Electrochemical Characterization of Ultra-Thin Silicon Films

THESIS

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Abstract

Silicon is a well-known and studied electrode material for use in Li-ion batteries. Its advantages include its high theoretical capacity (~3500 mAh/g) and abundance. Unfortunately, Si suffers from significant rate limitations, due to the slow diffusion of Li in Li-Si alloys, as well as capacity degradation, caused by the extreme volume change as the electrode is heavily lithiated and then delithiated. Typical techniques for deriving diffusion coefficients include CV, EIS, PITT, GITT among others. Because these techniques measure a variety of behaviors simultaneously, deconvolution of the diffusion constant from other processes can be difficult. Various factors also affect the diffusion rate, such as the crystalline or amorphous phase through which the Li diffuses and the thickness of the electrode. We have used a number of previously reported experimental techniques and models to derive Li diffusion constants within a thin film Si electrode. We have also carried out the slowest and most extended cyclic voltammetry scan (as far as we are aware) to observe how the electrode behavior changes over time and this has yielded some interesting data regarding phase reversibility in thin film Si electrodes. Our diffusion results differ somewhat from the previously reported values. We also present some preliminary data from a novel technique for the direct observation of Li concentration and movement within the electrode. We plan to use this technique,
known as neutron depth profiling to confirm or negate some of the results herein presented.
Acknowledgements

I would like to thank Dr. Anne Co for her guidance and mentorship through this research project. Our discussions of electrochemistry are among the most illuminating I’ve had in my chemistry education. I’d also like to thank members of the Co Group, particularly Danny Liu, Jose Lorie Lopez, and Nick Bashian. I would like to thank Dr. R. Gregory Downing for his forbearing instruction in the collection and analysis of neutron depth profiling data and the National Institute of Standards and Technology for the use of their facilities. Finally I thank the Ohio State University Department of Chemistry and Biochemistry for funding this research.
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Chapter 1: Background and Introduction

1.1 Li-ion Battery

Li-ion batteries are a well-studied and extensively utilized mobile power source. They are currently used for high energy applications such as cell phones, portable computers and most recently transportation. However, energy density, rate and safety limitations prevent them from being widely adopted in the pursuit of transport electrification. Much of the present research is focused on creating electrodes with high energy density. Two parameters are important for this goal, the electrochemical potential of the electrode and the amount of Li that can be stored within the electrode.

A promising alternative is Si, which can form a number of highly lithiated phases and has a potential only a few mV more positive than Li metal, meaning that if Si is the anode in a battery it will discharge at a voltage very similar to a battery with a Li metal anode, thus constituting a very energy dense electrode. The current state of the art anode, graphite has a theoretical capacity of 370 mAh/g. Much research into Si as a battery anode has already been performed. Ohara et al. achieved a capacity of 3500 mAh/g on a 500 angstrom thin film of Si for over 200 cycles. Song et al. interpenetrated a gel polymer binder into a Si nanoparticle electrode which gave excellent cyclability. Evanoff et al. coated a carbon nanotube fabric with Si to increase the capacity from the normal
370 mAh/g to 494 mAh/g for 150 cycles. Ma et al.\textsuperscript{5} pursued a strategy of chemically synthesizing a Si anode which was already in a semi-lithiated state (the Li$_{12}$Si$_7$ phase) resulting in better capacity retention for the bulk electrode. Unfortunately Si electrodes, particularly bulk electrodes, are prone to cracking and fragmenting due to the large volume change (~400\%) associated with repeated delithiation and lithiation\textsuperscript{6}. This leads to dramatic loss in capacity after just a few cycles. This issue has led to considerable interest in nanoscale or nano-patterned Si electrodes. Another challenge with Si is the rate capability, which determines how much current, and thus, power the battery can deliver. This parameter is of the utmost importance when it comes to the electrification of transportation since the power demand of an electric vehicle extends over a wide range. The rate is dependent upon the myriad processes occurring during the battery’s operation, such as diffusion of Li through the electrodes and electrolyte, and the charge transfer resistance/kinetics of the lithiation/delithiation reactions. However it is generally accepted that the slowest process at work (and thus the rate limiting process) is the solid state movement of Li within the Si electrode. There are two mechanisms of intra-electrode Li movement, diffusion and migration. Diffusion refers to a net Li movement due to a concentration gradient whereas migration denotes potential driven movement of a charged species within an electric field. Generally these two mechanisms are not deconvoluted in the measurement of the diffusivity in Si, or the migration contribution is assumed to be null (by assuming Li has been reduced to an oxidation state of 0, thus being unaffected by an electric field). The research performed
thus far on the room-temperature diffusivity of Li in a variety of Li-Si phases has yielded values in the $10^{-13} \text{ cm}^2/\text{s}$ range. Despite the challenges, the high capacity, large abundance and currently existing infrastructure for mining, purifying, and engineering Si makes it an anode material worth pursuing.

At room temperature there are 4 Li-Si phases, LiSi, Li$_{12}$Si$_7$, Li$_7$Si$_3$, and Li$_{13}$Si$_4$, shown in Figure 1. Obravac et al.\textsuperscript{8} report the formation of a Li$_{15}$Si$_4$ phase as well. It is clear from the phase diagram that the composition range over which the 3 most lithiated phases occurs is fairly narrow, from 50% to 20% (atomic) Si. This narrow compositional-phase range allows that during the electrochemical synthesis of Li$_x$Si$_y$ alloys a Si electrode may not completely convert to a single phase before part of it begins the next phase transformation giving an electrode which forms multiple phases simultaneously during lithiation, especially if the phase transformation kinetics are slow and the phases are close to each other thermodynamically. Table 1 gives a summary of the Li diffusion values that have been predicted computationally and measured experimentally. The values reported are spread over a range of $10^{-9}$ to $10^{-14} \text{ cm}^2/\text{s}$. The Li diffusion constant depends not only on the Li concentration within the electrode but also on the variable crystal structure (or lack thereof) of the host material which complicates the deconvolution of diffusion coefficients from the methods of measurement used to obtain them.\textsuperscript{9} In this work we have electrochemically characterized the behavior of the Si electrode and attempted to derive diffusion
coefficients using various models. Well known techniques such as cyclic voltammetry, potential holds and electrochemical impedance spectroscopy (EIS) are used. A novel technique for the accurate measurement of diffusion coefficients is neutron depth profiling which will be further addressed in chapter 5. Neutron depth profiling (NDP), unlike standard electrochemical methods, allows direct observation of the Li distribution within an electrode, providing information about the concentration and diffusion of Li which does not need to be deconvoluted from external process signals.
Figure 1. Phase diagram of Li-Si Alloys
Table 1. Reported room temperature Li diffusion constants in Li-Si alloys.

<table>
<thead>
<tr>
<th>Diffusion Coefficient (cm²/second)</th>
<th>Method</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>$5.1 \times 10^{-12}$ (CV) 3 $\times 10^{-12}$ (EIS)</td>
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1.2 Electrochemical Techniques

1.2.1 Cyclic Voltammetry

Cyclic Voltammetry entails sweeping the voltage (relative to a reference electrode) on a working electrode at a chosen rate between 2 voltage limits. The counter electrode, the electrode from which the working electrode draws current, may or may not be the same as the reference electrode. In most battery literature the counter and the reference electrodes are the same piece of Li metal, this is referred to as a 2-electrode since there are only two electrodes in the cell, such as in the case of our coin-cell type experiments. Our work occasionally requires us to use a different configuration where separate electrodes are used for the counter and reference. This setup is referred to as a 3-electrode setup. The benefit of a 3-electrode experimental set-up is that the current-potential relationship obtained is only a result of processes occurring in and at the working electrode against a fixed reference point. Since only infinitesimal current flows between the working and the reference, there is little to no electrochemical change at the reference electrode enabling it to maintain the fixed reference point against which the working is measured. If the counter is the same electrode as the reference, (known as a 2 electrode set-up) this is not guaranteed since the counter/reference may be modified over the course of the experiment as a result of the large current flowing between it and the working. Finally the signal obtained from a 2-electrode set-up is a combination of signal from the working and the counter and it
cannot be deconvoluted. In our experiments both configurations were used. Kinetic information about a chemical process can be obtained by changing the sweep rate since for slow processes a fast sweep rate does not allow the system to relax fully to an equilibrium state before it is perturbed to the next potential. A common use of the technique involves sweeping the working electrode from its open circuit potential to a more negative potential, generating cathodic peaks (indicating there is a reduction process occurring at the working electrode); and then sweeping it back to a chosen more positive potential generating anodic peaks (indicating there is some oxidation process at the working electrode). This constitutes one cycle and multiple cycles are often run to see how the behavior of the working electrode changes.

Window opening is a specific CV technique used to determine which redox process are coupled to each other. It involves progressively sweeping a working electrode to wider potentials limits with each cycle. A constant potential is chosen to be the starting point and every cycle ends and starts at this point. This technique allows any new cathodic peaks observed as the scan window increases to be correlated to new anodic peaks observed on the reverse sweep back to the constant chosen potential starting point.

1.2.2 Potential Holds

Potential holds are a technique where the working electrode is held at a constant potential for a time interval so that the current behavior over time can be
observed. This technique is useful for obtaining kinetic information about the processes occurring at the working electrode. The reference and counter electrodes may or may not be the same electrode in this technique.

