I. Chapter Heading (Heading 1)

I.1.A. Silicon Electrolyte Interface Stabilization Deep Dive (Sandia National Laboratories)

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I.1.A.1. Abstract

Objectives

- Establish protocol for testing
  - Develop Standard Samples, thin film Si on Cu
  - Develop Standard Samples, Si
  - Develop Preparation Protocol
  - Develop Standard Test Protocol
  - Execute Round Robin
- Establish Initial Experiments with Lithium Silicates
  - Establish deposition methods
  - Establish analytic methods
  - Expose samples to electrolyte in static conditions
  - Analyze samples
- Test Cell Development

Accomplishments (0Apr_Blue-Heading)

- Established protocol for sample preparation and testing
  - Completed Round Robin on Cu samples
  - Initiated Round Robin on Si Samples
- Established deposition conditions for controlled Li:Si ratio silicates
  - Deposited Li:Si 0 to over 8
  - Deposited Test samples
  - Characterized film evolution on model SEIs in lithiated and nonlithiated states
- Test Cells Built, tested, and distributed to teams

Future Achievements (0Apr_Blue-Heading)

- Develop full variation of Li:Si silicates for electrochemical and chemical testing

    - Understand impact of prelithiation on SEI time evolution
    - Understand effect of Li:Si in underlying alloy to SEI formation

- Develop Next Generation Cell Prototype and Distribute
    - Include current design changes
    - Establish design for spectroscopic cell version
    - Establish electrolyte recovery system in cell design

- Characterize film growth as a function of Li:Si in substrate and interface film
    - Characterize with ATRIR, XRR, ECAFM, XPS

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I.1.A.2. Technical Discussion (Heading 4)

Background (APR_Gray Shaded_Heading)

Text (0APR_para STANDARD Paragraphs)

Introduction

This report summarizes the activities that Sandia National Laboratories undertook in support of the Si anode Fundamentals program managed by the Vehicle Technology Office of the Department of Energy. The program is led by the National Renewable Energy Laboratory, and Sandia is one of four laboratories (including Oak Ridge National Laboratories and Berkeley National Laboratories) included in the program. The initial set of activities included establishing the baseline protocols for cell assembly and testing, and executing a number of round robin style tests to compare data collected under nominally identical conditions at each of the participating laboratories to ensure that similar results were obtained and that no extraneous secondary factors were affecting the results. Because the nature of the interface between electrode and electrolyte was in question, as well as how the interface evolved over time and electrochemical cycling, an effort to build "model" interfaces based upon previously observed lithium silicate structures within the native film.

Approach

The first set of activities for the program involved the establishment of a standard set of samples and a standard set of test protocols. Sandia sent our commercial Cu foils to the labs capable of sputtering Si and SiO2 on them, and then those labs that could do so sent the sputtered films to all the laboratories, where they were evaluated according to the established test protocol. This let the team see where variances in the observed data were arising. Once established, a standard set of test environments on Si wafers, using a standard test cell, were also developed, and Sandia supplied the manufacturing support for the NREL designed test cell and supplied these to the partner organizations. At the same time, Sandia, partnering with UC Boulder and ORNL, were establishing a set of standard thin film lithium silicates to be used to understand how lithiated SEI would interact with electrolytes.

Results (APR_Gray Shaded_Heading)

Support of Round Robin Tests

The first activity was the establishment of the necessary protocols and sample preparation methods to ensure uniform results across the various laboratories. To do this, a set of procedures were negotiated which included the preparation of the sample, the counterelectrode, the separator, the electrolyte to be used, and any preclean methods. In addition, the procedure for electrochemical treatment of the samples was defined to ensure that the samples all saw the same electrochemical cycling at the same rate. Samples of battery grade copper foil (18um thick, XXX tech) were sent to those laboratory sites which had Si/SiO2 PVD film deposition capability. Films were generated by these methods to the same standard (Cu foil, followed by 200nm of Si, followed by a varying amount of SiO2, either native, 30nm, or 100nm). Cathode disks 0.62" in diameter were punched from these foils and assembled with Celgard 2325 separators into a CR2032 coin cell case. Standard Tomiyama 2nd generation electrolyte for Si anodes (EC:EMC 3:7, 1.2M LiPF6, no FEC) was used as the electrolyte. The counterelectrode was a cold welded 0.5 mil Li metal foil cold welded to 18um thick Cu foil. 2 such samples were created and tested, and the discharge results are shown in Figure 1.

