SURFACE STUDIES OF LI-ION AND MG BATTERY ELECTRODES

BY

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DISSERTATION

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Abstract

This dissertation focuses on studies of the surfaces of both Li-ion and Mg-ion battery electrodes. A fundamental understanding of processes occurring at the electrode surface is vital to the development of advanced battery systems. Additionally, modifications to the electrode surfaces are made and further characterized for improved performance.

LiMn$_2$O$_4$ Cathodes for Li-ion Batteries: Effect of Mn in electrolyte on anode and Au coating to minimize dissolution: LiMn$_2$O$_4$ (LMO) is known to dissolve Mn ions with cycling. This section focuses on both the effect of the dissolution of Mn$^{2+}$ into the electrolyte as well as Au coating on the LMO to improve electrochemical performance. Electrochemical quartz crystal microbalance (EQCM) was used to monitor changes in mass on the anode, SEM and AES were used to observe changes in surface morphology and chemical composition, and potentiostatic voltammetry was used to monitor charge and discharge capacity. The effect of Cu$^{2+}$ addition in place of Mn$^{2+}$ was also studied, as Cu is known to form an underpotential deposition (UPD) monolayer on Au electrodes.

Following this, LMO particles were coated with a Au shell by a simple and scalable electroless deposition for use as Li-ion battery cathodes. The Au shell was intended to limit the capacity fade commonly seen with LMO cathodes by reducing the dissolution of Mn. Characterization by SEM, TEM, EELS, and AFM showed that the Au shell was approximately 3 nm thick. The Au shell prevented much of the Mn from dissolving in the electrolyte with 82% and 88% less dissolved Mn in the electrolyte at room temperature and 65 ºC, respectively, as compared to the uncoated LMO. Electrochemical performance studies with half cells showed
that the Au shell maintained a higher discharge capacity over 400 cycles by nearly 30% with 110 mA hr g\(^{-1}\) for the 400th cycle as compared to a commercial LMO at 85 mA hr g\(^{-1}\). Similarly, the capacity fade was reduced in full cells: the coated LMO had 47% greater capacity after 400 cycles over the control.

*Dimensionally Controlled Lithiation of Thin Film and Multilayer Conversion Li-ion Battery Anodes:* Oxide conversion reactions are an alternative approach for high capacity Li-ion batteries, but are known to suffer from structural irreversibility associated with the phase separation and reconstitution of reduced metal species and Li\(_2\)O. The morphology of the reduced metal species is thought to play a critical role in the electrochemical properties of a conversion material. In this section, a model electrode is used with alternating layers of Cr and CrO\(_x\) to better understand and control these phase changes in real-time and at molecular length scales. Despite lacking crystallinity at the atomic scale, this superstructure is observed (with XR) to lithiate and delithiate in a purely one-dimensional manner, preserving the layered structure. The XR data show that the metal layers act as nucleation sites for the reduction of chromium in the conversion reaction. Irreversibility during delithiation is due to the formation of a ternary phase, LiCrO\(_2\), which can be further delithiated at higher potentials. The results reveal that the combination of confining lithiation to nanoscale sheets of Li\(_2\)O and the availability of reaction sites in the metal layers in the layered structure is a strategy for improving the reversibility and mass transport properties that can be used in a wide range of conversion materials.

Following the Cr/CrO\(_x\) study, the next step was to study intermetallics which can electrochemically alloy to Li\(_{4.4}\)M (M = Si, Ge, Sn, etc.), providing order-of-magnitude increases in energy density. The energy density of Si may be combined with the structural reversibility of
an intercalation material using a Si/metal silicide multilayer (ML). In operando XR confirms the ML’s structural reversibility during Li insertion and extraction, despite an overall 3.3-fold vertical expansion. The ML electrodes also show enhanced long-term cyclability and rate capabilities relative to a comparable Si thin film electrode. This intercalation behavior found by dimensionally constraining Si lithiation promises applicability to a range of conversion reactions.

Improving Electrodeposition of Mg through an Open Circuit Potential Hold: In this section, in situ XRD, XPS, SEM and electrochemical methods were used to interrogate the mechanism of Mg electrodeposition from PhMgCl/AlCl₃ (APC) and EtMgCl electrolytes. An open circuit potential (OCP) pause following Mg deposition led to retained enhancement of Mg deposition and stripping kinetics along with lowered overpotentials for both. In situ XRD demonstrated that the OCP pause led to a more polycrystalline deposits relative to that without the pause, while SEM presented micrographs that showed smaller deposits with an OCP hold. The improvement is attributed to an ‘enhancement layer’ that formed on the electrode during the OCP hold. Analysis of XPS data suggests that this ‘enhancement layer’ consists of Mg and Cl retained on the electrode surface, possibly following electrode depassivation.
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Chapter 1

Introduction

1.1 Motivation

1.1.1 Energy: Current State and Goals for the Future

Energy sustainability and security is a key focus for scientists, government leaders, and society at large across the world. Energy consumption has increased drastically over the last several decades.\(^1\) However, sources of energy have not drastically changed. If energy consumption continues to follow the projection from the last 50 years, the demand will not be met by current energy sources; of particular concern is the diminishing supply of non-renewable fossil fuels.\(^2\) Because of the rate at which fossil fuels are used and the millions of years needed to create additional stores, fossil fuels are considered non-renewable resources.\(^3,4\) In addition to the limited supply, fossil fuels and many other non-renewable energy sources create harmful side-effects on health and the environment, such as the production of greenhouse gases.\(^5,6\) This further emphasizes the need for a drastic shift in energy production and utilization away from non-renewable energy sources to renewable sources and energy efficiency.\(^1-5\)

In 2014, 82% of the energy used in the US was obtained from non-renewable sources including fossil fuels, natural gas, and coal (see figure 1.1).\(^7\) Less than 10% of energy consumed in the US that year was from renewable sources including hydroelectric, solar, wind, and biofuels.\(^2\) Additionally, while the US consumption of renewable energy increased by 10.8% from 2013 to 2014, the consumption of non-renewable energy still increased by 1.2% during that time.\(^2\) This continued increased use of an unsustainable energy source is alarming.
The increase in both non-renewable and renewable energy sources from 2013 to 2014 demonstrates the increase in overall energy consumption. Overall energy consumption has risen 41% over the last 40 years.\textsuperscript{1} This increase has been attributed to both population growth as well as increased energy use in countries with developing economies.\textsuperscript{8,9} 2013 estimated power consumption worldwide was 5273 Mtoe (million tons of oil equivalent) (see figure 1.2).\textsuperscript{1} Energy use is expected to triple by 2050.\textsuperscript{2} This constant rise in the worldwide demand for energy drives the transition to renewable energy sources.
Figure 1.2: Historic world energy consumption by source over the last 40 years in Mtoe.¹

Additional concerns with the continued use of non-renewable energies include the detrimental effect of the production and consumption of such sources on both health and the environment. The combustion of fossil fuels forms dangerous greenhouse gases including carbon dioxide (CO₂), which accounts for 40% of total emissions.³,¹⁰ Greenhouse gases include CO₂, water vapor (H₂O), ozone (O₃), nitrous oxide (N₂O), and methane (CH₃), which collect in the atmosphere and absorb and emit increasing amounts of radiation from the earth and sun. These gases contribute to the rise in the earth’s surface temperature over time.⁵,⁶ Calculations project this increase in surface temperature will eventually create an atmosphere that is unsustainable because of weather changes and extreme climates.⁵,⁶ The International Energy Agency has made a goal to limit the world’s temperature increase to 2 °C by 2050 in their most recent report.⁵

Finally, in addition to the unsustainability and environmental damage, the purchase of non-renewable energy sources can be greatly affected by political factors. The international relations the US has with countries that have large sources of fossil fuels can significantly
influence the availability of these energy resources and the energy security.\textsuperscript{1,9} While oil production in the U.S. is possible, the political factors further encourage a transition to renewable energy sources.\textsuperscript{9}

1.1.2 Future Energy Demands Efficient Energy Storage

To obtain a sustainable and secure energy future, the most promising option is to transition away from fossil fuels and other non-renewable energy sources and towards the primary use of renewable energy sources.\textsuperscript{3} However, fossil fuels are convenient because they are easy to store, there is already a developed infrastructure for the transportation of fuel, and they produce energy when needed.\textsuperscript{11,12} On the other hand, renewable energy is often intermittent. Solar, wind, and hydrothermal all rely on the environment, and intrinsically, they cannot produce energy on demand.\textsuperscript{11} In order for these renewable sources to be feasible in society and able to power the US electrical grid, efficient energy storage will be vital.\textsuperscript{8} Efficient energy storage will store energy at times of low demand and will produce energy at times of low production and high demand, enabling the use of these intermittent renewable energy sources.\textsuperscript{8} Current energy storage devices include capacitors, batteries, and fuel cells (see figure 1.3).\textsuperscript{11}

One of the greatest challenges is energy storage appropriate for automobiles. Gasoline is a great energy source and society has become accustomed to the high power and large ranges in their vehicles obtained with gasoline. Because of the extensive use of gasoline, the transportation sector accounts for 27\% of greenhouse gas emissions in the US in 2013. With the diminishing fossil fuel supply, a transition to a new energy source is necessary. Many other energy technologies are not feasible in vehicles (see figure 1.4). In addition to limitations in
energy density, safety, reliability, and environmental benignity are of significant concern for electric vehicles. This poses a great challenge to energy storage devices.

Figure 1.3: Specific power and energy of various energy storage devices.\textsuperscript{11}

Figure 1.4: Total greenhouse gas emissions by source in 2013.\textsuperscript{5}
A great effort is currently underway to develop hybrid electrical vehicles and plug-in hybrid vehicles. Over the last five years, the energy density (Wh·L$^{-1}$) of commercial batteries has increased by a factor of 2 and the battery cost ($\cdot$kW$^{-1}$·h$^{-1}$) has dropped nearly 70% (see figure 1.5). Currently, the DOE has set target to further improve energy density and cost by 2022; the goal being to improve the energy density from 150 Wh·L$^{-1}$ to 400 Wh·L$^{-1}$ and the battery cost from $250$ kW$^{-1}$·h$^{-1}$ to $125$ kW$^{-1}$·h$^{-1}$. Because of the significant improvements necessary to make electric vehicles more attractive, promising new battery systems are being considered including Mg, Li-S.