1.2.3 Electrochemical Impedance Spectroscopy (EIS)

In EIS the working electrode is held at a constant potential (either at or away from the open circuit potential), and an oscillating potential (usually 5-10 mV) is applied over the DC bias. The frequency of this oscillating potential is changed continuously, generally starting at 100kHz and ending at 0.1 Hz, this allows processes that occur on different timescales to be probed. Since all electric circuits have characteristic voltage-current behaviors, the electrochemical system is approximated as an electric circuit and the EIS spectra (usually displayed as a reactance vs resistance plot referred to as a Nyquist plot) can be fitted to various circuits and parameters of the circuit elements (common circuit elements include ideal /non-ideal capacitors, resistors, and Warburg elements) can be obtained. A common circuit used to model electrochemical systems in the Randles Cell, which consists of a resistor in series with a parallel grouping of a second resistor in series with a Warburg element and a capacitor. Figure 2 shows this circuit along with a typical Nyquist plot that it can be fitted to. The challenge with this technique is interpreting the fitted circuit to actual electrochemical processes in the system. This technique can be run as a two electrode cell but the contributions of the working and counter electrode will be convoluted in the spectra. Generally three-
electrode setups are used so that the spectra can be attributed solely to the behavior of
the working electrode.

Figure 2. Randles Cell which represents an electrochemical system with kinetic and
charge transfer contributions. $R_s$ represents the resistance of the electrolyte and the
electrochemical measurement set-up. $R_{ct}$ represent the resistance of an electron
crossing the electrode-electrolyte interface to reduce a species at the surface of the
electrode. W is a Warburg element, it represents the diffusion of the relevant species
throughout the system. $C_{dl}$ represents the double layer capacitance that forms between
the electrode and the electrolyte. The arrows show the features in the Nyquist plot
which arise from these specific circuit elements. The y axis of the Nyquist plot is the
reactance in the circuit and the x-axis the resistance.
1.2.4 Constant Current Discharge

This technique involves drawing a constant current from the cell and allowing the voltage to change such that the cell can supply that current. Voltage limits are set and the cell cycles between them.

1.3 Neutron Depth Profiling

Unlike most other experimental methods which probe multiple processes in a system (so that the diffusion process must be deconvoluted from the total signal) neutron depth profiling allows direct observation of diffusion of Li through an electrode. The technique involves penetrating the substance with a cold neutron beam. The beam line used (National Institute of Standards and Technology, Gaithersburg Maryland) provides a “cold” neutron (~5 meV) beam\(^{22}\) with thermal equivalent fluence rate of \(1 \times 10^9\) neutrons/ cm\(^2\) s with a nominal beam area of 110 mm\(^2\). The neutrons will react with the Li in the sample according to the equation below.

\[
^6\text{Li} + n \rightarrow ^3\text{H} + \alpha \quad \text{(Reaction 1)}
\]

where the \(^3\text{H}\) (triton) has an initial energy of 2.73 MeV and the \(\alpha\) particle has initial energy of 2.05 MeV. As the tritons travels through the sample it loses energy, dependent on the stopping power of the sample. By looking at the quantity and energy of the triton particles detected, information about the depth (from a depth-energy model calculated in TRIM) and concentration of Li within the sample can be obtained.
Chapter 2: Experimental

2.1 General Procedures

To prepare the electrode samples Si was evaporated onto copper foil to achieve a thickness of 100 nm (the thickness was determined with the use of a crystal quartz microbalance suspended in the evaporation chamber) using a Denton DV-502A E-Gun Evaporator in the Nanotech West Lab Facility (Columbus, Ohio). The pressure during the deposition was $2 \times 10^{-6}$ torr the operating voltage 7.5 kV, and the current throughout the deposition was adjusted (~80 mA) to give a stable deposition rate of between 1.5-2 Angstroms/second. Total deposition time was about 10 minutes. The target was a manually scribed Si wafer (110, N-type, P-doped, 1-10 ohm/cm resistivity purchased from MTI Corp). Electrodes of 13mm (for the coin cells) and 16mm (for the swagelok cells) diameters were punched out using a Swanstrom Tool USA Round Disc Cutter. In later sections, where appropriate, values will be reported normalized to the area of the electrode in contact with the electrolyte. The Si electrodes were gently washed with acetone, methanol and isopropyl Alcohol before being hand-dried with a Kim-wipe and then left in a drying oven overnight at 55 degrees Celsius. The two electrode coin cells were assembled according to Figure 3. The electrolyte in all tests was 1M LiPF$_6$ 1:1
volume DMC:EC (Novolyte, Purolite A5 series). For coin cells Celguard 2400 separator (25 micron thick) was used after being soaked in the electrolyte. The coin cells (CR 2032) were crimped in a MSK-110 Hydraulic Crimping Machine (MTI) at pressures of ~600 psi. All cells were assembled in a glove box maintained at <0.5ppm water and oxygen levels. All electrochemical tests (except for some capacity cycling of coin cells and CV/EIS test) were performed on multi-channel Biologic VMP3 potentiostat. Coin cell capacity cycling was performed on a MTI 8 channel battery analyzer. The CV/EIS test was performed on a Princeton Applied Research potentiostat model 263A coupled with a Solarton SI 1260 Impedance Analyzer. The various experiments and their specifics are detailed below.

Figure 3: Expanded view of the assembly of a coin cell. Images of the assembled cell.
2.2. Slow scan CV

A slow scan CV was performed in a coin cell to obtain detailed information on the SEI formation and lithiation behavior of the thin-film Si electrode. The working electrode was thin-film Si and reference/counter was a Li disc. The cell was cycled between 0.005V and 2.5V at a scan rate of 5 μV/s.

2.3 Window Opening

A window opening experiment was performed in a 3 electrode Swagelok cell with Li foil and the counter and reference electrodes and thin film Si as the working electrode. The cell was cycled repeatedly between an upper limit of 1.5V (vs Li reference) and sequentially decreasing lower limits down to 5 mV (vs Li reference) at 50 μV/s.

2.4 Potential Hold

The potential hold experiment was performed in a 3 electrode Swagelok cell with Li foil and the counter and reference electrodes and thin film Si as the working electrode. The cell was held at all voltages for 2 hours. The order of voltage holds was 1.5V → 1.0V → 0.9V and then steps of 25 mV down to 0.005V vs Li/Li⁺ and then back up to 1.5V symmetrically.
2.5 Variable Scan Rate CV

Multiple CVs were run at various scan rates on a 3-electrode cell to determine how the magnitude and position of the peaks changed. Again the working electrode was thin-film Si on copper and reference and counter electrodes were Li.

2.6 CV/EIS

The CV/EIS experiment was performed in a 3 electrode Swagelok cell with Li foil and the counter and reference electrodes and thin film Si as the working electrode. The cell was swept in 25 mV increments at a 50 μV/s scan rate. After each sweep segment 3 sequential EIS measurements were made with a superimposed alternating potential of 10 mV over a directly applied potential equal to the end potential of the previous sweep.

2.7 Neutron Depth Profiling

A coin cell with a hole cut in the top and an airtight 7.5 um thick kapton window fitted was placed in the vacuum chamber of the NIST neutron beam line. The triton permeable aperture was 0.5 cm in diameter. The working electrode was a 13mm diameter disc of NMC material (Li$_{1.21}$Ni$_{0.15}$Mn$_{0.54}$Co$_{10}$O$_{79}$ ) coated on 20 um of aluminum current collector, obtained from a collaborator. The chamber pressure was pumped down to below 1 millitorr. The cell could not be charged in-situ because the high vacuum within the NDP chamber pulled the contents of the cell apart leading to
instability under vacuum. Thus the cell was measured by NDP in the as received fully discharged state and then charged outside the chamber up to 4.9V vs Li/Li⁺ at 38.5 uA/cm² after which it was again probed by NDP.

2.8 CV Coin cell cycling

In the cycling test the coin cells, with 100 nm e-beam evaporated Si on Cu as the working electrodes were discharged down to 0.00V vs the Li counter/reference and charged up to 2.5V repeatedly at a fixed current.
3.1 Probing phase transition in voltammogram at quasi-equilibrium.

In order to characterize the electrochemical behavior of thin film Si a slow scan CV was performed. This slow scanning speed allows the electrode to remain in a quasi-relaxed state during the scan. The intent is that electrode not be pushed to new potentials before the electrochemical processes appropriate for a particular potential are completed. With faster scanning the slow kinetics of a certain process prevents that process from coming to equilibrium before the electrode is scanned to another potential. In fast scans the resolution of a CV suffers because the potential changes so fast that many different process (each thermodynamically located within a particular discrete, narrow potential range) occur over a wide range of potentials and thus the current over that range cannot be assigned to discrete processes. Depending on the kinetics of the various electrochemical reactions between Si and Li (reported to be very slow), an even slower scan rate may yield more information about the phase transitions. There are various alloying reactions between Si and Li that have been reported. Figure 4\textsuperscript{23} shows an equilibrium titration curve of the Li-Si phase formation (black line). The peaks in our CV correspond well to these theoretical potentials and the charge passed corresponds to some widely reported Li-Si phases as will be discussed later.
Figure 4. Equilibrium titration curve (black line) for LiSi phase formation.  