The results show the voltage of the sputtered Si relative to the Li counterelectrode with a constant 5uA discharge on the cell to a terminal potential of 50mV vs. Li. The cells are identical in every way, and were assembled at the same time and discharge in the same way, but there are distinct differences between the two. In addition, they show no terminal lithiation. For 100nm of Si lithiating to Li17Si4 at 5uA, the total time to reach this level of lithiation should be roughly 26 hours, so the full lithiation of these samples may not have taken place. However, known plateaus of various lithiation alloy compositions are evident, and compare similarly to other data from other institutions.

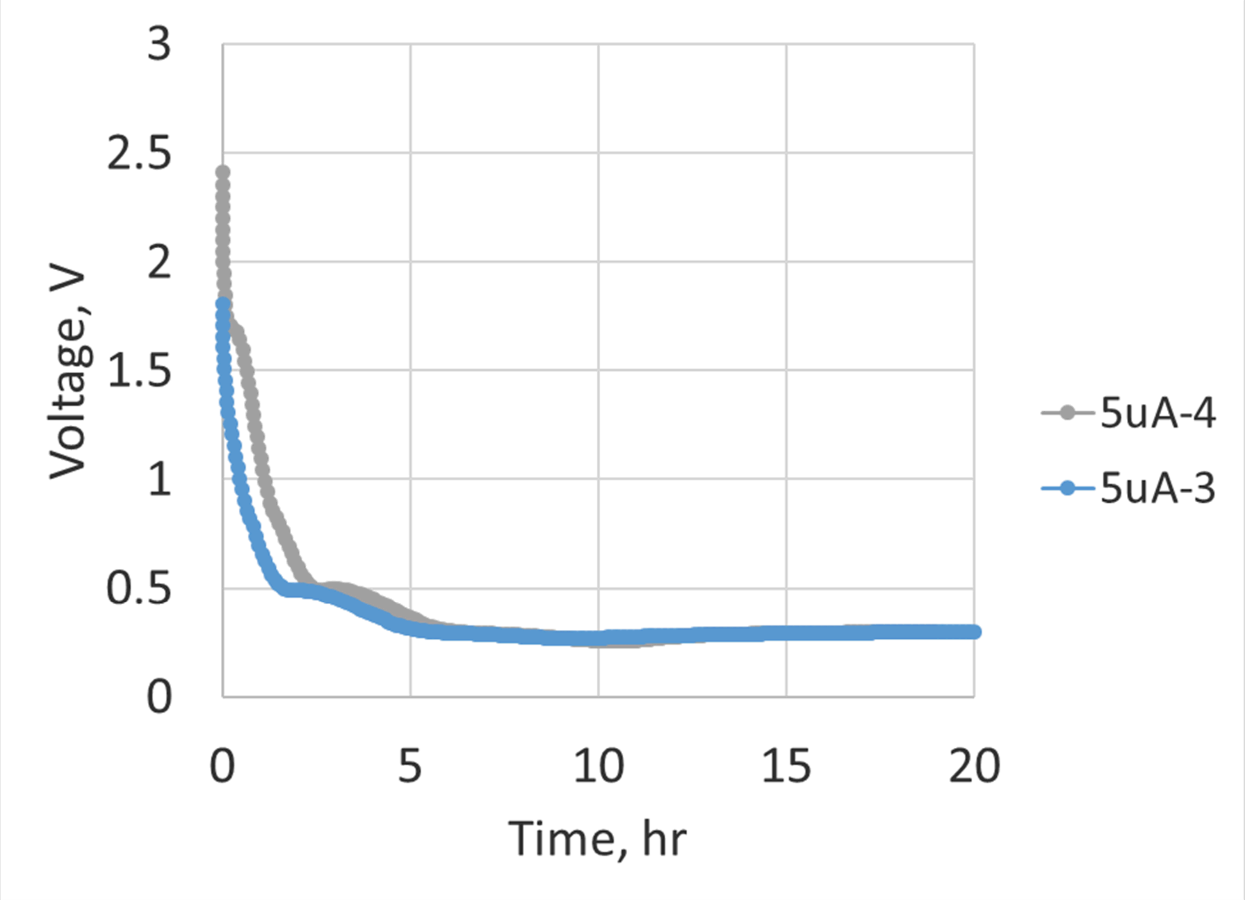

Figure I-1: First discharge of round robin Si on Cu foil samples. Conditions: Room temperature, 5uA rate, Li CE, EC:EMC 3:7 1.2M LiPF6 electrolyte, Celgard 2325 separator, 100nm sputtered Si on Cu foil.

XPS analysis of starting material

In addition to the base round robin tests, additional samples were prepared and analyzed using depth profiling XPS to determine the composition and bonding states of the elements as films of varying compositions were exposed to electrolyte for various amounts of times. Samples similar to those used in the round robin were prepared with either a ~50nm thick SiO2, or a 50nm thick Li:Si 1:1 ratio film (nominally Li2Si2O5). The depth profiles were taken every ~30A along a profile depth (based upon the sputter rate of pure SiO2 as a standard). Composition and bonding states for C, Cu, F, Li, O, Si, and P were collected. The results are shown in Figure 2 for SiO2, and Figure 3 for Li2Si2O5.

