The study of polymeric binders and their role in concomitant solid-electrolyte interphase formation on silicon anodes

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Claudia Rawn, Major Professor

We have read this thesis and recommend its acceptance:

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(Original signatures are on file with official student records.)
The study of polymeric binders and their role in concomitant solid-electrolyte interphase formation on silicon anodes

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Katie Lee Browning
August 2019
ACKNOWLEDGEMENTS

I have been fortunate in my early career to be surrounded by a multitude of people who have guided and shaped my research interests. First, I would like to thank my committee, Drs. Gabriel Veith, Claudia Rawn, and David Keffer for their guidance and feedback throughout this process. I thank Dr. Rawn for her encouragement and her belief in me.

My sincerest thanks to the Energy Storage and Membrane Materials Group for my time spent both before and during my Master’s. It was filled with great professional growth and an environment of collaborative effort and constructive criticism.

Many thanks to Beth Armstrong from whom I have learned a great deal of how to be an experimentalist (and have fun). Thank you for your advice and belief in me, it means a lot. Thank you to Robert Sacci for your willingness to help out anytime. Thank you to Mathieu Doucet for your help in performing experiments and especially with data analysis.

My deepest gratitude to my parents, Jim and Tina for your encouragement and support, always. To my dad, it has been a fantastic experience to work with my role model. To my mom, I wish I had half of your work ethic. To my siblings, Jimmy and Haley, thank you for listening to me complain.

Finally, but most certainly not least, I would like to thank Gabriel Veith. I have learned many things, most of which should not be repeated in a written document. All joking aside, I owe you a great debt of gratitude. Your mentorship has resulted in the development of skills that will carry me through my career. Your willingness to work with me and allow me to learn from my mistakes has boosted my confidence as a researcher. The people I’ve been fortunate to work with is beyond compare and I look forward to working with you in the future.
ABSTRACT

Silicon is a promising material for next generation anodes because of its order of magnitude higher specific capacity than the currently used graphite; however, as a result of the electrochemical alloying mechanism by which it stores Li, it undergoes large volume changes. This leads to stresses within the Si resulting in capacity fade and poor cell performance. One solution is the use of a polymeric binder to promote particle-to-particle cohesion, mitigation of volume expansion, and adhesion to the current collector. The presence of a binder may affect the formation of the solid-electrolyte interphase (SEI), an interfacial layer on the surface of an anode, that acts as a passivating layer. The SEI is crucial to cell performance, if it does not form properly excess electrolyte decomposition results in poor lifetime of the battery. The SEI is extremely sensitive to surface functionalities, cycling procedures, reaction with impurities, etc. Therefore, a better understanding about the relationship between the polymeric binder and the formation of the SEI is needed to improve battery performance as well as binder selection for Si anodes.

The first part of this study investigates how PEFM, an electronically conductive binder mediates the formation and composition of the SEI on the surface of an amorphous Si (a-Si) thin film electrode. The SEI layer is probed using in situ neutron reflectometry to understand the thickness, roughness and/or diffuseness of the layer. In addition, information related to the chemical composition is gained from the measured scattering length density value. Results indicate a large layer, ~ 800 Å thick forms on the surface of the anode.

The second part of this study investigates the commonly used binder for Si anodes, polyacrylic acid (PAA), and its effect on SEI formation. Reflectometry experiments were coupled with electrochemical quartz crystal microbalance (EQCM) studies to understand the viscoelastic response of the polymer layer as the anode is reduced. Initially the PAA suppresses any new layer formation, confirmed through EQCM and NR results, until the start of lithiation. As the cell is lithiated/ delithiated the SEI layer changes in chemical composition and thickness based on its state of lithiation.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si</td>
<td>Amorphous Si</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline Si</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluoroethylene carbonate</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>LiPAA</td>
<td>Lithium substituted polyacrylic acid</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron reflectometry</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>R</td>
<td>Reflectivity</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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CHAPTER 1: INTRODUCTION AND MOTIVATION
1.1 Silicon anodes

Most standard commercial Li-ion batteries utilize an intercalation reaction, where Li is stored between the sheets of a graphite anode. Though this is a fairly efficient mechanism it does not provide large current densities, averaging around 370 mAh g\(^{-1}\). Therefore, high energy density materials are being investigated through the use of metals that electrochemically alloy with Li. In an alloying-based reaction, the Li combines with the host metal (Sn, Sb, Si, etc.) resulting in some cases an order of magnitude higher energy densities when compared to graphite (Table 1.1). In particular the largest energy density of the alloying metals is Si, with a theoretical capacity of \(\sim 3600\) mAh g\(^{-1}\) and has been the focus of an intensive research effort.\(^{1-3}\) However, upon lithiation the volume expansion of the Si is around 300\% causing significant stresses of the anode resulting in decreased cycling performance as the material fatigues.\(^{4}\) The electrochemical alloying reaction results in a number of different phases that are evident in the voltage profile of Si anodes, that is dependent on a number of factors ranging from the size of the Si used to the cycling rate. During discharge the Si is lithiated while charge results in the removal of Li. The electrochemical (de)lithiation reaction of crystalline Si is described below where c-Si denotes crystalline Si and a-Si denotes amorphous Si (modified from reference 1):

\[
\text{Lithiation: } c\text{-Si} \rightarrow a\text{-Li}_{1.5}\text{Si} \rightarrow a\text{-Li}_{2}\text{Si} \rightarrow c\text{-Li}_{15}\text{Si}_4 \\
\text{Delithiation: } c\text{-Li}_{15}\text{Si}_4 \rightarrow a\text{-Li}_{2}\text{Si} \rightarrow a\text{-Si}
\]

The Li-Si system has four distinct phases that have been studied for some time; however, most of these phases exist at higher temperature (415\°C).\(^{5}\) The four Li rich phases found by coulombic titration measurements were \(\text{Li}_{12}\text{Si}_7\), \(\text{Li}_7\text{Si}_3\), \(\text{Li}_{13}\text{Si}_4\), and \(\text{Li}_{22}\text{Si}_5\) (Figure 1.1, dashed profile), where these phases were often used to calculate the theoretical capacity of 4200 mAh g\(^{-1}\) for Si based electrodes; however, these phases only occur at elevated temperatures. It has been determined the room temperature composition of the Li-Si alloy is \(\text{Li}_{15}\text{Si}_4\) which has a capacity of 3579 mAh g\(^{-1}\).\(^6\) Figure 1.1 depicts the voltage profile for elevated vs room temperature lithiation of Si anodes where the plateaus are indicative of the four phases (dashed line), which are not observed in the room temperature curve.\(^2\) In the following sections the electrochemical lithiation behavior of c-Si and a-Si are discussed as well as the mechanical properties of Si.
Table 1.1. A comparison of the specific and volumetric capacities of alloy-based anodes at full lithiation compared with non-alloy anodes graphite and lithium titanate (Li₄Ti₅O₁₂).

<table>
<thead>
<tr>
<th>Anode</th>
<th>Specific Capacity [mAh/g]</th>
<th>Volumetric capacity [Ah/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>350</td>
<td>719</td>
</tr>
<tr>
<td>Li₄Ti₅O₁₂</td>
<td>175</td>
<td>613</td>
</tr>
<tr>
<td>Bi</td>
<td>385</td>
<td>1662</td>
</tr>
<tr>
<td>Zn</td>
<td>410</td>
<td>1476</td>
</tr>
<tr>
<td>Ag</td>
<td>432-670</td>
<td>1798-2093</td>
</tr>
<tr>
<td>Pb</td>
<td>582</td>
<td>2052</td>
</tr>
<tr>
<td>Sb</td>
<td>660</td>
<td>1771</td>
</tr>
<tr>
<td>Al</td>
<td>993</td>
<td>1411</td>
</tr>
<tr>
<td>Sn</td>
<td>993</td>
<td>2111</td>
</tr>
<tr>
<td>Mg</td>
<td>0-2150</td>
<td>0-1658</td>
</tr>
<tr>
<td>Si</td>
<td>3579</td>
<td>2194</td>
</tr>
</tbody>
</table>

*aValues adapted from references 1 and 3*

Figure 1.1. The electrochemical titration curve for Si at room temperature (solid line) and 415°C (dashed). The stepped profile is indicative of different phases that have been added in for clarification to the reader.

Figure reprinted from reference 2
1.1.1 Crystalline Si

Elemental Si forms in the diamond cubic crystal structure; however, when fabricating electrodes, a crystalline or amorphous phase of Si can be utilized. Irrespective of the starting structure of Si (c-Si or a-Si), the subsequent lithiation and delithiation of the material results in drastic structural changes and after the first cycle the material exists in the amorphous state. Pristine Si anodes are devoid of Li and as such the cell must be polarized to lower potentials (discharged) to lithiate the Si, which occurs around 170 mV (vs Li/Li⁺). As Li is driven into the crystal structure of the Si, rearrangement of Si atoms occurs resulting in the amorphization of the crystalline Si. It was determined the alloying process arises via electrochemical solid-state amorphization of the crystalline material akin to forming a glass-like phase.⁷–⁹ The Si-Si bonds are broken apart which leads to the loss of the crystal structure of the Si. Interestingly, at high states of lithiation a sudden re-crystallization of the a-LiₓSi alloy occurs and as such many studies have focused on the transition of crystalline Si to amorphous Si as a result of electrochemical lithiation.⁶,⁹–¹¹ For instances, with the use of nuclear magnetic resonance (NMR) techniques, Key et al. were able to determine the Si structure as lithiation proceeds.¹²,¹³ The authors determined that the first lithiation results in a mixture of isolated Si and Si-Si clusters. Further lithiation results in the break-up of the clusters resulting in isolated Si which later forms the crystalline phase. Prior to this highly lithiated state, the Si atoms are well dispersed and surrounded by Li. The insertion of Li results in a rearrangement of the crystalline Si lattice where it eventually leads to the formation of a crystalline phase at high states of lithiation.⁷,⁹,¹²,¹⁴

This crystalline phase occurs at potentials less than 60 mV and identified as Li₁₅Si₁₄ at room temperature thus confirming the theoretical capacity of room temperature Si based anodes as 3579 mAh g⁻¹.⁶,¹⁰ This phase is thermodynamically unfavorable resulting in a metastable state. Through the use of in situ transmission electron microscopy (TEM) a distinct interface between pure c-Si and the a-LiₓSi alloy was observed and the crystalline to amorphous reaction was preceded by a reaction front approximately 1 nm thick.¹⁵ This further highlights the importance of interfaces within batteries across large length scales ranging from the nano- to the micro-scale. This large reaction front is the most likely cause of the large volume expansion of the material as it suggests a large activation energy is needed to break up the Si-Si bonds. Li and Dahn performed a detailed XRD study to follow the various phase transformations of the electrochemical alloying of Li with c-Si, as depicted in the phase diagram in Figure 1.2.¹⁰ The first discharge (Figure 1.2 blue box) is dominated by the two phase reaction between crystalline Si and the amorphous LiₓSi phase.
0.15 V the Li$_y$Si phase converts to a-Li$_x$Si. The amorphous phase is converted to the crystalline Li$_{15}$Si$_4$ at 0.05 V. Delithiation (Fig.1.2 green box) shows some initial presence of the Li$_{15}$Si$_4$ phase at the beginning of charge before conversion to a-Li$_x$Si phase. Additional cycling results in the purely amorphous phase at the start of lithiation (Fig.1.2 red). The sudden amorphous to crystalline transition has attracted much attention to the mechanism by which this occurs. Through the use of TEM, Gu et al. determined the spontaneous amorphous to crystalline transition is solely dependent on the Li concentration with a critical value of x=3.75 in the a-Li$_x$Si phase, and the favorability of the Li$_{15}$Si$_4$ as opposed to more Li rich phases is the similarity in the electronic structure of the two phases.\textsuperscript{14} The lithiation of c-Si can be difficult because of the breaking up of the crystalline lattice and as such research has turned to starting with the amorphous Si structure.

![Graph showing electrochemical lithiation mechanism for crystalline Si and the subsequent phases formed as a result of lithiation and delithiation.](image)

Figure 1.2. The electrochemical lithiation mechanism for crystalline Si and the subsequent phases formed as a result of lithiation and delithiation.

Figure reprinted from reference 10
1.1.2 Amorphous Si

The electrochemical lithiation of a-Si precedes in much of the same manner as c-Si. A similar reaction front observed in c-Si, where TEM showed a distinct interface between the pristine a-Si and a-Li₅Si core. This study confirmed a-Si proceeds in a two-phase reaction mechanism. The voltage profile for a-Si has two plateau like features that suggests how lithiation is proceeding. If the ratio of Li to Si is x<2 Li enters with one or more Si nearest neighbors, while if x>2.3 Li will be inserted where its nearest neighbor is another Li. This is representative of Li breaking up Si-Si bonds at the lower Li content region, while the higher Li content is indicative of Si surrounded by Li atoms. Early in the lithiation process, the Si becomes clustered due to the break-up of the crystal lattice resulting in isolation of the Si as lithiation continues as determined through nuclear magnetic resonance (NMR). In the amorphous phase the Li required to break the Si-Si bonds requires a lower activation energy than c-Si indicating less stresses during lithiation and a viable starting material for Si anodes.

One common fabrication technique for a-Si is through thin films. Thin films of a-Si have shown outstanding cycling performance; however, it is dependent on the film thickness. Maranchi et al. compared the cycling performance of a 250 nm a-Si thin film with a 1 µm thick film and demonstrated the thinner film had superior cycling performance which they attributed to less stresses on the film. Hatchard and Dahn used XRD measurements to follow lithiation of a-Si and determined the film will crystallize below 30 mV only within the critical film thickness around 2 µm. Figure 1.3 depicts the relationship between film thickness and lithiation where the arrow indicates the crystalline phase. It should be noted keeping lithiation above 0.1 V prevented the formation of the crystalline film. Thin films provide an ideal platform for fundamental studies as they often do not include additional materials present in composites (binders and conductive additives) allowing for a controlled study of the active material. Additionally, with the well-controlled interface it allows for an ideal platform to study interfacial chemistry of the anode.
Figure 1.3. The electrochemical lithiation of a-Si thin films of varying thickness as depicted by the potential vs capacity curves (a,c,e) and accompanying dQ/dV plots (b,d,f). The arrow indicates the formation of the crystalline phase Li_{15}Si_{4} in films with thicknesses greater than 2.4 µm.

Figure reprinted from reference 19
1.1.3 Stress and fracture associated with lithiation of Si

In general, the stresses associated with Si are dependent on a number of factors ranging from the size and/or morphology of the starting Si material. For instances, the stresses associated with c-Si are higher than those for a-Si, as a result of the higher energies needed to break up the crystalline structure. In addition, if the two-phase mechanism is present then the expansion will be greater than the one-phase mechanism when lithiating to above 50 mV to prevent formation of the crystalline phase. When cycling thin films of Si the electrode is shown to crack, known as “mud-cracking” due to the lateral stresses of lithiation (depicted in Figure 1.4). It has been found that the use of nanostructured Si reduces the stress on the particle or other structure. Chon et al. measured the stresses of c-Si upon initial lithiation and delithiation cycle where it was determined ~0.5 GPa of compressive force is exerted on the material as a result of the crystalline to amorphous phase transition.\(^\text{20}\) Through the use of optical and atomic force microscopy, the lithiation of a thin film occurs perpendicular to the substrate and is constrained laterly.\(^\text{4}\) This volume change, regardless of the structure of the Si used, leads to fresh surfaces being exposed resulting in poor cell performance. There have been many attempts to mitigate cracking and destruction of the Si, one such method is through the use of polymeric binders to inhibit expansion and to promote particle-to-particle cohesion and prevent delamination from the current collector.

![Optical image showing the “mud-cracking” as a result of large stresses during delithiation.](image)

Figure 1.4. Optical image showing the “mud-cracking” as a result of large stresses during delithiation.

Figure reprinted from reference 20
1.2 Binders

When fabricating anodes or cathodes, whether at the industrial scale or bench top, a binder is needed for adhesion of the working electrode to the metal current collector. The binder also serves to adhere the active materials and other conducting additives together to maintain electronic conductivity through particle-to-particle adhesion. This is crucial for alloying based reactions, where optical observations have shown particles crashing into one another, overlapping, become inactive through detachment of the active network as a result of large volume expansions in composite electrodes.\(^\text{21}\) The selection of binder can improve or hinder electrochemical performance, which is particularly important for Si because of \(~300\%\) expansion upon lithiation.\(^\text{22}\)

Many factors must be taken into account when analyzing a binder system’s performance such as its mechanical properties, its interaction with the electrolyte, and if it will be oxidized or reduced in the working environment of the battery. In addition, there are questions as to the final architecture of the binder within the cast electrode and fundamental questions regarding the insulating nature of a polymer. For example, beyond the mechanical properties of a binder, how does the presence of an insulating polymer effect ionic/electronic conductivity of the system? In addition, how does the binder effect the formation and chemical composition of the SEI layer? Understanding the role of binders in Si anodes has occurred in parallel with the understanding of the effect of Si particle size on cycling performance. This has led to an extensive research thrust in binder chemistries and developments within the last decade.\(^\text{23–27}\)

Several classes of polymers have been investigated for use in Si anodes and will be explored in the following sections.

1.2.1 Homopolymers

**PVDF.** The most common binder used in the battery industry is polyvinylidene fluoride (PVDF); however, for Si chemistries it fails to maintain particle cohesion. Initially, the use of PVDF for Si anods resulted from knowledge gained from graphite chemistry research and PVDF’s effectiveness as a binder for graphite composite electrodes. However, one important distinction is graphite only expands by at most 10% at lithiation. Early studies of binders were often performed on unoptimized systems because the importance of Si size, morphology and cut off voltages was still not fully understood.\(^\text{28}\)

The mechanical properties of a polymer are attributed to the binding ability and adhesion among active particles and the current collectors. Therefore, important parameters are the elongation until failure, the tensile strength of the polymer, and how these properties change in the dry state as opposed to the wet state when electrolyte is introduced.\(^\text{25}\) This led to the...
development of what is known as the tether model. This proposed mechanism would utilize elastomeric polymers that could accommodate large volume expansion in amorphous alloying electrodes through adhesion strength among the active particles. Wachtler et al. studied the effect of PVDF morphology on the cyclability of Sn/SnSb alloys in which PVDF was dispersed or dissolved within the alloy composite electrode. This work resulted in the understanding that beyond binder choice, the distribution and morphology within the composite leads to cycling improvements or detriments.

Liu et al. observed a Si electrode with 8 wt% PVDF could no longer charge/discharge after 8 cycles and attributed this to the poor electrical contact between the particles. Choi et al. observed similar effects of PVDF failure attributed to low tensile strength (18.8 MPa) of the binder causing collapse of the conduction pathways that prevented Li\(^+\) extraction during the charging states. This resulted in a first Coulombic efficiency of ~ 29%. PVDF was shown to be a poor binder for a-Si and a-SiSn alloy where Chen et al. attributed the poor cyclability of these electrodes to the mechanical properties of PVDF. The authors compared conventional PVDF with a modified commercial version, PVDF-TFE-P, which is a terpolymer elastomer. This resulted in improvement of cycling performance from improved mechanical properties of the elastomer. Standard PVDF could elongate less than 1%; however, their modified PVDF could elongate to 100% strain. Another study involved heat treating Si composite electrodes with PVDF binder. The authors believed the better distribution of the binder after heat treatment leads to better cycling performance than un-heated PVDF, thus concluding the importance of the architecture of the binder in addition to the binder choice. PVDF was believed to be the ideal polymer because of its ability to undergo large elongation until failure (>20%) which could accommodate volume expansion of the Si; however, the early studies proved other mechanisms were needed for alloying chemistries. The first viable polymer specifically for crystalline Si was sodium carboxymethyl cellulose (Na-CMC).

