

ELECTROCHEMICAL CHARACTERIZATION OF FLAME FORMED CARBON NANOFIBERS AND NANOTUBES

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Introduction

The flame formed carbon nanotubes recently developed at NASA Glenn Research Center were grown using a number of different catalysts on a number of different substrates[1]. The carbon nanotubes have been examined using SEM and TEM. The electrochemical properties of the nanotubes were studied recently. This report compares the effects of catalysts and substrates used during the fabrication process on the multi-wall carbon nanotube's behaviors during the cycles of lithium intercalation-deintercalation. Four different catalysts (Ni, Cu, Co, and Fe) and two different substrate materials (Ni foil and Stainless steel mesh) were used in this study.

The objectives of this research were (1) to understand how the catalysts and substrates affect the properties of the final carbon nanotube products, and (2) to explore the possibility of using carbon nanotubes as the anode material in lithium-ion batteries.

Experimental

The carbon nanotube fabrication process was described elsewhere. TEM results indicated that the carbon materials made from nickel catalyst/stainless steel mesh substrate were different from the other samples in that they were not hollow. They were actually nanofibers. The nanotubes and nanofibers examined in this study were divided into 3 groups:

- (1) Nanotubes/nanofibers made from the Ni, Cu and Co catalysts on stainless steel mesh,
- (2) Nanotubes made from Cu and Fe catalysts on the nickel foil substrate, and
- (3) Nanofibers made from nickel catalysts on stainless steel mesh, with the samples post-treated by 1000°C nitrogen and/or CVD carbon coating,

Individual nanocarbons grown on the substrates were then placed in a cell as the working electrode. The cell used ethylene carbonate and dimethyl carbonate 50/50 (volume %) mixture as the electrolyte, saturated LiI as the lithium salt, and lithium metal

as the material for both reference and counter electrodes. The nanotubes or nanofibers then went through cycles of charge-discharge using a current of 30 mA/gm of nanocarbon.

Results and Discussion

Figure 1 shows the voltage of the nanotube anodes made from Cu and Fe catalyst on nickel foil during the first cycle of lithium insertion-release. This figure indicates that:

(1) For both sample, the voltage values during the lithium-release period went up from zero to 0.3V slowly, then accelerated as the voltage getting higher than 0.3V. This is similar to the voltage curves for typical lithium intercalation into graphite materials. Hard carbon, on the other hand, has a voltage curves rise quickly from zero to > 0.3V. The results suggest that, in terms of the chemical reactivity, the carbon nanotubes obtained from this method were graphite-like.

(2) At the beginning of the 1st lithium insertion, the voltage values stayed at about 2.5V for some time. This means that in the nanotubes, there were a significant amount of defects, possibly in the form of loose electrons that readily bonded to lithium ion.

Such chemical reactivity of the loose electrons in carbon materials was not observed before. Previous research works [2, 3, 4] on nanotubes did not have this plateau at 2.5V, possibly because the majority of the loose electrons had already bonded to the more reactive lithium salt (e.g., LiPF₆, LiClO₄) before the charge-discharge cycling. (The research works in this report used the less reactive LiI). Previous research works when LiI was used [5,6] did not have this plateau, either, possibly because the carbon materials being examined were not nanocarbons.

(3) The voltage curves have plateau at about 0.8V. This is in agreement with all previous research works on nanotubes [2,3,4]. The plateau at 0.8V is believed to be the result of solvent decomposition [7]. This plateau is believed to be defect-related, and the length of the plateau is believed to be proportional to the defect density of the carbon materials.

Figure 2 shows the voltage of the nanocarbon anodes during the first cycle of lithium insertion-release. Three samples were made using stainless steel mesh as substrate and Cu, Co, and Ni as catalysts. The fourth sample used the nickel catalyzed nanofibers post heat treated at 1000°C in nitrogen as the anode. The heat treatment was made to cause carbonization that reduced the defects in the carbon material.

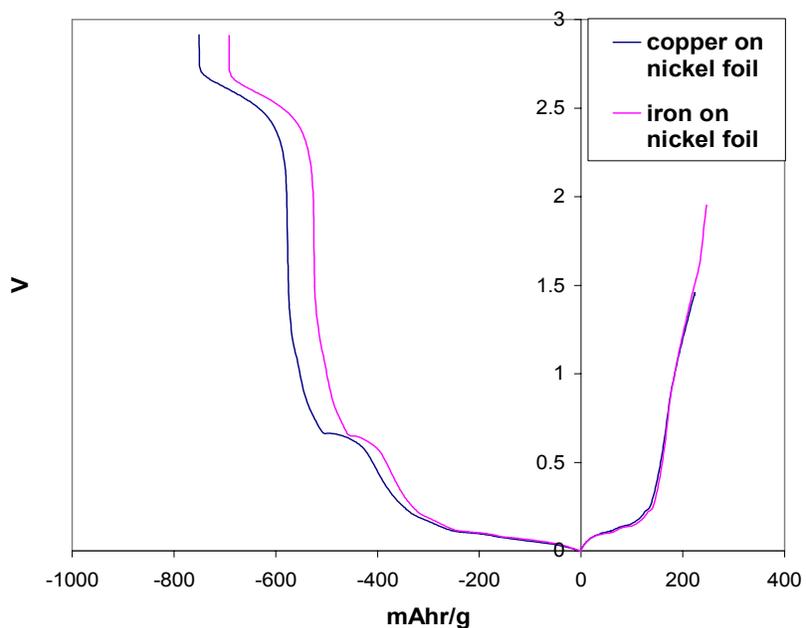


Figure 1. Voltage of anodes made from carbon nanotubes fabricated using copper or iron catalyst /nickel foil substrate during the first cycle of lithium insertion-release