![Figure 1.5: Energy density and battery cost evolution over five years. Cost projections based on a production of 100,000 batteries per year for batteries that meet DOE and USABC requirements.](image)

And finally, improved energy storage will benefit handheld electronic devices such as laptop computers, cellular phones, and other personal electronics. The increased use of such devices over the years has created a demand for smaller, lighter, longer lasting batteries.
Devices with energy densities that exceed those of current Li-ion batteries will be vital to obtain a sustainable energy future.\textsuperscript{8}

1.1.3 Batteries as a Promising Electrical Energy Storage Device

Batteries are a promising energy storage device as compared to fuel cells and capacitors due to currently higher energy and power densities. Various types of batteries are commercially used and under research (see figure 1.6).\textsuperscript{14} Li-ion batteries are among the highest energy densities of commercially available batteries.\textsuperscript{14,15} Li-air and Li-S batteries have some of the most promising theoretical capacities.\textsuperscript{14,16} Mg-ion batteries are additionally attractive for increased volumetric energy density.\textsuperscript{14}

![Figure 1.6: Energy densities of various batteries, both commercially available and currently under research.\textsuperscript{14}](image)

\textsuperscript{14}
In this thesis, Li-ion and Mg-ion batteries will be of particular interest. Modifications to Li-ion batteries to improve the electrochemical performance were studied. Additionally, fundamental studies on the nature of the Mg electrodeposition were done to further understand the processes necessary for a functional and efficient Mg-ion battery.

1.2 Basic Principles of Batteries

1.2.1 Batteries

Batteries may be classified in two categories — primary batteries (not rechargeable) and secondary batteries (rechargeable). Secondary batteries convert chemical energy to electrical energy and back in a reversible process through oxidation and reduction reactions. These reactions take place at two different electrodes (see figure 1.7). The electrode which is oxidized during discharge is the anode and the electrode which is reduced during discharge is the cathode. These electrodes are physically separated, but with an ion bridge between them, often an electrolyte. Many batteries have a separator between the electrodes to ensure that they do not touch and short the battery. This separator is often an ion permeable polymer.\textsuperscript{17,18}
1.2.2 Electrochemical Testing Techniques and Setups for Batteries

Most electrochemical testing took place in a two electrode or three electrode cell. The three electrode cell (see figure 1.8) has a working electrode, counter electrode, and reference electrode. The current is passed between the working and counter electrodes while the reference electrode measures the potential between the working and counter electrodes. In a two electrode cell, the counter electrode acts as both the counter and reference electrodes, monitoring both current and potential between the counter and working electrodes.\textsuperscript{17, 19}
These cells are often set up in beaker cells, coin cells, pouch cells, Swagelok cells, and prismatic cells. The most common of these are beaker cells and coin cells. In a beaker cell, the electrodes are immersed in an electrolyte in a beaker or beaker-like container with some physical distance between the electrodes (see figure 1.9a). If the materials are air-sensitive as they are in Li-ion and Mg-ion, these cells must be tested in an inert environment — a glove box or glove bag. In a coin cell (standard are 2032 cells), the cell materials are layered closely together and sealed with an O-ring between two metal casings (see figure 1.9b) so that an inert environment is maintained inside the cell even if it is brought into the atmosphere. Because the electrodes are closely layered, a separator is needed between the electrodes to keep them from shorting. This separator is an ion-permeable polymer that is soaked in electrolyte to facilitate ion transport between the electrodes.\(^\text{17}\)
The cells (beaker or coin cells) are often electrochemically tested using cyclic voltammetry, galvanostatic charge/discharge cycling, and electrochemical impedance spectroscopy. Voltammetry measures current as a function of potential. The current observed corresponds to electrochemical reactions occurring between the electrodes and the solution at the measured potential. When the potential is swept back and forth across a potential range at a given rate, this is known as cyclic voltammetry (CV) (see figure 1.10).19

Galvanostatic charge/discharge cycling (chronopotentiometry) applies a fixed current for and measures changes in potential. The current can be applied for a set amount of time or until a particular potential is reached. Charge/discharge cycling of batteries involves switching between positive and negative currents in charging and discharging steps (see figure 1.11).19

Figure 1.9: (a) Illustration of a beaker cell set up and (b) diagram of materials layered in a 2032 coin cell.
Electrochemical impedance spectroscopy is a method of characterizing limitations and losses of a cell. It identifies three main sources of potential losses — charge transfer activation, ohmic losses, and mass transfer losses. This separates and quantifies the sources of polarization
allowing for quantitative and qualitative information to be obtained on the system to better understand the limitations and how to improve.\textsuperscript{19}

### 1.2.3 Metrics for Battery Performance

When reporting battery performance, certain metrics are commonly accepted. The capacity, mA·h, of a battery describes how long a battery can provide a given current, mA. The efficiency of a battery is described by the ratio of the capacity released by the battery during discharge to the capacity stored during the charge. This is called the Coulombic efficiency. Power, W, describes the current, mA, that a battery can provide at a specific potential, V. The amount of time the battery can sustain that power is described by the energy, Wh.\textsuperscript{17}

Most battery metrics are normalized to the mass of active material or the area of active electrode. For example, CVs are often reported with mA·cm\textsuperscript{-2}. Capacity is often normalized to mass (gravimetric capacity, mA·h·g\textsuperscript{-1}) or volume (volumetric capacity, mA·h·cm\textsuperscript{3}). These normalized metrics make it possible to compare performance of various battery systems across many different experimental set-ups.\textsuperscript{17}

### 1.3 Li-Ion Batteries

#### 1.3.1 History and Basic Principles

First commercialized by Sony in 1991, the Li-ion battery changed the world of portable electronic devices.\textsuperscript{20} Li-ion batteries are the most common battery in consumer portable electronics including laptop computers, cell phones, tablets, music players, and more. The Li-ion battery is so popular because of the high operating voltage of 3.6 V and its sensible capacity of 100 to 265 Wh·kg\textsuperscript{-1}.\textsuperscript{20} Because energy is directly related to both the potential and capacity,
batteries with higher energy density will be developed from materials with higher operating voltages and/or higher capacities.

Li-ion batteries are charged when an external power supply moves current from the cathode to the anode (for example Li-ion battery see figure 1.12).\textsuperscript{17,21} When this occurs, Li ions are removed from the cathode and inserted into the anode.\textsuperscript{17,21} During discharge, the current moves from the anode to the cathode and the Li ions move the same direction.\textsuperscript{17,21} The process of Li ions being removed from an electrode is called delithiation while the reverse process (Li ions being added to an electrode) is called lithiation.\textsuperscript{17,21} For an intercalation electrode, such as graphite or LiCoO\textsubscript{2}, it is also referred to as deintercalation and intercalation, respectively.\textsuperscript{17,21}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Diagram of a Li-ion battery demonstrating the anode, cathode, electrolyte, and movement of Li\textsuperscript{+} ions and electrons.\textsuperscript{21}}
\end{figure}
The discharge of a Li-ion battery is the thermodynamically favorable process.\textsuperscript{17, 22} When this occurs, electrons travel from the anode to the cathode and the \( \text{Li}^+ \) ions move in the same direction through the electrolyte. The reactions that occur are shown for the example Li-ion battery system (figure 1.12) below:

\textit{Discharge Reactions:}

\[
\text{Li}_x\text{C}_6 \rightarrow \text{C}_6 + x\text{Li}^+ + xe^- \quad \text{(anode)}
\]

\[
\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2 \quad \text{(cathode)}
\]

In discharging, the graphite is delithiated, creating both \( \text{Li}^+ \) ions and electrons.\textsuperscript{17, 22} These travel to the cathode where the delithiated \( \text{LiCoO}_2 \) is then lithiated. The \( \text{Li} \) ions intercalate into the cathode, changing the oxidation state of the transition metal in the cathode active material. Charging is the opposite of these processes where the cathode is delithiated and the anode is lithiated.\textsuperscript{17, 22}

The Li-ion battery is a promising candidate for electrical energy storage in future applications because of their proven success. However, there are limits to the energy densities of Li-ion batteries, so additional systems are being studied in order to develop more advanced batteries.\textsuperscript{23-27} In order for Li-ion batteries to reach the goals for electric vehicles, the specific capacity must be increase by two or three-fold.\textsuperscript{13} However, even with these limitations, it is possible that Li-ion batteries will be the most common commercial battery system for the immediate future.
1.3.2 Li-ion Battery Cathodes- Current State and Issues

The cathode, or the positive electrode, reduces upon discharge. Often, this is done by intercalating Li into the crystal structure along with the reduction of some element in the active material. The main requirements for a material to be a cathode in a Li-ion battery include:

- The material must be low-cost, stable, and environmentally benign.\(^{28}\)
- The material must contain an easily reduced or oxidized ion, most often a transition metal ion.\(^{28,29}\)
- The material must conduct electricity which allows for the movement of electrons during the reactions. If the material is sufficiently conductive, no inactive conductive materials would be needed which would improve the energy density.\(^{28,29}\)
- The material must react reversibly with Li, most often an intercalation reaction so that the material’s structure does not change significantly with the addition of Li.\(^{28,30}\)
- The reaction with Li must be a fast reaction for both intercalation and deintercalation. This provides greater power density.\(^{29,30}\)
- The material must react with Li in a thermodynamically favorable reaction. Higher capacity and voltages are preferred (often around one Li per metal ion and 4 V, respectively) as this provides greater energy storage.\(^{28}\)

Over the last two decades, the leading cathode material for Li-ion batteries has been LiCoO\(_2\).\(^{28,30}\) This material is easy to make and use along with stable cycling and good performance.\(^{30}\) However, concerns of the cost and the safety have led to the development of
alternative cathode materials. Additionally, to use Li-ion batteries for transportation, improved energy densities will be necessary to further reduce the weight, size, and cost of battery packs for vehicles. Most research and commercial use of cathodes have focused on two types of materials. First, layered materials where the anions are close-packed or nearly close-packed with a transition metal ion in alternate layers between the anions. The Li intercalates into the remaining empty layers (see figure 1.13a). This group includes LiCoO₂, LiNi₀.₈₀Co₀.₁₅Al₀.₀₅O₂, and LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂. The second group includes spinel, olivine, and open structures such as LiMn₂O₄, LiFePO₄, and V₂O₅, respectively (see figure 1.13b-c). While the first group has a benefit of more energy stored per volume, the materials in the second group may have lower cost.