**Sodium carboxymethyl cellulose.** With the advancement of better Si starting materials, one of the first binders to replace PVDF was a styrene-butadiene-rubber (SBR) mixed with sodium carboxymethyl cellulose (CMC). SBR was mixed with CMC to be used in a binder with ball milled Si and ball milled Si coated with C resulting in improvements in cycle life when compared to PVDF alone. The authors acknowledge the system was not optimized which they attributed to an induction period where lithiation was harder to achieve as a result of binder coverage on the
Chen et al. saw better performance of C/Si electrodes with acrylic adhesive and CMC when compared with PVDF. Capacity retention for the acrylic adhesive alone was 79% after 50 cycles; however, when CMC was added the capacity retention was increased to 90% after 50 cycles. The authors attributed the improved performance to the dispersing effect CMC had on the slurry which resulted in improved uniformity of the cast electrode. This further highlights the importance between processing parameters of the cast electrodes in addition to the choice of binder. Buqa et al. looked at graphite/Si/C electrodes with PVDF, Na-CMC, SBR, and a combination of Na-CMC and SBR in low weight percent composites (~1 wt%). They determined mechanical properties were similar among all binder systems; however, Na-CMC exhibited less first cycle capacity loss. It was subsequently suggested binder content of SBR and Na-CMC should be restricted to 5-6 wt% of the slurry. It is important to note this study looked at electrodes with a significant amount of graphite (~75 wt%), this would already restrict the volume expansion of the electrode. Li et al. demonstrated the effectiveness of CMC binder for use in pure Si electrodes with micron sized particles. Utilizing a cutoff potential of 0.17 V (vs Li/Li⁺), 1100 mAh g⁻¹ was achieved. The authors concluded the use of a stiff (very little elongation at failure), and brittle polymer would be effective for alloy materials. This study showed the effectiveness of CMC alone as a binder for Si composite anodes.

The success of CMC was somewhat counterintuitive because its mechanical properties would not prevent expansion of the Si alloy. Thus, studies began to correlate acidic slurry processing conditions to enhanced capacity retention leading to the belief CMC was not an efficient binder because of mechanical properties, but because of its ability to form chemical bonds with the surface of the Si. Lestriez et al. demonstrated adjusting the pH of the slurry the confirmation of the CMC to the Si improved the network among carbon black/CMC/Si particles. It was determined that CMC forms covalent bonds with the native oxide layer found on the Si surface. Hochgatterer et al. proposed a covalent bond is formed between the carboxylic acid sites on the CMC with the native SiO₂ layer of the Si particle through a condensation reaction as described in Figure 1.5. The importance of the SiO₂ layer and the binder interaction were thoroughly investigated with surface sensitive techniques that concluded the layer is needed for the attachment of the CMC binder. Mazouzi et al. and Ding et al. explored this further and found the reaction is enhanced through pH effects of the slurry. In addition, by varying the degree of substitution the binder shows enhances efficiency. One downside to the preparation of CMC is the inability to control the carboxylic acid distribution.
Figure 1.5. The esterification reaction between the carboxylic acid groups present in the CMC binder with the hydroxy groups on the surface of the Si.

Figure reprinted from reference 39
**Polyacrylic acid.** To date, the most commonly recognized binder outside of CMC for Si based chemistries is polyacrylic acid (PAA). PAA is a polyelectrolyte with carboxylic groups similar to CMC. The appeal of PAA is the varying molecule weight ability, processability in water and other organic solvents, ease of substitution, and the ability to form covalent bonds with the surface oxide layer on Si. Magasinski et al. first demonstrated the effectiveness of PAA and attributed the improvement in cyclability to the larger number of carboxylic groups. The presence of the COOH groups will form a strong hydrogen bond to the surface of the Si because of the native oxygen with the OH groups on the surface of the anode, similar to the process observed in the CMC binder. One disadvantage is the Li substitution as a result of the ion exchange at the site of the H group. Komaba et al. showed when added to graphite composites the PAA uniformly coats the surface of the graphite particles creating an “artificial SEI” that prevents the cointercalaction of PC into the graphite. The same group studied the effectiveness of PAA on SiO electrodes and found PAA uniformly coats the particles leading to better cycling efficiency. The enhanced performance from PAA is depicted in Figure 1.6 where PAA effectively coats the active materials to form an artificial SEI to reduce electrolyte decomposition.

![Figure 1.6](image)

Figure 1.6. Schematic of the non-uniform coating of the binder PVdF on SiO electrode materials (a) as compared the uniform coverage of PAA binder (b).

Figure reprinted from reference 45
First cycle Coulombic efficiency losses when using PAA binder are attributed to the \textit{in situ} Li substitution of the proton groups of the PAA. To mitigate this, PAA can be neutralized by around 80\% by the substitution of the acidic proton group with the basic LiOH solution creating LiPAA.\textsuperscript{46} LiPAA was first demonstrated in graphite based chemistries where it was determined the LiPAA uniformly coated the graphite surface as a result of a more favorable conformation of the polymer when compared to PAA alone.\textsuperscript{47} In a silicon/graphite composite electrode the use of substituted polyacrylates led to improved dispersion of the composite components resulting in better cycling performance.\textsuperscript{46} It is believed LiPAA results in a better SEI layer as a result of better coating of the Si particles. A comparison of PAA and LiPAA binders in Si-graphite electrodes cycled in a full cell configuration yielded better performance in electrodes with the LiPAA binder.\textsuperscript{48} This is attributed to excess water content in the PAA binder as compared with the LiPAA. PAA is a well-known superabsorber of water and it is difficult to remove excess water from the polymer.\textsuperscript{48} In addition, it cannot be processed above 150\(^\circ\)C as it results in cross-linking and adverse anhydride formation.

\textbf{Natural binders.} Additional binders that have been explored come from naturally occurring sources. For example, an alginate-based binder derived from brown algae has been investigated. The alginate binder was determined to have favorable surface chemistry with the Si as a result of the naturally occurring carboxylic acid groups on the surface of the polymer chain. The binder resulted in a lithiation capacity of 1200 mAh g\(^{-1}\) for well over a thousand cycles.\textsuperscript{49} Another example is chitosan as it has favorable H-bonding between the polar groups of the chitosan and the hydroxylated Si surface.\textsuperscript{50} After 100 cycles a specific capacity of 2000 mAh g\(^{-1}\) was achieved. Another binder was derived from mussels, the catecholic binder, and was conjugated onto alginate (Alg\textsuperscript{C}) or PAA (PAA\textsuperscript{C}). A biopolymer known as guar gum (GG), was proposed as a binder utilizing a large number of hydroxyl groups found in the molecule. In addition, it was suggested the polymer could transfer Li\textsuperscript{+} to the surface of the Si, similar to the Li transfer in polyethylene oxide. Electrodes fabricated with the GG binder resulted in capacity of 2222 mAh g\(^{-1}\) after 100 cycles at a current density of 2100 mA g\(^{-1}\).\textsuperscript{51}

\textbf{1.2.2 Cross-linked and self-healing binders}

When cross-linking polymer binders the idea is to form a three-dimensional interconnected network, which can act as a self-healing mechanism during delithiation. With the superior
capabilities of the CMC and PAA binders, many studies have focused on crosslinking polymers of desirable characteristics with CMC and/or PAA to achieve properties of both polymers. For example, Koo et al. cross-linked PAA and CMC and achieved a reversible capacity of 2000 mAh g\(^{-1}\) after 100 cycles. However, cycling protocols were performed at an elevated temperature of 30\(^\circ\)C which could account for some of the improved performance from better wetting properties of the electrolyte. The authors noted at a high C rate (10C) the anode achieved a delithiation capacity of 850 mAh g\(^{-1}\) at room temperature. It was stated binder resistance to mechanical strain was accomplished through the three dimensional network formed by crosslinking.\(^{25,52}\) Another example utilizing the properties of PAA, were shown by Jeena et al. through the copolymerization of PAA with polyvinyl alcohol (PVA). This co-polymer was designed to include desirable functional groups, specifically carboxylic acid, carboxyl and hydroxyl groups in the polymer backbone to promote the strong surface reactions of the PAA with the improved viscosity of the PVA. At an optimized ratio of 60:40 acid-to-alcohol, a charge capacity of 2000 mAh g\(^{-1}\) for over 30 cycles was achieved.\(^{53}\) Song et al. showed through thermal crosslinking of the PAA-PVA system an interpenetrated gel binder network was formed. Figure 1.7 represents the crosslinking mechanism between the PAA-PVA and the oxide on Si surface, in addition to a schematic of how the gel network keeps the lithiated anode together. This system resulted in a specific capacity 1663 mAh g\(^{-1}\) for 300 cycles and a Columbic efficiency of 99.3\%.\(^{54}\)

![Figure 1.7](image)

Figure 1.7. The crosslinked network of PAA and PVA (left) forming an interpenetrated gel binder network (right) capable of accommodating large volume changes of the Si anode.

Figure reprinted from reference 54
Kang et al. incorporated the idea of dynamic ionic bonding to promote autonomous healing. This was achieved through the functionalization of the Si particles with an amine group that forms an ionic bond with the carboxylic acid group of the PAA. The bonding mechanism was confirmed through the use of XPS and Raman spectroscopy. The electrodes with the dynamic bonding showed a capacity retention of 80% for 400 cycles as a rate of C/2.\textsuperscript{55}

Recent advances in polymeric binders have focused on the ability of “self-healing” where after crack propagation in the electrode the binder can act as a sealant. This has been approached through a number of techniques ranging from a net like configuration of the binder, to utilizing the bonding of certain functional groups (-COOH, -OH) to the surface of the Si. Wang and co-workers developed a self-healing polymer designed to be stretchable, up to three times is original length, to enable healing of cracks as they occur as depicted in Figure 1.8.\textsuperscript{56} The polymer achieves this capability through a low glass transition temperature where after cracking the polymer chains are able to rearrange and intermix to reform hydrogen bonds. The micro-Si anode with the SHP binder showed a discharge cumbolic efficiency of 95\% after 50 cycles with a current density of 0.4 A g\textsuperscript{-1}.\textsuperscript{56} The group also demonstrated extended cycling (140 cycles) using large Si particles through 3D spatial arrangement of the SHP within the electrode.\textsuperscript{57} Another example of a self-healing polymer incorporated polyotaxanes with PAA. The polyrotaxane acted as a pulley along the PAA chain enabling a sliding network keeping pulverized microsilicon together.\textsuperscript{58}
Figure 1.8. The schematic representation of the self-healing polymer (a) and chemical structure of the polymer (b).

Figure reprinted from reference 56
1.2.3 Conductive binders

The development of conductive based polymers has sparked interest in the ability for their use in electrochemical devices since their inception in the 1970’s. Conductive polymers utilize \( \pi \) bonds, either C=C or C≡C, that alternate along the polymer chain. The conductive additive forms a conduction pathway through interaction with other particles; however, when Li\(^+\) is alloyed with the Si the expansion causes loss of contact among the conductive particles. Eliminating the conductive additive and replacing with an electronically conductive polymer would form a conductive network around the Si and eliminate the loss of contact among conductive additives. For example, one group utilized \textit{in situ} polymerization of conductive polyaniline (PANi) to form a hydrogel network that conformally coats the surface of the Si. The resulting anode achieved 5000 cycles with an average Coulombic efficiency of 99.8%. The authors proposed the \textit{in situ} processing allowed for a uniform conductive coating of the Si nanoparticles resulting in a conductive matrix with free space to allow for expansion, in addition to channels for ionic and conductive transfer.\(^{59}\) With the hydrogel, the electronic pathways would be maintained without the need for additional conductive additives. One disadvantage to PANi is its tendency to lose its p-type conduction under the reducing environments of Si anodes.

Work by Gao Liu and co-workers have focused on the optimization of electronically conductive binders through careful addition of polymer groups. These are identified through a mixture of experimental techniques (x-ray spectroscopy, materials synthesis, and cell testing) and computational work (density functional theory).\(^ {60}\) This led to the systemically designed polymers Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) and Poly(2,7-9,9-dioctylfluorene-co-2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene-co-2,7-fluorenene-co-2,5-1-methylbenzoate ester) (PEFM).\(^ {60,61}\) The PFM polymer exhibited a specific capacity of 2100 mAh g\(^{-1}\) for 650 cycles of the Si.\(^ {60}\) The PFM/PEFM binder exhibited a conductivity of 4.9 \( \mu \)S cm\(^{-1}\) after \textit{in situ} Li-doping during the first lithiation cycle.\(^ {61}\) The electronic conductivity is below acetylene black (AB) which is in the range of 0.1 to 100 S cm\(^{-1}\); however, there is evidence of a loss of electrical conductivity as a result of the AB particles being pushed apart when lithiation of the Si occurs.\(^ {61}\) PEFM was developed as a multifunctional binder where high electrical conductivity could be maintained, having good mechanical adhesion/ductility, and electrolyte uptake properties. The addition of triethyleneoxide monomethylether, “E” group, to the PFM binder resulted in a 3-fold increased electrolyte uptake as a result of the increased polarity of the binder. Figure 1.9 shows the PEFM molecule with the functional groups and their properties. The authors
indicate the swelling of the binder will allow for better Li-transport through the binder to the active Si surface. \textsuperscript{61,62} Improved cycling performance, reaching the full theoretical capacity of Si after 50 cycles was achieved with the modified binder (Figure 1.9 bottom). \textsuperscript{61}

Another conductive polymer of interest comes from the solar cell industry, poly(3,4-ethylenedioxy thiophene):poly(4-styrenesulfonate) (PEDOT:PSS). Higgins et al. used PEDOT:PSS in place of a conductive additive in addition to serving as the binder allowing for an electrode with 95 wt\% of active Si material. \textsuperscript{63} Through \textit{in situ} doping with formic acid, an electrode with 80 wt\% Si saw a capacity of 1950 mAh g\textsuperscript{-1} after 100 cycles. In addition, Park et al. looked at using PEDOT:PSS to create a core-shell on Si/SiO\textsubscript{x} resulting in initial reversible capacity of 968 mAh g\textsuperscript{-1}. \textsuperscript{64} One advantage of the PEDOT:PSS system is the ability to be processed in aqueous conditions; however, the polymer forms very acidic solutions (pH of 2 to 3).

![Figure 1.9](image1.png)

\textbf{Figure 1.9.} The strategically designed electronically conductive polymer, PEFM, molecular structure (top) and cycling performance (bottom).

Figure modified from reference 61
Additional conductive polymers that have been investigated include: poly(phenanthrenequinine) (PPQ), poly(1-pyrenemethyl methacrylate) (PPy), poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA). PPQ shows good dispersion among Si nanoparticles, and was optimized to 10 wt% resulting in a Columbic efficiency of 81% for the initial cycles. The initial low Columbic efficiency, comparable to LiPAA (82%), is attributed to Li trapping in the binder; however, after the first two cycles the Columbic efficiency increases to 97%. PPy was utilized in a graphite/nano-Si composite electrode for enhanced Columbic efficiency and specific capacity when compared to graphite and nano-Si alone. In addition, PPy was shown to impede lithiation as a result of selective uptake of electrolyte components (diethylene carbonate, DEC in this study) accelerating electrolyte decomposition when studied in model Si electrodes with a spin coated polymer layer. The authors propose in a composite electrode configuration lack of conformal coating on the Si surface could aide in reducing these effects. Finally, PPyMAA was determined to be a good binder for high tap density nano Si, a low surface area material, that suffers from larger stresses than conventional nano-Si. The authors concluded the co-polymer resulted in comparable adhesion strength to PAA on nano-Si.

The fabrication of composite electrodes for battery cells involves the formulation of a slurry composed of the active material, a conductive additive such as C black, and a polymeric binder. The above section highlights the extensive research into binders within the last couple of decades, but are often focused on the mechanical stability of the binder. However, slurries can contain a large weight percent of binder leading to the question of how the presence of an insulating polymer affects the interfacial chemistry of the active material and the binder.

1.3 Solid-electrolyte interphase

Of all the complex interactions within any battery, one of the most crucial and least understood is the electrolyte/anode interfacial chemistry, known as the solid-electrolyte interphase (SEI). The SEI forms on the surface of the anode as a result of reductive decomposition of the electrolyte from operating outside its voltage window. This interface dictates most of the functions of a battery ranging from safe storage to efficient cycling conditions. Interestingly, though the importance and understanding of what happens when a SEI does not form correctly is known, there are still many fundamental questions about the exact composition, structure, formation pathways, thickness, etc. that are not fully understood within the battery community.
this layer was first noted on Li metal, where when submerged in non-aqueous electrolyte the chemical formation of the SEI was discovered. Peled noted the layer formed instantaneously in contact with the electrolyte and consisted of insoluble reaction products between the Li metal and electrolyte. The layer was also found to be electronically insulating but ionically conducting. With the introduction of the Li-ion battery and its use of graphite anodes, as opposed to Li metal, the focus shifted to the electrochemically formed SEI on graphite/carbonaceous anodes. Peled et al. proposed a patchwork, or mosaic makeup, where inorganic components of the SEI sit on the surface of the electrode, while a more porous layer closest to the electrolyte is composed of organic/polymeric moieties. Which has been observed in atomic force microscopy and photoelectron spectroscopy studies. The main composition of the SEI appears to be decomposition products of the carbonate solvents, particularly ethylene carbonate (EC), and identified as lithium ethylene dicarbonate (LEDC). The insoluble products are mainly composed of salt decomposition products, such as LiF and solvent decomposition products such as Li$_2$CO$_3$. The exact composition of the SEI can change based on the solvents, salts, the anode material, cycling protocols, electrolyte additives, et cetra. However, with the ubiquitous rise of power electronics, an increasing need for higher capacity anodes, as compared to graphite, has driven research towards silicon. Thus, leading to the need for a better understanding of the SEI formed on Si based anodes.

The formation of the interphase requires a significant amount of capacity resulting in an irreversible capacity loss in the first cycle. The first cycle Columbic efficiency (CE), a metric for the charge efficiency related to the ratio of the total charge extracted to the total charge put in, is often low as a result of the SEI formation. However, CE will increase with cycling if the layer becomes stabilized. The SEI is essential for safe operation of the cell, if it does not form correctly further electrolyte degradation leads to limited performance. If the layer is ionically conducting which allows for Li$^+$ conduction pathways, but electronically insulating to suppress further electrolyte reduction. The SEI is of particular concern for alloying materials due to the cracking of the material exposing fresh surfaces to the electrolyte resulting in further electrolyte degradation and thicker SEI layers and poor cell performance. A good SEI has many characteristics such as mechanical rigidity, yet flexible enough to allow for volume changes during lithiation of the electrode. In addition, products should not be soluble in the electrolyte and the layer should be stable across a wide range of voltage windows. The following sections explore SEI chemistry and structure on different anode materials.
1.3.1 Electrolytes

The electrolyte serves to promote the conduction of ions between the anode and the cathode. The standard electrolyte in commercial Li-ion cells with liquid electrolyte, are composed of an organic solvent with a conductive salt. More importantly, the composition of the SEI is highly dependent on the chemical composition of the electrolyte. An ideal electrolyte system requires the following properties: a high dielectric constant to ensure solubility of the salts, low viscosity, inert to the cell, remains liquid in the voltage operating window, and be non-toxic for environmental integrity. However, due to the strong oxidizing and reducing environments within a battery, not all of these properties can be met and no single solvent has been identified with all of these properties. Indeed, the inability of an electrolyte to meet all these requirements leads to the interphase formation on the surface of the electrodes. As a result of no singular solvent, standard nonaqueous electrolyte systems utilize a two-solvent compilation with a cyclic carbonate, most commonly ethylene carbonate (EC) and a linear carbonate or carboxylic ester. A conductive salt is then added to the solvent mixtures to form the electrolyte.

