UNDERSTANDING THE EVOLUTION OF THE SILICON ELECTRODE SEI THROUGH MODEL LITHIUM SILICATE THIN FILM LAYERS

Christopher Apblett, Sandia National Laboratories, USA
caabple@sandia.gov
Jaclyn Coyle, National Renewable Energy Laboratory
Gabriel Veith, Oak Ridge National Laboratory
Michael Brumbach, Sandia National Laboratory, USA

Key Words: Silicon, Anode, Electrochemistry, SEI, Silicates.

Development of higher capacity anodes in lithium ion batteries for use in electric vehicles is necessary to further enhance their energy density. Silicon anodes are being considered for these lithium ion batteries due to their high specific capacity. One drawback to silicon anodes is the formation of an unstable solid electrolyte interface (SEI). A major cause of this instability is due to silicon anode volume expansion of up to 300% during cycling. To this end, there remains much to learn about the chemical reactions occurring at the silicon surface. Because of this expansion, composite Si-graphite electrodes exhibit poor cycling performance, as well as significant capacity loss even at open circuit, “shelf” conditions in the absence of electrochemical cycling. Implicated in these processes is the role of the solid/electrolyte interphase (SEI) region between the Si solid material and the electrolyte systems that forms upon initial exposure to the electrolyte, and evolves over time. Thermodynamic arguments suggest that the formation of lithium silicate (Li$_x$Si$_{2-y}$O$_y$) phases from the decomposition of the electrolyte at the silicon electrochemical potential play a role in SEI formation and evolution.

To better understand the evolution of the SEI layer and the nature of silicates formed prior to any cycling of the silicon anode and how it impacts the performance of the silicon anode, model SEI layers were deposited on silicon thin films using RF magnetron co-sputtering. Thin film chemistries from SiO$_2$ to Li$_3$SiO$_x$ were synthesized to model the proposed lithiation of the oxide layer during the first cycle. The composition and structure of these thin films prior to exposure to electrolyte were analyzed. In order to observe the chemical reactivity of these model silicate thin films, they were soaked in 1.2M LiPF$_6$ in EC:EMC 3:7 wt% electrolyte for up to 3 days, removed, rinsed and studied using Attenuated Total Reflectance Infrared Spectroscopy (ATR IR), X-ray Photoelectron spectroscopy (XPS) and Focused Ion Beam Cross-sections (FIB CS). Half cells with these same silicate model films were cycled to observe any differences in SEI formation or cell performance during electrochemical cycling.

Results on these model films after soaking in the electrolyte indicate a dependence on stoichiometry for surface reactivity over time. For low order silicates the composition and thickness are unchanged, but as the lithium content in the film increases, increasing fluorine content is observed through the film, along with reductions in thickness, indicating attack of the film by the electrolyte or its byproducts. It is theorized that this increased reaction rate is a function of the amount of non-bridging oxygens terminated by lithium metal ions in the silicate film. From electrochemical measurements, the presence of lithiated silicates at the surface of the silicon anode affects the kinetics of the initial lithiation of the silicon anode as well as the stability of the cell with continued cycling. These model systems have started to tease apart the complexity of the surface reactivity and lithiation kinetics that manifest during storage and cycling of silicon anodes.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

Figure 1: Illustration of thickness and compositional changes of a) SiO$_2$, b) Li$_2$Si$_{3}$O$_5$, c) Li$_2$SiO$_3$, and d) Li$_3$SiO$_x$ films exposed to electrolyte over time.