![Figure 1.13: Crystal structures of (a) LiCoO₂, (b) LiMn₂O₄, and (c) LiFePO₄. Li atoms are represented by green spheres.](image)

Recently, much research has been done to improve high-performance cathodes. The issues driving research on the layered system LiCoO₂ include the use of only 50% of the capacity (necessary to maintain the structure), the high cost of cobalt, and the dissolution of added transition metal ions. In order to enhance the amount of theoretical capacity that is useable and
to defray the costs, LiCoO$_2$ has been modified to include Ni and Mn ions. By doing this, not only are the costs reduced, but also the capacity increases from 140 mA·h·g$^{-1}$ to 240 mA·h·g$^{-1}$. However, problems still arise in the form of capacity fade at elevated temperatures (60 °C) due to Ni and other active transition metal ions dissolving in the electrolyte. Additionally, dissolved Ni may form NiO on the surface which limits lithiation.

Other high performance materials include Li rich transition oxides. These active materials may be described by Li(Li$_x$M$_{1-x}$)O$_2$ and xLi$_2$MnO$_3$. (1x)LiMO$_2$, where M is a transition metal such as Mn, Co, or Ni. For the first of these materials, a Li is doped in a transition-metal site and the oxidation number of the transition metal increases with this additional Li. The second of these materials introduces a new phase in which there are domains of Li$_2$MnO$_3$ and LiMO$_2$. Li$_2$MnO$_3$ is inactive at potentials below 4.5 V vs. Li/Li$^+$, so this reduces the capacity as compared to LiMO$_2$. However, at potentials above 4.5 V vs. Li/Li$^+$, the Li$_2$MnO$_3$ may be activated which leads to more Li at higher potentials, creating a promising high energy density cathode.

LiMn$_2$O$_4$ spinel is another cathode which has been studied due to the low cost, benign characteristic in the environment, safe and controlled cycling, and high power. However, this material suffers from significant capacity fade after just a few cycles. This capacity fade is attributed to three main factors: dissolution of Mn ions from the cathode, formation of SEI on the electrode, and a Jahn-Teller distortion when cycling. The dissolution of Mn causes not only a reduction in the active material of the cathode, but also the Mn$^{2+}$ ion inhibits the performance of the anode. These issues have been addressed by doping the LiMn$_2$O$_4$ with elements of lower valence states (i.e., Li or Al). However, this reduces the reversible capacity of the cathode material. Another approach to prevent Mn dissolution is to coat the cathode with
various materials. Coatings that have been studied include: C, LaF$_3$, and various oxides (semiconductors, insulating oxides, and even other cathode materials). Additionally, additives to the electrolyte that form a thick SEI can be effective at preventing the Mn from moving towards the anode.

LiFePO$_4$ is another cathode material that has been considered to have excellent safety characteristics and is environmentally benign. While the Li transport through this cathode material is very slow, studies have developed nano-structured LiFePO$_4$ in order to reduce the length of the diffusion path, thereby enhancing the electrochemical performance. Additionally, a conductive coating has been shown to further improve the performance of the cathode by enhancing the conductivity of the material. Even with this improved performance, LiFePO$_4$ remains a lower power cathode due to a lower working potential.

Other less common cathodes include LiNiCoAlO$_2$, Li$_4$Ti$_5$O$_{12}$, and V$_2$O$_5$. LiNiCoAlO$_2$ provides high capacity and working potential; however, it is also expensive and has various safety concerns. Li$_4$Ti$_5$O$_{12}$ has a low capacity; however, it is a very safe, reliable cathode. V$_2$O$_5$, while having a higher capacity than many other materials, suffers from significant capacity fade and has a low working potential. A summary of the performance of various cathodes is provided in Table 1.1.
1.3.3 Li-ion Battery Anodes - Current State and Issues

The primary anode in commercial batteries is graphite. Graphite has proven to have a high capacity, great working potential, and good safety. While cathodes have been thoroughly studied, anodes have been of less interest. This is because, the specific capacity of commercial cathodes are 120-160 mA·h·g\(^{-1}\) while the specific capacity of commercial anodes are 330-370 mA·h·g\(^{-1}\). To improve the specific capacity of a full battery, the cathode is currently the limiting factor.

Regardless, other anode materials have been studied. One material of particular interest is Si. Rather than an intercalation electrode as many cathodes and graphite are, Si is a conversion material (see figure 1.14). The Li reacts with the Si to make Li\(_{4.4}\)Si. This leads to an incredibly high specific capacity of 4212 mA·h·g\(^{-1}\). However, conversion materials also come with drawbacks, including significant volumetric expansion which leads to obliteration of the surface. This can cause electrical contact issues and problems with

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Table 1.1: Potential and capacity of various cathode materials.\(^{45}\)

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Working Potential (V vs. Li/Li(^+))</th>
<th>Reversible capacity (mA·h·g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO(_2) (LCO)</td>
<td>3.9</td>
<td>140</td>
</tr>
<tr>
<td>LiMn(_2)O(_4) (LMO)</td>
<td>4.1</td>
<td>120</td>
</tr>
<tr>
<td>LiFePO(_4) (LFP)</td>
<td>3.45</td>
<td>160</td>
</tr>
<tr>
<td>LiCo(<em>{1/3})Ni(</em>{1/3})Mn(_{1/3})O(_2) (NMC)</td>
<td>3.8</td>
<td>160</td>
</tr>
<tr>
<td>LiNiCoAlO(_2) (NCA)</td>
<td>3.8</td>
<td>180</td>
</tr>
<tr>
<td>Li(_4)Ti(_5)O(_12) (LTO)</td>
<td>1.6</td>
<td>150</td>
</tr>
<tr>
<td>V(_2)O(_5)</td>
<td>3.7</td>
<td>220</td>
</tr>
</tbody>
</table>
Li diffusion as well as increased SEI formation on new surfaces exposed from cracking.\textsuperscript{49} Because of this, many studies have considered microstructured Si, coating Si, and more to reduce these effects while maintaining the significantly enhanced capacity.\textsuperscript{50}

![Diagram of the intercalation of Li into the cathode (LiCoO$_2$, left) and the anode (graphite, right) and (b) diagram of a conversion reaction showing the lithiation of Si.\textsuperscript{51}}

Similar to Si, Ge has a high specific capacity due to its conversion to Li$_4$Ge.\textsuperscript{49} While less significant, Ge does still suffer from large volumetric expansion and structural demolition upon cycling.\textsuperscript{49} However, Ge has been considered for some specialized applications that require high capacity where cost is not an issue.\textsuperscript{52}

Li$_4$Ti$_5$O$_{12}$, a potential cathode material, is also a possible anode.\textsuperscript{45} However, as an anode, the working potential is much higher than others.\textsuperscript{45} While a very safe and stable anode, Li$_4$Ti$_5$O$_{12}$ is a very low power battery.\textsuperscript{45} A summary of the performance of various anodes is provided in Table 1.2.
Table 1.2: Potential and capacity of various anode materials.\textsuperscript{45}

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Working Potential $\textit{(V vs. Li/Li}^{+})$</th>
<th>Reversible capacity $(\text{mA}$·$\text{h}$·$\text{g}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (LiC$_6$)</td>
<td>0.1-0.2</td>
<td>372</td>
</tr>
<tr>
<td>Titanate (Li$_4$Ti$<em>5$O$</em>{12}$)</td>
<td>1-2</td>
<td>160</td>
</tr>
<tr>
<td>Si (Li$_{4.4}$Si)</td>
<td>0.5-1</td>
<td>4212</td>
</tr>
<tr>
<td>Ge (Li$_{4.4}$Ge)</td>
<td>0.7-1.2</td>
<td>1624</td>
</tr>
</tbody>
</table>

1.3.4 Li-ion Battery Electrolytes- Current State and Issues

Electrolytes in Li-ion batteries are typically a Li salt dissolved in some organic carbonate. Common salts include lithium hexafluorophosphate (LiPF$_6$), lithium tetrafluoroborate (LiBF$_6$), and lithium perchlorate (LiClO$_4$). Common solvents include ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC).\textsuperscript{17} Other less common electrolytes include utilizing ionic liquids as the solvent,\textsuperscript{53} enhancing common solvents with additives,\textsuperscript{44} and current studies in solid electrolytes.

While these electrolytes are common in commercial batteries, issues still arise. The main problem with these electrolytes is that over time, they decompose at the electrode surfaces, forming a layer of decomposition products over the electrodes.\textsuperscript{54} The decomposition of the electrolyte at the anode has been well studied while the decomposition of the electrolyte at the cathode is still currently being studied.\textsuperscript{55,56}

The organic carbonate solvents in Li-ion batteries reduce at the anode surface during charging. This reduction forms a layer of decomposition products on the surface that is often called the solid electrolyte interphase (SEI) (see figure 1.15).\textsuperscript{57,58} The SEI is very difficult to characterize because of the similarity to the electrolyte, the multiple components, the air
sensitive nature of the materials, and the time sensitivity of observing its formation which is dependent on electrochemical cycling.\textsuperscript{57,58} Because of this, while it has been studied extensively, little is known about the exact composition and mechanism of the formation of the SEI. It is understood that the SEI layer has of both conductive and insulating regions. The insulating regions create a protective passivation layer on the anode and can be beneficial to the battery.\textsuperscript{57,58}

The advantages of the SEI include protecting the anode material from degradation while cycling and preventing further decomposition of the electrolyte by blocking electron conductivity while allowing Li ion transport.\textsuperscript{58} Because of this, the SEI is an important component for ideal battery operation. However, SEI formation can be problematic if the layer becomes too thick for the transport of Li ions.\textsuperscript{57,58}

![Figure 1.15: A proposed model of a complex SEI with many different components on a graphite electrode.\textsuperscript{9}](image)

The thickness of the SEI layer has been reported as ranging between several to tens or hundreds of Å in thickness.\textsuperscript{57,58} A fundamental understanding of the composition of the SEI is
vital to construct Li-ion batteries with ideal SEI properties. Models of the SEI layer have been designed by several research groups. These studies suggest that the SEI is composed of inorganic species closer to the graphite anode (including LiF and Li$_2$CO$_3$) along with a porous organic region closer to the electrolyte.$^{59-63}$ Crystals of LiF have been additionally been reported as found throughout the SEI layer.$^{59,60}$