Between these two films, it can be clearly seen that the time evolution of the structure and composition of the film are markedly different, indicating that surface chemistry of the starting film will affect how the SEI forms and its subsequent structure evolution. For the SiO2 film, very little evolution of the surface layer is evident at short time, while the surface layer in the lithiated film more clearly indicates film growth over time. In addition, there is some evidence of fluorine in the films evolved at the surface (and penetrating into the film over time), even though this electrolyte does not contain FEC; fluorine here must be coming from penetration of the salt anion into the film structure, although the phosphorus signal does not indicate phosphorus penetration to the same extent. It is worth noting that these samples were deposited on copper foil, which had a relatively high roughness and therefore will skew some of the thickness measurements due to that roughness.

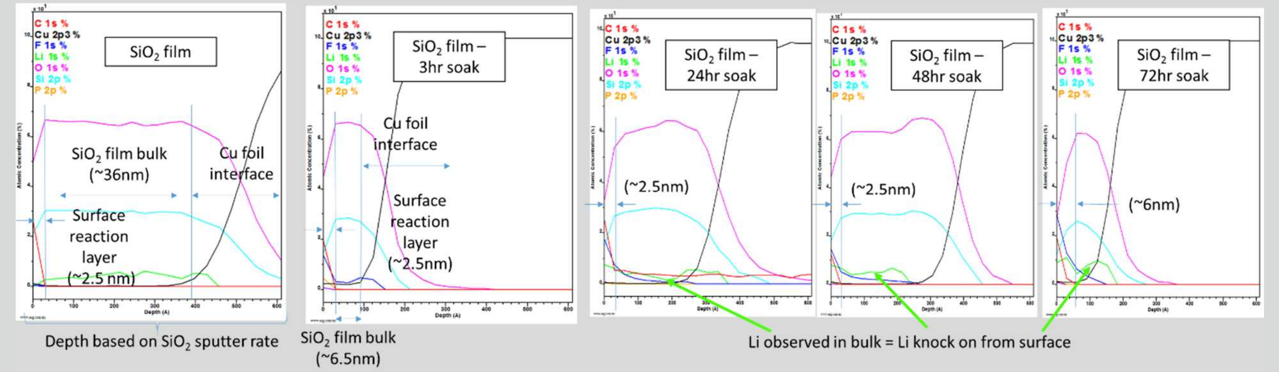

Figure I-2: Time evolution of XPS depth profiles on SiO2 sputtered on Cu foil exposed to electrolyte, from as deposited (left) to exposed for 72 hours (right). The film evolution and surface is seen to establish rapidly, but affects the SiO2 depth over time.

