



Goal: To test for improvements in Life Cycle and Charge Capacity when modifying the Graphite Anode with Silicon.

Introduction

Lithium-Ion batteries are quickly becoming a widely-implemented technology being adopted by industries that have both small and large power demands alike. As demand for better batteries increases, the race for battery optimizations continues to accelerate, different avenues of research are being probed in the search for the best solution. One avenue of study concerns the material modifications of core battery elements like the anode and cathode. In this study, we research the effects of different thicknesses of **microcrystalline columnar silicon** on the life cycle of a typical coin-cell battery.

Theory

Modern Rechargeable Batteries consist of one cathode-anode pair, a separator that partitions the electrodes, and an electrolyte that allows the ions to flow between the cathode and anode. Graphite is the most commonly used anode material in Lithium Ion Batteries (LiB), as it is very safe and cheap to produce. However, it lacks a high specific charge capacity (372 mAh/g) and has generally poor cycling efficiency. These two setbacks limit its application for devices that require higher power and storage.

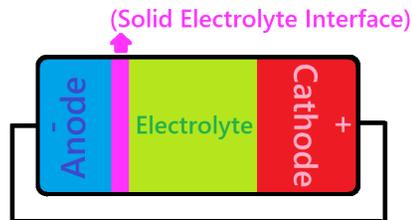


Figure 1a. Schematic of a typical lithium-ion battery (LiB) with an electrolyte and Solid Electrolyte Interface (SEI) between the anode and cathode.

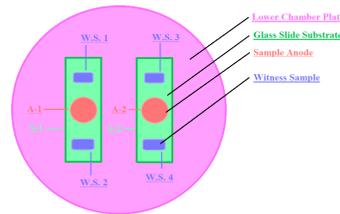


Figure 1b. Representative schematic of a graphite anode with a thin film of silicon and an SEI layer of a new composition distinct from 1a.

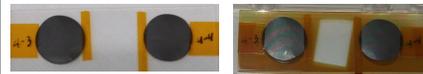
Combining graphite and a very high specific capacity (~3500 mAh/g, more than 10x graphite), but it is a very poor choice for an anode material due to the volume expansion of +300% that occurs when saturated with lithium. Like graphite, however, it is very cheap to manufacture. In light of the low cost and high manufacturability of both silicon and graphite, one major avenue of research is to explore what happens when they two are combined. A combination of graphite and silicon would be expected to have the effect of enhancing the overall cycling efficiency of a battery while minimizing the volume expansion and degradation that comes with a thick film of silicon.

Approach & Study

Deposition Experimental Setup



2. Schematic for Experimental Setup for Graphite Anodes inside PECVD chamber.



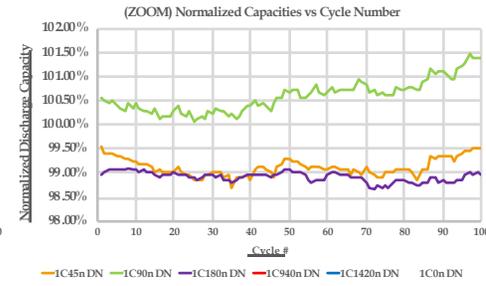
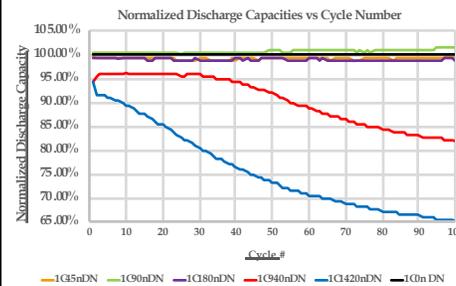
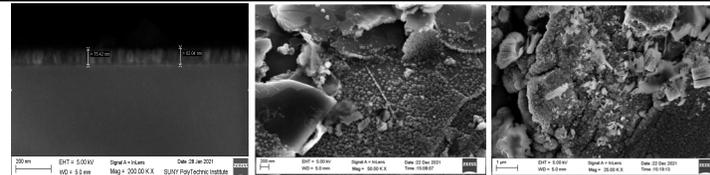
- Silicon thin films were deposited on top of graphite through a deposition method called Plasma Enhanced Chemical Vapor Deposition (PECVD). This method uses ionized argon gas to dissociate precursor gases for deposition of a material onto a substrate. Silane (SiH₄) was the precursor gas used to generate the silicon film.
- The experimental setup for the silicon deposition is shown to the left. 18 mm coin anodes were placed onto glass substrates and bound by the edges with vacuum tape. Witness samples were placed above and below the anode samples for SEM analysis of the silicon structure.
- Batteries were assembled using the modified Si-Gr anodes and Nickel-Manganese-Cobalt (NMC) cathodes with LiPF₅ as the electrolyte. The components of the battery were constructed using an EL-PAT Cell and tested using Wavenow Potentiostats with Gamry testing software, Aftermath graphical software, and ArbinSys graphical and testing software.

