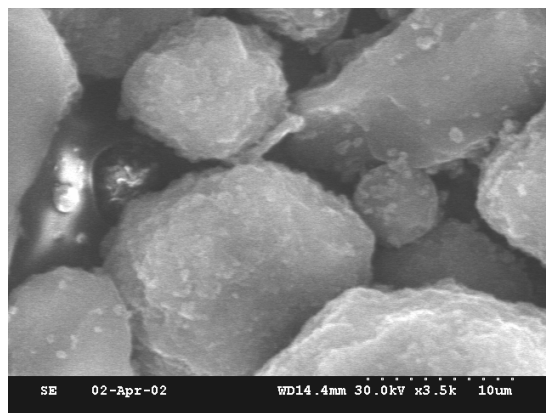
(c) MER, 12K magnification.



(d) SES Research, 10K magnification.



(e) Nanolab, 40K magnification.



(f) MCMB25 graphite, 3.5K magnification.

Figure 1.—SEM pictures of commercial off the shelf CNT powders and carbon: (a) Rice, (b) CNI, (c) MER, (d)SES Research, (e) Nanolab, (f) MCMB graphite.

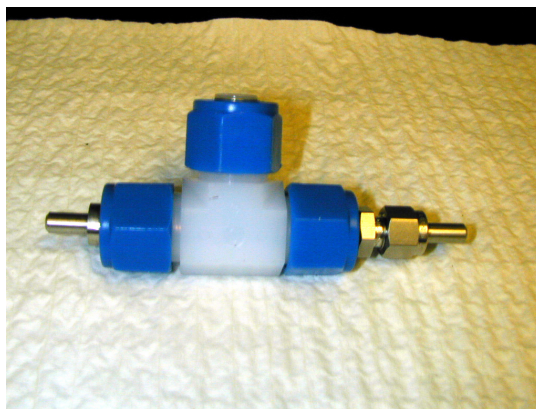


Figure 2.—T-cell for half cell cycle testing.

Half-Cell Construction

A conventional T-cell (fig. 2), fabricated in-house, was employed for all half-cell cycle testing using lithium foil (Aldrich) as the counter electrode. A 1-inch diameter Celgard 2500 separator, wetted with 1 M LiPF_6 in 50/50 (v/o) mixture of ethylene carbonate/dimethyl carbonate (LP30, Merck Corporation) was sandwiched between the 7/16 in. diameter CNT working electrode and 1/2 in. lithium counter electrode to prevent electrical shorting while allowing ionic conduction. All cells were assembled and tested in a glove box (Braun) filled with purified argon gas (<1 ppm H_2O , <1 ppm O_2).

Electrochemical Testing

Galvanostatic deintercalation and intercalation, coulombic efficiency, and voltage profile are three parameters used in this study to reflect cell cycling performance.

Galvanostatic experiments were conducted between 0.010 and 3.0 V using an Arbin cyler (Arbin BT-2000) at a current of 30 mA/g. The specific Li capacities (amount of Li measured per unit of carbon, mAh/g-C) were calculated from the time and the current used per unit weight.

Results and Discussions

High discharge capacity is necessary to satisfy the increasing demand for energy density. Loss of lithium ions results in fading capacity. Some lithium ions may be exhausted in the SEI film-formation process during the first charge. Superior coulombic efficiency is advantageous for reaching optimal discharge capacity.

Galvanostatic Deintercalation/Intercalation of CNT Electrodes

Electrodes made from Single Walled Carbon Nanotubes (SWNT).—The cycling characteristics of the CNT electrodes were studied (in galvanostatic mode) by cycling half cells at room temperature. Initial testing was performed on electrodes made from SWNTs (Rice, MER, CNI). Figure 3 displays the discharge capacity performance of these three SWNT electrodes and the MCMB graphite electrode as a function of cycles. Initial capacities of SWNT electrodes from Rice, MER and CNI are 131 mAh/g, 103 mAh/g, and 77 mAH/g respectively with slight decrease on succeeding cycles. For comparison, the initial capacity of the MCMB graphite electrode is 270 mAH/g, which is about 2 to 4 times higher than the CNT electrodes. Rice SWNTs show faster capacity fading compared to the MER and CNI SWNT electrodes with the MER SWNT electrode displaying an almost constant capacity for 5 cycles while the capacity of the MCMB graphite electrode increased to approximately 115 percent of its initial capacity value.