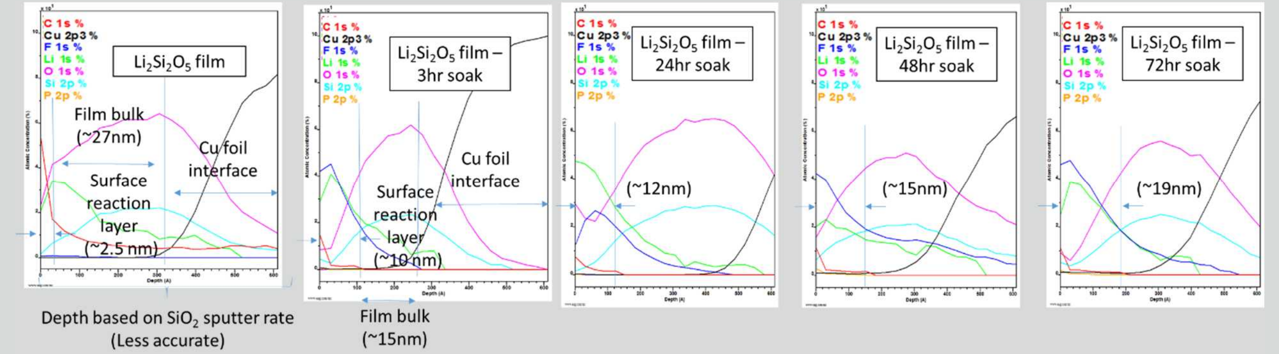

Figure I-3: Time evolution of XPS depth profiles on Li2Si2O5 sputtered on Cu foil exposed to electrolyte, from as deposited (left) to exposed for 72 hours (right). The time evolution of the film and thickness of the interface layer are markedly different than in the SiO2 case.

A similar trend towards formation of more complex structures can be seen using ATR-IR. Although the two sample sets (SiO2 and Li2Si2O5) look similar in the as deposited state (save for some expected differences in the region near 800 cm-1 attributed to the presence of the lithium in the silicate structure), the time evolution of these films on exposure to electrolyte is markedly different. In Figure 4A, a sample of SiO2 grown on Cu is exposed to the electrolyte for increasing amounts of time, and the ATRIR spectra is collected on the same sample after exposure. Five regions of interest exist, with the region around 550 cm-1 being attributed to adsorbed or residual LiPF6 from the electrolyte that was not removed upon rinsing. The region from 700 to 900 cm-1 is associated with a number of phosphate and carbonate groups that contain lithium replacements for hydrogen. The region between 1000 and 1250 is normally associated with O-Si-O stretching of the silicate peak. The region of 1400-1500 cm-1 is associated principally with a lithiated version of carbonic acid, and the region from 1700 to 1800 cm-1 is associated with alkyl carbonates and ethylene carbonate from the electrolyte. As can be seen in the figure, relatively little evolution of the surface is seen until longer times, and what is seen primarily is evidence of salt decomposition due to the formation of the phosphates and residual LiPF6 trapped on the surface. Additionally, some minor decomposition of the EC is visible as retained product on the surface at long times. Note also the broad peak in the O-Si-O region, indicating the network is relatively unperturbed up to 72 hours.

Contrast this with a starting film of the 1:1 Li:Si lithium silicate (Figure 4B). Significant decomposition products were appearing in as little as 1.5 hours of exposure to the electrolyte, and the region of salt decomposition products is showing much higher levels of salt residuals and phosphate byproducts than in the SiO2 case. The region for stretching of the silicate network has evolved several distinct peaks, which may indicate disruption of the network expected during lithiation. Also, the evolution of the lithiated carbonic acid on the surface, and generation (and possible subsequent extinction) of the alkyl carbonates from the electrolyte decomposition occurring on the surface. Clearly, having lithium in the starting film evokes a much richer time evolution of the SEI formation, even with no active electrochemistry being performed.

