

# HIGH ENERGY ANODE MATERIALS AND NOVEL ELECTRODE ARCHITECTURE FOR LITHIUM ION BATTERIES

*Junbing Yang, Wenquan Lu, Khalil Amine*

Chemical Sciences and Engineering Division, Argonne  
National Laboratory, Argonne, Illinois 60439, USA

*Chian Q. Liu*

X-ray Science Division, Argonne National Laboratory,  
Argonne, Illinois 60439, USA

## Introduction

Development of a safe and cost-effective lithium-ion battery (LIB) for a plug in hybrid electric vehicle (PHEV) with a 40 mile all electric range that meets or exceeds all performance goals set by the US Advanced Battery Consortium (USABC) represents a major challenge in the battery research society. Among all the components, anode plays an important role in achieving these goals. Current anode materials for LIB consist of two types of materials: intercalation and alloy-forming materials. Graphite is a material based on intercalating lithium ion into its layers for storage of lithium. It exhibits good cycle stability but low capacity (theoretical capacity is 372 mAh/g based on  $\text{LiC}_6$ ). Alloy-forming materials include Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, and Mg, which store lithium via formation of a lithium alloy. Among these materials, silicon is most attractive since it has low discharge potential, the highest known theoretical capacity (4200 mAh/g based on  $\text{Li}_{1.4}\text{Si}$ ), and a large natural reserve (silicon is the second most abundant element on earth). The disadvantage of alloy-forming materials like silicon is the fast capacity fading due to huge volume expansion, which results in pulverization of the electrode and electric contact loss between electrode materials. (Silicon undergoes up to 400% volume change during the alloying and de-alloying process). To develop high energy density LIBs for PHEVs, we prepared a silicon-coated carbon nanotube (Si-CNT) core-sheath structured material as the anode material for LIB to increase the anode energy density. The idea is to use carbon nanotubes as the support material to stabilize a high capacity alloy-forming material like silicon. The CNTs were further organized in an aligned status (ACNT) and thus can form a novel electrode structure, which brings additional benefits to LIB compared to the non-aligned configuration.

## Experimental

The CNTs were prepared through a one-step, chemical vapor deposition (CVD) process using inexpensive aromatic hydrocarbons and transition metal compounds [1]. Briefly, a liquid mixture of aromatics and volatile transition metal organometallics, such as xylene and Ferrocene, is injected into the low-temperature zone of a CVD reactor and is fully vaporized. The vapor mixture is carried downstream to the high temperature zone by hydrogen and inert gas and is subsequently decomposed over a quartz substrate. The silicon

deposition was carried on by DC magnetron sputtering in the Advanced Photon Source (APS) deposition lab at Argonne National Laboratory (ANL) [2]. The silicon layer thicknesses were controlled by the linear translation speed of the sample carrier and were calculated to be about 100 nm. The electrode was made by casting slurry of 90 wt% Si-CNT composites, and 10 wt% polyvinylidene fluoride (PVDF, Kureha 1100) dispersed in N-methyl-2-pyrrolidone on a copper foil. The electrodes were then dried completely in a vacuum oven at 75 °C for overnight. The performance of the Si-CNT composites materials were evaluated in 2032-type coin cells. The cell was configured with a lithium foil as negative electrode, a 25  $\mu\text{m}$  Microporous Trilayer Membrane (Celgard 2325) as separator, the above prepared electrode as positive electrode, and an appropriate amount of electrolyte. The electrolyte was 1.2M  $\text{LiPF}_6$  dissolved in the mixture solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a ratio of 3:7 by volume. The electrochemical performance of the Si-CNT composites materials were investigated by cycling the cell between 0 to 1.5 V with a constant current of C/2 using a computerized battery test systems manufactured by Maccor, Inc.

## Results and Discussion

Figure 1 shows the SEM image of CNTs. The CNTs typically have diameters in the range of 2 to 50 nm and length in the range of 5 to 50  $\mu\text{m}$ , which fall in the typical thickness of a battery electrode. At elevated temperatures, the Ferrocene decompose to finely dispersed, equally sized iron nanocrystallites over the quartz substrate. The iron crystallites act as the catalytic centers to decompose and convert xylene into a graphene plane during the carbonization. The graphene layer subsequently folds and grows around the catalytic center into individual multi-layer carbon nanotubes. Due to the even distribution of the iron particles, the carbon nanotubes grow parallel to each other at equal rate to form a dense, uniform layer with the identical vertical alignment to the substrate.