Below are the labeled reactions and their positions in our slow scan CV based on the theoretical potential ranges.

\[
\begin{align*}
7 \text{Si} + 12 \text{Li}^+ + 12 \text{e}^- & \rightarrow \text{Li}_{12}\text{Si}_7 \quad E = 0.33 \text{V (vs Li/Li}^+) \quad \text{(Reaction 2, peak C3)} \\
\text{Li}_{12}\text{Si}_7 + \frac{13}{21} \text{Li}^+ + \frac{13}{21} \text{e}^- & \rightarrow \text{Li}_7\text{Si}_3 \quad E = 0.27 \text{V (vs Li/Li}^+) \quad \text{(Reaction 3, peak C1)} \\
\text{Li}_7\text{Si}_3 + \frac{11}{12} \text{Li}^+ + \frac{11}{12} \text{e}^- & \rightarrow \text{Li}_{13}\text{Si}_4 \quad E = 0.15 \text{V (vs Li/Li}^+) \quad \text{(Reaction 4, peak C1)}
\end{align*}
\]
\[
Li_{13}Si_4 + \frac{23}{20} Li^+ + \frac{23}{20} e^- \rightarrow Li_{22}Si_5 \quad E = 0.05 \text{ (vs Li/Li}^+)\] 

(Reaction 5, peak C2)

Figure 5 shows the scans run at a slow scan rate of 5 μV/sec for 7 continuous cycles between 2.5V and 0.005V (vs Li/Li^+). In the first cycle we see two peak that do not show up in subsequent cycles. One small peak at 1.75V (C5) and another at 0.6V (C4). For the remaining cycles there are 3 constant cathodic peaks that shift gradually over time but the peak positions more or less stabilize after the 4th cycle. The cathodic shoulder peak around ~0.3V (C3) does not show up in CVs performed at faster scan rates. This voltammogram indicates there are 3 separate cathodic lithiation events but the first two are so close in potential they superimpose at fast scan rates. As the cell is scanned multiple times the shoulder peak (C3) migrates to more negative voltages until it is enveloped by the 0.2V (C1) cathodic peak. Table 2 quantifies the charge transferred in the peaks as the cell is cycled. Because of the small inter-scan peak movements the integration limits were changed by several millivolts, these changes are denoted by the “±” symbol in the table. It is seen in Figure 5 that as the shoulder peak (C3) moves to the left the C1 peak gets bigger. The sum of the charge passed in these two peaks remains constant over multiple scans (3-7) as shown in Figure 6. In addition the sum of charge passed by the 2 most negative cathodic peaks C1 and C2 is very close to the charge passed by the anodic peaks, A1 and A2, on the reverse scan. This is shown in Figure 8 where the cathodic charge is compared to anodic charge as well as the columbic efficiencies. It is seen that the charge passed by all 3 cathodic peaks is significantly
higher than the charge passed in the anodic peaks but the charge passed by the two most negative cathodic peaks is nearly identical to the charge passed by anodic peaks.
Figure 5. Slow scan (5 μV/second) CV performed on 2 electrode coin cell. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counter was Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). Insets show close up of the 1.75V peak (top), and entire voltage range of the scan (bottom). Black arrows show changes as scan number increased.
Table 2. Charge (in Coulombs) passed in different segments of the slow scan CV over multiple scans.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C1 + C3</strong></td>
<td>0.490 V – (0.130 V ± 0.01 V)</td>
<td>0.242</td>
<td>0.177</td>
<td>0.185</td>
<td>0.190</td>
<td>0.186</td>
<td>0.179</td>
</tr>
<tr>
<td><strong>C1+C2</strong></td>
<td>(0.130 V ± 0.01 V) – 0.005 V – (0.105 V ± 0.02 V)</td>
<td>0.317</td>
<td>0.284</td>
<td>0.293</td>
<td>0.297</td>
<td>0.294</td>
<td>0.290</td>
</tr>
<tr>
<td><strong>C1+C2+C3</strong></td>
<td>0.490 V – 0.005 V – (0.105 V ± 0.02 V)</td>
<td>0.407</td>
<td>0.348</td>
<td>0.341</td>
<td>0.338</td>
<td>0.328</td>
<td>0.314</td>
</tr>
<tr>
<td><strong>A1+A2</strong></td>
<td>(0.105 V ± 0.02 V) – 1.2 V</td>
<td>0.281</td>
<td>0.263</td>
<td>0.293</td>
<td>0.295</td>
<td>0.292</td>
<td>0.287</td>
</tr>
</tbody>
</table>

Table 3. Theoretical and experimental tracking of charge movement on the cathodic portion of the slow scan CV, cycle 7.

<table>
<thead>
<tr>
<th>Process</th>
<th>Li&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;y&lt;/sub&gt;</th>
<th>Theoretical (electrons per Si)</th>
<th>Experimental (electron per Si)</th>
<th>E regions measured (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lithiation</strong></td>
<td></td>
<td>Δ(e−/Si)</td>
<td>Total (e−/Si)</td>
<td>Δ(e−/Si)</td>
</tr>
<tr>
<td><strong>Li&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;y&lt;/sub&gt; formation</strong></td>
<td>Si → Li&lt;sub&gt;12&lt;/sub&gt;Si&lt;sub&gt;7&lt;/sub&gt;</td>
<td>1.71</td>
<td>1.71</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>Li&lt;sub&gt;12&lt;/sub&gt;Si&lt;sub&gt;7&lt;/sub&gt; → Li&lt;sub&gt;7&lt;/sub&gt;Si&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.62</td>
<td>2.33</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Li&lt;sub&gt;7&lt;/sub&gt;Si&lt;sub&gt;3&lt;/sub&gt; → Li&lt;sub&gt;13&lt;/sub&gt;Si&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.92</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Li&lt;sub&gt;13&lt;/sub&gt;Si&lt;sub&gt;4&lt;/sub&gt; → Li&lt;sub&gt;15&lt;/sub&gt;Si&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.5</td>
<td>3.75</td>
<td>0.83</td>
</tr>
</tbody>
</table>
Figure 6. Per-cycle charge passed during the 0.2V and shoulder peaks.
Figure 7. Per-cycle/cumulative charge passed during the shoulder peak.
Figure 8. Comparisons of the charge passed in the peaks during the CV. The red line is the total charge passed in all the cathodic peaks, read off the left axis. The orange line is the charge passed in the cathodic peaks excluding the shoulder peak. The blue line is the charge passed by the anodic peaks. The Coulombic efficiency counting all cathodic peaks is low ~85%, seen as the yellow line read off the right axis whereas if the shoulder peak is excluded, shown by the green line, the efficiency is close to 1.
Our interpretation of this is that the cathodic shoulder peak is some initial irreversible lithiation process that is not completed on the first scan although a large portion of the electrode is converted. The cathodic peaks C1 is a second lithiation process which uses the product of the shoulder peak, C3, as its reactant, this is why the C2 peak increases in intensity as the shoulder peak disappears. Over many scans the electrode becomes completely converted to the product of the shoulder peak (even when the electrode is in its most delithiated state, after the anodic sweep on each scan) so there is more reactant for the C1 peak and it grows. We think this is reasonable because, as stated before, the charge passed on the anodic sweep is quite close to the charge passed by the C1 and C2 peaks over multiple scans. This suggests that only the two most negative cathodic processes are reversible on the anodic sweep. In this analysis we do not consider the 1st cycle to be representative of the cell because there are one-time reactions that occur such as SEI formation and oxide reduction. Figure 7 shows the per-cycle and cumulative charge passed by the shoulder peak. It is seen that the shoulder peak decreases in charge passed with increasing cycle number. Assuming the shoulder peak is irreversible lithiation process which occurs less over cycling as more of the electrode is converted to that phase, the charge passed (over all cycles) corresponds to a formation of Li$_{1.93}$Si which is close to the Li$_{12}$Si$_7$ reported by Wen et al.$^{24}$ to form between 332 mV and 288 mV which corresponds well with the shoulder peak position in our CV. After the initial irreversible lithiation the second cathodic peak is reached and we calculate (based on the 7th cycle) a transformation of Li$_{1.93}$Si to Li$_{2.92}$Si a ratio in
between the reported phases of Li$_7$Si$_3$ ($\text{Li}_{2.33}\text{Si}$) and Li$_{13}$Si$_4$ ($\text{Li}_{3.25}\text{Si}$). This second peak sits within the voltage range of 275 mV to 110 mV which corresponds well to the values reported by Wen et al.$^{24}$, Li$_7$Si$_3$ forms between 288 mV and 158 mV and Li$_{13}$Si$_7$ between 157 mV and 44 mV. Again using cycle 7 the charge passed in the most negative cathodic peak (C2) gives a transformation of Li$_{2.92}$Si to Li$_{3.75}$Si, in good agreement with the reported$^{8}$ most lithiated phase of Li$_{15}$Si$_4$ ($\text{Li}_{3.75}\text{Si}$). This experimental data is compared to the theoretical charge in Table 3. In section 3.2 a window opening experiment was performed which shows that the A2/C2 peaks and A1/C1 peaks are coupled.