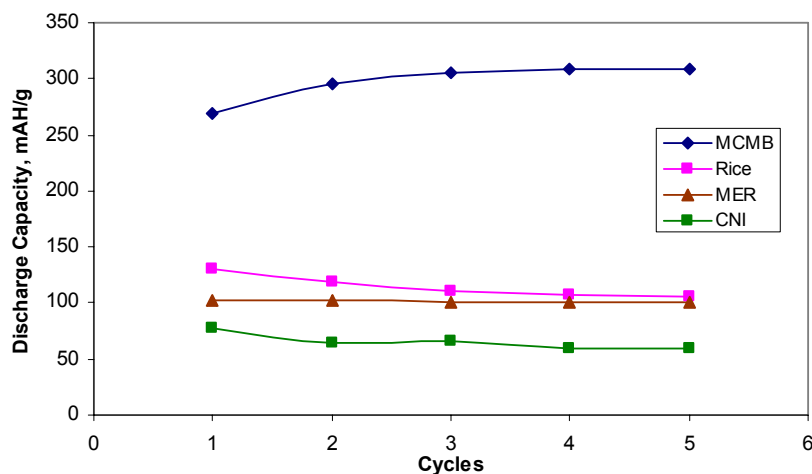


Figure 3.—Cell performance of SWNT and graphite electrodes.

Figure 4 shows the voltage profiles of these SWNT electrodes compared to the MCMB electrode for the initial two cycles. Table 2 depicts the capacity values of these electrodes. All of the anodes made from the SWNT show a significant permanent capacity loss during the initial cycle due to the anode surface passivation film formation. The permanent capacity loss, defined as the capacity difference between the first and second discharge, is called *irreversible capacity*. This surface film is formed in alkali metal systems, and in particular, lithium metal anodes and lithium intercalated carbon anodes due to the relatively low potential and high reactivity of lithium toward organic electrolyte. Compared to the first cycle irreversible capacity of the MCMB graphite electrode significant values are depicted on the first cycle of all the three CNT electrodes with Rice and CNI having the highest values. *Irreversible capacity* ranged between 392 to 1250 mAh/g (table 2) for the CNT electrodes. The MCMB graphite electrode has about 5 to 16 times lower irreversible capacity value of 77 mAh/g compared to CNT electrodes. *Reversible capacity*, which is defined as the capacity difference between the first discharge and the second charge, is in the range of 76 to 131 mAh/g for the CNT electrodes while the MCMB graphite electrode is about 2 to 3.5 times higher than those of the CNT electrodes as summarized in table 2.

TABLE 2.—IRREVERSIBLE AND REVERSIBLE CAPACITIES OF BOTH SWNT AND GRAPHITE ELECTRODES

| Electrode | Irrev. Cap, mAh/g | Irrev. Cap, % | Rev. Cap, mAh/g |
|-------------|-------------------|---------------|-----------------|
| MER | 392 | 79 | 103 |
| Rice | 801 | 85 | 131 |
| CNI | 1250 | 94 | 76 |
| MCMB | 77 | 22 | 268 |

The first discharge profiles of the three SWNT electrodes, as well as the MCMB graphite electrodes, showed definite plateaus in the voltage range of 0.5 to 0.8 (fig. 4). These phenomena correspond to the electrolyte decomposition and cause the formation of a passive film or solid electrolyte interface (SEI) layer on the carbon surface (ref. 10). This film formation protects lithium from further reaction with the solvent. These plateaus were observed only in the first discharge cycle.

Following the voltage plateaus at around 0.8 to 0.9 V, the voltage declined with a sloping profile, and the majority of Li was inserted into the CNTs below 0.2 V. No voltage plateau was observed below 0.2 V in the charge/discharge curves, indicating the absence of a well defined insertion staging phenomena in the CNTs.

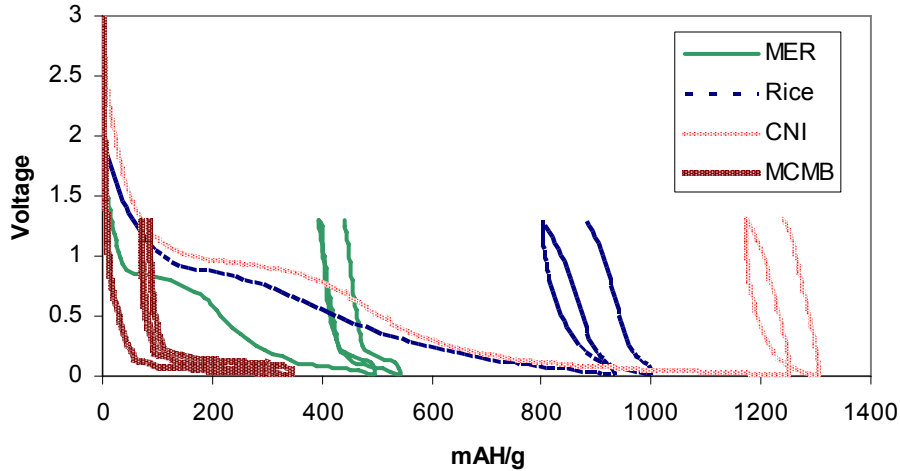


Figure 4.—Voltage profiles of SWNTs and MCMB graphite electrodes (1st two cycles).