Solvents. Extensive research has focused on the use of protic cyclic carbonates as the primary solvent for Li-ion chemistries. Before the use of Li-ion batteries and with the prevalence of Li metal as the main anode, the primary electrolyte solvent was propylene carbonate (PC). However, with the inability to prevent Li dendrite formation, graphite anodes came into use due to graphite’s ability to intercalate Li between its layers. Graphite is sensitive to exfoliation of the layers as a result of PC cointercalaction, but exfoliation can be prevented through the use of EC. This led to the use of EC as the primary solvent in Li-ion technology because of its ability to passivate the graphite surface. In addition, EC has an extremely high dielectric constant (ε~90) making dissociation of the conductive salt easy. However, the problem with EC arises from its extremely low viscosity at room temperature. A low viscosity leads to interfacial instability at the electrode surface.

In order to remedy the low viscosity of EC at room temperature, a co-solvent was introduced using linear carbonates. The linear carbonates are similar to the cyclic based carbonates, however the linear versions demonstrate a lower viscosity, a lower dielectric constant, and a lower boiling point than those of the cyclic molecules. The first successful co-solvent formulation was EC mixed with dimethyl carbonate (DMC). This mixture brought the viscosity down, allowing for better Li-ion conduction in addition to keeping the desirable properties of both
components, i.e. high dielectric constant of the EC and high ionic conductivity of the DMC. In addition, the reduction of DMC is not as severe as EC, thus most decomposition products making up the interfacial layer on the surface of the anode are from EC.

Salts. The conductive based salt has several requirements for useful operation within the cell. These are summarized as follows: the ability to fully dissolve/dissociate within the solvents, stability against oxidative decomposition, inertness of the anion, and finally inert to other components within the cell such as the polymeric separator. Lithium hexafluorophosphate (LiPF₆) has been the industry standard for Li-ion batteries because of its high conductivity. However, LiPF₆ suffers from extreme reactivity with moisture even in trace amounts and is not thermally stable at elevated temperature. The reaction with water produces several undesirable products that result in their incorporation within the SEI layer and are described as follows:

\[
\text{LiPF}_6(\text{soln.}) + \text{H}_2\text{O} \rightleftharpoons \text{LiF(s)} + 2\text{HF(soln.)} + \text{POF}_3(\text{soln.})
\]
\[
\text{PF}_5 + \text{H}_2\text{O} \rightleftharpoons 2\text{HF} + \text{POF}_3(\text{soln.})
\]

An ideal electrolyte system has not been identified for Si based chemistries, as carbonate-based solvents do not passivate the Si surface.

1.3.2 Formation mechanisms and composition

Most Li-ion battery electrolytes with carbonate-based solvents include ethylene carbonate (EC), making it an important component in SEI chemistry. Early investigations of the SEI involved the instantaneous formation on the surface of Li metal. Nazri and Muller proposed an SEI composition of Li₂CO₃ and polymeric moieties on the Li surface in propylene carbonate-based electrolytes (PC). The authors also noted when water was present a new species was identified as Li₂O. Aurbach et al. proposed the presence of Li₂CO₃ is a result of moisture sensitivity (Figure 1.10) of the primary SEI component which they identified as lithium ethylene dicarbonate (LEDC, (CH₂OCO₂Li)₂). Through the synthesis of the pristine materials and several analytical techniques, a reaction mechanism was proposed for the formation of Li₂CO₃ as a result of water content as depicted in Figure 1.10. Kanamura et al. determined the stability of the salt anions were dependent on the solvent used and noted the presence of LiF (or LiCl depending on the anion) on the Li surface. They also proposed the presence of alkyl carbonates in the surface layer on
Li. When the salt LiPF₆ is reduced the products are LiF and/or LiₓPFᵧ. Composition wise, LiF (or LiCl) persist in the SEI regardless of the surface. Irrespective of the anode the SEI is highly reactive and fragile and as such difficult to correctly identify all of its components as some compositions react upon contact with small amounts of water. This has been part of the debate as to whether certain moieties exist or are only present as a result of contamination from ex situ handling. Other species identified include LiOH and Li semicarbonates.

In comparison with Li metal, the SEI formed on graphite anodes occurs via electrochemical formation as opposed to chemically. There is debate to the exact potential the SEI formation begins, but is commonly valued at 0.8 V (vs. Li/Li⁺). As a result of competing and parallel decomposition reactions a combination of inorganic and organic species, from the solvent and salt, makeup the SEI on the graphite surface. The SEI formed on graphite has been extensively studied because of the prevalence of Li-ion batteries. It has been suggested the growth of the SEI occurs in a two-step reaction process where initially the decomposition of the organic electrolytes occurs via a reductive process. The exact formation pathways are a topic of debate with two commonly held beliefs. One belief is a one electron reaction process resulting in intermediates formed from solvent reductions as depicted in Figure 1.11 where the anion would undergo further reduction to form LEDC.

Figure 1.10. Two possible reaction mechanisms for LEDC reaction with water.

Figure reprinted from reference 84
The other proposed mechanism is a two-electron process where the solvated Li$^+$ forms intermediate compounds from co-intercalation into the graphite that are reduced to form the SEI.\textsuperscript{81,86,89,90} Many of the species identified on Li metal are also found on graphite. The SEI for graphite is dominated by Li$_2$CO$_3$.\textsuperscript{86} The variability of the layer is further shown on graphite as even different planes or types of carbons will result in different SEI compositions and structures.\textsuperscript{86,91–93} Using x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry (TOFSIMS), Peled, et al. showed compositional and morphological differences between basal and cross-sectional plane graphite. The basal plane had a thinner SEI with more organic compounds, while the cross-section showed a SEI with high salt reduction products.\textsuperscript{93} This highlights the importance of surface terminations on various anodes and the effect on SEI chemistries. In conclusion, the commonly observed chemical compounds of the SEI on graphite surfaces includes precipitates of LiF and Li$_x$PF$_y$ from salt decomposition as well as carbonates (Li$_2$CO$_3$) and lithium alkyl carbonates (ROCO$_2$Li) from solvent decomposition.\textsuperscript{86}

### 1.3.3 Structure

The exact structure of the SEI has been a topic of debate within the community for some time. The general concept includes a bilayer model in which a compact layer composed of inorganics (LiF, Li$_2$CO$_3$, Li$_2$O etc.) sits on the surface of the anode and a porous layer composed of organic/polymeric materials is closest to the electrolyte. Peled refers to this as a mosaic structure composed of microphases resulting in a polyhetero structure. This results in a polycrystalline layer that allows for Li$^+$ conduction through interstitial or point defects.\textsuperscript{73}
mosaic model is presented in Figure 1.12a, which shows a patchwork makeup of various solvent/salt decomposition products precipitated onto the surface of the anode. Edström et al. modified this model, as shown in Figure 1.12b, to show a heterogeneous distribution of products dominated by LiF and Li$_2$CO$_3$ close to the graphite particle with a porous organic layer on top of the inorganic layer. These simplified models most likely provide a generalized or simplified version of the true structure. The initial formation cycle results in a few angstroms thick layer. However, upon repeated cycles the SEI appears to continue reducing the electrolyte resulting in thicker SEIs. This growth is particularly bad for alloying anodes because of the repeated expansion and contraction of the material. These volume changes result in cracking of the surface which can lead to fresh active material reacting with the electrolyte resulting in thick SEIs and extensive electrolyte reduction.

![Figure 1.12](image-url)

Figure 1.12. a) The mosaic SEI model representing inorganic and insoluble products on the anode surface while polymeric products are close to the electrolyte. b) An updated model representing a compact inorganic layer on the surface of the graphite while a porous polymeric layer on the outer surface.

Figure 1.12a reprinted from reference 73
Figure 1.12b reprinted from reference 76
1.3.4 SEI formed on Si anodes

The SEI layer is considered to be the limiting factor of Si anodes as the continual expansion and contraction leads to cracking of the material resulting in further electrolyte reduction. The morphology of the starting Si material, i.e. nanoparticles, nanowires, etc. play a role in the SEI formation as a result of different stresses on the varying morphologies. During the first lithiation a compact SEI layer forms on the expanding silicon nanoparticle (SiNP); however, during the first discharge as the SiNP shrinks a porous secondary layer is formed as a result of decreased surface area. As the SiNPs are cycled the secondary SEI becomes denser and thicker. Arreaga-Salas et al. studied the SEI formation on binder free hydrogen terminated amorphous Si (a-Si:H) using Raman, infrared and x-ray photoelectron spectroscopy techniques to look at the initial SEI formation. The start of electrolyte and solvent decomposition occurred at 1.8 V, these decomposed components contributed to the SEI formation from 1.8 to 0.6 V. The first lithiation occurred at less than 0.4 V and the SEI components on the surface of the a-Si:H were primarily composed of LiF species with a small concentration of LiPF$_6$, Li$_x$PF$_y$, and PF$_y$. The presence of fluoride species is prevalent within Si SEI’s. Similar species to those found on graphite have also been identified on Si surfaces. The primary SEI products of a Si anode without the presence of a binder resulted in LEDC, LiF species in addition to Li$_x$SiO$_y$ (originating from the native oxide layer). Unlike graphite, Si has a native oxide layer which raises the question as to how the oxide will change the composition of the SEI as Li will react with SiO$_2$ before the pristine Si. Philippe and collaborators used x-ray photoelectron spectroscopy (XPS) with hard and soft x-rays to alter the penetration depth to study SEI formation on Si composite electrodes. This study showed the formation of a silicate, Li$_x$SiO$_y$ when lithiation begins, and noted the presence of Li$_2$O in the SEI. Upon full lithiation of 10 mV the Li$_2$O content increased; however, upon charging the cell the Li$_2$O was no longer present. A schematic of the SEI formation as a function of lithiation is depicted in Figure 1.13. The presence of this native oxide alters not only the chemistry of the interface, but the composition as well. Indeed, in a study comparing SEI formation on Si with and without the native oxide, the authors determined an SEI abundant with Li$_2$O in Si without the native oxide. Additional work by Philippe et al. suggests the presence of the Li$_2$O is a result of HF. Hypothesized from their observation of a fluorinated Si species (SiO$_x$F$_y$), upon cycling, at the interface between the Si and SEI was attributed to HF from the degradation of LiPF$_6$. In an a-Si thin film, Ferraresi et al. observed the reversible lithiation/delithiation of the SiO$_2$ layer studied through XPS.
There is evidence of varying SEI composition as a function of the state of charge of Si. Schroder et al. observed different SEI morphologies based on the electrochemical cycling technique used to charge and discharge the Si anode. Cycling cells with cyclic voltammetry and linear sweep voltammetry resulted in an SEI with an organic oxide and suppression of carbonate species when compared to samples cycled by chronoamperometry. Chan et al used XPS to study the SEI formation on the surface of silicon nanowires. The authors observed voltage dependency on the SEI thickness, where at low potentials a thick SEI was observed. However, as the potential was increased the SEI partially dissolved and cracks appeared.

1.3.5 SEI formation as a function of binder

An additional question with the SEI formation on Si is how the chemistry of the layer is changed as a function of the polymeric binders used to maintain the anode structural integrity. In battery processing, there is no set amount of binder added to the slurry and can vary based on the binder of choice. A few studies have investigated the relationship between binder and SEI formation. Through the use of soft and hard x-rays, the resulting SEI using the binder CMC was followed where there was evidence of a thin SEI before the start of lithiation resulting in the presence of Li$_2$CO$_3$ and lithium alkyl carbonates similar to graphitic SEI. The stable cycling and Columbic efficiency of 99.9% achieved by Si anodes alginate binder was attributed to the

Figure 1.13. Schematic of the SEI formation on a Si particle as a function of potential in a composite electrode probed with x-ray photoelectron spectroscopy.
formation of a stable SEI layer. The chemistry of the SEI layer was studied using XPS where it was observed there were minimal changes in the C1s, O1s and F1s peak between the 10th and 200th cycle suggesting stable layer formation.49 One advantage of the CMC binder is the belief that it helps form a stable SEI layer. With solid-state nuclear magnetic resonance (ssNMR), Si anodes with CMC binder and without binder were investigated. The authors noted in the electrode with CMC binder the formation of inorganic LiOH species were present, but not observed in the binder free Si anodes. The formation of LiOH was attributed to excess water in the polymer.102,103 Additionally, Key et al. observed via NMR, cells fully lithiated to the metastable Li15Si4, with CMC, suppressing the self-discharge when compared to binder-less cells. Thus, suggesting the binder inhibits side reactions with the electrolyte that would result in capacity fade.12 In a conductive based binder, poly 1-pyrenemethyl methacrylate spin coated onto a crystalline Si wafer the authors concluded the presence of the binder alters the interfacial chemistry.68 Several systemic studies have looked at PAA, CMC, and PVDF and their effect of the SEI as well as cycling performance.104,105 PAA was observed to form LiF and Li3PF5O2 as a result of LiPF6 decomposition.104 Both PAA and CMC based electrodes indicate a mature SEI by 30 cycles dominated by LiF formation.105 Most studies point to the dissolution of the salt, LiPF6, and subsequent excess formation of LiF as a result of higher water concentration from the binder leading to increased attack by hydrofluoric acid (HF).68,102,104–106

The principal hindrance to the study of SEI formation is the lack of in situ techniques, because ex situ investigations can alter the reactive and fragile SEI layer. The preparation method for ex situ studies requires the rinsing of the sample with DMC to reduce the amount of salt on the surface of the electrode. However, in doing so the fragile upper layer of the SEI is often altered or washed away because of the reactivity of the layer. One of the fundamental questions of this work is how a conductive binder, PEFM, and the commonly used binder, PAA, effect SEI formation on model thin film electrodes. Thin films create a well-defined interface between the Si surface and binder allowing them to be probed with in situ and ex situ techniques to observe how PEFM and PAA mediates the SEI formation. The tools to investigate the binder/electrode interfacial chemistry are outlined in the next section.
1.4 Characterization techniques

The propensity for the chemical species in the SEI to convert as result of trace amounts of water and other contaminants makes it difficult to study. A number of widely used techniques for studying SEI species are *ex situ*. In order for the electrode to be probed sample preparation involves a rinsing procedure to eliminate excess salt deposits on the surface, that would otherwise dominate the signal of commonly used techniques. Thus, highlighting the need for *in situ* techniques. In order to better understand the interfacial chemistries, as a function of polymeric binders used in Si anodes, neutron reflectometry (NR), x-ray photoelectron spectroscopy (XPS), and electrochemical quartz microbalance (EQCM) were used. This section highlights the three characterization tools used in this thesis to characterize the formation of the SEI on Si anodes both *in situ* and *ex situ*.

1.4.1 Neutron reflectometry

The absence of charge of a neutron gives rise to a deeply penetrating particle allowing for their use as a probe to study materials in complex environments. Because of their wave like nature they can be reflected and/or refracted off of surfaces separating materials of different indices of refraction in a way analogous to electromagnetic radiation, that is, neutrons obey Snell’s Law. This gives rise to a neutron scattering technique sensitive to surfaces and interfaces known as neutron reflectometry (NR). Reflectometry is an elastic scattering technique, i.e. there is no energy exchange when neutrons, or x-rays, interact with matter. In the case of neutrons, unlike electromagnetic radiation, the indices of refraction of most materials is less than one. As a result of neutron interaction with the nucleus as opposed to the electrons, the technique is not limited by Z number. This is of particular importance in materials for energy storage due to the presence of Li and H. In addition, neutrons are sensitive to isotopes which can be exploited to allow for contrast variation within a single experiment. For example, in battery related studies $^6\text{Li}$ has a scattering length of 2 fm while $^7\text{Li}$ has a negative scattering length of -2.22 fm, a difference Huger et al. used to study the permeation of Li nanosized amorphous Si layers.

The specular reflection of neutrons off different layers of a material results in the wave vector transfer (Q) described by the following term:

\[ Q = k_f - k_i = \frac{4\pi}{\lambda} \sin \theta \]

Eqn. 1: Wave vector transfer
where $\theta$ is the angle of incidence, and $\lambda$ the neutron wavelength. Probed length scales range from 1-500 nm with sub-nm resolution. Reflectivity ($R$) is a measure of the ratio of reflected neutrons to those that fall incident on the surface. Data collection results in a plot of $R$ vs. $Q$. Through a fitting routine, the thickness, roughness, and/or diffuseness of the layers is determined. However, the most important parameter determined is the scattering length density (SLD) which gives information on the composition of the measured layer as defined by:

$$ SLD = \beta = \frac{\rho N}{M} \sum_i b_i $$

Eqn. 2: Scattering length density

where $\rho$ is the materials density, $N$ Avogadro’s number, $M$ the molar mass, and $b_i$ the scattering length of each individual scatter within the molecular volume. Modeled data results in a SLD plot, a one-dimensional representation of the heterostructures of the system separated by the interfacial roughness between the layers. Figure 1.14 shows an example of a SLD plot after fitting the neutron reflectivity data of SEI growth on a Cu thin film.$^{108}$

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Figure 1.14. An example of a SLD plot obtained from fitting neutron reflectivity curves.

Figure reprinted from reference 108
The technique was first used to study the SEI formation on a non-intercalating electrode, Cu at different potentials as depicted in Figure 1.14 where the interface on the surface of the Cu changes with potential. In recent years NR has been used to study Si anodes and SEI formation due to the ability to see buried interfaces within a sample in situ. Jerliu et al. demonstrated the ability to measure the volume expansion of an amorphous Si electrode as a function of lithiation with operando NR experiments. The authors noted the presence of the SEI after delithiation of the sample but did not observe the SEI during the lithiation steps. Veith et al. have used NR for studying SEI formation at various states of charge of a-Si electrodes. The authors reported an initial chemical reactivity of the a-Si surface in contact with a carbonate-based electrolyte (1.2 M LiPF$_6$ in EC/DMC 3:7) evidenced by the decrease in the Si layer and the additional formation layer on the surface akin to a pre-SEI. A follow-on experiment showed the in situ formation of the SEI where a “breathing” like mechanism was observed in which the SEI swells during delithiation and shrinks during lithiation. Additionally, when the electrolyte additive fluoroethylene carbonate (FEC) was added the “breathing” of the SEI layer occurred in the opposite direction, i.e. shrinking during lithiation and swelling during delithiation. The results for the experiment with and without FEC additive are shown in the schematic in Figure 1.15. NR has also been used to study crystalline Si. The lithiation of c-Si was measured operando where the authors determined a concentration profile where initial lithiation occurred at the electrode surface and the final step was deep lithiation. These experiments highlight the power of NR as a tool to study the complex interfaces within a battery environment.
Figure 1.15. A schematic depicting the results for *in situ* neutron reflectometry experiments looking at a-Si thin film anodes in standard electrolyte composition versus with the additive FEC. These studies highlighted the “breathing” like mechanism of the SEI layer and its compositional change as a function of electrolyte additive.