### 3.2 Identifying coupled reactions

Coupled transitions can be identified by repeatedly cycling the potential to various potential vertex points, referred to as window opening. No appreciable current appears in the window opening experiment until cathodic potentials of 0.275V (vs Li/Li$^+$) are reached. At that potential and below the significant cathodic current is observed increasing in magnitude as lower voltage limits are probed. On the reverse sweep anodic peaks are observed. Figure 9 shows that until down to 0.125 V a single cathodic peak is observed as well a single anodic peak. As the cathodic peaks increases in size so does the anodic peak indicating that these two peaks are forward and reverse directions of a single process (lithiation). Below 0.125V a second cathodic peaks grows in and on the positive sweep a second anodic peaks appears. We conclude that the cathodic peak
at 0.175V (C1) is coupled with the anodic peak at 0.475V (A1) and the cathodic peaks 0.05 V (C2) is coupled with the anodic peaks at 0.3V (A2). Note that the peak potential for C1 shifts to a slightly more positive potential only after the C2 and A2 appear. This suggests that the C2/A2 process changes the Si electrode in such a way as to make the C1 process occur at a more positive potential. A plausible explanation for this is the well documented Si cracking that occurs when large amounts of Li get inserted into the electrode to effect a significant change in the structure. This change could be pulverization of the electrode, although the cycling life of these electrodes as shown in our coin cell cycling test cast doubt on this idea; or it could be the electrode going through crystalline/amorphous phase changes\textsuperscript{25-26} and incompletely converting back and forth between the various Li-Si phases. Dahn \textit{et al.}\textsuperscript{27} report the first lithiation process forms an amorphous Li\textsubscript{x}Si alloy whereas at potentials lower than 60 mV (vs Li/Li\textsuperscript{+}) a crystalline phase Li\textsubscript{15}Si\textsubscript{4} forms. Since the most lithiated phase has both a greater quantity of Li packed into the Si and also a crystalline structure it seems reasonable that this would be sufficient to cause structural change in the electrode, whereas the first process, merely forming an amorphous Li\textsubscript{x}Si alloy of lesser Li content would not necessitate drastic structural pulverization of the electrode.
Figure 9. Window opening experiment performed on 3 electrode Swagelok cell. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counters were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). Inset show entire voltage range of the scan. Black arrows specify coupled peaks.
Chapter 4: Quantifying Diffusion Behavior in Li\textsubscript{x}Si\textsubscript{y}

4.1 General Overview

The diffusion constant of Li in Si and Li-Si alloys as before stated is of import with regards to the rate capability of this battery chemistry. Many techniques are available however all require some kind of deconvolution to obtain the constant. Because the constant is not directly obtainable from experimental data, various models are proposed through which the value can be obtained, and the variety of models introduces a wide range of values, as shown in Table 1. In this work we have followed several techniques from literature, compared our values with theirs and given some thoughts on the strengths and weakness of various models. Because battery chemistry is relatively unique in electrochemistry in that it involves the compositional change of the working electrode it seems the diffusion coefficient modeling will be more complex than for more standard electrochemical situations such as heterogeneous catalysis. Various attempts have thus far been made to measure the diffusion coefficient. Pell\textsuperscript{11} reports a constant value of $\sim 3 \times 10^{-15}$ cm$^2$/s from his method of observing the change in capacitance in a p-n junction due to the diffusion of Li into the junction. Kuzubov \textit{et al.}\textsuperscript{15} obtain a value between $10^{-14}$ and $10^{-16}$ cm$^2$/s depending on the Li concentration within
the alloy, on their modeling of a initial adsorption of Li atoms to a 100 Si surface. Hüger et al.\textsuperscript{19} used neutron reflectometry to monitor the change in $^{6}\text{Li}/^{7}\text{Li}$ isotope ratios in reservoirs separated by 10nm layers of Si, they obtain a tracer diffusivity constant of $6 \times 10^{-13} \text{ cm}^2/\text{s}$. Xie et al.\textsuperscript{13} observed coefficients on the order of $10^{-12}$ and $10^{-14} \text{ cm}^2/\text{s}$ using PITT and EIS techniques on a sputtered amorphous Si electrode. Section 4.1 discusses our potential hold results in which we hold the Si electrode at a variety of potentials for a time interval and observe the current transient. From this transient and a model we can derive the diffusion constant. In section 4.2 we perform multiple CVs with varying scan rate. By observing the current density as a function of scan rate diffusion constants can be obtained via the Randles-Sevcik equation (a Nernstien model, as well as other models). A third method is taking electrochemical impedance spectra at various potentials in the CV and modeling part of the spectra as a Warburg impedance, which represents the diffusion of Li through the Si electrode.

4.2 Probing diffusion at constant potential

The mathematical model for calculating diffusion coefficients from the potential holds was taken from Wen et. al\textsuperscript{28} with slight modification (involving the directionality of the diffusion) of the boundary conditions. Fick’s second law (1) describes the 1-dimensional diffusion of a species into a medium, in this case the Si thin-film electrode. $C_L$ is the local concentration within the electrode, $D$ the chemical diffusion coefficient and $x$ is the distance into the electrode from the electrode-electrolyte interface.
\[ \frac{\partial C_{Li}}{\partial t} = D \frac{\partial^2 C_{Li}}{\partial x^2} \quad (1) \]

3 boundary conditions are imposed

\[ C_{Li} = 0: \quad 0 \leq x \leq L, \ t = 0 \quad (2) \]
\[ C_{Li} = C_s: \quad x = 0, \ t > 0 \quad (3) \]
\[ \frac{\partial C_{Li}}{\partial x} = 0: \quad x = L, \ t \geq 0 \quad (4) \]

(2) indicates that initially there is no Li inside the electrode. (3) indicates that at the interface, at all times after potential is applied, the local concentration is equal to the surface concentration \((C_s)\), which is determined by the applied voltage. (4) indicates that at all times the change in concentration at the back of the electrode is 0, it is impermeable to the diffusing species. Figure 10 below schematic shows the model.

![Figure 10](image)

Figure 10. Figure showing the surface reduction of Li cations and their diffusion through the bulk of the electrode.
Applying these boundary conditions to (1) two solutions for planar diffusion are obtained, a long-time and short-time variant. Because the potential holds were for 2 hours, the long-time variant will be used in the calculation.

\[
\frac{C_{Li}(x, t) - C_s}{C_s - C_0} = -\frac{4}{\pi} \sum_{n=0}^{\infty} \left[ \frac{1}{2n + 1} \sin \left( \frac{(2n + 1)\pi x}{2L} \right) e^{-\frac{(2n+1)^2\pi^2Dt}{4L^2}} \right]
\]

(5)

The current during the potential hold can be related to the interface concentration by (6).

\[
I(t) = -z_A FSD \left( \frac{\partial C_{Li}}{\partial x} \right)_{x=0}
\]

(6)

Using equations (5) and (6) we obtain:

\[
I(t) = \frac{2z_{Li} FSD (C_s - C_0) D}{L} e^{-\frac{\pi^2Dt}{4L^2}}
\]

(7)

(7) is valid only if:

\[
t \gg \frac{L^2}{D}
\]

(8)

Taking the natural logarithm of both sides of (7) we obtain:

\[
\ln(I(t)) = \ln(\text{constant}) - \frac{\pi^2D}{4L^2} t
\]

(9)
Therefore the current transients are plotted as Ln(I(t)) versus time and the slope takes the value ($\pi^2D/4L^2$). Rearrange for $D$ giving:

$$D = -\frac{(slope \times 4L^2)}{\pi^2}$$  \hspace{1cm} (10)

Figure 11 shows the current transients obtained at potential holds of 0.2, 0.05, 0.3 and 0.475V. These potentials were chosen because the final (semi-stable) current values in the 2 hour current transients indicated that faradaic processes were occurring at theses potentials. These final current values as a function of potential are shown in Figure 12. At potentials at which non-faradaic processes occur there is initial capacitive current when the hold begins but decays to an insignificant value relatively quickly as the “capacitor” interface is charged completely for that potential. The current transients show two regions in which the slope differs significantly. This suggests that there are two diffusion coefficients for Li being probed. However, because the current is limited by the slowest kinetic step at all times, it appears that the rate is limited by a certain diffusion coefficient (obtained from the orange current) and then at a later time limited by a different diffusion constant (obtained from the grey current). This may indicate that there multiple phases present in the electrode, and that the Li diffuses through a certain phase and then once that phase has been lithiated it forms a second phase with a different diffusion constant. Table 4 shows the slopes obtained from the various segments and the diffusion coefficients calculated from them. We obtain diffusion
coefficient on the order of $10^{-15}$ cm$^2$/s, which is about 2 orders of magnitude lower than is widely reported. From Table 4 it can be seen that the values for the diffusion constants derived from the orange portion are similar in value and also that the values for the constants derived from the grey portion also are similar. This leads us to believe that all 4 orange segments are the measurement of a single diffusion constant and the same for the grey segments. The orange constant is about double the grey one. We suspect that the fast diffusion constant is belongs to the diffusion of Li through a Li-Si alloy and the slower diffusion constant belongs to the diffusion of Li through bare silicon. It makes sense that Li might diffuse faster through a lattice that has already been expanded by pre-lithiation than through bare silicon.
Figure 11. 2 hour current transients from a 3 electrode cell. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counters were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). The holds at 0.05 and 0.2V are the cathodic peaks and the holds at 0.3 and 0.475V are the anodic peaks. Two regions (orange and grey) with different slopes have been linearly fitted. These two regions are different slopes indicating two different values for $D_L$ within the Si electrode. A multi-phase electrode may be the cause of the diffusion constant variation.
Figure 12. Current values at the end of 2 hour potential holds. The peaks in this spectra show the potentials at which faradaic processes are occurring.
Figure 13 below shows how we envision the electrode lithiates and delithiates.