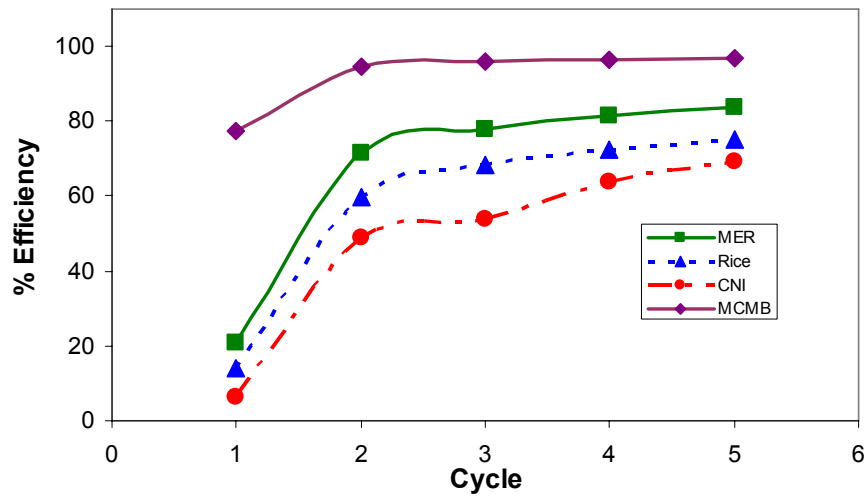


Figure 5.—Efficiency versus cycles of SWNTs.

Figure 5 illustrates the coulombic efficiency of the three SWNT and the MCMB graphite electrodes. Coulombic efficiency, Eff, is the ratio of the discharge or deintercalation capacity, Q_{dis} , to the charge or intercalation capacity, Q_{chg} .

$$Eff = (Q_{dis}/Q_{chg}) \times 100\% \quad (1)$$

A low initial efficiency was depicted for all three CNTs. The value jumps higher at cycle 2 and levels off the succeeding cycles. MER SWNT electrode has the highest efficiency at 84 percent followed by the Rice SWNT electrode at 75 percent and SWNT from CNI at 70 percent. However, none of the SWNT materials approached the performance of the MCMB electrode which has an average value of 64 percent higher efficiency at the beginning of the cycle and about 13 to 27 percent higher after the fifth cycle than those of the SWNT electrodes.

An optimal carbon material for Li-ion cells should have a higher reversible capacity than the ideal theoretical value of 372 mA/h/g for graphite, while keeping a small irreversible capacity. In all cases of the SWNT CNTs electrodes reported above, the reversible capacities are lower than the graphite while the irreversible capacities are extremely high. These represent the fraction of lithium irreversibly trapped

which requires an additional mass of cathode material. It is also assumed that the SEI formation mainly contributes to the value of the irreversible capacity.

Effect of conductive diluent.—The addition of carbon black to the SWNTs was evaluated as a means to improve the specific capacity and high irreversible capacity of the anodes. Carbon black aids in improving the performance of standard graphite anodes by increasing effective electrical conductivity of the electrode by contributing to overall electrical contact among the anode particles throughout the electrode (12). Figures 6 and 7 illustrate the comparison between electrodes with and without addition of carbon black (Super P Li, Timcal). Both irreversible and reversible capacities (also summarized in table 3) increased with the addition of carbon black (5 wt%) for both the MCMB graphite and SWNT electrodes, with a significantly larger increase in the irreversible capacities for both types of electrodes—5 times and 37 times with the graphite and CNT electrodes respectively. It is desirable for electrodes to have higher reversible capacity but undesirable to have high irreversible capacity. Since the addition of carbon black will increase reversible capacity, other additives or sample preparation procedures are needed to reduce the first cycle irreversible capacity.