Figure reprinted from reference 119
1.4.2 X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique that utilizes the photoelectric effect to determine chemical composition and oxidative states of a material. In XPS, the sample is irradiated with a fixed energy x-ray source, typically Al Kα (1486.6 eV) or Mg Kα (1253.6 eV), which results in a single electron process where an electron is emitted from an inner-electron core as a result of the binding energy being less than the energy of the x-ray. The kinetic energy (KE) of the emitted electron is measured by a spectrometer giving rise to a spectrum representing the energy of the atomic electron orbitals. The KE of the emitted electrons is described as follows:

\[ E_k = \hbar \nu - E_b - \Phi_{sp} \]

Eqn. 3: Kinetic energy of an emitted electron

where \( \hbar \nu \) is the energy of the x-ray, \( E_b \) is the binding energy and \( \Phi_{sp} \) is the work function of the material. The electrons that leave the surface without energy loss are the resulting spectrum, while those that inelastically interact result in the background. XPS is performed under ultra-high vacuum (10\(^{-9}\) - 10\(^{-10}\) Torr) conditions to prevent collisions among ejected materials and matter from ambient conditions. Due to the attenuation of the photoelectrons within the bulk after emission, the technique only probes the top ~ 10 nm of a sample thereby making it a surface sensitive technique.

From the elemental peak positions relative to binding energy qualitative information of the elemental and chemical nature of the material can be identified. As a result of chemical potential differences and polarizability within a sample, information on the chemical state of the material can be determined. Quantitative analysis can be done to understand the chemical moieties and atomic percent of the constituents through a peak fitting routine. The shifts in binding energy can be attributed to changes in chemical species; however, non-conducting species, such as those found in the SEI, can result in charging effects causing shifts in the spectrum making peak identification difficult. These charging effects can be corrected through peak shifting based on a known peak position, typically the C-C bond of the C1s peak. Sputtering with inert gas such as Ar allows the top surface of the material being probed, to be cleaned off. However, in battery related materials this method has been shown to convert SEI products.

XPS is an ideal technique to study the many interfaces of a battery, particularly the SEI layer. Edström et al. used XPS to show Li\(_2\)CO\(_3\) was not present in the SEI grown on graphite electrode that were maintained in a hermetically sealed environment. The dynamic nature of
batteries makes identification of species difficult e.g. changes based on lithiated/de-lithiated state, different species formation based on state of charge, exposure to contaminants, etc. can all lead to shifts in the binding energies. This concept is depicted in Figure 1.16 which highlights the complexity in battery electrodes, especially composite based, and the varying states of the battery can lead to peak position shifts.\textsuperscript{125} In addition, as a result of the rinsing procedure used for XPS sample preparation the SIE layer can be altered. For example, Fears et al. compared \textit{in situ} NR results of a Si anode to \textit{ex situ} XPS. The authors determined upwards of a 20 nm discrepancy between SEI thicknesses measurements from NR to those calculated from XPS. It was hypothesized the top 20 nm were composed of weakly bound species of the SEI.\textsuperscript{118} Regardless, XPS is one of the most prolific probes used to study SEI chemistries on the surface of Si anodes. When coupled with neutron reflectometry, chemical information gained from XPS can guide in the fitting routine by providing information on the chemical moieties present in the system.

Figure 1.16. Description of how photoelectron spectroscopy is used to determine the chemical composition of the SEI layer.

Figure reprinted from reference 125
1.4.3 Quartz crystal microbalance

Quartz crystal microbalance (QCM) is a technique sensitive to changes in the mass of a system as a result of the changes in the frequency of the quartz crystal resonator. Electrodes are deposited on either side of the quartz crystal and when an AC electric field is applied the changes in frequency can be determined through the mechanical oscillations because of quartz’s piezoelectric properties. Therefore, an increase of mass on the surface of the electrode will correlate with a decrease in the frequency of the crystal. This relationship is described by the Sauerbray equation which accounts for purely elastic mass changes as described in the following relationship:

\[ \Delta m = -C_f \Delta f \]

Eqn. 4: The Sauerbray Equation

Where \( \Delta m \) is the change in mass, \( C_f \) is the integrated QCM sensitivity, and \( \Delta f \) is the change in frequency. The limitations of the Sauerbray equation is the assumption the measured film is both thin and adsorbed on the surface and does not take into account viscoelastic properties (a material that behaves elastic and viscous when deformed) of the film. However, in the case of battery interfaces the viscoelasticity of a material needs to also be taken into account as the SEI is a bilayer like structure and could exhibit different properties from the interface at the electrode to the interface at the anode. Viscoelastic measurements can be achieved by coupling dissipation measurements with the crystal. Figure 1.17 depicts how an electrode can be measured in situ through changes in frequency, attributed to changes in mass, while the changes in resistance indicate a roughing of the electrode.\textsuperscript{126}

![Figure 1.17](image-url)  
Figure 1.17. An example of a QCM experiment that measures the change in frequency and resistance as a result of quartz’s piezoelectric properties.

Figure reprinted from reference 126
Electrochemical quartz crystal microbalance with dissipation (EQCM-D) is an ideal technique for in situ measurements on the surface of an electrode because not only are mass changes being taken into account, but the viscoelasticity of the layers under electrochemical cycling conditions are as well. This technique is particularly useful to study three categories of electrodes: nonporous solid electrodes that are thin and stiff, stiff porous electrodes, and soft coatings thereby giving information on gravimetric and nongravimetric measurements. For example, the SEI layer formed on Sn electrodes as a function of lithiation was measured where the authors not only determined thickness changes as the cell was cycled but also the quantified the shear elastic modulus and shear viscosity. Lee et al. combined NR with EQCM-D to determine the constituents of the SEI on a non-intercalating electrode to better understand the bilayer structure and how to measure this property in situ. The authors determined the initial SEI growth around 265 ng cm\(^{-2}\) and proposed organic species are deposited around 0.5 to 0.75 V while inorganics are deposited below 0.35 V. EQCM-D is an ideal tool to study the interfaces of a battery, with the additional benefit of experiments performed in situ. In this work EQCM was coupled with NR measurements to better understand the effect a thin layer of PAA binder has on the interfacial chemistry at the surface of the anode.

### 1.5 Project motivation and objectives

Polymeric binders play a key role in the cycle life performance of a Si anode by maintaining structural integrity of the electrode. Binders are typically introduced into a composite slurry after being dissolved/dispersed in a solvent. There is not a universal amount added in Si composite configurations, but account for at least 5 wt% of the slurry. This leads to many questions of how the binder is interacting with the active materials once a battery is cycled. In particular, how does the presence of an insulating binder affect the SEI formation on the surface of the anode. Due to the reactive nature of the SEI layer with even trace amounts of water, in situ techniques are crucial to better understand how the SEI is forming under working conditions. With the extensive number of interfaces within a battery an ideally suited technique is reflectometry. Through either neutrons or x-rays, reflectivity plots can provide insightful information pertaining to the layered interfaces within a system. Neutrons penetrate more deeply into a sample then complimentary x-rays, as well as not being limited by Z number. Therefore, neutron reflectometry is ideal for studying layers of battery materials in thin film architectures as the battery is being cycled. This platform reduces the complexity of composite slurries and isolates the binder/Si interaction enabling the
study of the interfacial chemistry. When coupled with other techniques, such as XPS, the thickness, roughness/diffuseness, and chemical composition of the SEI layer can be determined.

Chapter 2 focuses on the SEI formation as a function of an electronically conductive binder, PEFM. The main goal is to better understand how the PEFM layer is affecting the formation of the SEI during the first lithiation cycle. In addition, if the polymer binder is completely encapsulating the Si surface determining where the SEI is formed i.e. the surface of the Si or the surface of the binder. This was achieved through the use of neutron reflectometry to probe the first formation cycle of the SEI. The results were subsequently compared to XPS spectra from witness samples cycled under the same conditions as the NR experiments to better understand the chemical composition of the SEI layer.

The objective of chapter 3 was to characterize how the commonly used binder, PAA, mediates the SEI formation on a Si electrode. Neutron reflectometry was used to study the SEI in situ as a function of the state of charge. The anode was first cycled in a stepped potential procedure to capture the initial formation of the SEI. The cell was then cycled between a lithiated and delithiated state to better understand how the SEI changes as a function of cycling. The reflectivity measurements were coupled with electrochemical quartz crystal microbalance to understand the viscoelastic response of the polymer and subsequent layer formation. In addition, to resolve the stability of the SEI layer as it was cycled, electrochemical impedance spectroscopy (EIS) was used.
1.6 References


39. Hochgatterer, N. S. et al. Silicon/Graphite Composite Electrodes for High-Capacity


TARASCON, J. & GUYOMARD, D. New electrolyte compositions stable over the 0 to 5 V voltage range and compatible with the Li1+xMn2O4/carbon Li-ion cells. *Solid State Ionics* **69**, 293–305 (1994).


104. Nguyen, C. C., Yoon, T., Seo, D. M., Guduru, P. & Lucht, B. L. Systematic Investigation of Binders for Silicon Anodes: Interactions of Binder with Silicon Particles and


116. DeCaluwe, S. C. *et al.* Pore collapse and regrowth in silicon electrodes for rechargeable


CHAPTER 2: ROLE OF CONDUCTIVE BINDER TO DIRECT SOLID-ELECTROLYTE INTERPHASE FORMATION OVER SILICON ANODES
2.1 Disclosure
This chapter is based off a manuscript submitted to Physical Chemistry Chemical Physics (PCCP) (K.L. Browning, J.F. Browning, M. Doucet, N.L. Yamada, G. Liu, and G.M. Veith, “Role of conductive binder to direct solid-electrolyte interphase formation over silicon anodes,” PCCP, Accepted). The full list of authors includes: Katie L. Browning, James F. Browning, Mathieu Doucet, Norifumi L. Yamada, Gao Liu, and Gabriel M. Veith.

2.2 Abstract
With the use of in situ neutron reflectometry (NR) we show how the addition of an electronically conductive polymeric binder, PEFM, mediates the solid-electrolyte interphase (SEI) formation and composition on an amorphous Si (a-Si) electrode as a function of the state-of-charge. Upon initial contact with the electrolyte a Li rich, 41 Å thick, layer forms on the surface of the anode below the polymer layer. At 0.8 V (vs. Li/Li\(^+\)), a distinct SEI layer forms from the incorporation of electrolyte decomposition products in the reaction layer that is organic in nature. In addition, solvent uptake in the PEFM layer occurs resulting in the layer swelling to ~200 Å. Upon further polarization to 0.4 and 0.15 V (vs. Li/Li\(^+\)) a thick layer (800 Å) on the surface of the Si is evident where a diffuse interface between the PEFM and SEI occurs resulting in a matrix between the two layers, as the binder has taken up a large amount of electrolyte. The two layers appear to be interchanging solvent molecules from the PEFM to the SEI to the Si surface preventing the lithiation of the a-Si. By 0.05 V (vs. Li/Li\(^+\)) a Li rich, 72 Å thick, SEI layer condenses on the surface of the anode, and a 121 Å intermixed layer on top of the SEI with LiF and Li-C-O species is present with the rest blended in to the electrolyte.

2.3 Introduction
When fabricating composite battery electrodes, a slurry is prepared by dispersing the active material (electrode of study), conductive additive (typically a form of C), and a polymeric binder, used for mechanical strength and adhesion, in a solvent. After thorough mixing the slurry is cast onto a metal foil which acts as the current collector. The binder enhances the adhesion to the current collector in addition to providing mechanical integrity among the blend of different materials. The choice of binder is particularly important for silicon anodes due to the extreme expansion, around 300%, during lithiation of the Si, where mechanical integrity is needed to
prevent electronic isolation and pulverization of Si nanoparticles.\textsuperscript{1,2} There is no standardized amount of binder added to the system but on average accounts for ~15 wt% of the total slurry.\textsuperscript{3}

The most commonly used binder in the battery industry has been polyvinylidene fluoride (PVDF); however, Si based anodes with PVDF as the binder result in poor cycling performance.\textsuperscript{3-5} This has led to an intensive research effort exploring different binders for use in Si anodes. The most commonly used binders to date have been polyacrylic acid (PAA) and Li substituted polyacrylic acid (LiPAA).\textsuperscript{3,6} Their success as binders is attributed to the carboxylic groups that interact and bind with the -OH groups found on the native oxide layer on Si.\textsuperscript{3} There has also been interest in electronically conductive binders in order to eliminate the need for conductive additives such as carbon black. One such example is PEFM, which was designed to incorporate different functional groups to create a n-type conductive polymer modified to uptake electrolyte and maintain mechanical stability.\textsuperscript{7}

As a result of the volume changes in Si anodes, the Si surface cracks leading to exposure of fresh active surfaces causing further electrolyte degradation and the formation of additional SEI products leading to poor performance. Based on surface area and the large weight percent of added binder the surface of the Si should be fully coated, assuming a uniform dispersion, leading to the question of how this coating affects SEI formation? Does this SEI differ from that found on just Si? Furthermore, how does the ion transport or reduction processes occur within and/or through the insulating polymer layer? Only a few studies have focused on the complexity of binder interaction and their influence on SEI formation. For instance, in a photoelectron spectroscopy study looking at graphite-based anodes with water processable binders, the authors determined binder functional groups positively influence SEI formation.\textsuperscript{8} Nguyen et al. compared SEI composition and formation on Si as a function of binder (PVDF, PAA, CMC, and a cross-linked PAA-CMC) using XPS.\textsuperscript{9} The PVDF resulted in a thick SEI dominated by carbonate moieties in comparison with the PAA which accelerated the LiPF\textsubscript{6} decomposition leading to LiF and Li\textsubscript{x}PF\textsubscript{6}O\textsubscript{2}, and a thin SEI that suppressed the reduction of the solvent decomposition.\textsuperscript{9} This highlights the complex interactions among active material, binder, and conductive additive that are, in part, due to a large number of interfaces within cast electrodes.

The goal of this study is to explore some of these fundamental questions of the polymer/SEI interactions. To this end we use neutron reflectometry which allows the SEI growth and composition to be observed \textit{in situ}. The technique utilizes thin films allowing for a controlled architecture and interface of a conductive binder and an amorphous Si (a-Si) thin film electrode.
The chemical composition of the SEI can be further probed and characterized with x-ray photoelectron spectroscopy (XPS); however, due to the need to wash samples before using the technique some of the organic species are washed away or chemically altered. As a result, the combination of NR with XPS provides an extremely valuable tool to study and measure the SEI layer both in situ and ex situ.

Neutron reflectometry (NR) is ideally suited to study buried interfaces in situ. Neutrons can be reflected or refracted from interfaces between materials. Specular reflectivity is the probability of a neutron being reflected off of a surface as a function of the wave vector transfer Q perpendicular to the sample surface as expressed by Equation 1. Modeling of the measured reflectivity yields information about the scattering length density (SLD, β) profile as a function of depth. The SLD is indicative of the material composition of the layer and is expressed by Equation 2.

This technique has been utilized to study the SEI formation on amorphous Si anodes (a-Si).10–13 These studies showed in direct contact with LiPF₆ electrolyte, a Li rich reaction layer forms atop the Si surface.10 Studies using reflectometry have determined a “breathing” like behavior of the SEI where upon lithiation the layer thins and thickens upon de-lithiation.11,12 Interestingly in another NR experiment looking at the SEI formation on Si with the addition of the additive fluoroethylene carbonate (FEC), the opposite effect was observed in which the SEI thickens during lithiation and thins during de-lithiation.13

In this study, the effect of the polymeric binder, Poly(2,7-9,9-dioctylfluorene-co-2,7-9,9-(di(oxy-2,5,8-trioxadecane))fluorene-co-2,7-fluorenone-co-2,5-1-methylbenzoate ester) (PEFM), on the SEI layer composition was studied using in situ neutron reflectometry. The functional groups of the polymer include polyfluorene (P), fluorene (E), fluorenone (F), and a methyl benzoate ester (M).7 PEFM was chosen as it was designed to incorporate components of what is believed to make a good binder, i.e., swelling when in contact with the electrolyte, mechanical integrity, and electronic conductivity to reduce the need for a conductive additive such as C.7 in this work cells were cycled to various potentials associated with electrolyte reduction and lithiation of the silicon and NR data was collected. Ex situ experiments using x-ray photoelectron spectroscopy (XPS) were performed to further characterize species of the SEI at various formation potentials.
2.4 Experimental

Sample electrodes for this experiment were prepared by a combination of physical vapor deposition and spin coating. A single crystal 51 mm diameter, 5 mm thick silicon wafer was used as a substrate. The films were deposited using an in-house sputtering system utilizing RF magnetron sputtering and reaching base pressures in the $10^{-6}$ Torr range. A 6 nm Cu layer was deposited using a commercially available Cu target (99.99%, Plasmaterials). The Cu layer is used as a current collector, a contrast layer, and in addition, prevents lithiation of the single crystal Si substrate. Without breaking vacuum, a 50 nm a-Si (99.999%, Kurt J. Lesker) film was deposited atop the Cu film as the working electrode. The PEFM polymer binder was dissolved in chloroform to make a 0.1 wt% solution which was then pipetted onto the a-Si layer and then spun at 5000 rpm for 30 seconds. Samples were dried under vacuum at 80°C for two hours to remove excess solvent and were subsequently vacuum sealed in order to prevent further air exposure.

The battery electrolyte was prepared using deuterated ethylene carbonate (d-EC, Sigma Aldrich, 99%) and deuterated dimethyl carbonate (d-DMC, Sigma Aldrich, 99%) in a 30:70 wt% and dried over zeolites in an Ar filled glovebox. A thin strip of Li was placed in the solvents in order to react away impurities. The LiPF$_6$ salt (BASF, 99.99% battery grade) was added to form a ~1.1 M solution.