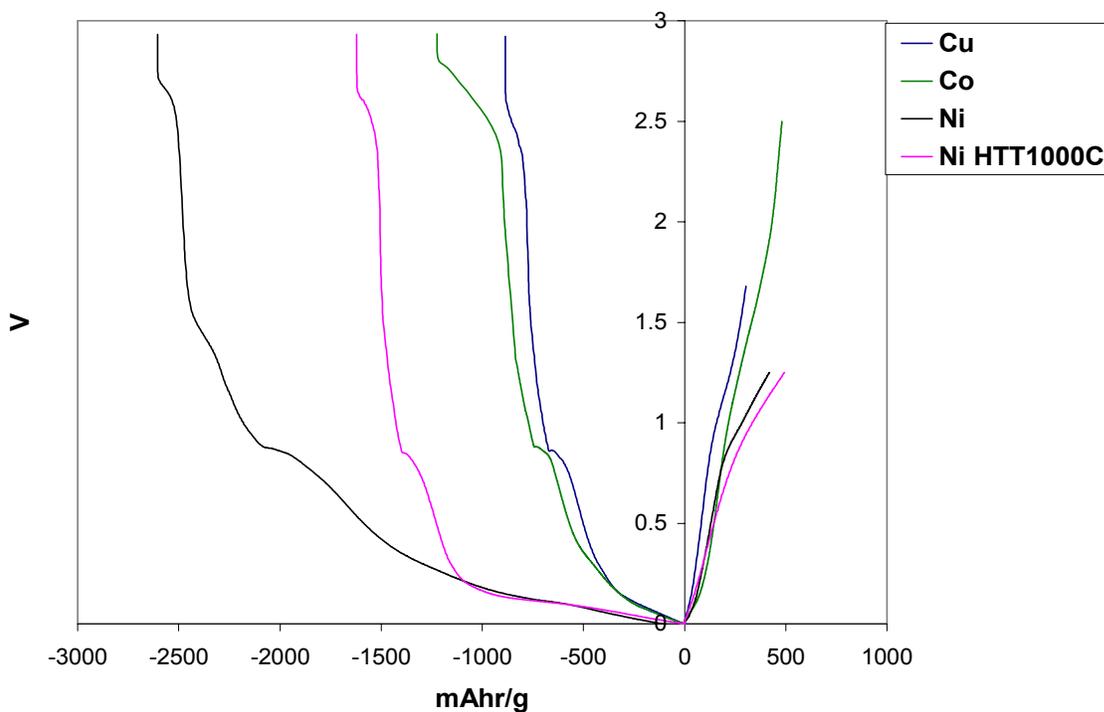


Figure 2. Voltage of anodes made from carbon nanotubes fabricated using different catalysts/stainless steel substrate during the first cycle of lithium insertion-release

Figure 2 indicated that:

(1) Nickel catalyzed carbon nanofiber anode had the highest irreversible and reversible capacity. If the cut-off voltage for the cycling was between 0 and 2.5V, the reversible capacity was larger than the 372 mAh/g., the theoretical maximum for a graphite sample. This suggests the mechanism for lithium insertion into these nanofibers was different from that for graphite. The high irreversible suggests that the samples contained a large number of defects. Heat treatment at 1000°C in nitrogen reduced the defects significantly, but far from completion.

(2) The voltage values during the lithium-release period went up from zero to >0.3V quickly. These results suggest that, contrary to the graphite-like nanotubes grown from the nickel substrate and described in Figure 1, the nanotubes and nanofibers grown from the stainless steel mesh were similar to hard carbon.

(3) The 2.5V and 0.8V plateau of the voltage curves in Figure 2 are similar to those described in Figure 1. This suggests the two set of the nanocarbon has similar types of defects.

The long Plateaus at 2.5V and 0.8V indicate that carbon nanotube would have a very high irreversible capacity if it is used as the anode material in lithium-ion batteries. In order to reduce the lengths of the plateau and to understand the defects that cause the plateau, five nanotube samples were made from the same process and then treated differently before the electrochemical experiments. The nanofiber samples were grown using nickel catalysts on stainless steel substrate. The post-treatments involved 1000°C heat treatment in nitrogen, which resulted in defect reduction by carbonization and changes of carbon bulk structure, and CVD carbon coating, which resulted in defect reduction by surface carbon reactions only. The post-treatment of these five samples and their reversible and irreversible capacities after one insertion-release cycle were summarized in Table 1. The voltage during the 1st half cycle of lithium insertion are described in Figure 3.