At this time, there is no consensus on the composition of the SEI layer. This is due, in part, to the difficulty of characterization and limitations in sampling. Additionally, changes in the composition are expected with changes in the electrode and electrolyte materials used. However, while no consensus has been made, the key components of the SEI that have been proposed include Li$_2$CO$_3$,$^{64}$ LiF,$^{65}$ Li$_2$O,$^{66}$ LiOH, Li$_2$C$_2$O$_4$,$^{67}$ HCOLi,$^{68}$ polycarbonates,$^{65,69}$ ROLi,$^{70}$ Li ethylene carbonate ((CH$_2$OCO$_2$Li)$_2$),$^{71}$ and ROCO$_2$Li.$^{72}$ These have been found by a variety of techniques including x-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES), Fourier transform infrared spectroscopy (FTIR), attenuated total reflection infrared spectroscopy, electrochemical methods (cyclic voltammetry), Raman spectroscopy, Auger electron spectroscopy (AES), atomic adsorption spectroscopy (AAS), temperature-programmed decomposition mass spectrometry (TPD-MS), ion chromatography (IC), TOF SIMS and MALDI-TOF mass spectrometry, and scanning electron microscopy (SEM).$^{57,73,74}$

1.4 Mg Batteries

1.4.1 History and Basic Principles

Li-ion batteries have been the commercial standard for rechargeable batteries.$^{20}$ The development of consumer electronics and interest in electric cars has created a demand for high
quality energy storage systems. One system of interest is Mg batteries. Mg has a low reduction potential of 2.37 V (H⁺/H₂, the lowest reduction potential after Li at -3.0 V). Additionally, Mg has a high volumetric capacity at 3,833 mA·h·cm⁻³ (compared to Li at 2,046 mA·h·cm⁻³), is low cost, and is abundant (Mg is the fifth most abundant element in the earth’s crust).

In a Li-ion battery, Li ions interact with the anode and cathode either by intercalation or a conversion reaction. In a Mg battery, the anode is often Mg metal and Mg ions electrodeposit onto the surface of the anode (see figure 1.16). In this way, Mg batteries are based on the electrodeposition and stripping of Mg. The direct deposition of Mg on the anode (as opposed to the intercalation or conversion with some other anode material) maximizes the voltage window of operation, providing a higher power battery. Mg ions often intercalate into cathode materials, similar to that in a Li-ion battery.

![Diagram of a Mg battery.](image)

Figure 1.16: Diagram of a Mg battery.
While the first Mg battery prototype was proposed in 2000, Mg electrodeposition and stripping has been studied since the early twentieth century. In the 1920s the first working electrolyte for Mg deposition and stripping was reported. Further research proposed the first non-Grignard based organo-borate electrolyte for Mg deposition and stripping in the 1980s. However, the electrochemical window was still very narrow at about 2 V. In 1971, Chevrel et al. reported the first prominent intercalation material for a Mg battery cathode, Mo$_6$S$_8$, named the Chevrel phase.

1.4.2 Mg Battery Cathodes- Current State and Issues

The intercalation of Mg ions into a cathode material is analogous to the intercalation of Li ions into cathode materials. However, Mg has proven to be a greater challenge. While in both cases, the ions move between available sites in the host lattice, Li ion diffusion is much faster than Mg diffusion. While the ionic radii for the ions are similar (Li$^+$ is 0.76 Å and Mg$^{2+}$ is 0.72 Å), the divalent nature of Mg$^{2+}$ causes very slow kinetics in the intercalation process. This is due to both the strong attraction between the Mg$^{2+}$ and the host and the strong repulsion between Mg$^{2+}$ ions.

In addition to sluggish kinetics, three other challenges arise: (1) structural instability of the cathode material, (2) surface film formed on the cathode which may prevent Mg$^{2+}$ transport, and (3) corrosion of the current collector. While these issues are all of concern, the primary goal of recent studies has been to improve the kinetics of Mg$^{2+}$ transport to and through the cathode material to improve the rate of charge/discharge.

Co$_3$O$_4$ was an early cathode material studied in the 1990s. This cathode was reported to have a capacity of 74 mA·h·g$^{-1}$, operated between 1.5 and 2 V (Mg/Mg$^{2+}$), and had
60% capacity retention after 30 cycles. While this material was one of the better materials of the time, it still was not competitive with Li-ion cathode materials. Further modification of this material to MgCo$_2$O$_4$ presented a higher operating voltage, however, voltage decay was observed with cycling due to a high polarization from the slow intercalation of Mg$^{2+}$ ions.

V$_2$O$_5$ was another thoroughly studied cathode material for Mg batteries. While the material could theoretically contain up to 2 moles of Mg$^{2+}$ per mole of V$_2$O$_5$, the maximum content of Mg observed was 0.6 moles. When a xerogel of V$_2$O$_5$ was used, a much higher magnesiation was obtained, resulting in 1.84 moles of Mg. This increased amount of Mg resulted in a capacity of 600 mA·h·g$^{-1}$ with an operating voltage of 3 V (Mg/Mg$^{2+}$).

Molybdenum based cathodes are additionally of interest. One of the most notable cathodes is the Chevrel phase, Mo$_6$S$_8$. This cathode reports excellent stability at less than 15% capacity fade over 2000 cycles. However, low operating voltages at 1.2 V (Mg/Mg$^{2+}$) and capacities at 110 mA·h·g$^{-1}$ limit these materials. Additional materials utilizing Mo have proven to be some of the best cathodes currently available for Mg batteries including MoS$_2$ with a reported operating voltage of 1.8 V and capacity of 170 mA·h·g$^{-1}$.

The final remaining major group of Mg battery cathodes are MnO$_2$ cathodes. MnO$_2$ is a widely used cathode for various systems, having been reported for Li, Zn, and Mg battery systems. While these cathodes provide good initial capacities at 240 mA·h·g$^{-1}$, the structural instability with magnesiation has proven detrimental to the further use of these materials.

The primary goal of recent Mg battery cathode research has been to find materials with high operating voltages and good Mg transport kinetics. In addition to these requirements, reasonable energy capacities are necessary.
1.4.3 Mg Battery Anodes- Current State and Issues

One of the attractive features of using Mg in a battery stems from the use of Mg metal as an anode. While some studies have been done on Mg intercalation anodes, most proposed battery systems utilize Mg metal as an anode. This improves the operating voltage and energy capacity. The analogous Li metal anode for a Li battery provides 3,862 mA·h·g⁻¹ as compared to using an intercalation graphite anode which provides 372 mA·h·g⁻¹. Moving from an intercalation anode to a deposition anode improves the energy capacity by an order of magnitude. However, for Li, Li deposition and stripping is not a sustainable battery as Li deposits are dendritic and could cause short circuiting. However, Mg forms more compact deposits, allowing for Mg metal anodes to be a possibility. A Mg metal anode provides 2,205 mA·h·g⁻¹, an order of magnitude greater than most Mg intercalation anodes (reported at 298 to 384 mA·h·g⁻¹).

While utilizing a Mg metal anode simplifies the system, the interaction of the Mg metal and the electrolyte becomes very important. Because Mg is very reactive, the Mg metal anode and deposits may interact with the electrolyte forming a surface layer. This surface layer can be detrimental to a battery as it can block or slow down the transport of Mg²⁺ to the anode. While in Li-ion battery systems, this layer is Li permeable and actually improves the battery, using conventional battery electrolytes in Mg battery systems creates a Mg impermeable layer. Because of this, much research has been done into electrolyte systems that effectively work with Mg metal anodes and fundamental studies of the Mg metal-electrolyte interface have been done.

To avoid the issues with the reactivity of the Mg metal anode with the electrolytes, Mg intercalation anodes have also been studied. However, as mentioned earlier, the intercalation
anodes have a significantly reduced energy capacity. These anodes have additional challenges including large volumetric expansion with magnesiation and slow Mg transport kinetics.\textsuperscript{107,108} The first report of Mg insertion anodes was using Bi, Sb, and Bi-Sb alloys.\textsuperscript{107} These materials were reported to have energy densities of up to 298 mA·h·g\textsuperscript{-1}. Additional studies reported Sn to have an energy capacity of 903 mA·h·g\textsuperscript{-1}.\textsuperscript{108} Nanostructuring of the materials improved the capacity retention of the anodes.\textsuperscript{113-115}

Discussions and studies on Mg battery anodes focus on the interfaces formed between the anode and the electrolyte. A fundamental understanding of these interfaces would support the development of improved anodes or electrolytes for enhanced electrochemical performance.

\subsection*{1.4.4 Mg Battery Electrolytes- Current State and Issues}

Three main types of electrolytes have been developed over the last several decades. These include Grignard-based electrolytes, non-Grignard based solutions, and Mg(TFSI)\textsubscript{2}- based electrolytes. The earliest used electrolytes were the Grignard-based electrolytes. These electrolytes, including RMgBr or RMgCl (R= alkyl or aryl) often in THF or poly-ether solvents, while maintaining good cycling capabilities, were very air sensitive and unstable.\textsuperscript{81} Further development of Grignard-based electrolytes led to the dichloro-complex (DCC) which was composed of Bu\textsubscript{2}Mg and EtAlCl\textsubscript{2}.\textsuperscript{79,116-118} This solution had high conductivity, a wide electrochemical window of 2.4 V and 100\% efficiency for Mg deposition and stripping.\textsuperscript{79,116,117}

The electrochemical window was determined to be limited by β-H elimination.\textsuperscript{118-120} Because of this, further studies moved towards organic groups that contain no H atoms at the
This led to the development of the all phenyl complex (APC) which is the mixture of PhMgCl and PhₙAlCl₃₋ₓ. This electrolyte has an electrochemical window of 3.3 V and deposition/stripping efficiencies of up to 100%. However, due to the instability and high cost of Grignard-based electrolytes, studies moving towards non-Grignard based electrolytes have been done. From this, the most notable electrolyte reported has been the magnesium aluminum chloro complex (MACC) which is composed of MgCl₂ and AlCl₃ in THF or a poly-ether solvent. The wide electrochemical window of 3.1 V and deposition/stripping efficiencies of up to 99% have made the electrolyte of great interest. However, recent studies have demonstrated the need for the electrolyte to be “conditioned” to obtain such high efficiencies. To date, the conditioning process is not fully understood.