An *in situ* electrochemical half-cell was constructed using the Cu/a-Si thin film. A TiZr ($\text{Ti}_{0.47}\text{Zr}_{0.53}$) substrate was used for the Li counter/reference electrode as it does not react with Li metal in addition to being a null neutron scatterer. A Teflon coated Viton o-ring, with a 1 mm cross-sectional area and 49 mm inner diameter, was placed between the a-Si and lithium coated TiZr to prevent shorting and define the working area of the electrode. A Teflon top was placed between the TiZr and cell top to prevent shorting and 4 mL of electrolyte were introduced into the cell. A conductive Ag epoxy (ITW Electronics) was used for an electrical contact and did not come into contact with the electrolyte. The scattering orientation and photo of the electrochemical cell is shown in Figure A.1. Cells were cycled at a C/3 rate and charged to the following potentials: 1.5, 1.2, 0.8, 0.4, 0.15, and 0.05 V (vs. Li/Li$^+$) using a Biologic VSP potentiostat. Once the potential was reached under galvanostatic conditions the current response was measured under potentiostatic conditions. After reaching the desired potentials the cell was allowed to equilibrate for ten minutes and NR data was collected. Before acquiring *in situ* measurements, samples were measured in air in order to determine the SLD profiles of the deposited layers.
Experiments were performed on the Soft Interface Analyzer (SOFIA) instrument (Beamline 16) at the Materials and Life Science Experimental Facility (MLF) located at the Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan.\textsuperscript{14,15} SOFIA is a horizontal geometry instrument that utilizes the time-of-flight method. The incident neutron energy ranges from 0.11 < \lambda < 0.88 \text{ nm} with a theta range of 0.3, 0.7, 1.6, 3.5° for in-air samples and 0.3, 0.7, 1.4, 2.4° for samples collected in the \textit{in situ} cell. Data fitting was performed using the Motofit software developed by A. Nelson.\textsuperscript{16}

\textit{Ex situ} experiments using x-ray photoelectron spectroscopy (XPS) were performed using a PHI 3056 spectrometer with a Mg anode operated at a 15 kV with an applied power of 350 W. A low-resolution survey scan was collected with a pass energy of 93.5 eV, while high resolution scans utilized a pass energy of 23.6 eV. Spectra were corrected to 284.8 eV, the primary C peak for all samples as evidence of charging was present in the lithiated samples. Witness samples were prepared in the same manner as the NR sample; however, films were deposited onto Cu foil as opposed to a Si substrate. After spin coating the electrodes were cycled in a coin cell using the same electrochemical procedure as the NR experiment looking at OCV, 1.2 V, 0.8 V, 0.15 V, and 0.05 V. After reaching the desired potential the cells were disassembled and soaked in DMC to remove excess salt deposits and were then transported in a vacuum sealed container to the XPS.

\section*{2.5 Results}

\subsection*{2.5.1 As-prepared Si anode}

The a-Si anode used in the NR studies was initially measured in air to determine the as-prepared structure of the sample and is shown in the top of Figure 2.1. The refinement of the data (Figure 2.1 middle) results in a SLD distribution (Fig.2.1 bottom) which represents the structure of the film as a function of depth, as schematically shown on the SLD plot on the bottom of Figure 2.1. From the refinement, the Si layer was determined to have a thickness of ~464 Å with an SLD of 2.07 \times 10^{-6} \text{ Å}^2 (for simplicity the unit for the SLD \textit{[}x10^{-6} \text{ Å}^{-2}\text{]} will be omitted from this point on), which is in agreement with the theoretical SLD of Si (2.07) indicating a uniform and dense a-Si film. There was no evidence of an oxide layer on the a-Si surface, which doesn’t preclude the existence of one as such a thin layer is often hidden by roughness between adjacent layers or an SLD close to that of the a-Si or PEFM films.\textsuperscript{13} The Cu film was approximately 200 Å thick with an SLD of 6.54 which is also in good agreement to that of the theoretical value of 6.59, while the
native oxide layer present on the substrate was ~17 Å thick. The PEFM polymer binder was spin coated to a thickness of 41.9 Å, which was ideal in order to allow lithiation and prevent creation of an insulating layer. The fit resulted in an SLD of 1.56. With Equation 2 and the measured SLD value the density and areal density for the PEFM binder layer were calculated to be 0.35 g cm$^{-3}$ and 0.15 µg cm$^{-2}$, respectively. Witness samples fabricated for XPS show the C1s peak with a significant amount of C-C/C-H (284.8 eV) on the surface most likely originating from the binder which has a complex structure made up of C ring backbones (Figure 2.3). Approximately 25.4 at% of the C1s spectra (Figure A.6) was made up of a C-O species with concurrent peaks observed in the O1s spectra (532.5 eV, Figure 2.4). There was additional evidence of carbonyl groups with a binding energy of 531.26 eV. The Si2p peak (Figure A.2) is still evident which is expected as the binder layer is only a few nanometers thick while the depth probed by XPS is on the order of 10 nm.
Figure 2.1. A representation of how data is collected on the thin film assembly (top) for the in-air measurements to determine the as-prepared sample. Data collections (middle) results in a reflectivity (R) vs. Q plot (open circles) and the resulting fit (solid line). The fit produces an SLD plot (bottom) representing a one-dimensional representation of the film the heterostructures and separated by the layer interfaces.
Figure 2.2. Neutron reflectivity data with open holes representing collected data and the fit shown as a solid line (top). The SLD profile from resulting fit (bottom).
2.5.2 Open circuit voltage

After the cell was constructed and alignment complete the electrolyte was in contact with the anode for ~ 30 min and the OCV equilibrated to 2.8 V (vs Li/Li+) before data collection. Figure 2.2 shows NR data collected for the sample in the cell (top) and resulting SLD vs thickness profiles (bottom) used to fit the data. Individual SLD depth profiles for each state of charge can be found in the supplemental section (Figure A.7). Results for the thickness, SLD, and goodness of fit ($\chi^2$) for the PEFM, SEI, and a-Si films are summarized in Table 2.1. Changes in the reflectivity from air to OCV are evident, with the resulting fit indicating a decrease in the Si layer thickness (464.2 to 450.1 Å) and the addition of a new layer on the surface of the anode. The new film is attributed to a reaction layer that forms as a result of the chemical reactivity of the active Si surface with the electrolyte and is approximately 42 Å thick.\textsuperscript{10} The SLD value was 2.95 significantly lower than the electrolyte SLD (5.46) indicating the incorporation of a component with a low coherent scattering length needed to lower the SLD. Given the elemental makeup of the electrolyte components, i.e. D, O, F, and P (6.6, 5.8, 5.1, and 5.6 fm, respectively), have relatively high scattering lengths, the reaction layer is most likely Li rich, which has a bound coherent scattering length of -1.90 fm, and would originate from the LiPF$_6$ salt.\textsuperscript{10} The fitting routine of the neutron data attempted various models in terms of the placement of the reaction layer/SEI. When the layer was placed on the surface of the PEFM binder, the model resulted in a none physical representation of the system and could only be fitted with the layer underneath the binder. In addition, the only way to get a higher SLD is with the d-EC/d-DMC; therefore, the change has to be due to solvent at the a-Si interface. Turning to the XPS results the C1s spectra shows no statistical variation in C-C/C-H and C-O peaks between the in air and OCV witness samples (Figure 2.3). However, the O1s spectra shows the formation of C-O-C, P-O-F peak, as shown in Figure 2.4, attributed to the LiPF$_6$ salt in the electrolyte. There was a decrease of ~16 at% in the C=O while the C-O, Si-O peak stayed the same, in agreement with the C1s data (Figure A.6). Interestingly the PEFM layer stays fairly constant in thickness (Table 2.1) with a very slight increase in SLD from 1.56 to 1.73. This increase would indicate an incorporation of 0.05 volume fraction of electrolyte incursion within the PEFM film from porosity or absorption. The F1s peak shows evidence of P-F (688.6 eV, 39.8 at%) and P-O-F (686.4 eV, 60.2 at%) representative of the salt (Figure 2.5) and further supported by the P2p peak with the addition of P-O (134.4 eV, Figure A.3).
Table 2.1. Results for NR refinements of the PEFM, SEI, and a-Si layers.

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<td>Air</td>
<td>41.88±1</td>
<td>1.56±0.05</td>
<td>6.54±0.01</td>
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<td>7.79±1</td>
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<td>2.06±0.01</td>
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<td>1.5 V</td>
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<td>1.59±0.05</td>
<td>8.18±0.5</td>
<td>38.65±0.1</td>
<td>3.11±0.05</td>
<td>8.09±0.1</td>
<td>450.86±0.9</td>
<td>2.06±0.01</td>
<td>13.36±1</td>
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<tr>
<td>1.2 V</td>
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<td>63.71±2</td>
<td>54.23±2</td>
<td>4.08±0.06</td>
<td>16.96±5e-14</td>
<td>461.82±0.7</td>
<td>2.06±0.01</td>
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<tr>
<td>0.8 V</td>
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<td>5.21±0.03</td>
<td>6.72±0.8</td>
<td>54.82±2</td>
<td>5.52±0.04</td>
<td>7.66±1</td>
<td>472.51±0.4</td>
<td>2.06±0.01</td>
<td>7.66±1</td>
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<td>0.4 V</td>
<td>147.17±2</td>
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<td>19.75±1</td>
<td>130.39±4</td>
<td>4.47±0.03</td>
<td>37.39±1</td>
<td>484.52±0.4</td>
<td>1.92±0.03</td>
<td>6.46±0.30</td>
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<td>0.15 V</td>
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<td>68.60±1</td>
<td>556.13±4</td>
<td>3.91±0.03</td>
<td>5.14±0.14</td>
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<td>0.05 V</td>
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<td>0.433±0.03</td>
<td>6.54±2e-14</td>
<td>7.7</td>
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Figure 2.3. XPS results for C1s spectra

Figure 2.4. XPS results for O1s spectra
2.5.3 No lithiation (1.5 and 1.2 V)

Previous experiments have indicated trace impurities could be present within the deuterated solvents and as a precaution the 1.5 V (vs. Li/Li$^+$) potential is run at a higher C-rate to purify the electrolyte.\textsuperscript{11} No change in the SLD of the electrolyte was observed between OCV and the 1.5 V potential, remaining at 5.46 indicating no significant impurities within the electrolyte; therefore, this parameter was kept constant for the remainder of the fits. No changes are evident in the film heterostructures at 1.5 V as indicated by NR refinements.

At 1.2 V the SLD increases from 1.59 to 2.58 in the PEFM layer from the incorporation of electrolyte accounting for upwards of 26% volume fraction which is also confirmed by a ~ 50 Å thickness increase from OCV and 1.5 V. The SLD of the reaction layer increased to 4.08 indicating higher SLD components from the electrolyte reacting in the reaction layer on the surface of the a-Si anode commensurate with a ~ 16 Å growth in thickness, Table 2.1. The XPS witness sample showed a decrease in the overall C content by approximately 10 at% (61 to 51 at%) as depicted in Figure A.5 and the formation of a new spectra with a binding energy at 288.2 eV consistent with the formation of O-C=O (Figure 2.3). The O1s spectra showed an increase in the C-O, Si-O peak
by approximately 10 at% from the OCV content of 76 at% with a subsequent decrease in C=O from 9.54 to 3.13 at% (Figure A.6).

2.5.4 Initial SEI formation (0.8 V)

Refinements of the 0.8 V NR data indicates two distinct structures: the SEI layer on the surface of the anode and the PEFM on top of the SEI as depicted in Figure 2.2 by the purple SLD profile. The interface between the SEI and PEFM are distinct and well defined. The electrochemistry as a function of state of charge and current is depicted in Figure 2.6, highlighting the large current response resulting in the generation of 2 coulombs of charge at 0.8 V (Figure 2.6). The most likely explanation is binding of Li to the PEFM, which is designed to be cathodically doped in a reducing environment where Li will attach to the F group of the polymer. This is in conjunction with an increase in thickness of the PEFM to ~ 200 Å, from 93 Å from the previous potential. The significant increase in SLD of the PEFM layer to 5.21 (from 2.58) suggests a large incorporation of solvent within the polymer layer. Interestingly, NR shows no increase in thickness for the SEI (from the previous potential). However, there is a significant increase in the SLD from 4.08 at 1.2 V to 5.52 indicative of a significant change in chemistry of the SEI layer on the surface of the Si due to the reduction of the d-EC at this potential or uptake of Li⁺ into the bottom of the PEFM from the SEI layer. The close SLD value of the SEI layer at 5.5 is close to the SLD of the electrolyte at 5.46 indicates the layer of close chemical composition to the electrolyte. The ability to see the layer is a result of the presence of the polymer which has a SLD of 5.21.
The overall XPS spectra indicates an increase in the C content around 67.1 at%, up from 51.6 at% at 1.2 V; in addition, a slight increase of ~6 at% of O content from the as-prepared, OCV, and 1.2 V witness samples which averaged around ~12.3 at% (Figure A.5). While a decrease in the inorganic moieties, F and P, indicating the 0.8 V SEI layer was organic in nature as depicted in Figure 2.7 which compares the organic portions (C, O) with the inorganic components (F, P) overlaid with the SEI thickness and SLD. This is in conjunction with the high SLD value observed. Looking at the results for fits in Figure A.6 for C1s spectra, C-C/C-H species increased to 75 at% while a significant decrease in the C-O peak was observed (31.0 at% to 17.5 at%) and is also confirmed in the O1s spectra. The O-C=O moieties stayed the same. The O1s indicated a slight increase in the C-O-C, C-O-F as well as the C=O. The F1s and P2p both indicate a decrease in the P-O-F species. A new species was observed with a binding energy of 685.40 eV assigned to the formation of LiF (Figure 2.5). The XPS indicates an organic layer rich in C and O; however, a significant portion of this layer must have been removed with the rinsing of the witness sample as the Si$^0$ (Figure A.2) is still evident even though NR indicates a polymer layer ~20 nm thick beyond the maximum escape depth of the photoelectrons. The SLD of the PEFM layer is ~5.14, close to

Figure 2.6. Electrochemical data for \textit{in situ} neutron experiment with voltage profile highlighted in solid black and current profile highlighted in red. Neutron collection occurred after cell returned to equilibrium highlighted by dashed black line.
that of the electrolyte (5.46) which is in agreement with the XPS indicating a large amount of C, D, O, F incorporation into the layer all of which have high scattering cross sections.

### 2.5.5 Beginning of lithiation (0.4 and 0.15 V)

The lithiation of the a-Si layer begins at 0.4 V vs Li/Li⁺ as indicated in the NR refinements with the increase in the Si layer thickness from 472.5 to 484.5 Å. This is coupled with the lowering of the SLD to 1.92 (Table 2.1) indicating the incorporation of Li as it has a low scattering cross section which lowers the average SLD. From formalism developed by Chevrier and Dahn¹⁷ the extent of lithiation was estimated to be Li₀.₀₅Si, a very small Li content within the Si. Li is also becoming incorporated in the SEI layer as a significant decrease in the SLD, from 5.52 to 4.57, was observed as well as a swelling of the layer by over 70 Å (compared to the 0.8 V thickness). There is evidence of a more intermixed layer forming between the polymer and SEI as observed in the SLD profile (Figure 2.2) in which the distinct polymer layer at 0.8 V is no longer evident at 0.4 V. The SLD profile indicates a diffuse interface between the SEI and polymer layer. The large uptake of electrolyte results in a contrast match as the layers’ SLD become close to that of the electrolyte. By 0.15 V the PEFM and SEI layers results in a gradient where the interface between the two layers is no longer distinguishable. Interestingly, the SLD of the PEFM layer has decreased from 5.19 to 4.62 similar to the SEI layer which settles to 3.91 (as compared to 4.47 at 0.4 V) as shown in Figure 2.7. As the potential is decreasing and more Li⁺ is moving through the system it is most likely becoming incorporated in the PEFM as well as being consumed in the SEI leading to the small Li:Si ratio, Li₀.₀₉Si, being observed. The Si layer has only slightly changed in both thickness and SLD further supporting low concentrations of Li⁺ in the anode.

XPS supports a thick layer formation as indicated by the intensity of the Si2p peak which has significantly decreased due to the attenuation of the photoelectrons from the surface of the electrode. The overall C content decreases going from 0.8 to 0.15 V by as much as 46 at%, going from 67.1 at% at 0.8 V to 20.7 at% at 0.15 V (Figure A.5). The Li content accounting for 41.6 at%, is likely representative of the top layers of the sample both in the PEFM and SEI layers as opposed to the Si itself due to the thickness, ~ 800 Å of the two layers determined by NR. A significant amount of the layer must have been washed off due to the presence of Si2p spectrum (Figure A.2). Charging was observed in the sample and found to be caused by the increased LiF species which is insulating in nature (as depicted by the grey peak in Figure 2.3). The LiF content increased from 17.7 at % to 76.7 at%. The high content of LiF implies extensive reduction of the
LiPF$_6$ salt. This is further supported by the Li1s spectra which is entirely composed of LiF (56.15 eV). No significant changes in the P2p were observed. The C-C/C-H peak decreased significantly (27.2 at% total) while the C-O moieties increased from 17.5 to 40.2 at%. A new peak with a binding energy of 289.8 eV was observed and assigned to -CO$_3$ while no O-C=O was evident. Figure 2.4 shows the formation of a new species in the O1s spectra with a binding energy of 530.2 eV attributed to Li-O species.

2.5.6 Lithiated (0.05 V)

At 0.05 V the a-Si layer has been lithiated to Li$_{0.7}$Si based on thickness. Due to the low Li:Si ratio the Li was most likely consumed in the both the SEI and PEFM layer which is further evidenced by a decrease in the SLD of the SEI (3.91 to 1.63) and that of the PEFM (3.09 from 4.62). The SEI and PEFM layer/s appear to swell significantly at 0.15 V; however, at 0.05 V a distinct 71.6 Å SEI layer forms on the surface of the lithiated a-Si with an SLD of 1.63 (Figure 2.2, Table 2.1). This would indicate a fairly Li rich SEI due to the significant decrease in SLD from the previous two voltage states. Lithiation is also indicated by an increase in the a-Si layer increasing to 747.9 Å and lowering of the SLD to 0.43 indicative of Li$^+$ incorporation. The PEFM layer is most likely trapping Li as the lithiated Si layer has not reached the theoretical limit of Li$_{3.75}$Si. The PEFM layer compresses to 121.3 Å, a decrease of ~ 126 Å from the previous potential, as is crosslinks or expels solvent. Components within the PEFM layer are being dissolved back into the electrolyte. The Si2p peak points to the lithiation of an oxide layer on the surface of the Si as a peak consistent with Si-O-F is identified. However, given the total thickness of the surface layers on the surface of the anode, ~193 Å, a significant portion of the layers are being rinsed away. The XPS confirms a Li$_2$O peak with a binding energy of 55.8 eV as well as a significant amount of LiF. The insulating nature of both the LiF and Li-O resulted in significant charging evident in the C1s peak. The F1s and P2p peaks both show an increase in the P-O-species.
Figure 2.7. Atomic % of XPS witness samples at various states of charge overlaid with SEI SLD (green circle) and SEI thickness (blue triangle).
2.6 Discussion

The effect of the polymer binder, PEFM, on the SEI composition and formation on a Si anode is explored in the presented data through the use of *in situ* NR and *ex situ* XPS. A schematic of the film heterostructures, as determined by the NR refinements, is depicted in Figure 2.8. From the NR it is evident the polymer layer is continuously changing with higher states of lithiation through interactions with the electrolyte. At OCV, Li is concentrated at the surface of the anode, underneath the PEFM, in the reaction layer and a similar thickness and SLD is evident when compared to previous NR experiments (Table 2.2).\textsuperscript{10,11,13} As the cell is polarized to 1.2 V, the swelling of the PEFM layer is observed commensurate with an increase in SLD due to solvent uptake. There is a small increase in the SEI SLD due to D, C, O, F species (Figure 2.3), but not much change in the thickness of the SEI layer. At 0.8 V we observe a huge increase in the PEFM thickness and composition (increased SLD) which has to be due to solvent incorporation/swelling. We continue to see the SEI grow more organic due to solvent decomposition. This is further supported by the XPS results which shows a distinct Si spectrum of the witness sample (Figure A.2), as the polymeric/organic moieties are more susceptible to the rinsing procedure and would be redissolved in the wash which explains the much thinner layer observed in XPS at 0.8 V.\textsuperscript{18}

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Figure 2.8. Summary of heterostructures from NR refinements at various states-of-charge
At 0.4 V a thinning in the PEFM layer occurs in addition to swelling of the SEI to 130 Å with a small drop in SEI SLD (5.5 to 4.5) due to more solvent and more Li within in the SEI layer. If it was just related to solvent the SLD would be higher, whereas if it were related to salt alone the SLD would be much lower. The two layers (PEFM and SEI) are closely mixed and appear to be transferring solvent (C, O, F, D) from the PEFM to SEI resulting in a matrix between the two layers. The 0.15 V data shows a growth in the PEFM again through solvent and salt incorporation, but there is a larger swelling of the SEI layer to 556 Å corresponding with a decrease in the SLD which occurs because of solvent and salt concentration. The PEFM binder was designed to swell in electrolyte solutions, similar to PVDF, and shown to incorporate upwards of 50 wt% of solvent within its structure.\textsuperscript{7,19} The significant electrolyte uptake within the PEFM inhibits the bulk electrolyte from contacting the Si surface. The most likely explanation for a matrix from the electrolyte/PEFM/SEI interfaces, observed at 0.4 and 0.15 V is the result of electrolyte decomposition within the polymer and SEI layer altering the electrolyte composition that is interacting with the Si. This was recently observed in another binder poly (1-pyrenemethyl methacrylate) (PPy).\textsuperscript{20} The authors from this study determined the mechanism for passivation of the crystalline Si, in the presence of the PPy binder, was altered as a result of selective solvent uptake. This changed the distribution of the decomposition products resulting in ineffective passivation of the Si surface.\textsuperscript{20}

At 0.05 V a condensation process is observed in the PEFM/SEI matrix resulting in a now well-defined SEI layer on the surface of the lithiated Si (Figure 2.2 bottom green SLD plot). The PEFM is 121 Å with an SLD of 3.1 indicating less organics within the layer, while the SEI goes from 556 to 71 Å and an SLD of 3.9 to 1.6. Again, a less organic but Li\textsuperscript{+} rich SEI layer. Once the cell is polarized to 0.05 V there is enough of a driving force to push unreacted Li\textsuperscript{+} in the layers into the anode causing a reordering of the SEI and PEFM. However, due to the elemental makeup the PEFM layer is no longer the same as the as prepared resulting in an intermixed layer of electrolyte decomposition products and PEFM (Figure 2.8). The contraction of the SEI is a result of the changing composition and density of the layer. Due to the two unknowns within Equation 2, the density and exact chemical composition of the SEI layer cannot be determined from NR alone.

