

# LITHIUM RESERVOIR NANOCARBONS FOR LITHIUM ION BATTERIES

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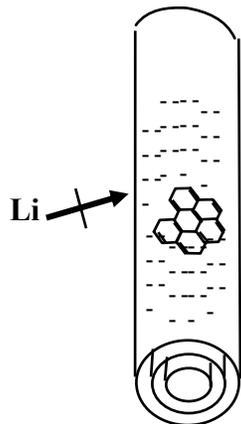
## Abstract

Carbon nanofibers (CNF) having a nested conical structure have been studied to determine their utility as an improved anode for lithium ion batteries. Their morphology allows greater access to the edges of graphitic planes than either conventional fullerene multiwall nanotubes (MWNT), or so-called bamboo carbon nanotubes (BCNT). Therefore, it is expected that CNF will be more easily intercalated with Li ions than other nanocarbons. The anticipated performance features are higher capacities and faster charge/discharge rates, both of which would have major operational advantages for Li-ion battery anodes. In this work CNF was formed into binderless, 6-mil thick paper electrodes for anode testing, with one smooth face suitable for making good electrical contact to a copper current collector. Other similar electrodes were prepared with silicon powder dopants for higher charge storage capacity. To date, high discharge rates and high capacities have been observed in some samples, but two issues remain. The high surface area of the nanofibers creates high irreversible capacity, and the samples with silicon rapidly lose capacity upon cycling. Strategies for dealing with these issues are reported.

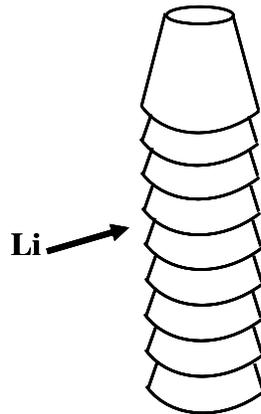
## Introduction

Over the past decade, lithium ion battery technology has achieved considerable commercial impact. As mature as this industry is, there are still good prospects for major performance improvements through the use of advanced materials. For example, recent literature suggests that new types of anode nanocarbons can yield large increases in energy storage and charge/discharge rate capability. Some single- and multiwalled carbon nanotubes have shown reversible intercalation capacities in excess of  $\text{LiC}_6$ : SWNT buckypaper produced  $460 \text{ mAhg}^{-1}$  (1), while one variety of slightly graphitized MWNT gave  $640 \text{ mAhg}^{-1}$ (2). These large capacity numbers have been explained by hypothesizing lithium occupancy at nano-defect locations and at sites between closely-spaced nanotubes. Theoretical calculations support the energetic favorability of hosting lithium atoms or nanoclusters in this way (3).

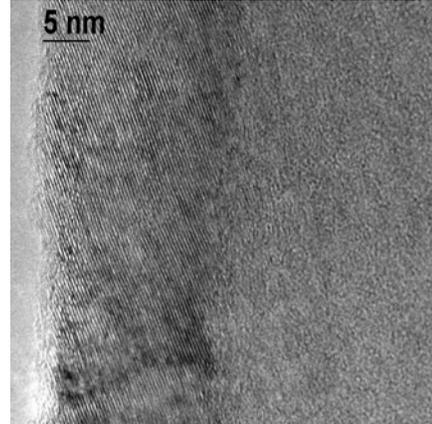
Calculations also show that it should be possible to store lithium within the inner core of a carbon nanotube (3). In other words, the hollow core of a nanotube could act as a reservoir of lithium nanoclusters, providing reversible storage capacity well in excess of  $\text{LiC}_6$ . Until very recently there has been no direct experimental evidence for this phenomenon, probably because the carbon nanotubes tested in the past have had unsuitable structures. Most multi-wall nanotubes have a concentric cylindrical structure (as shown in Figure 1) that provides only a high energy lithium diffusion path through the wall to the hollow tube core. In Figure 1, another path to the core is through the tube end, and these tube ends are often capped. Even when the ends are open, adsorption/co-insertion of electrolyte can inhibit lithium entry.