The final type of electrolyte is the Mg(TFSI)₂-based electrolytes. These electrolytes are of interest because of the simplicity of the system. Because it is simply the dissolution of a Mg salt into an organic solvent, the electrolyte is not as corrosive (particularly for the cathode), is not as reactive as the Grignard-based electrolytes, and is less air sensitive than the MACC electrolyte. However, the deposition of Mg from the Mg(TFSI)₂ electrolyte to the anode has proven difficult, limiting the use of Mg(TFSI)₂ electrolytes.

The further development of Mg battery electrolytes has many challenges. The electrolyte must be stable, low reactivity, cost effective, non-corrosive to the cathode, and able to deposit Mg on the anode. Additionally, the formation of a surface layer on the anode must be avoided to allow for Mg transport.
1.5 Summary

There is a great interest in developing improved electrical energy storage systems. To obtain this, a fundamental understanding of current energy storage systems is vital to engineer new solutions. Batteries are among the most promising electrical energy storage systems for long term solutions. This dissertation will focus on studying the processes at the electrode surfaces in Li-ion and Mg battery systems.

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Chapter 2

LiMn$_2$O$_4$ Cathodes for Li-ion Batteries:

Effect of Mn in electrolyte on anode and Au coating to minimize dissolution

2.1 Introduction

Li-ion batteries are a technology of great interest for applications in hand-held electronics and electric cars due to their high operating voltage and energy density. While substantial improvements in anode capacity have occurred over the past decade, cathode improvements have been slower. LiMn$_2$O$_4$ (LMO) is a great cathode material for a Li-ion battery due to its low cost, thermal stability, abundance, and lack of toxicity.$^{1-4}$ However, batteries using LMO cathodes suffer from significant capacity fade with cycling (see figure 2.1).$^{3,4}$ This capacity fading is attributed to three main factors: (1) the instability of the electrolyte at high potentials when charging cells, (2) a Jahn-Teller distortion of the MnO$_4$ center at the discharged state, converting from a cubic symmetry to a tetragonal symmetry, reducing the stability of the cathode structure with cycling, and (3) the dissolution of Mn into the electrolyte.$^{5-7}$

The dissolution of Mn has been considered a necessary issue to be solved to improve LMO cathodes. The amount of Mn dissolved into the electrolyte from a LMO cathode has been quantitatively analyzed by ion chromatography and concentrations up to 31 ppm Mn$^{2+}$ have been found.$^9$ The dissolution of Mn may be hastened with an increased concentration of acid, particularly HF forming from the hydrolysis of LiPF$_6$, in the electrolyte.$^{10}$ Prior research has shown that Mn dissolution reduces battery capacity by two methods: (1) material loss at the cathode$^{11,12}$ and (2) Mn reduction at the anode, causing an increase in cell resistance.$^{13-15}$
Mn reduction on the anode has been studied on graphite using EDS, XRD, AFM, XPS, and electrochemical impedance spectroscopy.\textsuperscript{11,13,15,16} Additionally, a variety of methods have been used to reduce the effect of the dissolved Mn ions. These methods include adding inorganic electrolyte additives to prevent further reduction of Mn on the anode,\textsuperscript{17,18} substituting a fraction of the Mn atoms with other transition metal atoms in the cathode,\textsuperscript{8} redepositing the Mn on the cathode before depositing on the anode with cycling,\textsuperscript{19} and coating the cathode with various materials.\textsuperscript{20-23} A variety of coatings have been studied, primarily oxides, either on LMO particles or on the surface of the cathode.\textsuperscript{19,20,24-26} However, metal oxides often exhibit low conductivity and further reduce the conductivity of the cathode material. Coating LMO with a metal would be ideal, however, at the potentials used for charging and discharging LMO, many metals would strip. Au, however, does not strip at these potentials.
2.2 Effect of Mn Ion in Electrolyte


2.2.1 Summary

This section focuses on the effect of the dissolution of Mn$^{2+}$ into the electrolyte and the deposition of Mn on a model anode has on the SEI layer. Electrochemical quartz crystal microbalance (EQCM) was used to monitor changes in mass on the anode, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was used to observe changes in the oligomer formed in the SEI, SEM and AES were used to observe changes in surface morphology and chemical composition, and potentiostatic voltammetry was used to monitor charge and discharge capacity. We also examined the effect of Cu$^{2+}$ addition in place of Mn$^{2+}$, as Cu is known to form an underpotential deposition (UPD) monolayer on Au electrodes.$^{27}$

2.2.2 Experimental

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. All solutions were prepared in an argon glove box with [O$_2$] < 2 ppm. 1.0 M LiClO$_4$ (battery grade, 99.99 %) in 1:1 volume ratio of ethylene carbonate, dimethyl carbonate (EC:DMC) and 1.0 M LiPF$_6$ (battery grade, 99.99 %) in 1:1 EC:DMC formed the electrolyte solutions. Mn(ClO$_4$)$_2$:6H$_2$O, Cu(ClO$_4$)$_2$:6H$_2$O, CuSO$_4$, and MnSO$_4$·H$_2$O dried at 350 °C for 2 hours (Sigma-Aldrich) were added to the electrolyte solutions as indicated. Li metal foil
(Sigma-Aldrich) was used as counter and reference electrodes. Karl Fischer analysis showed water content of 5.3 ± 0.8 ppm, 8.2 ± 1.1 ppm, 7.8 ± 0.9 ppm (8.1 ± 1.5 ppm), 9.2 ± 1.3 ppm (8.7 ± 1.1 ppm) for EC:DMC, 1 M LiPF6 in EC:DMC, 0.27 mM MnSO4 (0.29 mM CuSO4) in 1 M LiPF6 EC:DMC, and 5.4 mM MnSO4 (5.8 mM CuSO4) in 1 M LiPF6 EC:DMC, respectively. Working electrodes were formed from 2.5 nm Cr and 250 nm Au evaporated onto pyrex substrates (Esco Optics) by using a Temescal six pocket E-Beam Evaporation System. The electrodes were annealed with a hydrogen flame for 5 minutes before use.

EQCM experiments used room-temperature-optimized 5 MHz quartz crystals with polished Au electrodes (Inficon, East Syracuse, NY). The crystals were cleaned in piranha solution for 10 minutes, rinsed with Milli-Q water (Millipore Inc., Billerica, MA), and dried with argon before using. The QCM cell was purged with Ar until the frequency stabilized and the probe was lowered into the solution until the frequency stabilized again. The QCM cell includes a water-jacketed beaker kept at 30 °C using a Neslab RTE 10 refrigerated bath (Thermo Electron Corporation, now Thermo Fisher Scientific Waltham, MA) and was maintained under a positive pressure of Ar. Upon frequency stabilization, the Li metal counter/reference electrode was lowered into the solution and the open circuit potential was measured. Data was collected from 0.1–2.0 V (vs. Li/Li+) at a scan rate of 0.2 mV·s⁻¹, starting at 2.00 V using a CV-27 (BASi West Lafayette, IN). The frequency was monitored with a Maxtek PM-710 plating monitor (Inficon, East Syracuse, NY). Both the frequency response and the electrochemical data were recorded using a home-built program written using LabVIEW (National Instruments, Austin, TX).

All other electrochemical measurements were performed using CH Instruments 760D and 760E Electrochemical Workstation (Austin, TX) and a three electrode cell under an
argon atmosphere at the scan rate of 0.2 mV·s\(^{-1}\). Potentials are reported with respect to Li/Li\(^+\).

The surface morphology of the working electrode surfaces were analyzed after completing electrochemical measurements using SEM (Jeol, JSM-7000F). The chemical composition of the electrode surfaces were analyzed after electrochemical measurements using AES (Physical Electronics, PHI 660).

Working electrodes were prepared for MALDI-TOF analysis by adding 10 µL of 0.1 M 2,5-dihydroxy benzoic acid (DHB) in acetonitrile to the surface of the electrode maintained in the glove box after completing electrochemical measurements. The samples were then analyzed using a UltrafleXtreme MALDI-TOF (Bruker Daltonics).

2.2.3 Results and Discussion

2.2.3.1 Mn Addition

Figure 2.2a shows cyclic voltammetry obtained from initial experiments of a Au electrode immersed in a solution containing 1.0 M LiClO\(_4\) in 1:1 vol EC:DMC. Additional cyclic voltammetry of a Au electrode immersed in a solution containing 1.0 M LiPF\(_6\) in 1:1 vol EC:DMC demonstrated similar results and are shown in figure 2.1a. The voltammetry shows lithiation beginning around 0.17 V vs. Li/Li\(^+\) on the cathodic sweep and delithiation beginning around 0.32 V vs. Li/Li\(^+\) on the anodic sweep, and is similar to that reported previously.\(^{28}\) The two peaks on the delithiation are due to first, Li bulk dissolution and second, the decomposition of the Li-Au alloy.\(^{29}\) Increased capacity on the fifth cycle as compared to the first cycle is associated with roughening the Au electrode surface, exposing a greater surface area
of Au for lithiation and delithiation. \(^{30,31}\) This roughening of the electrode surface is due to the Li-Au dealloying process.

Figure 2.2: Cyclic voltammetry obtained at 0.2 mV s\(^{-1}\) in 1 M LiPF\(_6\) EC:DMC at first cycle (solid line) and fifth cycle (dashed line), and in 1 M LiClO\(_4\) EC:DMC (faded line) showing (a) no metal ion added, (b) one equivalent monolayer of Mn\(^{2+}\) added to electrolyte initially, (c) one equivalent monolayer of Mn\(^{2+}\) added to electrolyte after one cycle, and (d) 20 equivalent monolayers of Mn\(^{2+}\) added to electrolyte initially. MnSO\(_4\) was used with the LiPF\(_6\) electrolyte (solid and dashed lines) and Mn(ClO\(_4\))\(_2\)\(\cdot\)6H\(_2\)O was used with the LiClO\(_4\) electrolyte (faded line) as the Mn salts.