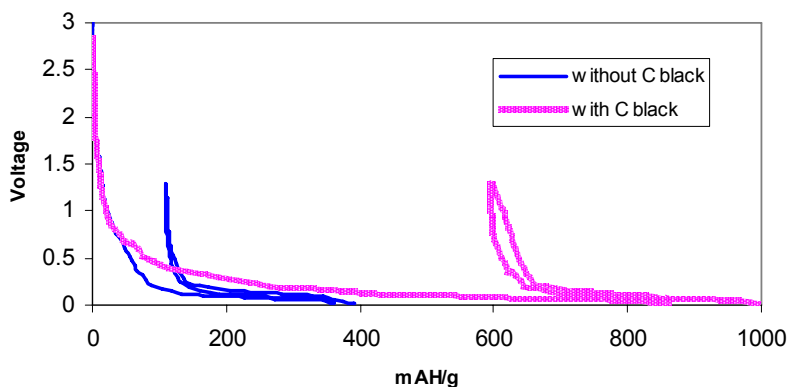


Figure 6.—Comparison of the voltage profiles of MCMB graphite electrode with and without C black.

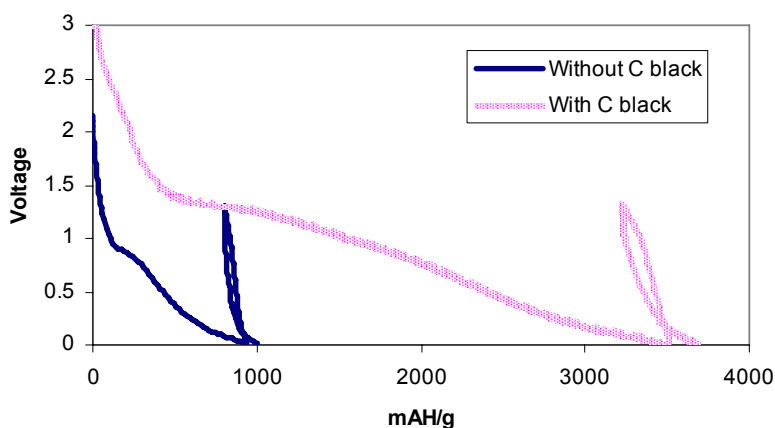


Figure 7.—Comparison of the voltage profiles of Rice SWNT with and without C black.

TABLE 3.—IRREVERSIBLE AND REVERSIBLE CAPACITIES OF SWNT AND MCMB GRAPHITE-BASED ELECTRODES (1ST CYCLE)

| Electrode | Irrev. Cap, mAh/g | Irrev. Cap, % | Rev. Cap, mAh/g |
|----------------------|-------------------|---------------|-----------------|
| SWNT with C black | 3222 | 91 | 288 |
| SWNT without C black | 801 | 85 | 131 |
| MCMB with C black | 77 | 22 | 268 |
| MCMB without C black | 110 | 30 | 252 |

Electrodes made from Multiwall Carbon Nanotubes (MWNT).—COTS multi-walled nanotubes (MWNT) from MER, Nanolab and SES Research were also evaluated. Cycling test results of electrodes made of these materials as compared with the MCMB graphite electrodes are shown in figures 8, 9, and 10 and summarized in table 4. As can be seen in figure 8, the MER, Nanolab, and SES electrodes depict almost constant discharge capacities with cycling, with the MER having the highest capacity of 175 mA/h/g. The Nanolab and SES MWNTs demonstrated capacities of 85 and 104 mA/h/g respectively. The coulombic efficiency of the three MWNT CNTs as shown in figure 10, have the same profiles as those of the SWNT CNTs (fig. 5) but at higher values (70 to 84 percent and 85 to 96 percent, respectively).

The MWNT from MER with >90 percent MWNT and <0.1 percent Fe metal content has an irreversible capacity of almost twice as high as that of the MER SWNT electrodes (605 mA/h/g for the MWNT and 392 mA/h/g for the SWNT) as shown in figures 4 and 9 and tables 2 and 3. The MER MWNT electrode has the highest irreversible and reversible capacities of all the MWNT electrodes tested. Figure 10 shows the efficiency values of the MWNT as compared to the MCMB graphite electrodes. Again, similar trend was depicted as the SWNT showed smaller differences between the MWNTs and the graphite electrodes, especially after five cycles.