Figure 13. The blue represents un lithiated silicon. The green the electrolyte and the red circles the Li⁺ dissolved in it. The purple circles represent a Li atom after being reduced at the interface and diffusing through the electrode. In (a), at a reducing potential, a reduction event occurs at the surface of the electrode and the reduced Li diffuses through the Li-Si alloy with a certain diffusion coefficient, $D_{LiSi}$. After a given time enough Li accumulates in the interface region such that the Li must diffuse into and through the unlithiated part of the electrode with another diffusion coefficient, $D_{Si}$. In (b) at a more negative potential, Li is continually reduced at the surface and the interface Li-Si alloys becomes more lithiated whereas the less lithiated Li-Si alloy moves further into the electrode. The diffusion constant, $D_{LiSi}$, is not significantly different in the more or less lithiated alloys. Eventually the Li-Si alloys become lithiated such that Li must again diffuse into the silicon electrode with diffusion constant $D_{Si}$. In (c) at an oxidizing potential, the interface is delithiated over time during which Li diffuses through the Li-Si alloy with diffusion constant $D_{LiSi}$. Eventually there is only silicon at the interface, thus Li must diffuse through the interfacial silicon with diffusion rate $D_{Si}$ to the interface where it can be oxidized. In (d) at a more oxidizing potential, the same thing occurs as in (c) except the Li-Si alloys present in the electrode are less lithiated.
Figure 14. NDP spectra of Al foil being delithiated over time. The Li comes out at the interface first leaving a large concentration within the bulk.\textsuperscript{29}

Liu \textit{et al.}\textsuperscript{29} have shown (Figure 14) via an in-situ imaging technique (NDP) that an aluminum electrode will delithiate at the interface first leaving a large section of the bulk still lithiated, which gives some support to our explanation of the multiple diffusion constant (Figure 13).
Table 4. Slopes and calculated diffusion constants at the 4 lithiation peak potentials.

<table>
<thead>
<tr>
<th>E (V vs Li/Li⁺)</th>
<th>Segment 1 slope (s⁻¹)</th>
<th>$D_1$ (cm²/s)</th>
<th>Segment 2 slope (s⁻¹)</th>
<th>$D_2$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 (C2)</td>
<td>-1.87 x 10⁻⁴</td>
<td>7.57 x 10⁻¹⁵</td>
<td>-9.61 x 10⁻⁵</td>
<td>3.90 x 10⁻¹⁵</td>
</tr>
<tr>
<td>0.2 (C1)</td>
<td>-2.18 x 10⁻⁴</td>
<td>8.82 x 10⁻¹⁵</td>
<td>-6.66 x 10⁻⁵</td>
<td>2.70 x 10⁻¹⁵</td>
</tr>
<tr>
<td>0.3 (A2)</td>
<td>-2.04 x 10⁻⁴</td>
<td>8.27 x 10⁻¹⁵</td>
<td>-1.34 x 10⁻⁴</td>
<td>5.43 x 10⁻¹⁵</td>
</tr>
<tr>
<td>0.475 (A1)</td>
<td>-2.05 x 10⁻⁴</td>
<td>8.31 x 10⁻¹⁵</td>
<td>-1.17 x 10⁻⁴</td>
<td>4.73 x 10⁻¹⁵</td>
</tr>
</tbody>
</table>

We now consider how to reconcile the disparity in our values from previous measurements, as before stated a difference of about 100x. The amount of charge passed in total during these potential holds matches well with the expected capacity of the electrode. The three electrode cell was disassembled and a dark spot on the working thin film Si electrode was observed shown in Figure 15. We take this to be the active area of the electrode (because of the cell design this area was the only part of the electrode exposed to the electrode), and we calculate a mass of Si in this active electrode to be 4.687 x 10⁻⁷ grams. From the charge – time relationship, shown in Figure 16, we can see that at the end of the cathodic potential holds a total charge of .25 C had been passed giving the electrode an initial capacity of 5320 mAh/g. This is reasonable considering the cathodic potential holds were carried out a fresh electrode and thus some of the charge passed was not lithiation current but possible surface oxide reduction as well as SEI formation. Furthermore if the anodic charge is counted starting
from the first anodic potential hold after the cathodic holds and ending with the final anodic potential hold at 1.5V the charge passed corresponds to 4.22 electrons for every Si atom, or very close to the Li$_{22}$Si$_5$ phase. The agreement between the theoretical capacity of Si (3500-4400 mAh/g) and the actual initial discharge capacity (5320 mAh/g) and charge capacity (~4400 mAh/g) of our electrode shows the system is behaving reasonably and gives credence to the calculated diffusion constant values. In addition Yoshimura et al$^{30}$ have suggested the diffusion coefficient of Li in Si decreases with the film thickness although their measurement of a 100 nm Si film (using potential holds and a similar mathematical model) yield a diffusion coefficient on the order of $10^{-13}$ cm$^2$/s. The reason for the discrepancy in our values in because they fitted a different part of the current transient. As shown in Figure 17 the data fitted is the initial current of the potential hold whereas the fitted current in our hold (Figure 11) passes long after start of the potential hold. We chose to fit the current after more time had passed because at that point the current can reasonably be assumes to be only from semi-steady-state lithiation of the Si electrode and to be limited by the slowest kinetic step in that process; presumably the diffusion of the Si through the Si or Si-Li alloy. At earlier times in the hold, capacitive and faradaic non-lithiation current are both contributing to the total current and probably exceeding the faradaic lithiation current. This test can also inform some of the earlier conclusions regarding the slow scan CV scan. That voltammogram (Figure 5) suggested that the Li$_{12}$Si$_7$ phase forming at around 350 mV was irreversible since no coupled anodic peak was observed. Notice in Figure 16 that the
cathodic charge begins to flow significantly only when the potential hold has been set around that potential region. This confirms what was seen in the slow scan CV.

Regarding the irreversibility of that Li$_{12}$Si$_7$ phase, at quite positive potentials in Figure 16 (0.6V to 1.5V) there is still significant charge coming out of the electrode, even though in the slow scan CV (Figure 5) no obvious peaks appeared there, although there was constant low value positive current over that entire voltage range. This suggests that the Li$_{12}$Si$_7$ phase is possible to delithiate but it occurs very slowly over a wide, very positive potential range.
Figure 15. Working thin film Si electrode after potential hold experiment. The dark spot in the middle is the part of the electrode that was exposed to electrolyte during the experiment. We take this to be the active area. The diameter is 8.5 mm.

![Image of thin film Si electrode]

Figure 16. Charge (orange) and voltage (blue) vs time. Cathodic charge (lithiation of the Si electrode) is passed significantly from about 0.5 to 0.005V reaching a maximum of 0.253C and then is mostly removed on the anodic potential holds from about 0.25 to 1.5V. This allows us to calculate the capacity of the electrode.
Figure 17. current transient with fitted line from which the diffusion constant was calculated\textsuperscript{30}. The data fitted is taken in the first two seconds of the potential hold.
4.3 Determining diffusion coefficient for lithiation rate dependence.

The lithium diffusion constant can be obtained from CVs performed at various scan rates. Many groups have done this using the Randles-Sevcik equation, shown below.

\[ I_p = 2.69 \times 10^5 n^{1.5} A D^{0.5} C_{Li} v^{0.5} \]  

(11)

Where \( I_p \) is the peak current (in A), \( n \), the number of electrons involved in the redox reaction (unit-less, presumed here to be 1 for the reduction of Li\(^+\)), \( A \) the surface area of the electrode (in cm\(^2\)), \( D \) the diffusion coefficient (in cm\(^2\)/s), \( C_{Li} \), the concentration of Li\(^+\) (in mol/cm\(^3\)), and \( v \) the scan rate (in V/s). The Randles Sevcik equation was developed for simple cases of fast reversible electrochemical reactions such as the ferrocene/ferrocenium couple. In this situation there is a reactant diffusing towards the electrode, being reduced and then diffusing away as product. The rate at which this occurs can be calculated from the current observed in the CV and is dependent on the diffusion rates and concentration of these species as well and the scan rate of the CV. As the equation above shows the faster the scan rate the more current must be passed in the same amount of time. This is because in this situation the measured potential is entirely due to the activity of oxidized and reduced species at electrode/electrolyte interface (Nernstian, assuming a very fast electron transfer). The surface (compositionally and structurally) of the electrode is relatively static since the reactant is merely arriving at the interface, experiencing an interfacial charge transfer and then
diffusing away. However in a battery this process is more complicated since the charge transfer event itself modifies the surface of the electrode. It modifies the electrode by changing the composition; the more negative charge passed on the cathodic CV scan, the more lithiated the surface of the Si electrode becomes. This is confirmed by comparing the OCP of the Si electrode before and after a cathodic CV sweep (it is lower after the sweep since it is electrochemically more similar to the Li counter it is being referenced against). It decreases from ~ 3.0V to ~0.2V depending on the amount of charge passed. Pushing more Li into the Si changes the intrinsic electron pressure within the electrode so that electrode is now very different in an electrochemical potential sense than it was at the beginning of the scan as pure Si. Instead of sharp interface between pure Si and Li in the electrolyte, we envision a multiphase interface of Li-Si alloys lithiated to various degrees. In addition unlike the simple ferrocene situation where the only diffusion is of reactant and product in the electrolyte towards and away from the electrode, in a battery there is diffusion of the reactant towards the electrode, and then diffusion of the product deeper into the electrode. The local state of lithiation of the electrode (which changes based on exactly what region of the electrode is being examines) also effects the rate at which the reduced Li can diffuse through the electrode, making the diffusion contribution to the current much more complicated than the ferrocene case. Since the measured potential is dependent upon this interface, the fact that it has become ill-defined presents a problem with using Randles-Sevcik since the equation is partially based on the assumption that the interface is static. In
addition with Si in particular a high degree of lithiation has been reported to cause
volume expansion and cracking thus modifying the surface morphology, so the active
surface area may change as the scan progresses. Previous studies have taken different
approaches to this issue. Arie et al.\textsuperscript{20} sidesteps the problem and treat the battery
electrode as a static object. They claim $D$ to be the diffusion coefficient of Li inside the
electrode and for $C$, they use the concentration of Li in the electrolyte. Ding et al.\textsuperscript{10} use
Randles Sevcik but for their $C_Li$ they use the concentration inside the electrode assuming
a particular Li-Si phase. We have performed the same analysis of our data and
compared it to their results. Figure 18 shows multiple CVs at various scan rates. Two
sequential scans were performed at each rate to ensure that the electrode had reached
a steady state. For all rates except 50 $\mu$V/s the cyclic voltammograms are very similar
for both scans. For the 50 $\mu$V/s scan the second scan was taken since the peaks were
better defined. As expected the current increases with scan rate. To determine
diffusion coefficient the maximum current (in Amperes) of each peak is plotted vs the
square root of the scan rate (in V/s). Figure 19 shows the plotted data with the fitted
lines and $R^2$ values. The linear fits to this data have a slope which is equivalent to $2.69 \times
10^5 n^{1.5} A D^{0.5} C_Li$. We take $n$ to be 1, $A$, to be 0.5672 cm$^2$, and $C_Li$ to be .001 mol/cm$^3$.
Therefore the Diffusion coefficient can be determined from the below equation.