Figure 2.2b shows the effect of addition of 0.13 mg of MnSO\(_4\) to the solution as well as the addition of 0.30 mg of Mn(ClO\(_4\))\(_2\)\(\cdot\)6H\(_2\)O (faded line). With an electrode surface area of 1.27 cm\(^2\) these amounts of Mn\(^{2+}\) correspond to one equivalent monolayer of metal. (The solution concentration in this case was 0.27 mM (1.27 ppm)). The voltammogram in figure 2.2b exhibits potentials of lithiation and delithiation similar to those obtained without added Mn\(^{2+}\). However, as Table 2.1 shows, the amount of lithiation for both the first and fifth cycles is substantially
(48 % and 44 %, respectively) lower than that obtained without added Mn$^{2+}$. Kumagai et al. observed similar decreases in capacity with the incorporation of Mn$^{2+}$ in the electrolyte on graphite electrodes.$^{14}$

Figure 2.2c shows the effect of the addition of one equivalent monolayer of Mn$^{2+}$ (1.27 ppm) after the first lithiation/delithiation cycle. As expected, the first cycle has nearly identical capacity as the first cycle of la, where no Mn$^{2+}$ was added. The figure shows the presence of significant capacity loss after the first cycle when the Mn$^{2+}$ was added. When 20 equivalent monolayers of Mn$^{2+}$ is added initially, very little lithiation and delithiation is found (figure 2.2d). The increased Mn$^{2+}$ concentration caused significantly decreased capacity. Thus, the presence of Mn$^{2+}$ in the electrolyte blocked lithiation and delithiation.

Table 2.1: Mass change on Anode during Lithiation/Delithiation with Addition of Mn$^{2+}$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>EQCM (µg·cm$^{-2}$ Li on anode)</th>
<th>Voltammetry (µg·cm$^{-2}$ Li on anode)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lithiation</td>
<td>Delithiation</td>
</tr>
<tr>
<td>1 equiv. ML Mn$^{2+}$ in electrolyte</td>
<td>1</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>56</td>
</tr>
<tr>
<td>1 equiv. ML Mn$^{3+}$ added after cycle 1</td>
<td>1</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37</td>
</tr>
<tr>
<td>No Mn$^{2+}$ added</td>
<td>1</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>103</td>
</tr>
</tbody>
</table>

As seen in figure 2.2, the electrochemistry of the LiClO$_4$ electrolyte is similar to the electrochemistry of the LiPF$_6$ electrolyte. Additionally, the addition of the waterless MnSO$_4$ as compared to the addition of the hydrated Mn(ClO$_4$)$_2$·6H$_2$O presented negligible differences in
the electrochemistry. Both electrolyte systems present equivalent electrochemistry and demonstrate the effect of Mn$^{2+}$ in the electrolyte on a model Au anode.

Figure 2.3a demonstrates mass changes recorded by EQCM when cycling with four different amounts of Mn$^{2+}$ added over five cycles. Changes in the frequency of the quartz crystal are related to mass changes on the electrode surface using the Sauerbrey equation.

$$\Delta f = C_f \Delta m$$

where $\Delta f$ is the change in frequency (Hz), $C_f$ is the sensitivity factor (Hz·cm$^2$·μg$^{-1}$) of the quartz crystal and $\Delta m$ is the change in mass (μg·cm$^{-2}$). The increase in mass following the first cycle in the system with no Mn$^{2+}$ added has been observed in prior studies.$^{32}$ This increase in mass is attributed to the formation of the SEI and the lithiation of the Au. The subsequent decrease in mass is attributed to the delithiation of Au. At the completion of a cycle, the remaining mass is primarily associated with the SEI, however some of this mass could be Li not completely removed from the Au electrode.$^{28}$ Prior studies have shown that at potentials below 0.2 V vs Li/Li$^+$ a Li–Au alloy is formed.$^{33}$ Most of the Li$^+$ will de-alloy during the anodic sweep, but some Li$^+$ will remain in the bulk, adding to the mass on the anode after a full cycle.

Figure 2.3a shows that greater mass remains on the electrode surface after delithiation on the first cycle when Mn$^{2+}$ is present. Subsequent cycles exhibit less mass increase in the systems with Mn$^{2+}$ when compared to that without Mn$^{2+}$. This result suggests that there is increased mass in the SEI in the presence of Mn$^{2+}$, and there is reduced capability to lithiate and delithiate, leading to higher residual masses and reduced mass increase/decreases with increasing Mn$^{2+}$ concentration.
Figure 2.3: Representative data from the EQCM showing the (a) mass changes as a function of number of cycles and (b) the residual mass as a function of number of cycles for (■) no metal ion added, (●) one equivalent monolayer of Mn$^{2+}$ added to electrolyte initially, (○) one equivalent monolayer of Mn$^{2+}$ added to electrolyte after one cycle, and (▲) 20 equivalent monolayers of Mn$^{2+}$ added to electrolyte initially. 0.2 M LiClO$_4$ 1:1 EC:DMC was used as the electrolyte with Mn(ClO$_4$)$_2$·6H$_2$O as the Mn salt (a lower concentration of Li salt was used to minimize Au delamination from the QCM disk).

Figure 2.3b shows that the residual mass, composed of the SEI and any Li$^+$ retained following delithiation at +2.0 V vs. Li/Li$^+$, is greater when Mn$^{2+}$ is incorporated in the electrolyte. When one equivalent monolayer of Mn$^{2+}$ is initially added to the electrolyte, there is 23 % more residual mass relative to that with no Mn$^{2+}$ added. When 20 equivalent monolayers of Mn$^{2+}$ is initially added to the electrolyte, there is nearly twice as much residual mass as that with no Mn$^{2+}$ added. After every cycle, the presence of Mn$^{2+}$ yields more residual mass retained on the electrode than the corresponding cycle without Mn$^{2+}$. With the addition of Mn$^{2+}$
following cycle one, this residual mass is evident on the very next cycle where 35 % more residual mass relative to the Mn-free situation is found. After five cycles, there is little difference in residual mass between one equivalent monolayer of Mn\(^{2+}\) added initially and that added after one cycle. This result indicates that adding Mn\(^{2+}\) initially or after one cycle makes little difference in the residual mass after a sufficient number of cycles.

Table 2.1 compares the degree of lithiation as inferred from EQCM measurements with that obtained from integration of the voltammetry using Mn(ClO\(_4\))\(_2\)·6H\(_2\)O as the Mn salt. By the fifth cycle, the two techniques produce results that are nearly identical with each other, with deviations on the order of 15 % or less. While the lithiation masses from EQCM measurements are initially greater than those from voltammetry measurements, these masses include not only lithiation, but also SEI formation and potentially Mn\(^{2+}\) adhering to the anode. Thus, the values for mass increase during lithiation measured by EQCM are expected to be greater than that measured by voltammetry. However, the mass decrease as measured by EQCM is primarily delithiation, thus the values for delithiation are similar between those measured by EQCM and those measured by voltammetry. This table demonstrates reasonable agreement between values for measurements by EQCM versus measurements by voltammetry.

In order to ascertain the origin of the increased mass in the presence of Mn\(^{2+}\), we used SEM to examine the electrodes following cycling. Figure 2.4a-d shows representative SEM images of the Au electrode at the delithiated state after five cycles. The initial annealed Au surface was nearly featureless on the 10 µm length scale (not shown). With lithiation and delithiation, the Au surface roughens, as has been observed previously.\(^{30,31}\) Figure 2.4a shows the effect of five cycles of lithiation and delithiation on a Au surface in the absence of Mn\(^{2+}\). This degree of roughening was also observed following the first cycle.
When Mn$^{2+}$ was added to the electrolyte prior to cycling, and the electrode cycled five times, the image in figure 2.4b was obtained. Figure 2.4b shows regions of roughness, similar to that found in figure 2.4a, and regions of a smooth surface, identical with that seen on the uncycled Au electrode. The amount of smooth area ranged from 40 % to 50 % of the interrogated electrode area, which is similar to the degree of drop in charge between the Mn-free and Mn-added systems on the first cycle as evidenced in figure 2.2.

Figure 2.4: SEM images of the Au electrode surface after 5 cycles with (a) no metal added, (b) one equivalent monolayer of Mn$^{2+}$ added to electrolyte initially, (c) one equivalent monolayer of Mn$^{2+}$ added to electrolyte after one cycle, and (d) 20 equivalent monolayers of Mn$^{2+}$ added to electrolyte initially. 1.0 M LiPF$_6$ 1:1 EC:DMC was used as the electrolyte with MnSO$_4$ as the Mn salt.
Figure 2.4c shows the SEM image obtained with addition of Mn$^{2+}$ following the first lithiation/delithiation cycle. The figure shows a texture similar to that found in SEM images obtained from Au surfaces without Mn$^{2+}$ addition. This result indicates that roughening occurs following the first cycle of lithiation and delithiation. However, the Mn$^{2+}$ in solution is still able to decorate the surface and inhibit lithiation.

Figure 2.4d shows the SEM image obtained when 20 monolayers of Mn$^{2+}$ was added to the electrolyte initially. Similar to figure 2.4b, there are regions of rough and smooth surfaces. The ratio of the smooth area ranged from 80 % to 90 % of the imaged electrode area. This ratio is similar to the amount of decrease in charge between the Mn-free and 20 equivalent monolayer Mn-added systems on the first cycle as evidenced in figure 2.2.

To determine where the Mn is on the surface of the electrode, Auger electron spectroscopy was conducted. Figure 2.5a-d presents representative AES spectra of the Au electrode after five cycles showing the differentiated Auger intensity for the kinetic energy range 520 to 670 eV. Mn is known to have peaks at energies of approximately 542, 589, and 636 eV while F is known to have a strong peak at energy 647 eV. Figure 2.5a shows the effect of five cycles of lithiation and delithiation on a Au surface in the absence of Mn$^{2+}$ followed by soaking in a 5.6 mM (25.4 ppm) MnSO$_4$ 1 M LiPF$_6$ EC:DMC or the equivalent to 20 ML of Mn$^{2+}$ in the electrolyte for 24 hours and rinsing with DMC. This spectrum demonstrates that there is no measureable amount of Mn present on the surface of the electrode, however a significant amount of F is present.
Figure 2.5: Auger electron spectra of the electrode surface after 5 cycles with (a) no metal added during cycling followed by 20 hours of soaking in a 20 equivalent monolayer of Mn$^{2+}$ electrolyte and washing, one equivalent monolayer of Mn$^{2+}$ added to electrolyte after one cycle probed in (b) a smooth surface region and (c) a rough surface region, and (d) 20 equivalent monolayers of Mn$^{2+}$ added to electrolyte initially. 1.0 M LiPF$_6$ 1:1 EC:DMC was used as the electrolyte with MnSO$_4$ as the Mn salt.