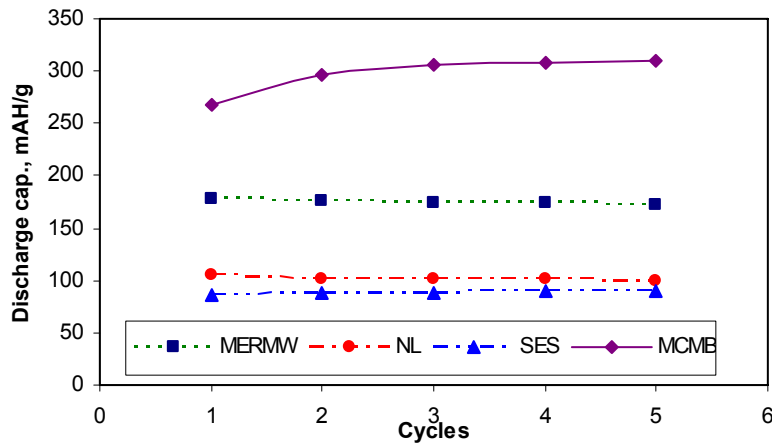


Figure 8.—Performance of MWNT electrodes as compared with MCMB graphite electrode.

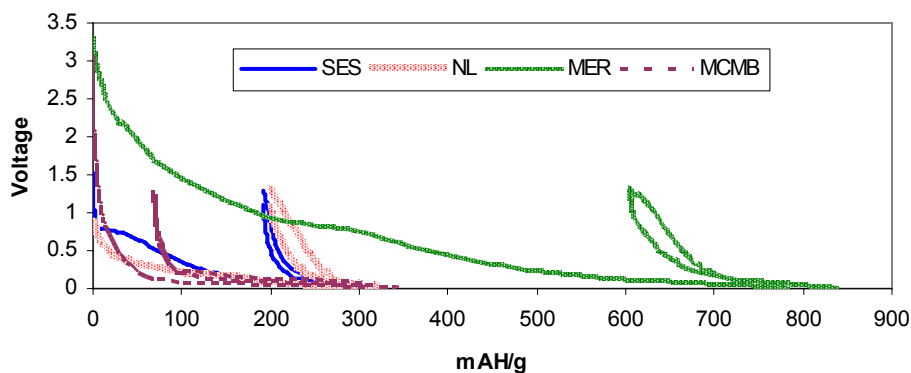


Figure 9.—Voltage profiles of MWNT electrodes.

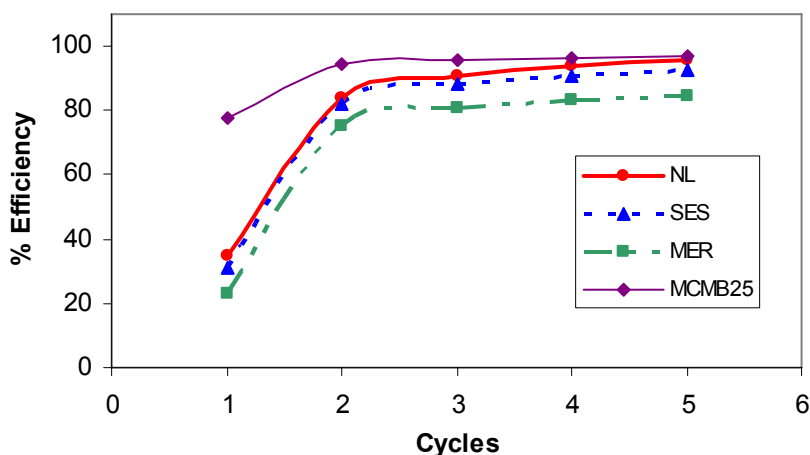


Figure 10.—Efficiency versus cycle of MWNT electrodes and compared with MCMB graphite electrode.

Effect of Purification

As mentioned earlier, one type of CNT purchased and evaluated went through an experimental purification process here at NASA GRC. The MWNT from SES Research was purified to about 85 percent CNT and compared with the *as received* MWNT as shown in table 4 and figures 11, 12, and 13. The irreversible capacity value of the *as received* SES MWNT is about 3.5 times higher (700 vs. 50 mAH/g respectively) than that of the *purified* SES MWNT. In addition, the reversible capacity of the *purified* SES MWNT is about 1.7 times higher (85 vs. 50 mAH/g respectively) than the *as received* SES MWNT as shown in table 4 and figures 11 and 12. The efficiency comparison between the *purified* and *received* SES MWNTs is also shown in figure 13. The gap between the *as received* and *purified* SES MWNT electrodes increased as the electrodes cycled.