\[
D = \left( \frac{slope}{0.5672 \times 2.69 \times 10^5 \times 0.001} \right)^2
\]  

(12)
Table 5 shows the diffusion coefficients calculated for each faradaic peak. These values are in fair agreement with Arie et al\textsuperscript{20}.
Figure 18. CVs run at various scan rates for the purpose of determining Li diffusion coefficient in Si electrode. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counters were Li foil. The electrolyte was 1 M LiPF₆ in DMC:EC (1:1 vol). Full range scan shown in inset.
Figure 19. Plot of the lithiation peaks of CV vs the square root of the scan rate the CV was taken at. Diffusion constants can be obtained from the slope of the fitted lines.
Table 5. Diffusion constant calculated from the standard Randles-Sevcik model.

<table>
<thead>
<tr>
<th>Peak</th>
<th>C1</th>
<th>C2</th>
<th>A1</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_Li$ (cm$^2$/second)</td>
<td>$2.42 \times 10^{-9}$</td>
<td>$3.33 \times 10^{-9}$</td>
<td>$4.13 \times 10^{-10}$</td>
<td>$8.70 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Kulova *et al.* take a completely different track. They derive a new expression for the diffusion coefficient shown below based on the inapplicability of Randles Sevcik to solid state diffusion.

\[
D = \frac{5}{\rho c F} \frac{dE}{dQ} \left( \frac{dj}{\sqrt{v}} \right)^2
\]  

(13)

Where \( \rho \) is the density of Si (2.32 g/cm\(^3\)), \( c \) concentration of Li in the electrode, \( F \) the Faraday constant, \( j \) the peak current (in Amperes) \( v \) the scan rate (in Volts/second). The quantity \( dE/dQ \) is taken from a discharge curve and relates the measured potential to the charge which has been incorporated into the working electrode. For our calculation we used the 2\(^{nd} \) scan of the 50 \( \mu \)V/s CV. The data is plotted as Potential vs Q/g, a discharge curve. This is shown in Figure 20. The slope of the graph is constant in the region from 250mV to \(~120 \) mV. We take this slope to be \( dE/dQ \), it is \( 3.0 \times 10^{-5} \), in close agreement with Kulova’s value of \( 2.8 \times 10^{-5} \). To determine \( c \) the integrated charge is calculated by integrating the discharge in Figure 20. This charge is assumed to be equal to Li that has been incorporated into the electrode. For this electrode that charge was \(~0.15C \), assuming a one electron reduction process, we obtain \( 1.59 \times 10^{-6} \) moles of Li reduced into the Si. We assume the volume of the Si electrode does not change (even though is very probably does) which gives us a Li concentration of 0.279 mol Li/cm\(^3\). Thus the Li diffusion coefficient will be calculated from the below equation.
\[ D = \frac{5}{(2.32)(0.279)(96485)} \frac{3.0E-5}{1} (slope)^2 \]  \tag{14}

Where the slopes are from Figure 19. Table 6 shows the diffusion constants calculated for the 4 peaks. Kulova’s values range from 4 - 9 \times 10^{-13}, but that is for alpha-Si:H Si prepared at high temperature which may explain the discrepancy in our values. In addition the concentration of Li in the electrode can vary by 2 order of magnitude based on the method used to calculate it. Our \( c \) value is quite high compared to other literature so that could account for our somewhat low diffusion coefficient values.
Figure 20. Potential vs Q/g plot derived from the cathodic sweep of the second 50 μV/second sweep. Constant slope region plotted in orange with the slope equation displayed.

\[ y = -3 \times 10^{-5}x + 0.3434 \]

\[ R^2 = 0.999 \]
Table 6. Diffusion constants calculated from the Kulova model.

<table>
<thead>
<tr>
<th>Peak</th>
<th>C1</th>
<th>C2</th>
<th>A1</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Li}$ (cm$^2$/second)</td>
<td>$1.35 \times 10^{-13}$</td>
<td>$1.86 \times 10^{-13}$</td>
<td>$2.31 \times 10^{-14}$</td>
<td>$4.86 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

### 4.4 Determining the diffusion coefficient from alternating current impedance spectroscopy

Figure 21 shows the potential sweeps performed on this cell. In between the end of one sweep and the beginning of the next triplicate EIS was taken. The cyclic voltammogram shows significant reductive faradaic processes from 5mV to ~500 mV and anodic processes from ~200 mV to ~800 mV. This matches well with the more traditionally acquired CVs in Chapter 3. The EIS spectra taken in between the voltage sweeps were examined. In EIS spectra semicircles can be fitted to circuit model of a capacitor and a resistor in parallel. These elements are generally taken to represent the capacitive nature of an electrode-electrolyte interface and the charge transfer event across that interface respectively. Figures 22 and 23 show the EIS spectra for the cathodic and anodic faradaic processes respectively at various potentials. The linear portion of the spectra can be modeled in part as Warburg elements. Warburg elements can represent the 1 dimensional semi-infinite diffusion of Li and thus diffusion constants can be obtained from them according to a model by Ding et al.$^{10}$
\[ D = \frac{1}{2} \left( \frac{V_m}{SFA} \right) \left( \frac{dE}{dx} \right)^2 \]  

(15)

Where \( V_m \) is the molar volume of Si (1.2054 \( \times \) 10\(^{-5} \) m\(^3\)/mol), \( S \) the active surface area of the electrode (5.6745 \( \times \) 10\(^{-5} \) m\(^2\)), \( F \) is Faraday’s constant (96,485 Coulombs/mol), \( A \) is the slope of the plotted -Z'' (reactance) vs \( 1/\sqrt{2\pi f} \), obtained from the Warburg impedances in the EIS spectra taken at the faradic potentials (units of \( \Omega \)s\(^{1/2}\)), and the quantity \( dE/dx \) (V) is the slope (within specific potential ranges) of the Galvanostatic cycle curves shown in Figure 26. The Warburg segments of the EIS spectra were picked by eye and then a brief calculation (the slope of the -Z'' vs Z' segment) was done to ensure a slope close to that of a Warburg elements. The slope should be 1 since the Warburg elements per its definition should have a 45 degree angle between the –Z” axis and the Z' axis. Tables 7 and 8 show the –Z” range for the segments picked from the EIS spectra and also the slope of those –Z” segments with their associated (not shown) Z’ values. It can be seen that the slopes range from 0.867 to 1.00. We accept this deviation from the correct value, 1.00 because the EIS spectra is a non-linear superposition of various processes, so for our “Warburgs” which do not have slope of one, we posit that they are convoluted up with some other electrochemical process within that frequency range. Figures 24 and 25 show the slopes of the Z” vs inverse frequency plots. These slopes are the quantity \( A \) in Equation 15. There is no slope for 0.3V because the EIS spectra taken at 0.3V on the anodic sweep did not exhibit a Warburg impedance that could be easily
identified. While the spectra can probably be fitted to include a Warburg impedance we have not included it here since it could not be identified in the same way as the other spectra. Figure 26 shows the galvanostatic cycling curve of a coin cell. The characteristic cycle capacity loss can be seen from the difference in the black curve and the red/blue ones. The 4th charge and 5th discharge cycles were chose to for the dE/dx analysis. This derivative takes into account the change in the voltage of the working electrode as a function of the change in the charge incorporated (and thus, its atomic composition). The slopes of the various voltage ranges are colored and displayed in the Figure 26. Tables 9 and 10 show the diffusion constant obtained for each voltage regime for the cathodic and anodic sweeps respectively.
Figure 21. 3 electrode Swagelok cell. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counters were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). The voltage was swept cathodically and then anodically in intervals. In between each sweep triplicate EIS was taken. The AC voltage was 10 mV imposed over a potential hold of the ending voltage of the previous sweep.
Figure 22. EIS spectra taken in between the cathodic voltage sweeps.