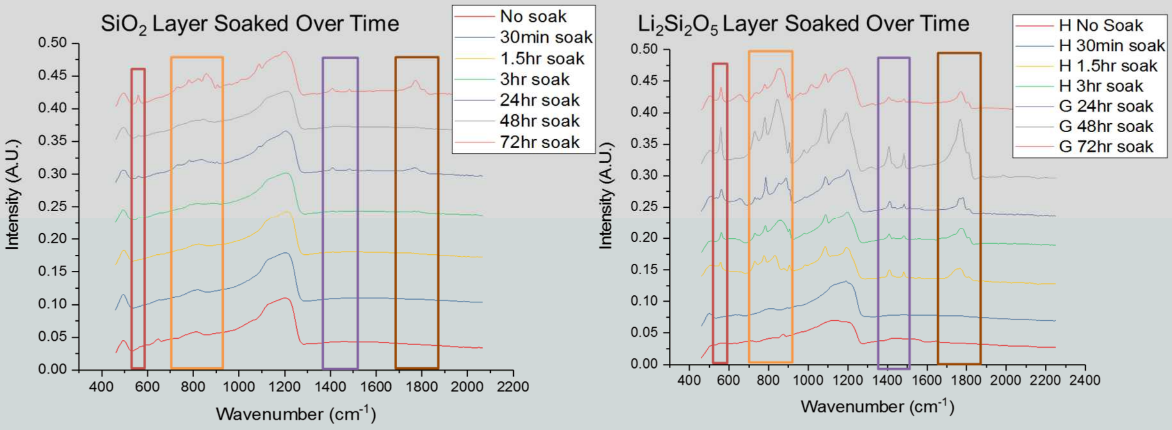

Figure I-4: A (left) ATRIR spectra of SiO2 film sputtered on Cu exposed to electrolyte for various lengths of time. Relatively minor evolution of surface species is noted, and the O-Si-O network is relatively unperturbed. B (right) Spectra of Li2Si2O5 film subjected to the same conditions. Although the ATRIR signals start out similarly, the time evolution of the surface products is very different, with more evidence of salt and electrolyte decomposition being noted.

Test Cell Design

The last area of effort for SNL was in the area of supporting the design and fabrication of a test cell for use with the bare bulk Si substrates provided by NREL, as an alternative to the sputtered thin films on Cu. These samples required a sealed, controlled volume of electrolyte within a standard electrochemical cell. NREL provided the first version of the design of the cell, and worked through most of the issues surrounding sealing and protecting the working, counter, and reference electrodes during cell operation. However, the initial design of the cell had issues with getting good backside electrical contact to the Si samples, since only the cell closing force was used to make electrode contact to the working electrode. A modification to this design was made to add a compression screw and a backside contacting plate to the original design, which would allow compression to be controlled independently of the cell closing compression, and allow for the Si to be in intimate contact with the working electrode contact. A total of 8 replicates of this design were manufactured at Sandia, and sent to the partner groups for use in their labs in replicating the NREL initial results. Using this method, an improved performance to the cell was noted. Additional design changes may be necessary, as all the teams have not had uniform success with this design. Depending on how the second set of round robin tests on Si substrates completes, the cell design may require further modification to ensure uniformity of data across the partner laboratories. A 3D design image of the modification to the cell design is shown in Figure 5.

