

# High Capacity Anode Materials for Lithium-Ion Batteries

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## Abstract

This paper examines high capacity anode materials for lithium-ion cells. Improvement in the cycleability of silicon was obtained by coating silicon particles with carbon using chemical vapor deposition. This material maintained 500mAh/g for more than 30 cycles in a voltage range of 10 mV – 0.70 V versus Li. In addition to silicon-based materials, commercial graphite materials, with carbon and silicon coatings, have also been studied for use as high capacity anode materials. These coated graphite materials exhibited a higher specific capacity compared to the 372 mAh/g for standard graphite.

## Introduction:

The use of lithium-ion batteries has increased in recent years in military, aerospace, and commercial applications. This increased demand is due to lithium-ion's favorable characteristics such as long cycle life and wide temperature range. As this technology continues to grow, research efforts continue to optimize higher energy and power densities.

Current lithium-ion battery systems utilize a carbonaceous anode, due to its exceptional reversibility and safety issues. One alternative to carbonaceous anode materials is silicon-based anodes. Typical carbon-based anodes have discharge capacities of approximately 290 mAh/g [1], where silicon has a theoretical capacity of 4000 mAh/g. Substituting silicon for carbon as an anode material could potentially increase the capacity of lithium-ion batteries. However, poor reversibility of the alloying reaction between lithium and silicon at room temperature is a major obstacle in commercializing silicon as an anode material in lithium-ion batteries [2, 3]. Carbon has been successfully coated onto silicon powder recently using a CVD method with toluene or benzene vapor and N<sub>2</sub> as a carrier gas [4]. Specific capacities reached 800mAh/g during coin cell cycling. Carbon coatings on graphites are also being researched so that graphitic anodes can be used with propylene carbonate based electrolytes. This PC-

based electrolyte would increase the low temperature range of lithium-ion batteries.

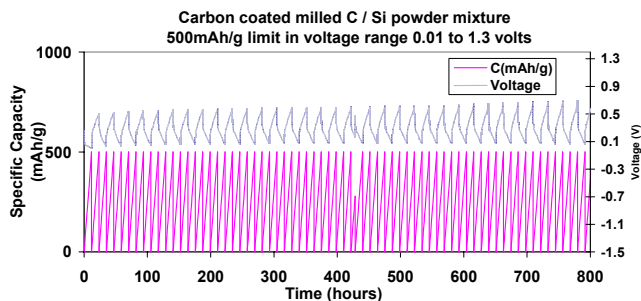
## Experimental:

Carbon was deposited on a milled mixture of silicon and diluent carbons. The CVD system included a reactor tube positioned vertically with a porous frit in the center. The milled silicon/carbon sample was placed on the frit and low-level (ppm) concentrations of an organic precursor were introduced to the system in nitrogen as a carrier gas. The temperatures and deposition times varied from 900°C to 1100°C and 0.5 to 2.0 hours, respectively. Samples were coated one to four times, using a mortar and pestle in between runs to break up agglomerates. The samples were then made into a slurry with and organic solvent and PVDF binder and coated onto a copper substrate. Coin cells were manufactured with the silicon-based electrodes against lithium metal and cycled from 0.01 to 1.3 V, with a 500mAh/g capacity cutoff.

Pure natural graphite materials were also coated with carbon and/or silicon via CVD. Four different samples were developed for electrochemical analysis. The graphite with no deposition was used as a baseline. It was compared to a carbon-coated graphite, a graphite with silicon embedded on the graphite surface, and lastly, a graphite with silicon on the surface coated with carbon. The first three samples were made into slurries containing an organic solvent and PVDF binder. Then they were coated onto a copper substrate and inserted into coin cells against lithium metal. The coin cells were cycled from 0.01 – 1.3 V with no capacity cutoff. All four samples were implemented into 7 Ah prismatic cells using a cathode made with LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub>.

## Results and Discussion:

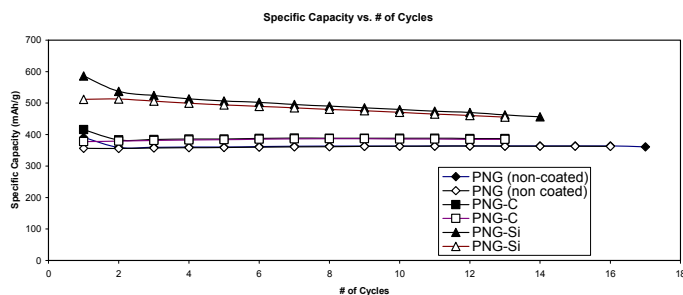
Specific capacity and voltage profiles for the initial 33 cycles of coin cell containing the carbon-coated silicon material are shown in figure 1.