TABLE 4.—IRREVERSIBLE AND REVERSIBLE CAPACITIES OF MWNT ELECTRODES

| Electrode | Irrev. Cap, mAh/g | Irrev. Cap, % | Rev. Cap, mAh/g |
|------------------------------|-------------------|---------------|-----------------|
| NanoLab MWNT | 304 | 66 | 105 |
| SES MWNT, <i>as received</i> | 700 | 93 | 50 |
| SES MWNT, <i>purified</i> | 192 | 69 | 65 |
| MER MWNT | 605 | 77 | 178 |
| MCMB graphite | 77 | 22 | 268 |

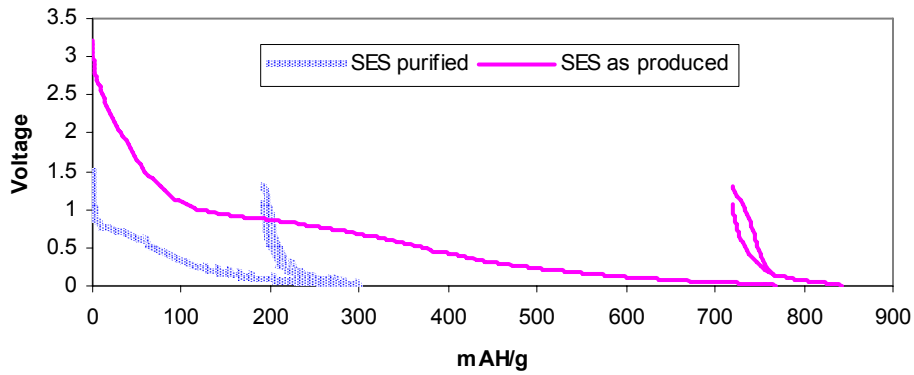


Figure 11.—Voltage comparison between the as received and purified SES Research MWNT.

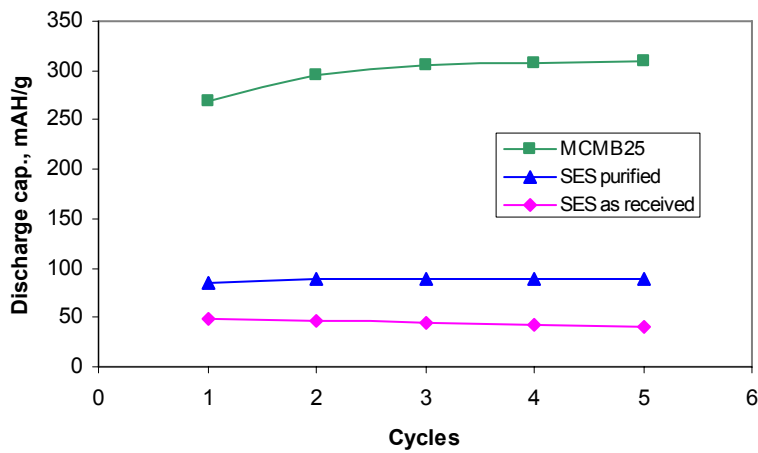


Figure 12.—Performance comparison between the purified and as received SES MWNT electrodes (compared with the MCMB graphite electrode).

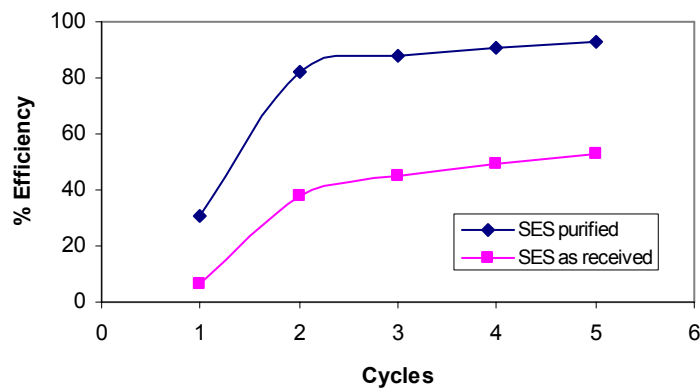


Figure 13.—Efficiency versus cycle comparison between the purified and as received SES MWNT electrodes.