Figure 2 shows the cycling performance of this Si-CNT material. The reversible capacity of this Si coated CNT is determined to be over 750 mAh/g. About 80% capacity retention is obtained after 60 cycles at room temperature. For comparison, silicon powder (~10  $\mu\text{m}$  average diameter) lost over 90% of its capacity after 10 cycles, as reported in the literature [3]. The results demonstrate that CNTs stabilized silicon during repeated alloying and de-alloying processes and possessed 2 times the reversible capacity of state-of-the-art graphite materials. In the Si-CNT material, the CNTs served as support materials and buffer layer for silicon, therefore, Si can expand without being in physical contact with the current collector where a problem of delamination usually occurs—a process that would jeopardize the integrity of the negative electrode. Higher stability of silicon during cycling is achieved due to the outstanding elastic deformability of carbon nanotubes, which accommodate the tensions caused by the huge silicon volume change. The voids between the nanotubes provide free space for silicon volume expansion and

contraction during the lithiation and de-lithiation processes. For the silicon powder or film, silicon is pulverized during repeated cycling. A schematic depiction of morphological changes of Si during electrochemical cycling is shown in figure 3.

Furthermore, The CNTs can be synthesized in an aligned status. The Si-ACNT materials offer a novel nanostructured electrode with a vertically-aligned one-dimensional structure, which has the potential to provide additional advantages to LIB. ACNTs will be grown directly on the metallic current collector substrate and be used as electrode. A schematic of the Si-ACNT anode configuration is shown in Fig. 4. Fast charge and discharge rates may be achieved because of the unique aligned structure of carbon nanotubes and their mesoporosity and high electronic conductivity. Further more; significant weight reduction and simplified electrode fabrication process can be achieved since the electrode will be formed during the Si-ACNT syntheses, which eliminate the need for binder, conductive additives, and the mixing step [4].

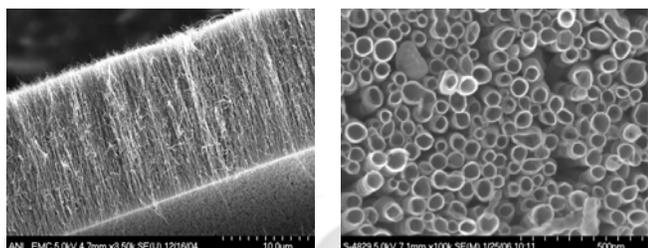


Fig. 1 SEM images of CNTs

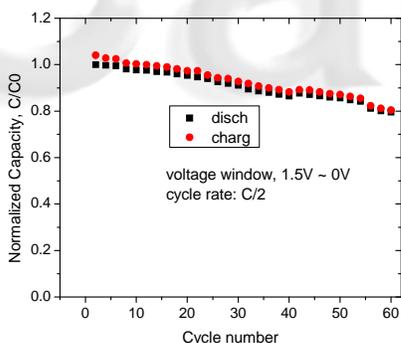


Fig. 2 Stability of Si-ACNT during cycling

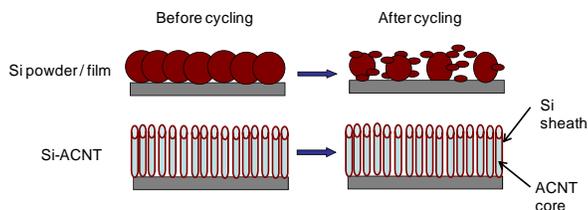


Fig. 3 Cartoon depiction of morphological changes of Si during electrochemical cycling

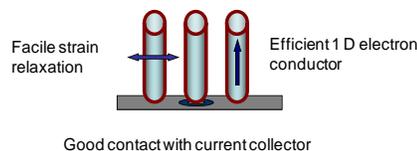


Fig. 4 Proposed structure and mechanism of Si-ACNT as anode material for Li-Ion battery

## Conclusions

We successfully prepared silicon coated carbon nanotubes through magnetron sputtering methods and tested it as anode materials for lithium ion battery. The reversible capacity of this Si coated ACNT is determined to be over 750 mAh/g. About 80% capacity retention is obtained after 60 cycles at room temperature. The results demonstrate that the CNTs stabilized the silicon during repeated alloying and de-alloying processes. We are working to further improve the capacity and cycle stability through different silicon deposition approaches and exploring the novel aligned carbon nanotube based battery electrode architecture.

**Acknowledgment.** The electron microscopy was performed at the Electron Microscopy Center for Materials Research at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

## References

- [1] Yang J, Liu D-J. Three-dimensionally structured electrode assembly for proton-exchange membrane fuel cell based on patterned and aligned carbon nanotubes. *Carbon*. 2007; 45(14):2845-8.
- [2] Liu C, Erdmann J, Macrander A. The APS Coating Facilities, SRI-CAT Newsletter, April 1997, Vol. 3, pp. 2-4, <http://www.aps.anl.gov/sricat/news.html>.
- [3] Ryu JH, Kim JW, Sung YE, Oh SM. Failure modes of silicon powder negative electrode in lithium secondary batteries. *Electrochemical and solid-state letters*. 2004;7:A306.
- [4] Yang J, Lu W. Nanotube composite anode materials suitable for lithium ion battery applications, US provisional patent application, filed on November, 5, 2009.