**Figure 1.** Concentric multi-wall nanotube with a carbon basal plane surface



**Figure 2.** Multi-wall nanotube with a nested conic structure



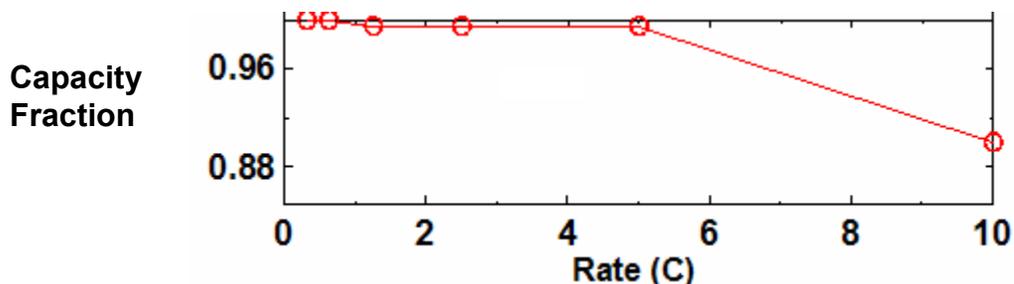
TEM image of PR-25 nanofiber wall and hollow core.

In contrast, Figure 2 is a tubular structure with carbon edge planes on the surface. Lithium can intercalate between the conical shells, diffuse to the inner core, and accumulate. Such a process has been reported in a recent study on similar “bamboo” carbon nanotubes with a structure close to Figure 2, but with segmented features that resemble bamboo(4). High Resolution TEM has shown that BCNTs develop nanocrystallites of lithium inside the tube cavity if the applied potential is zero volts vs. lithium or slightly below. The lithium nanocluster deposits disappear when the sample is de-intercalated (reservoir effect). A reversible capacity of  $460 \text{ mAhg}^{-1}$  is reported.

In this study, a nanofiber of similar structure from Applied Sciences, whose trade name is PR-25 is examined. It has the structure shown in Figure 2, namely an off-axis tubular arrangement of carbon planes with carbon edge sites at the nanotube surface, and its diameter is comparable to BCNTs, about 50-80nm. Two things distinguish PR-25 from BCNT. First, its structure down the tube length is more regular, without the segmented features of BCNT. Second, PR-25 is available in commercial quantities.

Another type of Applied Sciences nanofiber (PR-24, which is like PR-25 but with a thin amorphous carbon coating) has been previously examined for lithium ion intercalation. It showed 250-275 mAh/g of charge storage, a respectable but not stellar value for carbon. This is the charge storage observed if the sample is tested above zero volts vs. the lithium potential, with no attempt to produce the reservoir effect.

PR-24 nanofibers have also shown excellent rate features, as seen in Figure 3 below.



**Figure 3.** Fraction of charge storage capacity as a function of speed of charge/discharge for a PR-24 nanofiber electrode.

The graph shows that 90% of the full capacity of 260 mAh/g is retained at a 10C rate. A “1 C” rate means full charge or discharge in an hour, and so a 10 C rate means full charge in 1/10<sup>th</sup> the time, or six minutes. This is unusually fast for carbon materials in general, although nanomaterials often show good rates of charge/discharge due to their high surface areas.

### **Experimental**

Electrode sheets of pure PR-25 were prepared by a papermaking process at Inorganic Specialists, Miamisburg Ohio. Samples were generally 6-7 mils (0.15-0.18 mm) in thickness. The surface area was approximately 40 m<sup>2</sup>/g. Electrochemical half-cell testing was performed either by Professor J.R. Dahn at Dalhousie University in Canada, or at the General Motors Research facility in Warren Michigan.

### **Results**

To date, samples of PR-25 show higher reversible capacities (300mAh/g) than PR-24, and the capacity seems to increase with time. It is unclear whether this is an indication of the reservoir effect, since the potentials used in the testing were slightly above zero volts vs. lithium. As of this writing, testing below zero volts is being performed, a procedure that is usually avoided because this lithium plating potential can form lithium dendrites on electrode surfaces that short cells and cause fires. One can consider the reservoir effect as a lithium plating process that occurs on the inside of the tube. With the right structure of nanofiber, it is apparently energetically favored to accumulate lithium in the tube core rather than plate or form dendrites externally in a limited voltage range.

Since the structure of PR-25 is close to PR-24, comparable high rates of charge/discharge are expected. As mentioned above, this is partially due to the high surface areas of these nanomaterials. However, high surface area material tend to produce high irreversible capacity, which is lithium that is lost (scavenged) during the first discharge cycle as a solid electrolyte interphase (SEI) layer forms on the carbon surface. The irreversible capacity in PR-24 and PR-25 is about equivalent to the reversible capacity, and this is an unacceptable ratio for purposes of constructing practical batteries. Thus if nanofibers are to be used in practical batteries, it is necessary to reduce their high irreversible capacity.