**Figure 1.** Carbon Coated Milled C / Si Powder Mixture

This silicon sample was heated up to 950°C in ambient air. Using toluene in N<sub>2</sub>, carbon was deposited on the sample for 30 minutes. After one run, the sample was re-mixed and coated a second time. The current density for the initial cycling was 0.2 mA/cm<sup>2</sup>. While cycling at 100% coulombic efficiency (charge capacity to discharge capacity), the cell remained in a voltage range of 0.01 and 0.7 V for over 30 cycles.

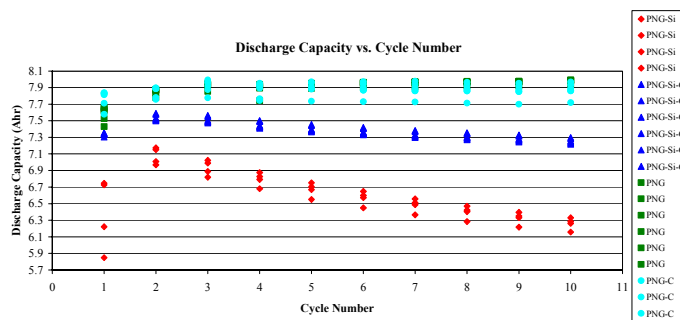
The graphite and coated graphite materials were inserted into coin cells for galvanostatic testing. Observing the capacities and reversibility of the three materials (figure 2), the carbon-coated graphite (PNG-C) exhibited a higher specific capacity, approximately 385 mAh/g, than seen with the baseline graphite (PNG).



**Figure 2.** Specific Capacity vs. # of Cycles

The graphite with silicon embedded on the surface (PNG-Si) showed a significant increase in initial capacity (over 500 mAh/g), indicating that the lithium is alloying with the silicon. Because of the poor reversibility of silicon, a capacity loss of approximately 10% per cycle occurs. By the tenth cycle, the specific capacity decreased to about 455 mAh/g.

The four graphite materials, PNG, PNG-C, PNG-Si, PNG-Si-C, were analyzed in 7 Ah prismatic cells. PNG refers to the baseline natural graphite. PNG-C is a carbon-coated version of PNG. PNG-Si refers to the natural graphite with silicon embedded onto the graphite surface. PNG-Si-C is a carbon-coated version of PNG-Si. The data in figure 3 is the first ten cycles for all of the 7 Ah cells. Four 7 Ah cells of PNG-Si were fabricated. The other three materials have six 7 Ah cells each.



**Figure 3.** Discharge Capacity vs. Cycle Number

Looking at the discharge capacities for the 7 Ah cells, significant differences exist between the carbon-coated Si material versus the Si material without carbon coating. The CVD procedure for carbon deposition improved specific capacity and the fade rate. The cells were limited to 8.0 Ah so that the cathode wouldn't be utilized beyond 165 mAh/g. The PNG cells and the PNG-C cells both produced about 7.9 Ah. The carbon coated material and the baseline material have similar cycling data through the first 10 cycles. The comparison between PNG-Si and PNG-Si-C shows the difference in capacity and capacity degradation. PNG-Si cells peaked at 7.1 Ah and faded to about 6.3 Ah by the tenth cycle. The PNG-Si-C cells had a higher capacity of 8.0 Ah, and a smaller fade rate that resulted in 7.3 Ah after 10 cycles. The coating of the silicon particles that are on the graphite surface have greater reversibility than seen with the silicon particles on PNG-Si.

### Conclusions:

Silicon-based anode materials showed improved electrochemical performance when the particles were carbon-coated via CVD. Milled silicon powder displays much less reversibility than the CVD coated version of silicon, which remained coulombically efficient for about 40 cycles. Optimizing the CVD system to produce more uniform and repeatable coatings can extend this cycle life.

The 7 Ah prismatic cells also point out the improved performance when the graphitic powders with surface silicon were coated with carbon. The fade rate was less with the carbon coating. Also, specific capacity increased with the coated material. Initial cycling of the PNG and PNG-C materials are similar in terms of reversibility and specific capacity. Cycle life could be improved with carbon coating on the graphite. This will be analyzed when more cycles are completed.

### Acknowledgements

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