3. Graphite Anodes: a. Before (Left) and b. After PECVD. (Right).

Results & Discussion

SEM Images

- 4a. (Left) ~80 nm Deposition of Microcrystalline Columnar Silicon.
- 4b. (Middle) ~940 nm Deposition of MC-Silicon
- 4c. (Right) ~1420 nm Deposition of MC-Silicon



5a. (Left) – Graph of Experimental Battery Capacities Relative to the Average Capacities Per Cycle of the Batteries with Pristine Graphite Anodes
5b. (Right) – Y-Axis scaled version of the left graph to observe the finer differences between the 45nm, 90nm, and 180 nm thickness results.

- The 90-nm (green) Si-Gr anodes did slightly, consistently better than the baseline. The comparative charge capacities range between 100.3% and 101.6%
- The 45-nm (orange) and 180-nm (purple) Si-Gr anodes did slightly, consistently worse than the baseline. The comparative charge capacities range between 98.0% and 99.7% for the entire 100 cycle run.
- The 940-nm (red) and 1420-nm (blue) Si-Gr anodes did significantly worse than the baseline with no silicon, starting off around 90-100% efficiency and quickly dropping in relative capacity over the test schedule. 940-nm drops to 81.8% by the 100th cycle, and 1420-nm drops to 65.1% by the 100th cycle.
- For all trends, there is a consistent increase in the slope of the normalized capacities, indicating that the cycling efficiencies of graphite anodes with any silicon in them increase relative to graphite anodes with no silicon. This may suggest that a Silicon deposition of ~100 nm may add a small bonus to both charge capacity and cell longevity.

Conclusion

- Silicon-Graphite anodes were created using the Plasma Enhanced Chemical Vapor Deposition process. The purpose of developing and testing Si-Gr composite anodes is to gather experimental data on the electrochemical effects of silicon modifications to a graphite anode base.
- Deposition of around 100 nm of microcrystalline columnar silicon on pristine graphite offers a slight 0.3-1.6% increase in capacity over the course of 100 cycles. Deposition of greater than 100nm of microcrystalline columnar silicon results in a significant decline in discharge capacity relative to a cell with no graphite.
- Any addition of silicon to a graphite anode results in a resistance to further decline in cycling efficiency over the life of the test cell.

Future Work

- The improvements shown to charge capacity and life cycle when adding a thin film of silicon show potential to be optimized. A deeper study of a narrower range of film thicknesses may prove useful to finding the maximum storage capacity boost of a single thin silicon layer.
- A study to determine the storage capacity of a thin film of silicon on a graphite anode vs an equimolar mixture of silicon and graphite may be studied to determine if the effects are dominated by composition or by specific geometry.

References

- Yemeserach Mekonnen, Aditya Sundararajan and Arif I. Sarwat. "A Review of Cathode and Anode Materials for Lithium-Ion Batteries". March 2016.
- Hunjoon Jung, Min Park, Yeo-Geon Yoon, Gi-Bum Kim and Seung-Ki Joo. "Amorphous silicon anode for lithium-ion rechargeable batteries". September 2002.
- Zhaojun Luo, Dongdong Fan, Xianlong Liu, Huanyu Mao, Caifang Yao and Zhongyi Deng. "High performance silicon carbon composite anode materials for lithium ion batteries".
- Lurie Nanofabrication Facility Wiki, April 2020, Web, https://inf.wiki.eecs.umich.edu/wiki/Plasma_enhanced_chemical_vapor_deposition

Acknowledgements

Haralabos Efsthadiadis, Amir Hegazy, Kevin Shah, Latika Susheel Chaudhary, Randall Wheeler, Yamini Kumaran