In comparison with previous work done by the group looking at a-Si anode in the same electrolyte\textsuperscript{11} and with addition of the electrolyte additive (FEC),\textsuperscript{13} there are evident trends among the three cases (Table 2.2). The OCV reaction layer among all three experiments is similar in
thickness and SLD, indicating similar reaction mechanism and chemical compositions. At 1.2 V, the PEFM and Si show a more organic SEI on the surface of the Si with similar chemical compositions. Interesting, in the case of the FEC the SLD remained fairly consistent throughout and is fairly Li⁺ rich. However, both the Si and FEC become inorganic as the cell is further polarized (0.4 to 0.15 V), while the PEFM remains organic. Together this data indicates the FEC is driving the surface far more inorganic in nature, while the PEFM promotes organic like interfaces. After lithiation the SEI always becomes mostly inorganic, but the PEFM delays this transition. Unlike the two previous cases, it is evident there is a bilayer present on the surface of the lithiated Si with a total thickness of ~193 Å. A dense and compact layer on the surface of the anode that is Li⁺ rich, and a more organic layer at the electrolyte interface similar to the suggested bilayer SEI structure.

The data points to the PEFM acting as a membrane where solvent molecules selectively concentrate to the surface of the Si. The PEFM acts as a barrier to lithiation of the anode, then is gets polymerized/condensed where it appears organics are redissolved into the electrolyte. The swelling of the PEFM binder is similar to what is observed for PVDF. Beyond the mechanical properties of the PVDF binder, the uptake of electrolyte within the binder system maybe determinantal to the performance of the Si cell. This hypothesis needs to be explored. If a polymer system could be designed to drive the salt to the surface with selective ion transport it may yield a better SEI and a “stable” Si anode.
Table 2.2. A comparison of SEI thicknesses and SLDs from NR experiments of PEFM, a Si anode, and Si with FEC additive.

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ORGANIC → INORGANIC
C, O, D → Li⁺

aData collected at 0.9 V vs. Li/Li⁺, bData collected at 0.12 V vs. Li/Li⁺
2.7 Conclusion

This study highlights the complicated role of the binder in SEI formation. The PEFM binder is a dynamic layer that hinders the lithiation of the anode until low potentials and concentrates organic solvent near the surface. There is a defined interface between the SEI and binder layer indicating the SEI still forms on the surface of the anode as opposed to the surface of the PEFM and a bilayer structure is evident at 0.05 V. This study focused on a model electrode representing a fully coated active particle. It would suggest that patchy coating of the binder would result in a different SEI formation and thickness; however, with the full coating of the binder a distinct two-layer SEI is observed on the surface of the lithiated anode. The membrane like behavior of the polymer indicates a binder that selectively brings salt to the surface, in addition to ion channels would perform better as opposed to uptake of solvent molecules.

2.8 Acknowledgments

This research at the Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725 was sponsored by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO) (Deputy Director: David Howell) SEISTa subprogram (Program Manager: Brian Cunningham) (KLB and GMV) and the Office of Basic Energy Sciences FWP-ERKCSNX (JFB, MD). The neutron experiment at the Materials and Life Science Experimental Facility of the J-PARC (NY) was performed under a user program (Proposal No. 2017AU1602).
2.9 References


Appendix A

Figure A.1. Schematic for the electrochemical cell used for the *in situ* NR experiment.

Figure A.2. XPS results for Si2p spectra.
Figure A.3. XPS results for P2p spectra.

Figure A.4. XPS results for Li1s spectra.
Figure A.5. Atomic percent of XPS witness samples.
Figure A.6. Atomic percent from fits of XPS witness samples.
Figure A.7. Individual SLD depth profiles for each state of charge.
CHAPTER 3: THE STUDY OF THE BINDER POLYACRYLIC ACID AND ITS ROLE IN CONCOMITANT SOLID-ELECTROLYTE INTERPHASE FORMATION ON SI ANODES
3.1 Disclosure

This chapter is based on a manuscript that was submitted to ACS Applied Materials and Interfaces, in review. The full list of authors includes: Katie L. Browning, Robert L. Sacci, Mathieu Doucet, James F. Browning, Joshua R. Kim, and Gabriel M. Veith

3.2 Abstract

We use neutron reflectometry to study how the polymeric binder, polyacrylic acid (PAA), affects the in situ formation and chemical composition of the solid electrolyte interphase formation (SEI) on a silicon anode at various states-of-charge. The use of model thin films allows for a well-controlled interface between the amorphous Si (a-Si) surface and the PAA layer. If the PAA perfectly coats the Si surface and standard processing conditions are used the binder will prevent the lithiation of the anode. The PAA suppresses the growth of new layer formation at early states of discharge (open circuit voltage to 0.8 V vs. Li/Li⁺). At 0.15 V the SEI layer underneath the PAA, increases in thickness and SLD as it incorporates components from the electrolyte. At lithiated and delithiated states the SEI layer changes in chemical composition and thickness dependent on the state of lithiation. The SEI layer grows with delithiation and shrinks during lithiation. The PAA layer keeps the SEI thin and inorganic in nature.

3.3 Introduction

One of the most crucial interfaces within any battery is the passivating layer that forms on the surface of the anode known as the solid electrolyte interphase, or SEI. The SEI is a result of electrolyte decomposition, as a consequence of operation outside the voltage window of commonly used electrolytes, and is ideally electronically insulating and ionically conducting. Irreversible capacity loss in the first charge/discharge cycle of a Li-ion battery is often attributed to the development of this layer. Without proper SEI formation the battery will fail to meet sufficient columbic efficiencies as a result of rapid capacity fade as the electrolyte is consumed. The SEI is often cited as the limiting factor for silicon-based chemistries due to the instability of the layer. Si at room temperature form a series of electrochemical alloy with Li, giving rise to a theoretical capacity of 3579 mAh g⁻¹, an order of magnitude higher than graphite (~372 mAh g⁻¹). This alloying reaction causes significant stresses within the material as a 300% volume expansion occurs as the Li alloys with the Si. Upon delithiation of the Si, the mismatch in materials results in the SEI dissolving or separating leading to fresh cracked surfaces being exposed to the
electrolyte. Because of these new surface’s interaction with the electrolyte, significant electrolyte degradation occurs in these anodes and leads to poor capacity retention over repeated charge/discharge cycles. In addition, Si is covered in a native oxide layer thus leading to questions of how the oxide will affect SEI chemistry.

Photoelectron spectroscopy measurements before lithiation of Si shows the SEI resembles the chemical composition found on graphite or carbonaceous anodes; however, at the start of lithiation the silicon oxide layer is lithiated first resulting in a silicate formation on the surface of the anode before lithiation of the bulk material. Another chemical moieties observed in Si SEI is a silicon oxyfluoride species most likely from the onset of hydrofluoric acid (HF) attack from ppm levels of water present in the electrolyte reacting with the salt forming HF. The presence of the oxide layer exemplifies the complex interfacial reactions between pristine Si and the electrolyte. These interfacial reactions are amplified within a composite electrode which contain additives such as conductive carbons and polymeric binders.

Binders, particularly polyvinylidene fluoride (PVDF), are an industry standard used in composite electrodes to bind active materials and additives such as C black to the metal current collector and to promote particle-to-particle cohesion. Though the final architecture of the binder matrix is not fully understood, there is interactions between the surface of the Si and the binder. This leads to the question of how the addition of an insulating polymeric binder, added to mitigate the effect of Si expansion in composite slurries, effects the SEI formation. We know the binder has a role in the electrochemistry, regardless of the anode. For example, the commonly used binder PVDF doesn’t work in silicon based chemistries, but the use of polyacrylic acid (PAA) does. In addition, the components of composite based electrodes can change the SEI. Indeed, one study looking at different surface area carbons, the choice of PAA and CMC binders led to an “artificial SEI” that enhanced the cyclicity. PAA has also been shown to create a protective layer, or act as an interfacial modifier on the surface of graphite in propylene carbonate based electrolytes.

PAA is composed of carboxyl groups that form a covalent bond to the hydroxyl groups present on the Si surface due to the native oxide layer. However, many questions still arise about how the binder interacts within a composite slurry. Indeed, very little is known about how PAA or any other binder affects the composition and formation of the SEI. For instances, how does the insulating nature of the PAA change or alter Li conduction pathways? Or if the Si nanoparticle is completely coated by PAA how does the electrolyte interact with the active material? Lastly, does
the SEI form on the surface of the polymer or the surface of the Si? Some of these questions are beginning to be explored where the presence of PAA in a composite Si electrode and appeared to accelerate the decomposition of the LiPF$_6$ salt resulting in significant LiF formation in the SEI, as seen in x-ray photoelectron spectroscopy (XPS). The authors of that study determined at full lithiation Li$_2$CO$_3$ and LiF were the dominate species as identified by x-ray photoelectron spectroscopy. Typical *ex situ* techniques used to explore SEI chemistries rely on a post-mortem preparation where the electrode is rinsed in a solvent to remove excess salts. This can lead to the removal or alteration of the fragile upper porous layer of the SEI, highlighting the need for both *in situ* and *ex situ* techniques to study this interface.

The ability to control the architecture between the Si surface and the binder enables a controlled study of the electrolyte/binder/Si surface. In this study model thin films with a spin coated PAA layer were probed using both *in situ* and *ex situ* techniques to better understand the chemistry, thickness, conductivity, and viscoelastic properties of the SEI. In conjunction with XPS, neutron reflectometry (NR) and electrochemical quartz crystal microbalance (EQCM) provides powerful tools to study SEI composition as a function of the state-of-charge both *in situ* and *ex situ*. Neutron reflectometry uses a beam of neutrons to probe buried interfaces to provide information on the composition, thickness, roughness and/or diffuseness of the layers. Electrochemical quartz crystal microbalance (EQCM) is an extremely sensitive tool that utilizes shifts in frequency of quartz, a piezoelectric material, to study changes in mass. In order to understand the ionic conduction of the surface layers electrochemical impedance spectroscopy (EIS) was performed during the neutron collection. The cell configuration utilizing thin films eliminates the need for conductive additives. Indeed, with the use of model electrodes the exact architecture of the binder is known which provides information on how Li is conducted through this layer, in addition to where the SEI forms.

### 3.4 Experimental

Magnetron sputtering was used to deposit a 10 nm Cu (Plasmaterials, 99.99%) thin film onto a single crystal Si substrate (Institute of Electronic Materials Technology, Warszawa, Poland). The Cu film acts as a current collector, a contrast layer between the a-Si and Si substrate, as well as a Li diffusion barrier. Without breaking vacuum, a 50 nm a-Si (Kurt J. Lesker, 99.999%) film was deposited on top of the Cu. Base pressures for the in-house system reached 10$^{-6}$ Torr. PAA (Sigma Aldrich M$_w$=1800) was dissolved in methanol to make a 1 wt% solution and spin
coated (Laurell WS-400B-6NPP/LITE/AS) atop the a-Si film at 3000 rpm. Samples were dried under vacuum at 140°C for ~ 18 hrs.\textsuperscript{25} After drying, samples were immediately placed in a He filled glovebox.

The electrolyte used in this experiment was homemade, where deuterated ethylene carbonate (d-EC, Sigma Aldrich 99%) was mixed with deuterated dimethyl carbonate (d-DMC, Sigma Aldrich 99%) in a 3:7 wt% solution and dried over 4Å sieves with a strip of Li to react with impurities in the solution. The salt, LiPF$_6$ (BASF) was mixed with the solvent in a ~1.2 M solution. Samples for XPS and EQCM also used a 1.2 M LiPF$_6$ EC:DMC 3:7 electrolyte without deuterium.

In this study, \textit{in situ} neutron reflectometry (NR) and \textit{ex situ} x-ray photoelectron spectroscopy (XPS) were performed to study the SEI formation on a-Si thin film as a result of PAA spin coated on the surface. Neutrons are an ideal probe for battery materials because they interact with the nucleus, therefore, are not limited by the Z number of a material allowing for lighter materials such as Li and H to be studied. In addition, they are extremely sensitive to isotopes allowing for contrast changes in a single experiment. Neutron reflectometry probes buried interfaces in complex environments providing information on the thickness, roughness and/or diffuseness of a sample. The most important parameter determined is the scattering length density (SLD) which provides information on the composition of the layer being probed as described by Equation 2.

Neutron reflectometry was performed on the Liquids Reflectometer (LR) located at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). The LR is a horizontal geometry time-of-flight reflectometer. A 3.5 Å bandwidth, extracted from a wavelength range of 2.5-17 Å, is used in conjunction with measurement angles of $\Theta$=0.60, 0.69, 1.19, and 2.34 to extend a Q range of 0.005 to 0.4 Å\textsuperscript{-1}. The footprint on the sample is kept constant through adjustments in the sample slit opening commensurate with the angle of incidence. Analysis was done using the Motofit analysis package and ORNL’s Web Interface (Webi).\textsuperscript{26,27} Specular reflection is a measurement of the wave vector transfer of the neutron expressed by $Q=4\pi\sin\theta/\lambda$, where $\theta$ is the angle of the incident beams and $\lambda$ is the wavelength of the neutron beam. Measurements result in a reflectivity (R) as a function of Q, which can be modeled to produce an SLD profile as a function of sample depth.

Samples for NR were placed in an \textit{in situ} cell assembled in a He filled glovebox. A Teflon coated o-ring with a 1 mm cross-sectional and 49 mm inner diameter, was placed on top of the a-Si/Cu/Si substrate. Li was rolled onto a Ti$_{0.47}$Zr$_{0.53}$ (TiZr) substrate. TiZr is used as it does not
react with metallic Li, in addition to being a null scatterer to minimize background. The TiZr was subsequently placed on top of the o-ring. A Teflon top is placed on the TiZr to prevent electrical shorting and ~3 mL of electrolyte was introduced into the cell. A Ag epoxy (ITW Electronics) was painted onto the a-Si substrate to create an electrical contact but was outside the Teflon coated o-ring and did not interact with the electrolyte.

Potentiostatic measurements were controlled with a Biologic VSP and driven to the following potentials: 1.5, 1.2, 0.8, 0.4, 0.15, 0.05 V, 1.5 V, and 0.05 V (vs Li/Li^+) at a rate corresponding to C/3 in a constant current/constant voltage process. All potentials stated in this paper are measured against Li/Li^+. After reaching the desired potential the cell was held for one hour while the current was measured. The cell was then allowed to relax back to OCV and NR was collected. Electrochemical Impedance Spectroscopy (EIS) was performed simultaneously with the NR data collection. A reference electrode was fabricated with a Pt wire (Alfa Aesar) and Ag/AgCl paste (Ercon). The reference electrode was placed inside the cell through one of the lurer locks and put in contact with the electrolyte. EIS scans (Biologic VSP) were conducted from 100 KHz to 100 mHz and then reversed and scanned from 100 mHz to 100 KHz at a 6 mV amplitude. Impedance was measured at OCV during NR collection at the following points: initial OCV, after the first lithiation, after the first delithiation, and after the second lithiation steps. Data processing was done with ZView software where an equivalent circuit model was utilized with each circuit component equivalent to a physical process occurring in the cell.

X-ray photoelectron spectroscopy (XPS) was performed on a Phi 3056 spectrometer using a Mg x-ray source. The source was operated at 15 KV and 350 W with a low-resolution survey scan with a pass energy of 93.5 eV and high-resolution spectra collected at 23.6 eV. Samples were cycled in 2032 coin cells with the same electrochemical procedure used for the NR, disassembled and submerged in DMC three times. Samples were transferred to the XPS in a vacuum sealed carry case to minimize exposure to ambient conditions. Data analysis was performed using the Multipak software suite. Charging was corrected for using the Si^0 peak for as-prepared through 0.15 V. (De)Lithiated samples (0.05, 1.5, and 0.05) were corrected using the C1s peak as the Si^0 is no longer present.

Electrochemical quartz crystal microbalance (EQCM) utilizes quartz’s piezoelectric properties to accurately measure mass changes on the surface of an electrode as a function of shifts in frequency. The changes in frequency can be correlated to changes in mass through the Sauerbrey equation, which assumes a homogenous and rigid film formation on the surface of the
electrode as described by Equation 4. Kanazawa and Gordon proposed a relationship that takes into account the changes in frequency of a crystal immersed in a solution as described by Equation 5:

$$\Delta f = \frac{f_0}{\sqrt{\pi}} \left( \frac{\rho_L \eta_L}{\mu_Q \rho_Q} \right)^{\frac{1}{2}}$$  \[5\]

where $f_0$ is the frequency of the dry crystal, $\rho_L$ and $\eta_L$ are the density and viscosity of the liquid, respectively, $\mu_Q$ is the elastic modulus of quartz and $\rho_Q$ the density of quartz. In addition to shifts in frequency, resistance changes can be monitored and related to mechanical properties of the films as described in the relation by Martin et al.:

$$\Delta R = 4\sqrt{\pi} f_u \frac{3}{2} L_u \left( \frac{\rho_L \eta_L}{\mu_Q \rho_Q} \right)^{\frac{1}{2}}$$  \[6\]

where $L_u$ is the piezoelectric inductance response of the natural quartz crystal. In order to account for changes in motional resistance as an effect of viscoelastic changes in the system affecting the changes in the frequency the following correction factor was used by combining equations 5 and 6:

$$\Delta \Gamma = \frac{\Delta R}{4\pi L_u} = \Delta f_{ve}$$  \[7\]

$$\Delta f_{\text{measured}} = \Delta f_{\text{ma}} + \Delta f_{ve}$$  \[8\]

where $f_{\text{ma}}$ is the frequency contribution from the mass and $f_{ve}$ is the frequency contribution from the viscoelastic changes.