Table 7. Warburg element range and slope for cathodic voltages.

<table>
<thead>
<tr>
<th>Potential (V vs Li/Li⁺)</th>
<th>-Z'' (Ω)</th>
<th>-Z''/Z'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>264-394</td>
<td>0.867</td>
</tr>
<tr>
<td>0.1</td>
<td>240-329</td>
<td>0.899</td>
</tr>
<tr>
<td>0.2</td>
<td>139-211</td>
<td>0.963</td>
</tr>
</tbody>
</table>
Figure 23. EIS spectra taken in between the anodic voltage sweeps.

Table 8. Warburg element range and slope for anodic voltages.

<table>
<thead>
<tr>
<th>Potential (V vs Li/Li⁺)</th>
<th>-Z'' (Ω)</th>
<th>-Z''/Z'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>266-399</td>
<td>0.993</td>
</tr>
<tr>
<td>0.2</td>
<td>248-329</td>
<td>0.900</td>
</tr>
<tr>
<td>0.4</td>
<td>202-302</td>
<td>0.909</td>
</tr>
<tr>
<td>0.5</td>
<td>207-354</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 24. Reactance vs inverse frequency from the EIS spectra at various voltages on the cathodic sweeps. The slopes are used in the calculation of the diffusion constant.
Figure 25. Reactance vs inverse frequency from the EIS spectra at various voltages on the anodic sweeps. The slopes are used in the calculation of the diffusion constant.
Figure 26. Galvanostatic cycle of a coin cell, various voltage ranges in the curves are fitted to obtain $\mathrm{dE/dx}$ slopes. The working electrode was e-beam evaporated 100nm Si on Cu, the reference and counters were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). Inset shows full range of data.
Table 9. Diffusion constants calculated for the cathodic potentials of 100 nm Si electrode.

<table>
<thead>
<tr>
<th>Potential (V vs Li/Li⁺)</th>
<th>dE/dx (V)</th>
<th>Z''/√2πf (Ω·s⁻¹/²)</th>
<th>D_{Li⁺} (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-0.1468</td>
<td>265.01</td>
<td>7.4366 x 10⁻¹⁵</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.1237</td>
<td>241.96</td>
<td>6.3343 x 10⁻¹⁵</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.2286</td>
<td>489.71</td>
<td>5.281 x 10⁻¹⁵</td>
</tr>
</tbody>
</table>

Table 10. Diffusion constants calculated for the anodic potentials of 100 nm Si electrode.

<table>
<thead>
<tr>
<th>Potential (V vs Li/Li⁺)</th>
<th>dE/dx (V)</th>
<th>Z''/√2πf (Ω·s⁻¹/²)</th>
<th>D_{Li⁺} (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-13.20</td>
<td>516.47</td>
<td>1.5831 x 10⁻¹¹</td>
</tr>
<tr>
<td>0.2</td>
<td>-1.645</td>
<td>319.92</td>
<td>6.4076 x 10⁻¹³</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.3076</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.4829</td>
<td>306.59</td>
<td>5.9994 x 10⁻¹⁴</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.6727</td>
<td>302.65</td>
<td>1.1973 x 10⁻¹³</td>
</tr>
</tbody>
</table>
Chapt 5: Neutron Depth Profiling

5.1 Modeling and Calibration

Neutron depth profiling involves penetrating the substance with a cold neutron beam. The neutrons will react with the Li in the sample according to the equation below.

\[ ^{6}\text{Li} + n \rightarrow ^{3}\text{H} (2.73\text{MeV}) + \alpha (2.05\text{MeV}) \]  

(Reaction 6) where the \(^{3}\text{H}\) (triton) has an initial energy of 2.73MeV and the \(\alpha\) particle has initial energy of 2.05 MeV. As the triton travels through the sample it loses energy, dependent on the stopping power of the sample (high Z elements have greater stopping power). By looking at the quantity and energy of the triton particles detected, information about the depth (from a depth-energy model calculated in TRIM) and concentration of Li within the sample can be obtained. The energy and depth calibration for this technique is non-trivial. The first step is to calibrate the detector to the energy of the particles that impact it. Two standards are used. A Li-6 standard and a B-10 standard. Below are the two neutron boron reactions, one which occurs 6% of the time, the other which occurs 94% of the time:

\[ 6\%: \text{B-10} + n \rightarrow \text{Li-7} (1.02 \text{ MeV}) + \alpha (1.78 \text{ MeV}) \]  

(Reaction 7)
Figures 27 and 28 show the spectra obtained from these standards. The sharp peaks in these spectra indicate reaction products that originate on the surface of the calibration standards. These particles retain their full energy as they travel to the detector since they only have to pass through the vacuum in the sample chamber. The declining signal to the left of the sharp peaks indicate the reaction particles that originate at various depths into the sample. Because these particles need to pass through the sample on their way to the detector they lose energy and are counted into lower detector channels. To make the channel-energy calibration 4 points are taken, the (channel, energy) data from the reaction products originating at the surface. These particles are shown on the calibration spectra. The 4 points are plotted in Figure 29, fitted, and a slope of 0.690 is obtained. This means that each channel in the detector collects particles within a 0.690 keV range, i.e. this is the resolution of the detector. The second step is to calibrate the counts collected by the detector to a concentration of Li in the sample. For this a B-10 standard with uniform and know B-10 concentration is used. The spectra collected from measurement of this concentration standard is shown in Figure 30. There are 4 peaks in this spectra, one peak for each of the reaction products shown in reactions 7 and 8. The calibration is done by integrating the peaks at channels 2000 and 2500. These peaks represent all the alpha particles generated by the two B-10 neutron reactions. This integration gives a number of counts that corresponds to the

\[
94\%: \text{B-10} + n \rightarrow \text{Li-7} (0.84 \text{ MeV}) + \alpha (1.47 \text{ MeV}) \quad \text{(Reaction 8)}
\]
known concentration of the B-10 concentration standard. Equation (16) shows the
calculation to go from the B-10 areal concentration to Li-7 concentration.

\[
\frac{(\text{std conc})(\text{std csa})(\text{sample cts})}{(\text{std cts})(\text{sample csa})} = \text{sample conc} = \frac{(5.5 \times 10^{15} \text{ B atoms/cm}^2)(3843 \text{ barns})}{(\text{std cts})(\text{sample cts})} = \frac{6 \text{ Li atoms/cm}^2}{(955 \text{ barns/Li atom})^{0.36}}
\]

(16)

In the above equation 0.36 is the value of the integration of the B-10 standard, $5.5 \times 10^{15}$
per square centimeter is the uniform areal density of B-10 in the concentration
standard. The “std csa” and the “sample csa” are the cross sectional absorption areas for
the two nuclei (B-10: 3843 barns, Li-6: 955 barns) at cold neutron temperature. This
parameter is measured in barns ($10^{-24} \text{ cm}^2/$barn) and represents the probability of the
nuclei to interact with a neutron to produce the reaction products. Li-6 is about one-
fourth (955 barns for Li-6 vs 3843 barns for B-10) as likely as a B-10 nucleus to react with
a cold neutron. After this calibration the Li-6 areal density is obtained and must be
normalized to the total (isotope independent) Li concentration as per the below
equation.

\[
\left(\frac{6 \text{ Li atoms}}{\text{cm}^2}\right) \left(\frac{100 \text{ Li atoms}}{7.5 \text{ }^6 \text{Li atom}}\right) = \frac{\text{Li atoms/cm}^2}{\text{cm}^2}
\]

(17)
Figure 27. Li-6 calibration standard.

Figure 28. B-10 calibration standard.
Figure 29. Energy-channel calibration.

Figure 30. Spectra of the B-10 concentration standard.
So far the electrode is modeled as a number of slices of indeterminate width located at various depths within the sample, each associated with a specific particle energy. Combining the channel-energy calibration with the concentration calibration we obtain the areal concentration of each slice of the sample. In order to obtain a volumetric concentration, a depth and width for each slice must be modeled and then the areal density (Li atoms/cm$^{2}$) divided by the width (cm) to obtain volumetric concentration (Li atoms/cm$^{3}$) of Li within that slice of the sample. The depth modeling is performed in a program called SRIM/TRIM (The Stopping and Range of Ions in Matter). The program takes into account the density and elemental composition of the sample and determines how particles (triton in this case) will interact with the sample as they pass through it on the way to the detector. Figure 31 shows the output of the TRIM simulation. The program produces a file detailing the escaped particles (the initial number and position of the particles is set by the user) and their energies. These energies are related to the depth at which the particles originated at. The simulation is run multiple times with different origin depths and a depth-energy calibration graph is produced, shown in Figure 32.
Figure 31. Output of SRIM simulation. Particles are originating 8 microns into the NMC sample, pass through the NMC layer, then through 20 microns of Aluminum and then through the 7.5 micron thick Kapton window. The particles lose energy as they travel through the sample. Some are deflected and do not escape the sample.
Figure 32. Depth-calibration graph. Smaller energies as measured by the detector indicates reaction products which originate deep within the sample. They lost energy as they escaped the sample before hitting the detector.