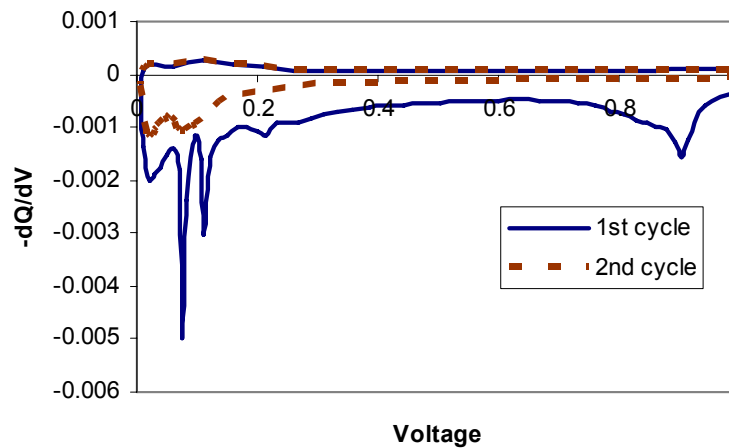
In this study, purification of the SES MWNT showed marginal improvements in performance. The *as received* CNT soot contains a large amount of impurities. The main impurities consist of graphite sheets, amorphous carbon, metal catalyst and the smaller fullerenes. These impurities interfere with many of the

CNTs desirable properties. It is preferable to obtain CNTs as pure as possible. Some of the common industrial techniques use strong oxidation and acid refluxing techniques, which have an adverse effect on the structure of the tubes. Materials used in this report have purities of ~75 to 90 percent.

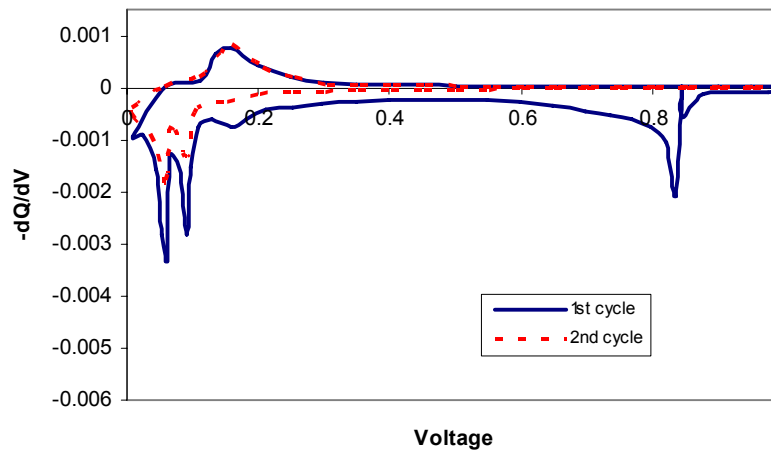
Raffaella's (ref. 12) highly purified SWNTs (over 99 percent) for Li-ion batteries achieved much greater reversible capacity than the purified CNTs (75 to 90 percent) used in this study. Degree of purification is an important factor needed in the development of high capacity carbon nanotube electrodes for Li-ion cells.

Differential Capacity Data

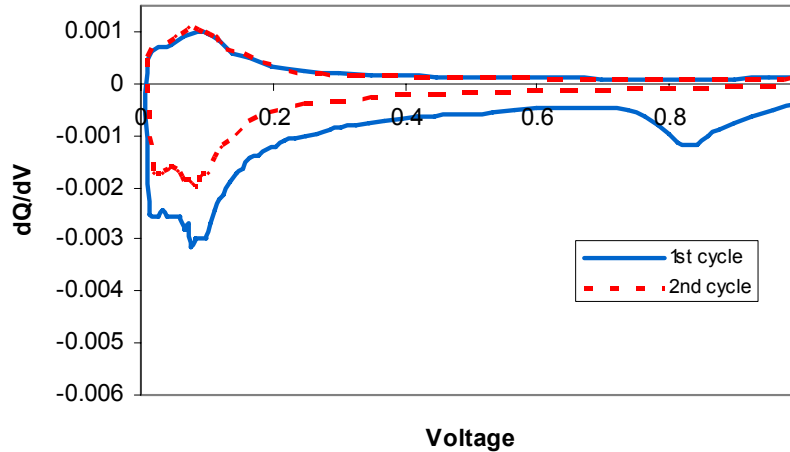
Differential capacity (dQ/dV) analysis was used to aid in identifying the stages of lithium insertion and other electrode processes (ref. 13). Plots of dQ/dV for CNT electrodes and MCMB graphite electrodes are compared in figures 14(a) to (d). In general, all samples clearly showed peaks corresponding to insertion of Li ions.