When one equivalent monolayer of Mn$^{2+}$ was added to the electrolyte prior to cycling, and the electrode cycled five times, SEM showed regions of smooth surface and regions of rough surface (figure 2.4b). Figure 2.5b shows the AES spectrum obtained of an area chosen with a smooth surface and figure 2.5c presents the AES spectrum of an area chosen with a rough surface. The spectrum of the smooth surface (figure 2.5b) indicates the presence of Mn and the reduced amount of F as compared to no Mn incorporated (figure 2.5a). However, the spectrum
of the rough surface (figure 2.5c) indicates no measurable amount of Mn and significantly more F present. Thus, we hypothesize that some of the Mn adheres to the surface with electrochemical cycling prior to lithiation and blocks the Li-Au alloy from forming in that region, preventing roughening with lithiation. This would explain the presence of Mn at the smooth surface and the lack of Mn at the rougher surfaces in addition to the correlation of the ratio of smooth surface on the electrode (figure 2.4b) to the drop in electrochemical capacity (figure 2.2b).

When 20 monolayers of Mn$^{2+}$ was added to the electrolyte prior to cycling, and the electrode cycled five times, and rinsed with DMC, the AES spectra shown in figure 2.5d was obtained. This spectra indicates the presence of Mn on the surface and very little F. Since figure 2.5a shows no Mn and significantly more F, these results indicate that the Mn adheres to the electrode surface due to the electrochemical cycling of the system. Additionally, when Mn was incorporated, there was a significantly reduced amount of lithiation and delithiation (see figure 2.2), which would likely reduce the amount of LiF on the surface, leading to a reduced amount of F on the surface.

In order to evaluate the effect of added Mn$^{2+}$ on the presence of an SEI layer on the electrode surface, we undertook mass spectrometry measurements from emersed electrodes. It has been previously reported that the SEI is in part associated with the formation of high molecular weight oligomers on anodes such as Au, C, and Sn in Li-ion battery systems.$^{32}$ MALDI-TOF MS measurements obtained from a Au electrode immersed in 1 M LiClO$_4$ in 1:1 vol EC:DMC revealed the presence of an oligomer with mass ratios up to 1500 m/z and a spacing of 177.5 m/z between peaks. We wondered whether the presence of Mn$^{2+}$ in the electrolyte might inhibit the formation of this oligomer.
Figure 2.6 reports the results of MALDI-TOF MS measurements obtained from the different electrodes studied here following five lithiation/delithiation cycles. The mass spectrometry shows that very similar high weight oligomers formed during five cycles with and without the addition of the Mn$^{2+}$ ion.

![Figure 2.6: MALDI-TOF mass spectrometry analysis, (a) no Mn$^{2+}$ added, (b) one equivalent monolayer of Mn$^{2+}$ added to electrolyte initially, (c) one equivalent monolayer of Mn$^{2+}$ added after one cycle, and (d) 20 equivalent monolayers of Mn$^{2+}$ added to electrolyte initially. 1.0 M LiClO$_4$ 1:1 EC:DMC was used as the electrolyte with Mn(ClO$_4$)$_2$·6H$_2$O as the Mn salt.](image)

Mass ratios up to 1600 m/z are obtained in the electrolyte without any metal ion added. The peak spacing for all electrolyte systems, both those with Mn$^{2+}$ added and without, is approximately 177 m/z. These results indicate that the same high weight oligomer is formed when a Mn$^{2+}$ ion is in the electrolyte as when there is no Mn$^{2+}$ ion added. No difference is
detected when the Mn$^{2+}$ is added initially or after the first cycle. Differences in peak intensity between the different samples may simply be reflective of different ionization efficiencies.

### 2.2.3.2 Cu Addition

To further study the effect of metal ion addition to the electrolyte, we examined the addition of Cu$^{2+}$ to the electrolyte. Cu is known to form a UPD layer on Au in aqueous and non-aqueous solutions. As with the addition of Mn$^{2+}$ to the electrolyte, when one equivalent monolayer of Cu$^{2+}$ was added to the electrolyte initially, figure 2.7b shows similar lithiation and delithiation potentials as that without Cu$^{2+}$ addition, however the capacity is substantially lower. When one equivalent monolayer of Cu$^{2+}$ is added after the first cycle, figure 2.7c is obtained. As expected, the first cycle has nearly identical capacity as that seen in the first cycle of figure 2.7a, where no Cu$^{2+}$ ion was added. Some capacity loss occurred after the first cycle when the Cu was added; however after 5 cycles, there was a slight capacity increase due to the roughening of the Au electrode surface. These figures show that the presence of Cu$^{2+}$ in the electrolyte also inhibits lithiation on a Au electrode.

Figure 2.8a shows EQCM data obtained for lithiation of Au in the presence of Cu$^{2+}$. As with the Mn$^{2+}$ case, all electrolyte systems exhibit substantial residual mass retained on the electrode surface following delithiation. Cu$^{2+}$ addition resulted in an increased mass after delithiation on the first cycle. Subsequent cycles exhibit less mass increase in the systems with Cu$^{2+}$ when compared to that without Cu$^{2+}$. Additionally, there is reduced capability to delithiate when Cu$^{2+}$ is in the electrolyte, leading to higher residual masses and reduced mass decreases during delithiation.
Figure 2.7: Cyclic voltammetry obtained at 0.2 mV·s\(^{-1}\) in 1 M LiPF\(_6\) EC:DMC at first cycle (solid line) and fifth cycle (dashed line), and in 1 M LiClO\(_4\) EC:DMC (faded line) showing (a) no metal ion added, (b) one equivalent monolayer of Cu\(^{2+}\) added to electrolyte initially at (solid line) first cycle and (dashed line) fifth cycle, and (c) one equivalent monolayer of Cu\(^{2+}\) added to electrolyte after one cycle at (solid line) first cycle and (dashed line) fifth cycle. CuSO\(_4\) was used as the Cu salt.

Figure 2.8b shows that the residual mass is greater when Cu\(^{2+}\) is added to the electrolyte. When one equivalent monolayer of Cu\(^{2+}\) is initially added to the electrolyte, there is 35% more residual mass as compared to that with no Cu\(^{2+}\) added after the first cycle. If Cu\(^{2+}\) is added after cycle one, there is no immediate increase in residual mass, however, after the second cycle, there is 30% more residual mass as compared to that with no Cu\(^{2+}\) added.

Table 2.2 compares the degree of lithiation obtained from EQCM measurements with that obtained from integration of the voltammetry. By the time of the fifth cycle, the two techniques produce delithiation results that are equivalent with deviations on the order of 10% or less. Table 2.2 exhibits reasonable agreement between values for measurements by EQCM versus measurements by voltammetry.
Figure 2.8: Representative data from the EQCM showing the (a) mass changes as a function of number of cycles and (b) the residual mass as a function of number of cycles for (■) no Cu\(^{2+}\) added, (●) one equivalent monolayer of Cu\(^{2+}\) added to electrolyte initially, and (○) one equivalent monolayer of Cu\(^{2+}\) added to electrolyte after one cycle. 1.0 M LiClO\(_4\) 1:1 EC:DMC was used as the electrolyte with Cu(ClO\(_4\))\(_2\)·6H\(_2\)O as the Cu salt.

Table 2.2: Mass change on Anode during Lithiation/Delithiation with Addition of Cu\(^{2+}\)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>EQCM (µg·cm(^{-2}) Li on anode)</th>
<th>Voltammetry (µg·cm(^{-2}) Li on anode)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lithiation</td>
<td>Delithiation</td>
</tr>
<tr>
<td>1 equiv. ML Cu(^{2+}) in electrolyte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>220</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>51</td>
<td>13</td>
</tr>
<tr>
<td>1 equiv. ML Cu(^{2+}) added after cycle 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>182</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>34</td>
</tr>
<tr>
<td>No Cu(^{2+}) added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>186</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>103</td>
<td>80</td>
</tr>
</tbody>
</table>
To fully compare the addition of Cu$^{2+}$ to the addition of Mn$^{2+}$ in the electrolyte, the samples exposed to Cu$^{2+}$ addition were observed with SEM. Figure 2.9a-b shows representative SEM images of the Au electrode after five cycles. The effect of five cycles of lithiation and delithiation on a Au surface in the absence of added Cu$^{2+}$ may be seen in figure 2.4a. When Cu$^{2+}$ was added to the electrolyte prior to cycling, and the electrode cycled five times, the image in figure 2.9a was obtained. Figure 2.9a shows, similar to figure 2.4b regions of roughness and regions of a smooth surface. The amount of smooth area ranged from 50 % to 60 %. This is similar to the drop in capacity on the first cycle between the system with no Cu$^{2+}$ added and that with an equivalent amount of Cu$^{2+}$.

![Figure 2.9: SEM images of the Au electrode surface after 5 cycles with (a) one equivalent monolayer of Cu$^{2+}$ added to electrolyte initially and (b) one equivalent monolayer of Cu$^{2+}$ added to electrolyte after one cycle. 1.0 M LiPF$_6$ 1:1 EC:DMC was used as the electrolyte with CuSO$_4$ as the Cu salt.](image)

Figure 2.9b shows the SEM image obtained with addition of Cu$^{2+}$ following the first lithiation/delithiation cycle. The figure shows a texture similar to that found in SEM images
obtained from Au surfaces without Cu\textsuperscript{2+} addition; however, the features are less well defined. These results are similar to those reported in figure 2.3 for the addition of Mn\textsuperscript{2+} to the electrolyte.

Figure 2.10 shows MALDI-TOF MS obtained from Au electrodes with the electrolytes considered here following five lithiation/delithiation cycles. The figure shows that when Cu\textsuperscript{2+} is added to the electrolyte, regardless as to whether it is initially in the electrolyte or if it is added after one full cycle, a high weight oligomer is observed on the surface. The spacing between subsequent peaks for all systems is approximately 177 m/z. Thus, these MALDI-TOF MS experiments cannot detect any changes to the high weight oligomer present in the SEI when Cu\textsuperscript{2+} is incorporated into the electrolyte as compared to no Cu\textsuperscript{2+} being added to the electrolyte.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure210.png}
\caption{MALDI-TOF MS analysis, (a) no Cu\textsuperscript{2+} added, (b) one equivalent monolayer of Cu\textsuperscript{2+} added to electrolyte initially, and (c) one equivalent monolayer of Cu\textsuperscript{2+} added after one cycle. 1.0 M LiClO\textsubscript{4} 1:1 EC:DMC was used as the electrolyte with Cu(ClO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O as the Cu salt.}
\end{figure}
Additionally, it is of interest to consider the oxidation state of the metal that is blocking lithiation. We are confident that the metal blocking lithiation of the anode in both the Cu\(^{2+}\) and Mn\(^{2+}\) addition cases is metallic. Based on the Pourbaix diagrams, the oxides of these metals are not formed for any pH until 2.8 V vs Li/Li\(^+\) and 2.7 V vs Li/Li\(^+\) for Cu and Mn, respectively.\(^{36}\) While the insight from the Pourbaix diagram is for aqueous systems, the general thermodynamics are clear. As all experiments were carried out at no higher than 2 V vs Li/Li\(^+\), the blocking of lithiation on the anode must be due to metallic Cu and Mn.