In this study, EQCM was utilized to study the mass changes and viscoelastic properties of the first lithiation of an a-Si anode with a spin coated PAA layer on the surface. EQCM experiments (SRS QCM 200) were performed in a homemade flow cell with a 5 MHz Ti/Au crystal (Maxtek) at a scale of 500 Hz. The a-Si thin film was deposited onto the Au electrode using a mask to keep the sputtered Si within the defined limit of the Au electrode. PAA binder was spin cast on the surface of the a-Si and dried at 140°C for 18 hours, the same procedure used for NR sample preparation. A Biologic SP-240 was used to cycle the cell with analog inputs that converted frequency and resistance measurements from the QCM to voltages. Initial electrochemical procedures failed to lithiate the cell and as such the experiment was restarted with a modified program using the same crystal.
3.5 Results

The schematic for the *in situ* cell used for the NR measurements, in addition to the scattering geometry through the cell and an image of the cell are depicted in Figure 3.1. The film heterostructure are shown in Figure 3.1b. Neutron reflectivity of an a-Si thin film anode was collected at various states of charge, Figure 3.2a. Fitting the data to a layered model resulted in the SLD depth profiles, Fig. 3.2b. The fitting parameters are tabulated for the a-Si, oxide/SEI layer, and PAA layers in the supplemental section (Table B.1). In addition, Figure 3.3 graphically depicts the thickness and SLD of the above-mentioned layers obtained from the NR fits. Finally, changes in the film heterostructures are pictorially illustrated in Table 3.1.

Figure 3.1. Schematic (a), scattering orientation (b) and photo (c) of the *in situ* electrochemical cell.
Table 3.1. Schematic representation of the heterostructures of the PAA/SEI layer, and a-Si as a function of the state of charge and the resulting thickness and SLD from NR refinements and mass gain from EQCM.

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<th>Schematic of heterostructures</th>
<th>Thickness [nm]/SLD [10⁻⁶ Å⁻²]</th>
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ᵃ Errors associated with NR measurements can be found in Table S1.ᵇ Mass change at potential hold with relax back to OCV.
Figure 3. 2. a) Neutron reflectivity curves (open circles) and fits (grey line) for PAA on a-Si thin film anode at different states of charge. Curves offset for clarity. b) The resulting SLD plots (bottom) from reflectivity fitting routine representing a one-dimensional view of the film heterostructures separated by interfacial roughness.
3.5.1 As-prepared

The processing conditions for the PAA layer is crucial to the cyclability of the anode. The first attempts at electrode fabrication utilized a 5 wt% solution of $M_w=450,000$ PAA, spin cast, and dried at 200°C for various amounts of time. At 200°C the PAA crosslinks and forms an anhydride,\(^{30}\) this resulted in the PAA layer being impermeable preventing lithiation of the a-Si (Figure B.1). This suggest that when casting anodes from composite slurries the polymer binder does not fully coat Si nanoparticles’ surfaces as this would prevent any cycling. In order to introduce the polymer to a thin film architecture that allowed for cycling, we evaluated different processing conditions. After trying different molecular weight and drying temperatures it was determined a $M_w=1800$ PAA dried at 140°C prevented crosslinking and enabled anode lithiation.

We constrained the parameter space for fitting the NR data by measuring the as-prepared heterostructures of the vapor deposited layers in air. The Cu and a-Si layers thickness were determined to be 17.0±0.01 nm and 58.80±0.04 nm, with a SLD of 6.58×10^{-6} Å^{-2}±0.01 and 1.7658×10^{-6} Å^{-2}±0.02, respectively (the SLD unit x10^{-6} Å^{-2} will be kept off for simplicity). These values agree with uniform dense layers of Cu and H incorporation into the a-Si layer (presumably during the sputtering process). It is important to note the SLD is a summation of each of the individual scatterers within a layer. As such, the incorporation of an element with a large scattering cross section, such as C (6.6 fm), D (6.6 fm), P (5.13 fm), and/or F (5.7 fm) will increase the overall SLD as a result of these elements’ large neutron cross-section. Likewise, in the case of Li
or H incorporation (-1.90, -3.7 fm respectively) a decrease in the SLD would be expected. In order to prevent water contamination, the PAA-coated sample was placed directly into the glovebox while still hot from drying. To determine the thickness and the SLD of the spin cast PAA, witness samples were made using the same spin coating and drying procedures directly onto the single crystal Si substrate, which were measured by NR promptly. The PAA thickness averaged around 30 nm with an SLD of 1.8, which is slightly lower than the theoretical SLD of PAA, around 1.96 assuming a density of 1.41 g cm$^{-3}$. The SLD of the Si substrate was 2.07 and had a thin oxide layer with a SLD of 3.5 which provided contrast to the PAA layer.

The witness samples of spin cast PAA on Si that was deposited onto Cu foil and punched into 13 mm discs were made for cycling and XPS analysis. The XPS spectra (Figure 3.4) of the as coated anode is consistent with PAA.$^{31}$ C1s spectrum shows peaks at 287.5 eV of the carboxylic acid and 289.4 eV corresponds to the ester groups. In the O1s spectra the peak with a binding energy of 534.9 eV is not typically observed in thin films of PAA and therefore is likely attributed to strong acid-base interactions between the PAA and oxidized Si surface.$^{32}$ There is a distinct Si$^0$ peak in the spin coated XPS samples on a-Si deposited Cu foil meaning less than a 10 nm PAA layer; however, this peak is absent in the spin coated Si wafer sample confirming >10 nm PAA layer in agreement with the NR measurements (Fig. B.2). With the presence of the elemental Si peak in all samples prepared on the Cu foil, it is evident that the layer is not as homogenous or consistent to that of atomically smooth Si. Because of these inconsistencies there cannot be a direct comparison between the NR results and the XPS on a witness foil as the thickness of the PAA layer is different. However, we can identify some reaction products that help with the data analysis.

![Figure 3.4](image.png)

Figure 3.4. The C1s (a), O1s (b), and the Si2p (c) XPS spectra for PAA on Cu foil.
3.5.2 OCV

The introduction of the electrolyte to the anode produced several changes in the reflectivity profile (Fig. 3.2). The electrolyte was in contact with the electrode for approximately 30 minutes before the initial measurement at OCV, 2.4 V. OCV NR data shows a 24% (8 nm) thickness expansion in the PAA layer and increase in the SLD (1.8 to 4.33±0.02). The increase in both thickness and SLD, suggests deuterated electrolyte uptake into the PAA layer. The uptake of the PAA was unexpected as it is not known to swell in carbonate based solvents. The swelling of the PAA in thin film orientation was observed by Urbanski et al. where the authors determined a gain of 15 wt% when placed in EC/DMC (1:1). In their study, a $M_w = 450,000$ PAA in a 0.5 wt% methanol solution was used with a significantly lower drying temperature and time (80°C for 2 hrs vs. 140°C for 18 hrs in this study). The incorporation of electrolyte is most likely an effect of the lower molecular weight polymer (1800 vs 450,000) and different orientation of the polymer chains, or packing density as a result of spin coating as compared to traditional slurry preparation. The one consistency between the two experiments is the preparation method i.e. spin coating suggesting in this configuration, PAA swells in the electrolyte; however, the degree appears to be dependent on the molecular weight and drying temperature.

The resulting SLD profile of the OCV measurement showed a layer between the a-Si and PAA with a thickness of 4.33±0.36 nm with a SLD of 1.38±0.17 (Figure 3.2 b, orange curve). This SLD is close to an interfacial Si hydroxide previously reported on sputtered a-Si thin films. This layer was not statistically relevant enough to fit the bare a-Si/air data, presumably due to not enough contrast between the layer and air. The use of deuterated electrolytes with high SLD (~5.3) enables contrast and thereby reflection at this buried interface. The a-Si layer thickness did not decrease with the introduction of the electrolyte, and with the low SLD, indicates the layer on the surface of the a-Si is not a reaction layer from the electrolyte decomposition and is different than what has been previously observed.

3.5.3 Before lithiation (1.5, 1.2, and 0.8 V)

There are no significant changes within the system at 1.5 V as expected, because this potential is typically used to clean up impurities within the electrolyte (Figure 3.3). Previous experiments have indicated the possibility of trace impurities within the deuterated electrolyte, and as such the 1.5 V potential is used to react away the impurities present and run at a higher current rate. No change is evident in the PAA layer. The a-Si layer remains at 56.54±0.15 nm with a
SLD of 1.79±0.03. At 1.2 V minimal changes were observed in the NR data (Figure 3.2), and all layer’s thickness and SLD remain unchanged statistically. Figure 3.3 highlights the stability within the three layers, in both the SLDs and thicknesses, up to 0.8 V. Typically, at potentials more negative than 1.2 V, electrolyte reduction and SEI formation occurs.\textsuperscript{2,23} This was not seen in the NR at 0.8 V; in fact the calculated scattering profile remains unchanged.

In order to better understand the reflectivity in addition to validate the models, electrochemical quartz crystal microbalance (EQCM) experiments were performed. EQCM has been utilized to study alloying based electrodes and subsequent SEI formation.\textsuperscript{37–40} An advantage of this technique is the ability to study dynamics of the electrode during polarization and subsequent relaxation. Thus, EQCM provides complimentary information to the NR measurements. In relation to Equations 5 and 6, neutrons provide a better picture of the change in chemical makeup and thickness, \( \rho \), while QCM provides information on the viscoelastic response, namely viscosity changes, \( \eta \). Figure 3.5a depicts the transient response of \( \Delta f \), \( \Delta \Gamma \), and the difference thereof. The colors are associated with a hold at potential and the relax back to OCV is denoted by the grey region. As Eqs.7 and 8 suggests, \( \Delta f \) (red curve) is a combination of the mass loading and viscoelastic change of the electrode, while \( \Delta \Gamma \) (blue curve) contains mostly the viscoelastic response. The difference, \( \Delta f-\Delta \Gamma \), is therefore more closely related to \( \Delta m \) of the film by Eq 8. The overall mass change of each step, potential hold (circles) and relaxation (square) is plotted in Figure 3.5b where circles corresponding with the potentials in Figure 3.5c depicting the total mass gain at the potential hold; in addition, the grey squares depict total mass change including the OCV state after the potential hold.
Figure 3.5. a) The shifts in frequency as depicted in the red curve ($\Delta f$), the change in resistance, in Hz, is the blue curve ($\Delta \Gamma$), and the corrected frequency shift in black ($\Delta f - \Delta \Gamma$). The holds in potential are depicted in the colored boxes and the relax back to OCV is depicted in the grey boxes. b) Total mass gain from beginning of the potential hold until end of hold (circles) or end of OCV relaxation period (squares). c) Applied potential and potential relaxation transient profile.
Before going into detail, it is important to note that the transient curve for $\Delta \Gamma$ shows little change during most of the applied potential and subsequent relation steps. There is a slight positive slope leading up to the point where the electrode is polarized to 0.05 V. This is important as the majority of the frequency change measured is due to mass change and not merely viscoelastic change of the PAA thin film. This is shown more clearly in Figure B.4 where initially the system is dominated by Sauerbrey conditions and mostly consists of mass gain; however, at later times in the measurement associated with higher degree of lithiation more viscoelastic response is observed before returning to Sauerbrey conditions. Interestingly, the PAA begins to thin around 0.4 V and could be the reason for the viscoelastic change. This is observed in Figure 3.5a where the corrected curve, $\Delta(f-\Gamma)$, maintains all the same features as $\Delta f$- they decrease as the potential becomes more reducing.

Clearly, the electrode gained mass between potential steps. The total area mass change, $\Delta m$, during potential steps as calculated from Eq 4 and 8 is shown in Figure 3.5b. $\Delta m$ during the first full lithiation of the Si (from OCV to 0.05 V) was 10.6 $\mu$g cm$^{-2}$. Potential ranges of 0.8 V and above are associated with decomposition of the electrolyte and as such $\Delta m$ here is associated with decomposition products of the electrolyte, that is SEI formation. However, there was no significant mass gain at the 1.5 V potential to 1.2 V; only 0.6 $\mu$g cm$^{-2}$ was added (Fig. 3.5b).
suggests that the PAA effectively coats the Si electrode and limits SEI growth at these voltages. This observation agrees with the NR profile results of the OCV, 1.5 V, and 1.2 V SLD plots (Figure 3.2b). At 0.8 V (Figure 3.5a, green box) and 0.4 V (Figure 3.5a, blue box) a mass decrease is observed at the beginning of these potential holds. The initial decrease in mass may be due to displacement of PF$_6^-$ anions within the polymer/SEI matrix. Similar effects in anion/cation adsorption resulting in increased mass have been observed in carbons in electrochemical double layer capacitors.\textsuperscript{41}

3.5.4 Lithiation of the Si (0.4, 0.15 V)

At 0.4 V the PAA layer thins down to 33.9 nm while maintaining its SLD at 4.55±0.02. There is a 2 nm increase in the a-Si layer (56 to 58.2±1.8 nm) with a decrease in the SLD from 1.76 to 1.25±0.04 (Fig. 3.3), indicating the beginning of lithiation of the sample as Li is a negative scatterer. However, NR implies little lithiation from thickness changes, but electrochemically the Li to Si ratio is estimated to be Li$_{0.2}$Si.

At 0.15 V the NR profile drastically changes. Here fringes between 0.04 Å$^{-1}$ to 0.1 Å$^{-1}$ are smoothed (Figure 3.2a, dark blue) indicating changes in layer thicknesses and compositions. The a-Si layer swells to 108.4±0.51 nm with a SLD of -0.29±0.04 suggesting composition of Li$_{1.6}$Si for the a-Si layer from the refined NR data. Assuming 100% Faradaic efficiency, the electrochemical derived composition is around Li$_{2.3}$Si. SEI is most likely being consumed to form the SEI layer. The oxide layer on the surface of the electrode increases in SLD from ~1.3 to 2.52±0.35. The increase in the SLD suggests a heavier scatter, such as C, D, O, F, P incorporation into the oxide film as opposed to Li. These components are all from the electrolyte, suggesting electrolyte decomposition products in the oxide layer, resulting in the formation of the SEI. The exact chemical composition cannot be determined from NR alone. A schematic representation of the changing heterostructures is shown in Table 3.1. The PAA layer at the electrolyte interface continued to thin, settling at 33±0.1 nm from 36 nm and decrease in SLD from 4.3 to 3.81±0.04. Due to the polarization of the cell at 0.15 V a significant amount of Li is being diffused into the Si and the lowering of the PAA SLD is the result of Li incorporation into the PAA layer.

XPS for witness samples that have been lithiated to 0.15 V are presented in Figure 3.6. The reader is cautioned that thickness inconsistencies are likely as a result of different film morphologies on the Cu foil to that of the Si wafer. Figure 3.6a depicts the C1s spectra where C-O species are present (~285.3 eV) and C-C, C-H species (284.2 eV), in addition to O-C=O
moieties. These species are indicative of electrolyte decomposition products, as a result of the polymerization or decomposition of the C=O species. The O1s peak confirms the decomposition of the solvent (Fig. 3.6b). There is also evidence of P-O-F moieties from salt decomposition. This is further confirmed by the presence of the P-F species in the F1s spectra (Fig. 3.6d). LiF denotes the decomposition of the LiPF₆ salts. The NR shows an increase in SLD of the SEI layer (the layer between the Si and PAA) from 1.25 at 0.4 V to 2.52 at 0.15 V as a result of a heavier scatter incorporation from the electrolyte solvent. From the XPS and large presence of LiF and Li-PF₆ it is most likely from the dissociation of the salt at this potential. The SLD of fully dense LiF is 2.3 while LiPF₆ is 2.1. Interestingly, the O1s spectra indicates the formation of an inorganic Li-O species, which is confirmed in the Li1s spectra (~57.1 eV). The Si2p peaks shows a new species with a binding energy of ~101 eV attributed to the lithiation of the native oxide layer on the surface of the Si forming a LiₓSiOᵧ species (Fig. 3.6c).
Figure 3.6. The C1s (a), O1s (b), Si2p (c), F1s (d), and Li1s (e) spectra at 0.15 V.
3.5.5 Cycled (0.05, 1.5, and 0.05 V)

The PAA layer has thinned by 10 nm at 0.05 V (30.1 to 20.2 nm), in addition to a change in the SLD to 3.56±0.09 (from 3.8 at 0.15 V). The thinning of the PAA from the start of 0.4 to 0.05 would suggest the PAA is dissociating into the electrolyte and is changing in composition at the beginning of lithiation (x>1). This could be attributed to Li exchange within the PAAH to LiPAA. The SEI layer decreases in SLD to 1.52±0.1 compared to 2.52 at 0.15 V, suggesting more Li in the film. The silicon is lithiated to Li$_{3.8}$Si which results in a thickness of 177.54±2 nm and SLD of -0.64±0.04. As the alloying reaction proceeded to higher states of lithiation (0.15 and 0.05 V) changes in the chemical composition and thicknesses of the SEI layer and PAA are observed and can be correlated back to the EQCM measurements to better understand the changes in the layer formations. Figure 3.5a shows that after a brief “break in” period $\Delta f$-$\Delta \Gamma$ begins to decrease substantially, relating to an increase in $\Delta m$ of ~2.6 $\mu$g cm$^{-2}$ during the 0.15 and 0.05 V potential holds (Fig. 3.5b). However, not all of this mass corresponds to Li gain. At the start of lithiation (0.15 V) approximately 3.15 g per mole of electrons (m/z) are gained. At 0.05 V there are approximately 1.95 m/z. This is not the full 7 m/z expected for the state of lithiation; thus, indicating consumption of Li$^+$ most likely in the formation of the SEI layer. Smaran et al. found that m/z <7 was attributed to SEI formation on the surface of Li metal in glyme based electrolytes.\textsuperscript{42} The relatively slow kinetics of the Li deposition at 0.05 V would suggest the small amount of Li deposits would react with the solvent and subsequent impurities, such as HF, resulting in low m/z ratio.\textsuperscript{43}

Upon delithiation to 1.5 V, the SEI layer grows to 15±0.2 nm with an increase in the SLD to 3.83±0.05 (from 1.52), reflecting a change in the chemistry of the layer as a result of the delithiation of the anode (Table 3.1). The increase in the SLD and thickness would be from the incorporation of solvent molecules such as C, O, D. The PAA layer increases in SLD to 4.66±0.03. The Si layer thins but the SLD (-0.3) indicates the anode was not fully delithiated, and from the electrochemistry the Li:Si is estimated to be Li$_{0.9}$Si. The second lithiation sees the PAA layer remain ~ 20 nm; however, the SLD returns to around 3.4 as in the first lithiation. The SEI layer shrinks to 11 nm with a decrease in the SLD to 1.13 (as opposed to 1.52 after the first lithiation). Both the SEI layer and PAA change in chemical composition and thickness based on the state of lithiation or delithiation.