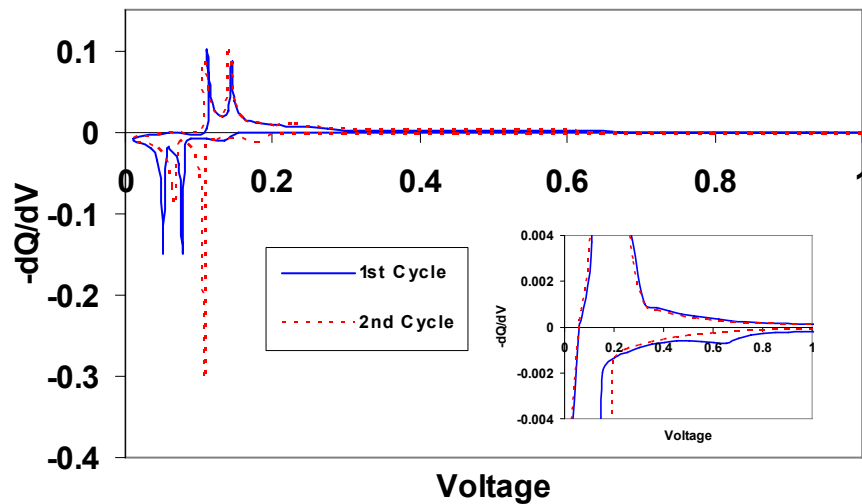
(a) Rice SWNT



(b) MER_SWNT



(c) MER_MWNT



(d) MCMB Graphite electrode

Figure 14.—Derivative plots of first and second cycles of CNTs and graphite electrodes.

A pronounced peak at 0.8 to 0.9 V, corresponding to SEI formation, appears in the first cycle and is broader for the MER_MWNT compared to the other CNTs. This peak vanishes after the first cycle, as expected. In comparison, the SEI-formation peak for MCMB electrode (fig. 14(d), inset) is much smaller than those in the CNT electrodes. Additional peaks also appear at ~ 0.051 and 0.078 V on discharge and 0.14 and 0.11 V on charge during the first cycle of the MCMB electrode. These peaks also appear in the second cycle but shifted towards higher voltages.

An optimal carbon material for lithium-ion cells should have a higher reversible capacity than graphite, while keeping a small irreversible capacity. The reversible capacities of the CNTs evaluated and reported here are consistently lower than the MCMC carbon control while the irreversible capacities are extremely high. It is assumed that the SEI formation mainly contributes to the value of the irreversible capacity. Another factor that needed to be addressed is the closed and relatively defect-free structure of the CNTs which makes the interior of the CNTs inaccessible for intercalation without processing. The closed-structured inner core spaces of the CNTs are usually not accessible for intercalation and Li can not diffuse through the carbon pentagons and hexagons under the current experimental conditions. Several methods have been developed to open and generate defects on the nanotubes. It has been reported that an

ultrasonic purification process can induce a considerable number of defects on the nanotubes (ref. 14) and decrease the length of the CNTs segments (ref. 15). Due to their relatively large diameters, considerable amounts of Li⁺ ions can readily diffuse into these structurally damaged CNTs through the opened ends and defects sites to give an enhanced capacity. Another way to increase capacity is to shorten the CNTs segments by chemically etching (ref. 16) or by using a chemical and heat treatment. Mechanical ball-milling of the CNTs may also lead to a significant enhancement of the reversible capacity and the reduction of the irreversible capacity (ref. 17).

Conclusion

A series of graphite and CNT electrodes was tested for electrochemical performance in lithium-ion cells. CNT samples showed lower reversible capacities and significantly higher irreversible capacities than the graphite electrodes. The problem with high irreversibly capacity and low reversible capacity is not well understood and will need further investigation. Another concern is the need to purify the CNTs. Different purification and processing methods used would resolve this low reversible and high irreversible capacity issue. Due to the importance of purification in nanotube research, nanotube manufacturers are exploring new methods in purifying both the SWNTs and the MWNTs. As more techniques become available, different results will be achieved. Care should be taken in choosing the technique as its effect on the entire sample will also depend on the composition and the amount of the active material. A desirable technique would involve tearing down the carbon impurities and metals without changing the structure of the nanotubes.

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| 14. ABSTRACT Rechargeable lithium ion (Li-ion) battery technology offers significant performance advantages over the nickel-based technologies used for energy storage for the majority of NASA's missions. Specifically Li-ion technology offers a threefold to fourfold increase in gravimetric and volumetric energy densities and produces voltages in excess of three times the value of typical nickel-based battery systems. As part of the Advanced Battery Technology program at NASA Glenn Research Center, a program on the evaluation of anodes for Li-ion cells and batteries was conducted. This study focused on the feasibility of using carbon nanotubes as anodes in Li-ion cells. Candidate materials from multiple sources were evaluated. Their performance was compared to a standard anode comprising mesocarbon microbeads. In all cases, the standard MCMB electrode exhibited superior performance. The details and results of the study are presented. | | | | | |
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