The data indicated that 1000°C post-treatment reduced the irreversible capacity, but improve the reversible capacity only slightly. CVD carbon coating, on the other hand, was more effective in improving the reversible capacity. When the sample was heat treated at 1000°C then carbon coated, the effect of reducing irreversible capacity and improving irreversible capacity became much enhanced. With more complete CVD carbon coating and carefully designed temperature histogram during heat treatment in other environment such as hydrogen [8], further increase in reversible capacity and reduction of irreversible capacity are believed possible.

Table 1. First cycle reversible and irreversible capacities to insert and release lithium for the five nanotube samples grown similarly from nickel catalysts on stainless steel substrate and post-treated differently

Post-treatment	1 st cycle reversible capacity (mAh/g)	Irreversible capacity after 1 st cycle (mAh/g)
None	5860	180
CVD carbon coating	1648	290
Heat treated at 1000°C in N ₂	1390	215
CVD carbon coating, then Heat treated at 1000°C in N ₂	1600	278
Heat treated at 1000°C in N ₂ , then CVD carbon coating	2130	580

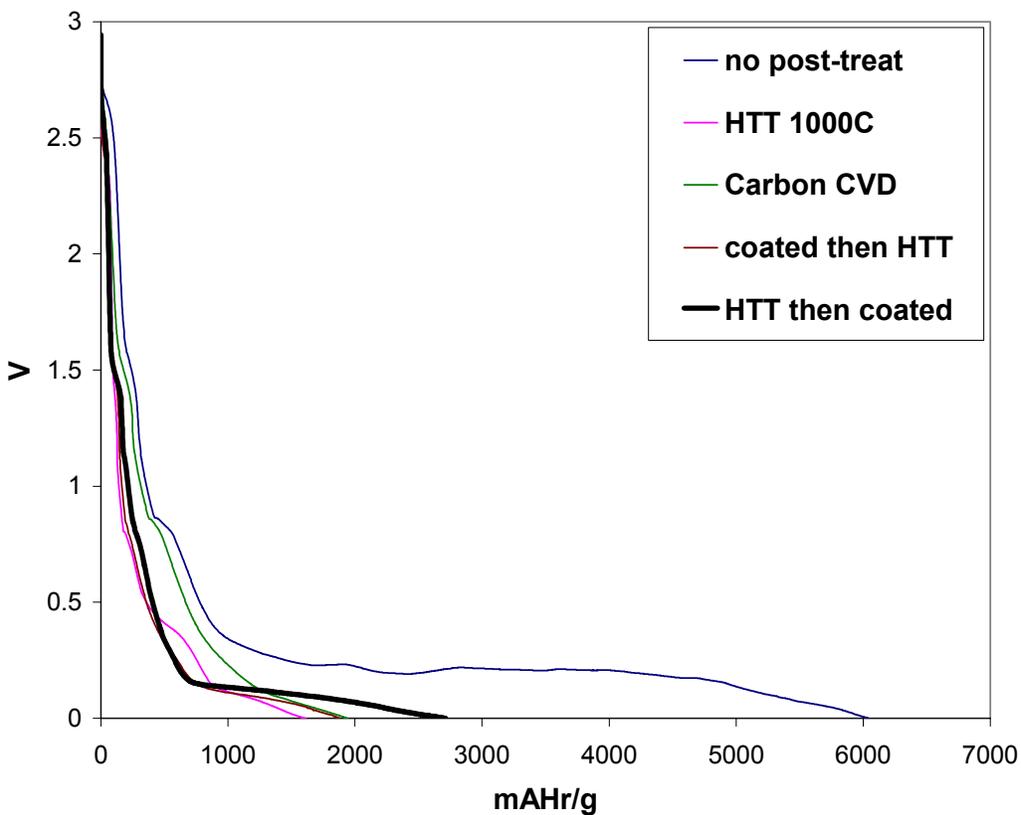


Figure 3. Voltage of anodes made from carbon nanotubes fabricated using from nickel catalyst/stainless steel substrate with 5 different post-treatment methods during first half cycles of lithium insertion

Conclusions

The carbon nanotubes/nanofibers grown from a nickel foil substrate and stainless steel mesh substrate were graphite-like and hard-carbon-like, respectively. Nickel catalysts produced carbon nanofibers that, when used as the anode material in lithium batteries, had a higher reversible capacity and higher irreversible capacity than the nanotubes produced by other catalysts. All nanocarbon has defects that were responsible for the long plateau for the voltage curves during the cycles of lithium insertion-release at constant rate. The defects responsible for the 2.5V plateau were believed to be loose electron that readily bonded to lithium ion. The defects responsible for the 0.8V plateau were commonly observed in the experiments of lithium intercalation of carbon materials. All defects can be reduced by 1000°C post-treatment in nitrogen and/or CVD carbon coating. The post-treatment of 1000°C post-treatment in nitrogen followed by CVD carbon coating was found to be best in reducing irreversible capacity and improve reversible capacity of the carbon nanotube as anode materials in lithium-ion batteries.

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