XPS shows the presence of O-C=O, C-C/C-D, and C-O all of which are consistent with the decomposition of the electrolyte (Figure 3.7a). The first lithiation O1s spectra shows a Li-O
species observed at 0.15 V. Interestingly the first delithiation indicates no presence of the Li-O species suggesting a reversible reaction process that forms during lithiation, but is consumed during delithiation thus further decomposing the electrolyte (Fig. 3.7g). This is further evidenced by the changes in SLD during the lithiation and delithiation steps. The grey peak at 283 eV (Fig. 3.7k) is most likely a result of charging effects due to the insulating nature of the LiF species. LiF is present in all cycled samples (Figure 3.7). The second delithiation state shows a drop in the C-C, C-H moieties (74 to 38 at%) accompanied by an increase in the C-O peak (12 to 49.1 at%) indicating the polymerization of electrolyte species. The O1s (Figure 3.7b) shows the reappearance of Li-O species in the second lithiation, in addition to other Li containing moieties attributed to Li$_2$O (528.8 eV).

Upon the delithiation of the sample the Li-O species disappears. This in agreement with previously reported results identifying the reversibility of the reaction forming Li$_2$O species is a result of reaction with P-F species. The Li1s peak indicates alloying of Li and Si as evidenced by the Li-Si peak at 55.1 eV (Fig. 3.7e). The delithiation sample shows evidence of the emergence of carbonate containing species most likely Li$_2$CO$_3$ that is not observed in the first lithiation, however, it remains in the second lithiation step (Fig. 3.7k). There is no evidence of a Li-Si peak within the Si2p spectra as a result of the thick layer formation found on the surface of the electrode in agreement with the NR results which indicate layer thickness greater than the escape depth of the photoelectrons. The LiF and P-O-F species, originating from the LiPF$_6$ salt combined with the emergence of the Si-O-F peak in the spectra indicates further decomposition of the salt.
Li\(^+\) transport resistance through the anode surface layers were estimated using electrochemical impedance spectroscopy (EIS) at the initial OCV, after the first lithiation/delithiation, and the second lithiation steps. Impedance was performed during the OCV after discharge to the stated potentials and occurred while NR data was being collected. Figure 3.8 shows the resulting impedance curves and fits. The equivalent circuit used to fit the impedance data is displayed in Figure 3.8 where elements of the circuit can be used to model physical behaviors within the system. \(R_1\) is the resistance of the electrolyte, \(R_2\) is the resistance through the surface layers on the Si, \(Q_1\) is a capacitive element, and \(W_s\) is the diffusion element. The average solution resistance between all measurements was \(\sim 0.2 \, \Omega \, \text{cm}^{-2}\). Initial surface resistance is high, \(1.3 \times 10^4 \, \Omega \, \text{cm}^{-2}\), at the onset OCV before measurements were taken (Figure 3.8). The first lithiation indicates the formation of an SEI layer (Figure 3.8, purple) as the presence of a semi-circle from that of the original OCV is observed. The resistance of this layer has decreased significantly from the purely resistive state of OCV, to approximately \(1.4 \, \Omega \, \text{cm}^{-2}\). This is also in

Figure 3.7. The C1s (a,f,k), O1s (b,g,l), Si2p (c,h,m), F1s (d,l,n), and Li1s (e,j,o) spectra at the 0.05 V first lithiation, 1.5 first delithiation, and 0.05 second lithiation, respectively.
agreement with the NR data which indicates a significant change in chemistry at 0.05 V (compared to 0.15). The delithiation of the anode shows a significant increase in the resistance of the layers on the surface of the anode; thus, indicating the SEI that formed at 0.05 V was not stable. This is also in conjunction with an increase in the SLD of the layer, and the emergence of Li-O type species. The second lithiation is much more resistive than the first lithiation cycle (Figure 3.8, teal curve). The EIS measurements were run in a forward scan and then reversed; however, for the second lithiation the data did not overlay the forward scan indicating the system was not at a steady-state which suggest sluggish Li\(^{+}\) transport. Overall the EIS points to an unstable or dynamic layer formation on the surface of the anode with resistances that change with the extend of Li content in the SEI.

Figure 3.8. Electrochemical impedance spectroscopy curves and resultant fit.
3.6 Discussion

The above data details the thickness and composition of the SEI layer that forms beneath a perfect PAA binder coating. Initially, the PAA uptakes solvent within the layer, but there is no evidence of the chemical reaction between the Si and the electrolyte. This is in contrast to previous NR experiments which observed a lithium rich layer segregating to the a-Si surface upon exposure to the electrolyte indicating that the PAA is protecting the silicon surface at OCV.\textsuperscript{34–36} Instead, under the PAA layer we observe the hydrogen terminated oxide layer grown on the a-Si from the reaction with the atmosphere. This suggests the PAA preferentially adsorbs the solvent, excluding the salt, which will play a role in the initial SEI formation and Li transport during lithiation.

There are few changes to the thickness and composition of the interfacial layers down to 0.4 V vs. Li/Li\textsuperscript{+}. This indicates that the PAA is effectively acting as an SEI by suppressing electrolyte decomposition while still allowing solvent to approach the silicon surface. This is in contrast to measurements collected on an amorphous silicon electrode which revealed the formation of a 25 nm thick inorganic-like SEI layer.\textsuperscript{36} This data indicates a well-defined PAA layer prevents electrolyte decomposition above 0.4 V which may be beneficial to other intermetallic anodes such as antimony. Below 0.4 V there are significant changes observed at the Si-PAA interface.

At 0.15 V lithium containing species have diffused to the silicon surface where they react (beneath the PAA layer) resulting in an inorganic-like SEI layer, Li\textsubscript{2}O and LiF, that is about 10 nm thick and the silicon electrode begins to lithiate. Simultaneously the PAA is thinning/decomposing and uptaking lithium within the PAA layer leading to a lithiated PAA-like composition. This inorganic SEI layer is similar to the surface measured without the PAA.\textsuperscript{36} Indeed, the composition is similar based on scattering length density (2.5 vs 2.9) but the PAA layer is much thinner: 9 nm vs 19 nm, respectively.\textsuperscript{36} This indicates the polymer is acting as an artificial SEI while still enabling the formation of a lithium containing SEI.\textsuperscript{44} This data is consistent with reports which claim after PAA is electrochemically reduced to form LiPAA, a protective layer of binder reduction products prevents the reduction of the carbonate based electrolyte and forms a relatively thin and more stable SEI.\textsuperscript{18} Similar effects on graphite anodes that contain PAA have been observed, where the binder suppressed the first lithiation decomposition of the electrolyte as a result of the PAA binder coverage.\textsuperscript{15,45}
Upon further lithiation below 0.05 V vs. Li/Li⁺ the SEI continues to change in composition as evident by the decrease in the SLD from 2.5 to 1.5. Interestingly, the thickness remains constant at 9 nm. This increase in Li content results in a much lower interfacial resistance as measured by impedance spectroscopy. Specifically, the charge transfer resistance drops from 12 kΩ cm⁻² to 1.4 Ω cm⁻². Furthermore, EQCM measurements indicate that there is a change in the viscoelastic response of the interfacial layers due to changes in the polymer/SEI chemistry.

The delithiation of the anode shows a significant increase in both the PAA and SEI layers. Specifically, the PAA layer increases in SLD from 3.6 to 4.7 and the SEI increases in SLD from 1.5 to 3.8. This increase is due to the removal of Li AND incorporation of solvent species as indicated by a change in thickness of the SEI layer. The PAA layer remains the same thickness but has lost Li. This trend was supported by the XPS data showing a loss of Li-containing species which are likely redissolved into the electrolyte. Furthermore, the EIS points to a significant increase in the interfacial resistance of the layer, 936.2 Ω cm⁻², most likely as result of more polymeric type species being formed, in addition to the removal of Li from the layers. The observed loss of Li/increase in organic content is consistent with data reported for the amorphous silicon without PAA.³⁶

Upon further cycling, the SEI returns to about 11 nm and the SLD drops to 1.1 indicating the incorporation of Li within the layer. The PAA returns to 3.4 which is similar to the composition with the first lithiation. This coincides with a decrease in the charge transfer resistance from 936.2 Ω cm⁻² to 9.8 Ω cm⁻². This data indicates the SEI and the PAA layers are dynamically incorporating and losing lithium with charging. This effect has previously been described as the SEI “breathing”. The PAA lowers the magnitude of the changes in thickness with cycling (~ 10 to 15 vs. 18 to 30 nm) consistent with it mediating SEI formation.³⁶ Similar mediation in breathing magnitude was observed for FEC containing electrolytes on the same amorphous silicon.³⁴ In both the FEC and PAA case the surfaces were becoming predominantly organic at the beginning indicating the need to form a polymer-like surface layer to prevent egregious electrolyte consumption.³⁴

This work can be related to composite electrodes and the processing needed to make such electrodes. As is clear from this work a fully coated Si particle behaves differently than one that has patchy coverage. If the binder fully encapsulates a Si particle and is cross-linked at high temperature from drying procedures, there will be no Li⁺ transport. This data would support the need to make a heterogenous PAA/Si structure to allow some Li transport. The challenge would
therefore be related to ensuring a minimal exposed silicon surface (which would react to form larger amounts of SEI) while maintaining some pathways for electrolyte to interact with the silicon surface. It would also explain why FEC works well with PAA based composite electrolytes in that it is resulting in the polymeric protective layer while maintaining Li transport pathways.\textsuperscript{46–50}

3.7 Conclusion

The effect of the binder, PAA, on the SEI formation on the surface of an a-Si electrode was explored using \textit{in situ} neutron reflectometry, electrochemical quartz crystal microbalance, and \textit{ex situ} x-ray photoelectron spectroscopy. The SEI forms on the surface of the anode, underneath the PAA binder. The initial processing condition i.e. molecular weight of the PAA and drying temperature, suggests the full coating of a Si particle under the same processing conditions would prevent the lithiation of the anode. Therefore, the processing parameters when using PAA need to be optimized. The model electrode with a full coating of the PAA binder used in this experiment resulted in little SEI formation up to 0.4 V. Upon further lithiation the PAA mediates the formation of a thinner SEI. The lithiated Si has an inorganic 10 nm SEI form on the surface of the anode, below the PAA. The SEI layer is dynamic in nature, changing in chemical composition and thickness as a result of lithiation and delithiation of the Si. Upon removal of the Li from the layers a more organic SEI is present as a result of more polymeric type species being formed. Interestingly the PAA layer changes in chemical composition in conjunction with the changes in the SEI layer as a result of the addition and removal of Li.

3.8 Acknowledgment

The authors would like to thank Dr. Kevin Hays for providing the PAA and discussion of processing parameters. This research at the Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, was sponsored by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO) (Deputy Director: David Howell) SEISTa subprogram (Program Manager: Brian Cunningham) (KLB and GMV). A portion of this research used data from the Liquids Reflectometer at the Spallation Neutron Source. This research was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (MD and JFB). EQCM and analysis was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering (RLS).
3.9 References

1. Peled, E. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in


4. Peled, E. Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and

5. Obrovac, M. N. & Christensen, L. Structural Changes in Silicon Anodes during Lithium

6. McDowell, M. T., Lee, S. W., Nix, W. D. & Cui, Y. 25th anniversary article:
Understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries.


9. Erk, C., Brezesinski, T., Sommer, H. & Schneider, R. Toward Silicon Anodes for Next-
Generation Lithium Ion Batteries: A Comparative Performance Study of Various Polymer
Binders and Silicon Nanopowders. (2013). doi:10.1021/am401642c

10. Rezvani, S. J. *et al.* Binder-induced surface structure evolution effects on Li-ion battery

11. Li, J., Lewis, R. B. & Dahn, J. R. Sodium Carboxymethyl Cellulose. *Electrochem. Solid-

12. Magasinski, A. *et al.* Toward efficient binders for Li-ion battery Si-based anodes:

13. Young, B. T. *et al.* Role of binders in solid electrolyte interphase formation in lithium ion


25. Hays, K. A. *et al.* What makes lithium substituted polyacrylic acid a better binder than


45. Ui, K. *et al.* Analysis of solid electrolyte interface formation reaction and surface deposit of natural graphite negative electrode employing polyacrylic acid as a binder. *J. Power Sources* 247, 981–990 (2014).
49. Bordes, A., Eom, K. & Fuller, T. F. The effect of fluoroethylene carbonate additive

## Appendix B

Table B.1. Tabulated values for NR refinements for the thickness, SLD, and roughness for the a-Si, interfacial layer, and PAA layers, respectively and goodness of fit ($\chi^2$).

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<td>1.31±0.41</td>
<td>4.33±0.36</td>
<td>1.38±0.17</td>
<td>3.25±0.12</td>
<td>36.14±0.16</td>
<td>4.33±0.02</td>
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<td>4.31±0.41</td>
<td>1.48±0.21</td>
<td>3.08±0.14</td>
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<td>1.40±0.71</td>
<td>4.75±0.65</td>
<td>1.42±0.21</td>
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<td>1.30±0.65</td>
<td>4.97±1.02</td>
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<td>0.4 V</td>
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<td>3.03±0.11</td>
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<td>6.93±0.34</td>
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Figure B.1. The reflectivity patterns, of PAA processed at 5 wt% and 200℃, that shows no change between the OCV measurement and 0.05 V.

Figure B.2. The Si2p from XPS of PAA coated on atomically smooth Si (red) and Cu foil
Figure B.3. The change in resistance (in ohms) at the different potential holds.

Figure B.4. Sauerbrey versus viscoelastic conditions as a function of lithiation.
Figure B.5. Atomic percent from XPS fits for 0.15, 0.05, 1.5, and 0.05 V
CHAPTER 4: CONCLUSION
4.1 Chapter conclusions

4.1.1 Role of conductive binder to direct solid-electrolyte interphase formation over silicon anodes

Chapter 2 focuses on the first lithiation and SEI formation cycle of an a-Si thin film spin coated with the conductive binder PEFM. The PEFM layer is dynamic, changing in thickness and composition based on the state-of-charge. The binder did not impede the electrolyte from interacting with the a-Si as determined from the observation of a reaction layer that formed on the surface of the electrode underneath the polymer binder. At 0.8 V (vs. Li/Li\(^+\)), the reaction layer becomes the SEI at it incorporates components from the decomposition of the electrolyte. The SEI is organic in nature and the interface between the SEI and the polymer is still well defined. The PEFM and SEI form a thick (~800 Å), diffuse layer resulting in a binder/SEI matrix at the start of lithiation. The high SLD of the layers indicates the binder acts as a membrane bringing the solvent molecules from the electrolyte to the surface of the anode and preventing the lithiation. By 0.05 V (vs. Li/Li\(^+\)), the SEI condenses to a 72 Å Li rich layer on the surface of the anode. The PEFM contracts to 122 Å as a result of crosslinking/expelling of the electrolyte with organic products dissolving into the electrolyte. This results in a bilayer structure with a dense and compact layer on the surface of the anode that is Li rich, and a more organic layer at the electrolyte interface.

4.1.2 The study of the binder polyacrylic acid and its role in concomitant solid-electrolyte interphase formation on Si anodes

Chapter 3 investigates the commonly used binder PAA, and its effect on the SEI formation on an a-Si anode. The PAA layer suppresses new film growth in early potentials (OCV to 0.8 V vs. Li/Li\(^+\)) as evidenced by no changes in the SLD or thickness of the system. There is no observed SEI formation at 0.8 V (vs. Li/Li\(^+\)), in fact the layers remain statistically the same from previous potentials. In order to better understand the lack of new film formation, EQCM was performed. The resistance response from the crystal indicates there are relatively no changes in the viscoelasticity of the polymer layer until the start of lithiation. In addition, little mass change at potentials above 0.15 V (vs. Li/Li\(^+\)) are observed similar to the results of the NR refinements. At the start of significant lithiation (x>2), the oxide layer on the surface of the Si changes in composition and thickness. The increase in the SLD indicates the incorporation of a heavier
scattering element. Given the elemental makeup of the system, C, D, O, F, P has to be coming from the decomposition of the electrolyte resulting in the formation of the SEI. In addition, the PAA layer decreases in SLD indicating Li within the polymer, and begins to thin by dissolving in the electrolyte and becoming part of the SEI. The lithiated Si has a thin, ~10 nm inorganic SEI, underneath the PAA binder. The SEI layer increases to ~14 nm and increases in SLD as the anode is delithiated becoming more organic. Upon cycling the SEI and the PAA change in chemical composition and thickness as a function of lithiation/delithiation and results in the poor passivation of the anode.

4.2 Impact and significance

Si anodes have many obstacles to overcome before fruition into a viable replacement for graphite. An understanding of the binder’s role in SEI formation can aide in optimizing a binder system for Si, similar to PVDF for graphite. The use of NR is important because it gives a better insight into where the SEI is forming i.e. on the surface of the anode or on top of the polymer. In both cases studied, the SEI is underneath the polymer binder on the surface of the a-Si. This result is an important finding that would be hard to see in common ex situ studies because of the need to rinse samples before measurements removing soluble species and reducing the thickness of the SEI. NR refinements also showed the large interactions between the electrolyte and the binder, by using deuterated solvents, that are otherwise hard to discern and highlights the complexity of the electrolyte within the polymer. In addition, the focus of these studies was on full binder coverage of the Si surface. The processing parameters for composite electrodes are key to better performance. This work showed that a fully coated particle surface would hinder the lithiation of the Si under certain drying temperatures or molecular weights of the polymer. The coverage of the binder altered the solvent that was interacting with the surface of the Si suggesting a different SEI thickness and composition when compared to a patchy binder coverage. A significant uptake in electrolyte results in Li consumption and prevents the cycling of the Si. Therefore, it is evident the salt content at the surface of the anode is beneficial to the SEI formation. As such, developing a membrane like polymer that selectively brings salt to the surface, in addition to ion channels would perform better than a polymer that brings solvent molecules to the Si surface. This could lead to a better SEI as well as a more stable Si anode.
4.3 Future work

This study focused on the use of model anode systems with full binder coverage; therefore, future work could be the implementation into composite electrode formulation as the Si system is far from optimized. It is evident the processing conditions will dictate the performance and when mixing a slurry, it is clear the Si is not being fully covered. This was evidenced by the PAA cell that underwent typical processing procedures where it was impenetrable to Li. Therefore, a better understanding of the science of processing is needed. A focus on where the binder is located after being cast onto a metal current collector is important, in addition to the confirmation of the polymer on the Si surface during the casting procedure. In addition, a slurry is a colloidal system and as such techniques to better understand the binder’s interaction within such a system are needed. The presence of the PAA binder was advantageous at early potentials as it delayed the solvent molecules from interacting with the Si surface; however, with the continued cycling of the anode a “breathing” mechanism contributed to further electrolyte decomposition. This “breathing” is a result of electrolyte species being dissolved and reformed as the cell is lithiated or delithiated resulting in the poor passivation of the anode. It would be beneficial to determine the effects of an electrolyte additive that promote a more stable SEI, such as fluoroethylene carbonate, on the mitigation of this “breathing” mechanism in the presence of PAA to prevent further decomposition of the electrolyte.
VITA

Katie Browning earned a bachelor’s of science degree from the University of Tennessee in the Materials Science and Engineering Department in 2015. Following graduation, she spent two years at Oak Ridge National Laboratory in the Energy Storage and Membranes Materials group under the direction of Dr. Gabriel Veith. Her work focused on materials for energy storage.