\[ y = -0.0165x + 20.307 \]

\( R^2 = 0.9976 \)
5.2 NDP measurement of NMC

Using the three calibration steps detailed above the experimental data of count number and channel number can be converted into a Li concentration and depth. When this experiment is carried out in-situ, that is to say a cell being cycled under constant neutron beam irradiation, changes in Li concentration as function of time can be calculated and thus also the diffusion coefficient. Liu et al.\textsuperscript{31} have obtained diffusion coefficients of Li in a thin film Sn electrode using this technique. Figure 33 shows a spectra of an NMC-like electrode (Nickel Manganese Cobalt Oxide, a cathode material for Li-ion batteries currently being widely researched) before and after an ex-situ charging interval. The difference in the Li concentration within the electrode is significant. The average Li concentration in the lithiated (discharged) state is measured to be 6.2 ± 8.0 x 10\textsuperscript{20} atoms/cm\textsuperscript{3} whereas the expected Li concentration based on the specifications from the material synthesizer is of 8.6 ± 1.4 x 10\textsuperscript{21} atoms/cm\textsuperscript{3}. According to the NDP spectra the Li concentration decreased by 51.5% ± 7.4% between the initial discharged state and the partially charged (delithiated) state. According to the electrochemical data we have removed 50.5% of the Li in the electrode originally by withdrawing 1.47 mAh from the cathode out of the total 2.91 mAh capacity. These calculations are obtained by integrating the area under the blue and orange curves between the black line and the graph origin. A plateau indicates a uniform Li concentration throughout the electrode and this is expected because between the end
of charging and the NDP measurement a period of several hours elapsed giving time for Li to diffuse throughout the electrode to yield a uniform distribution. The error associated with these measurements is counting error in the detector equal to the square root of the counts. Based on the charge passed during the charge we expect a decrease in the NDP signal of 50.5 %, and we observe a decrease of 51.5% ± 7.4%, in good agreement with the expected value.
Figure 33. NDP spectra of Cathode material. Original lithiated state (orange) with error boundaries (light orange), delithiated state (blue) with error boundaries (light blue), and instrument noise (grey). Modified coin cell with window was used with Li metal as the counter/reference and Li$_{1.21}$Ni$_{0.15}$Mn$_{0.54}$Co$_{0.10}$O$_{0.79}$ (NMC) as the cathode material. Electrolyte was 1M LiPF$_6$ salt in 1:1 (volume) DMC/EC electrolyte, separator was Celgard 2400 polymer.
Chapter 6. Coin Cell cycling

Figure 35 shows the cycling and Coulombic Efficiency results for a coin cell using the nano-film Si as the working electrode. The discharge capacity starts off around 1800 mAh/g and over the course of 120 cycles decays to about 900 mAh/g. The Coulombic efficiency is low on the first cycle, \( \sim 70\% \) and then improves to about 92\% getting better from there as the cycling continues and reaching about 98\% on the 120\textsuperscript{th} cycle. Figure 34 shows the similarity between the behavior of the cells we performed CV on for the diffusion measurements and the cells we used for Galvanostatic cycling tests.
Figure 34. Figure showing the similarity between a CV obtained from a coin cell and a Galvanostatic cycling data from a coin cell and the galvanostatic cycling data from a coin cell displayed as a dQ/dx plot. The consistency shows that the peaks in the CV show in the galvanostatic cycling curve as plateaus. In both cells the working electrode was e-beam evaporated 100nm Si on Cu, the reference/counter were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol).
Figure 35. Coin cell cycling data. The working electrode was e-beam evaporated 100nm Si on Cu, the reference/counter were Li foil. The electrolyte was 1 M LiPF$_6$ in DMC:EC (1:1 vol). The initial capacity (read off the left-hand axis) is ~ 1800 mAh/g and declines over 120 cycles to ~ 1000 mAh/g. Throughout the cycling the coulombic efficiency (read off the right hand axis) is close to 100%.
In conclusion, we have conducted an extremely slow scan (5 μV/s) CV on ultra-thin film Si (100 nm) to probe the quasi-equilibrium states during silicon lithiation. In these series of experiment the total amount of charge passed corresponds to the formation of a most lithiated state of Li_{15}Si_{4}. We also observed an irreversible peak (C3), which was not reported in the literature, around 350 mV, decayed over cycling indicating that it may be an irreversible process. The charge passed in this peak cumulatively corresponded to Li_{12}Si_{7} which was reported to form around the same potential range. We conducted a window opening experiment to identify coupled reactions which correlated our A1/C1 and A2/C2 pairs of peaks but we observed no coupled peak for the C3 peak, although on the anodic sweep there was small but significant current passed in the 500 mV to 1 V range. We used several methods to determine the diffusion constant of Li within the Si electrode. Table 11 shows our diffusion results from the various experiments and models used. We first performed a potential hold experiment at multiple potentials on the electrode. This experiment confirmed the Faradaic processes seen in our CV results and also indicated the presence of multiple diffusion constants at work at the same potential over a long period of time.
which suggests a multiphase electrode. We have proposed a model consistent with these observations and calculated the diffusion coefficients based on the model by Wen et al.\textsuperscript{28} We then performed a variable scan rate experiment to derive diffusion coefficients. There are multiple models in literature for this. We used a basic Randles-Sevcik model to calculate the diffusion coefficient and compared our results and method to literature. This model generated values which most deviated from our other diffusion results. We have attempted to specify generically the significant differences in battery electrochemistry from catalysis; for which Randles-Sevcik is typically used, to explain why it is not an appropriate model for batteries. We also use an alternative model from Kulova et al. to calculate the diffusion coefficient based on variable scan rate CV. This model takes into account the charge incorporated into the electrode and its intrinsic effect on electrode potential which we believe more accurately models the diffusion constant. Finally we used an EIS measurement to obtain diffusion constants through modeling of the obtained spectra as a Warburg element which represents the diffusion of lithium thorough the electrode. Looking at the agreement between the methods; the potential holds, the alternative variable CV experiments, and the EIS measurement all give diffusion constant in the $10^{-13}$ to $10^{-15}$ cm$^2$/s range whereas the Randles-Sevcik method gives values several orders of magnitude higher. Despite this spread of values, we do believe that the potential hold results indicate 2 distinct diffusion constants at work within the electrode, indicating a multiphase electrode due to very slow phase transformation kinetics. Diffusion constants obtained through all of
these models are inherently suspect because the value must be de-convoluted from the signal obtained. The effectiveness of this process is dependent upon how well the model represents the physical process. Neutron depth profiling (NDP) offers a solution for this problem because the signal obtained is a direct observation of the (relative) amount and location of Li within the sample. Unlike all other previous models the movement of Li is determined by observation of the Li itself, not by reference to the current over time, or reactance/resistance measurement which may be affected by other processes. We have shown proof of concept for the NDP technique with an NMC-like (Li$_{1.21}$Ni$_{0.15}$Mn$_{0.54}$Co$_{0.10}$O$_{0.79}$) electrode. Lastly we have performed a standard cycling at C/20 of our thin film Si and reported the results which show high Coulombic efficiency and capacity fade of about 45% over 120 cycles.
Table 11. Summary of diffusion constant obtained through various methods.

<table>
<thead>
<tr>
<th>Section</th>
<th>Region</th>
<th>$D_n$ (cm²/second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 Potential Holds</td>
<td>Potential vs Li/Li⁺ (V)</td>
<td>Orange/ Grey</td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>$8.82 \times 10^{-15}$ / $2.70 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td>$7.57 \times 10^{-15}$ / $3.90 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td>$8.27 \times 10^{-15}$ / $5.43 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.475</td>
<td></td>
<td>$8.31 \times 10^{-15}$ / $4.73 \times 10^{-15}$</td>
</tr>
<tr>
<td>3.4 Variable Scan Rate</td>
<td>Peaks</td>
<td>Randles-Sevcik /Kulova¹⁷</td>
</tr>
<tr>
<td>$C_1$</td>
<td></td>
<td>$2.42 \times 10^{-9}$ / $1.35 \times 10^{-13}$</td>
</tr>
<tr>
<td>$C_2$</td>
<td></td>
<td>$3.33 \times 10^{-9}$ / $1.86 \times 10^{-13}$</td>
</tr>
<tr>
<td>$A_1$</td>
<td></td>
<td>$4.13 \times 10^{-10}$ / $2.31 \times 10^{-14}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td></td>
<td>$8.70 \times 10^{-10}$ / $4.86 \times 10^{-14}$</td>
</tr>
<tr>
<td>4.1 CV/EIS</td>
<td>Potential vs Li/Li⁺ (V)</td>
<td></td>
</tr>
<tr>
<td>0.2 (cathodic sweep)</td>
<td></td>
<td>$7.44 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.1 (cathodic sweep)</td>
<td></td>
<td>$6.33 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.01 (cathodic sweep)</td>
<td></td>
<td>$5.28 \times 10^{-15}$</td>
</tr>
<tr>
<td>0.1 (anodic sweep)</td>
<td></td>
<td>$1.58 \times 10^{-11}$</td>
</tr>
<tr>
<td>0.2 (anodic sweep)</td>
<td></td>
<td>$6.41 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.4 (anodic sweep)</td>
<td></td>
<td>$6.00 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.5 (anodic sweep)</td>
<td></td>
<td>$1.20 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
References