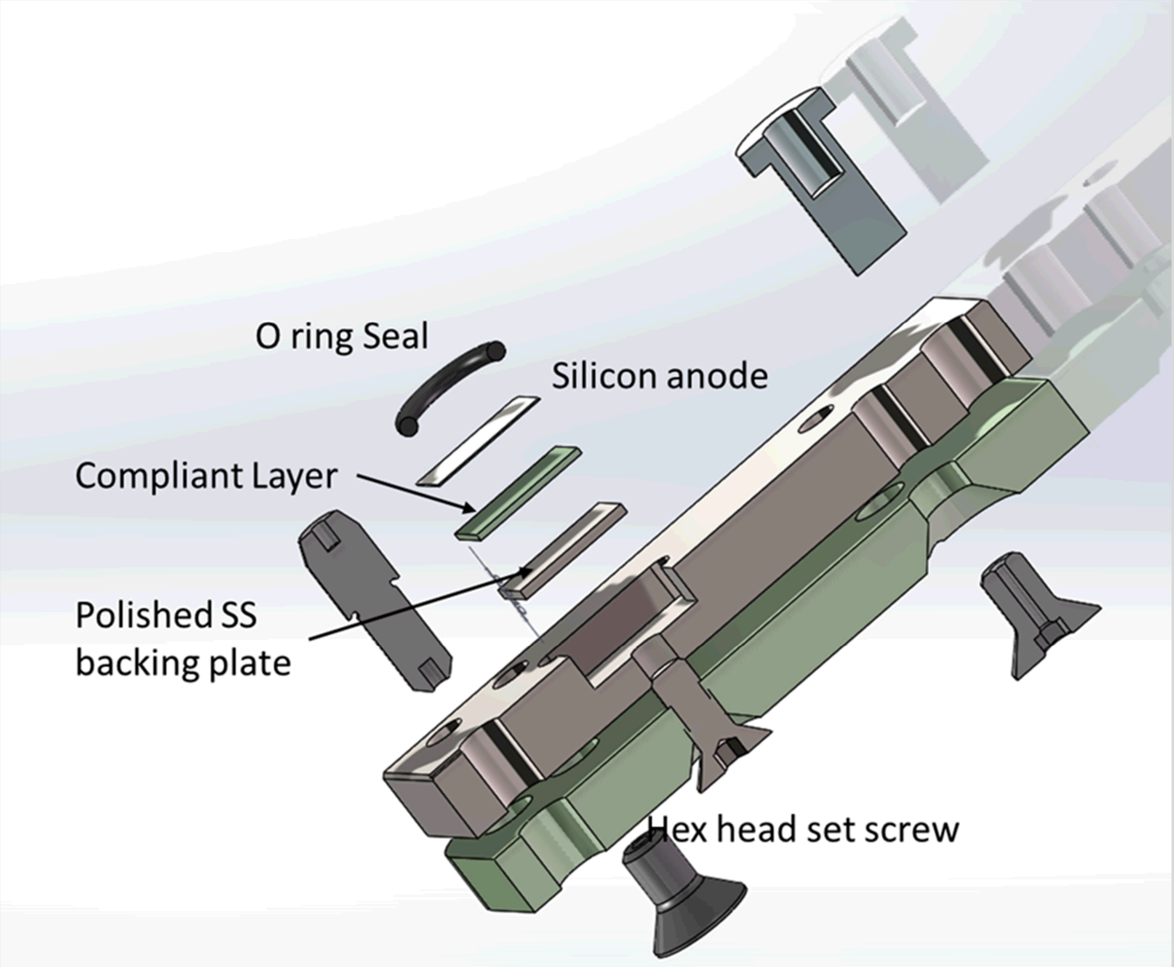

Figure I-5: Test Cell design modification for controlling working electrode contact pressure. The upper electrode assembly is removed in this image for clarity.

Conclusions

With the conclusion of the first round robins; the need for a unified test cell that produces similar results across the laboratories is critical so that modifications to the basis cells can be compared back to a known standard. This includes basis samples, and a new set of optically flat, controlled Si surface samples need to be mated to a well-controlled cell design. The cell design above has several challenges, and the results across the laboratories in using the cell are mixed. A set of redesigns will be completed to support the characterization milestones in Q1 of FY18, and then a spectroscopic version of the cell that allows interrogation of the working electrode as the SEI is formed and cycled will be developed. Finally, Sandia will support (using ATRIR, XPS, Raman, ECAFM) the investigation of silicate starting substrates at various stages of lithiation (from Li:Si 1:1 to 4:1) and investigate the time evolution of the surface chemistry from these different starting silicates.

Presentations/Publications/Patents

Coyle, J., Apblett, C. A., Stoldt, C., “Composition and Structure of Lithium Silicate Thin Film Electrolytes Deposited by Radio Frequency Magnetron Sputtering”, 229th ECS, San Diego, CA, May 29-June 2nd, 2016

Coyle, J., Stoldt, C., Apblett, C., “Initial Irreversible Capacity Loss Mitigation Through Engineered SEI Layer on Silicon Electrode”, 231st ECS, New Orleans, LA, May 28-June 1st, 2017

Coyle, J., Apblett, C., Brumbach, M., Ohlausen, A., Stoldt, C., “Structural and Compositional Characterization of RF Magnetron Co-Sputtered Lithium Silicate Films: From Li2Si2O5 to Lithium-Rich Li8SiO6”, JVST A, JVSTA-A-17-242, accepted.

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