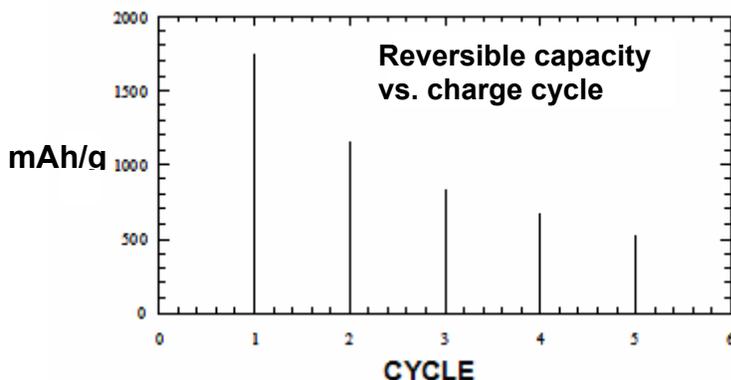
### **Nanofiber Combinations with Silicon**

The nanofiber's high irreversible capacity might be acceptable if an overwhelmingly high reversible capacity is created to make the irreversible capacity a small fraction of the total capacity. This can be achieved by using highly active additives incorporated into the nanofiber paper.

A focus of recent research in lithium ion batteries is the investigation of metals/alloys that form alloys with lithium, such as silicon. Such materials can store over 10 times the energy of today's negative electrodes made of carbon. These alloys are destined to create a revolution in batteries and impact a wide range of applications. The principal disadvantage of silicon is the huge volume change (250%) it undergoes as it incorporates and releases lithium during charge and discharge(5). It has been directly observed with in-situ microscopy that particulate forms of silicon will fragment and/or move as a result of these large volume changes, isolating them from electrical contact with rest of the electrode assembly. The net result is a rapid loss of capacity upon repeated charge and discharge. As one might expect, this problem is more associated with large particles than small ones due to less total structural stress. It is also manifested more with crystalline materials than amorphous silicon forms.

Silicon has a theoretical Li storage capacity of 4200 mAh/g. If silicon particulates in a nanofiber matrix can be made into a practical electrode, the high capacity of the silicon could produce an enormous reversible capacity that would mitigate the irreversible capacity of the nanofibers. For example, an electrode made with 50% silicon and 50% nanofibers could have a reversible capacity of about 2000 mAh/g and an irreversible capacity of about 200 mAh/g. Such silicon/nanofiber combinations are currently being studied.

These mixtures have yet to show the cycling features desired for commercial applications. Below is an example of a nanofiber/silicon mixture rapidly losing its capacity over the first few cycles. The capacity eventually stabilizes to a value that is close to the carbon component alone.

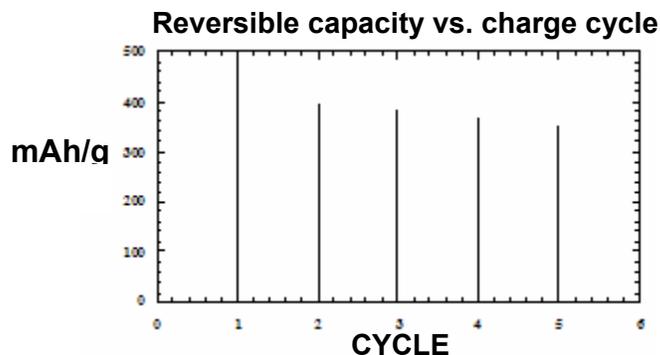


**Figure 4.** Reversible capacity vs. charge cycle for a nanofiber paper with 45% silicon content.

Three strategies are being pursued to improve cycling features. The first strategy is the use of tethering agents to bind the silicon to either the nanofibers or to an incorporated polymeric binder. The second strategy is to not fully utilize the capacity of the silicon. By charging the silicon with lithium to less than its full capacity, the silicon will swell less and be less likely to fragment. The third strategy is to immobilize the silicon by blending a carbonizable binder into the nanofiber/silicon mixture and firing the sample to create a rigid electrode.

The latter strategy is showing some success. Figure 5 shows how a sample made with a carbonized binder has a slower capacity loss relative to other samples. The

absolute value of the capacity in this example is still relatively low. Future work will focus on increasing the capacity while maintaining capacity over a large number of cycles.



**Figure 5.** The capacity vs. cycle plot for a nanofiber/silicon combination made with a carbonizable binder.

### Acknowledgement

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