### 2.2.4 Conclusions

The results presented here show that even very low concentrations of Mn\(^{2+}\) – equal to one equivalent monolayer of Mn – can strongly inhibit lithiation on a model Au electrode. SEM images obtained from surfaces initially exposed to a Mn\(^{2+}\) or Cu\(^{2+}\) containing electrolyte evince substantial (ca. 50%) areas of the surface which do not show the characteristic Au roughening found when Au is lithiated. Rather, the surface remains smooth. Because the amount of smooth area roughly corresponds with the drop in capacity following Mn\(^{2+}\) or Cu\(^{2+}\) addition we suggest that the effect of these cations is to form a monolayer or equivalent on the Au surface, which then prevents lithiation. On surfaces to which the foreign cation is added following the first cycle, the SEM evinces the rough structure seen in Mn\(^{2+}\) or Cu\(^{2+}\) -free electrolytes. However, it is reasonable to think that the foreign metal has deposited on this surface as well, albeit with less coverage due to the rougher surface, and slowly seals the Au from subsequent lithiation.

While the drop in electrode capacity for lithiation is associated with foreign metal cation addition, this addition does not seem to affect the formation of the SEI. In both the cation-free
and cation-added cases, MALDI-TOF MS shows that the high weight oligomer is formed in the SEI with or without the addition of Mn$^{2+}$ or Cu$^{2+}$. Additionally, the mass gains associated with the SEI seen in the EQCM are found with or without foreign metal cation addition. Indeed, EQCM data demonstrates that there is more initial mass gain on the anode with increasing concentration of Mn$^{2+}$. Thus, the SEI seems to be intact with or without addition of Mn$^{2+}$ or Cu$^{2+}$. Changes to the SEI are not the origin of the capacity loss in Li-ion battery anodes exposed to Mn$^{2+}$ containing solution.

These results suggest that Mn$^{2+}$ exposure to the anode results in a monolayer of material that is impermeable to Li. Similar behavior is found with Cu$^{2+}$. Preventing Mn$^{2+}$ from reaching the anode seems to be a solution to the capacity fade problem found with LMO cathodes.

2.3 LMO@Au Particles as Improved Li-Ion Battery Cathodes


2.3.1 Summary

LMO particles were coated with a Au shell by a simple and scalable electroless deposition for use as Li-ion battery cathodes. The Au shell was intended to limit the capacity fade commonly seen with LMO cathodes. Characterization by SEM, TEM, EELS, and AFM showed that the Au shell was approximately 3 nm thick. The Au shell prevented much of the Mn from dissolving in the electrolyte with 82 % and 88 % less dissolved Mn in the electrolyte at
room temperature and 65 ºC, respectively, as compared to the uncoated LMO. Electrochemical performance studies with half cells showed that the Au shell maintained a higher discharge capacity over 400 cycles by nearly 30 % with 110 mA·hr·g⁻¹ for the 400th cycle as compared to a commercial LMO at 85 mA·hr·g⁻¹. Similarly, the capacity fade was reduced in full cells, where the coated LMO had 47 % greater capacity after 400 cycles over the control.

2.3.2 Experimental

LMO (electrochemical grade, Sigma-Aldrich, St. Louis, MO) was combined in ethanol (200 proof, Decon Laboratories) with AuCl₃•3H₂O (99.9+ % metals basis, Sigma-Aldrich) in a 14.9:1 mass ratio (LMO: AuCl₃•3H₂O). The mixture was heated to 60 ºC with stirring. After equilibrating at 60 ºC, hydroquinone (Sigma-Aldrich) dissolved in Milli-Q water was added in a 1.25:1 mass ratio (LMO:hydroquinone). The mixture was stirred for 15 minutes, removed from heat, centrifuged, and washed three times with ethanol. The product was dried in a vacuum oven at 60 ºC for 8-12 hours. Cathodes were made by combining active material, conductive carbon (Super P Li, TimCal), and PVDF (2801, Kynar) in 80:10:10 mass ratio. N-Methyl-2-pyrrolidone (>99.0 %, TCI) was added and the slurry was cast with a doctor blade at 0.12 mm thickness. Cathodes were dried in a vacuum oven at 60 ºC overnight. Cathodes had an active material weight of 12.3 ± 0.4 mg·cm⁻².

The surface morphology of the LMO and the LMO@Au particles was analyzed using SEM (JEOL, JSM-7000F). The thickness of the Au coating was additionally evaluated by coating a glass slide partially occluded with a PDMS (Sylgard 184, Dow Corning) mask. Following Au deposition, the PDMS mask was removed by sonication in hexanes for 5 minutes and the slide was examined by using an AFM (Asylum Research MFP-3D AFM) for height.
differential between the occluded and bare areas. TEM and EELS (JEOL 2010F (S)TEM) were used to interrogate the core-shell structure of the LMO@Au particles. Further characterization was undertaken by using XPS (Kratos Axis ULTRA) and ICP-MS (PerkinElmer – SCIEX ELAN DRCe ICP-MS). XPS demonstrated the presence of Au on the surface with peaks at 84 and 88 eV. Mn dissolution stability of the bare and LMO@Au particles was determined by immersing 0.2 g of particles into 15 mL of solution containing 1 M LiPF$_6$ in EC/DMC (1:1) for a period of 72 hours at both room temperature and 65°C. Following immersion, the solution was filtered to remove the particles, the supernatant evaporated, and the precipitate redissolved in 5 mL of conc. HNO$_3$. Mn concentrations were determined by using ICP-MS. A pre-leaching was also done by leaving the particles in 1 M LiPF$_6$ in EC/DMC (1:1) for 4 days. The electrolyte was decanted and the particles were washed three times with DMC.

Potentiostatic electrochemical measurements were performed using a CH Instruments Electrochemical Workstation (Model 760D, Austin, TX) and a three electrode cell under an Ar atmosphere at a scan rate of 0.2 mV·s$^{-1}$. Counter and reference electrodes were formed from Li metal (Alfa Aesar). Potentials are reported with respect to Li/Li$^+$. Coin cells were made using Celgard 2325 separator, and an MTI automatic press. Commercial LMO cathode material and graphite anode material were purchased from MTI. Coin cells were cycled with an Arbin BT2000 cycler, half cells (using a Li counter electrode) were cycled between 3 and 4.3 V and full cells were cycled between 0.1 and 4.3 V at a 1C rate.
2.3.3 Results and Discussion

2.3.3.1 Deposit Characterization

SEM images of LMO and LMO@Au particles are shown in Figure 2.11. Figure 2.11a is an image of the bare LMO particle. The image shows the presence of a smooth surface representative of the as-synthesized LMO material. The particle size and shape is consistent with prior work.\textsuperscript{37,38} Figure 2.11b shows the surface of the LMO@Au particle following electroless deposition of Au. The figure shows that the particle exhibits a roughened surface which is associated with the Au-shell on the LMO particles. Au islands with lateral dimensions ranging from 5 to 20 nm in diameter are seen on the facets. Good dispersion of the Au is seen across the particles in SEM. An SEM image of the LMO@Au particle obtained following 25 charging/discharging cycles is shown in figure 2.11c. The roughened texture associated with the presence of Au is still observed on the surface of the particle.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure211.png}
\caption{SEM images (a) LMO particles, (b) LMO@Au particle, and (c) LMO@Au after being cycled 25 times.}
\end{figure}
In order to obtain an estimate of the thickness of the Au deposited on the LMO particle, TEM images were obtained from the particle edges. Figure 2.12 shows the TEM and the corresponding Mn concentration along the thick blue line moving from the interior of the particle to the edge with concentrations obtained using EELS. This measurement demonstrates a decrease in Mn concentration with the approach of the edge of the particle. The Mn concentration decreases to a negligible amount approximately 3.5 nm before the edge of the particle, indicating that little to no Mn is present in the outer 3.5 nm shell of the particle. While the EELS of Au overlaps with that of Li and is thus not informative in this case, the presence of the 3.5 nm edge suggests that the Au shell is approximately 3.5 nm thick. Electroless Au deposition thicknesses using this method are found to range from 0.2 to 100 nm, and the thickness found here is consistent with these values.\(^{39}\)

![Figure 2.12: TEM image of the edge of a LMO@Au particle. Graph overlays EELS measurement of Mn peak over a line scan of the sample.](image)
Figure 2.13 shows the surface morphology obtained by using AFM. Figure 2.13a shows AFM of two areas on a glass surface onto which Au has been deposited. In the area on the left, the bare glass surface was exposed to the deposition solution. In the area on the right, the glass was protected from the solution by using a polydimethylsulfoxide (PDMS) mask which was subsequently peeled from the surface following emersion of the glass from the deposition solution. The figure shows the presence of material on the left which is not present on the right. This material is associated with electrolessly deposited Au. Additionally, the average roughness (Ra, arithmetic average of absolute values) of the Au deposit is 640 pm while the average roughness of the protected area is 220 pm. Figure 2.13b is a line scan across the sample showing the difference in height between the protected and unprotected areas. The line scan shows that the height difference between the two is ca. 3.2 nm which is associated with the amount of Au deposited on the glass slide. The 3.2 nm Au deposit thickness found here is consistent with the ca. 3 nm value determined using TEM.

Au electroless deposition has been reported on numerous substrates, including metals, semiconductors, glass, PVDF, and ceramic oxides.\textsuperscript{40-42} The Au deposited using electroless methods ranges in thickness from 2 nm to several microns. On Si, a nonporous Au deposit with thicknesses between 20-100 nm was reported.\textsuperscript{31} On many substrates, the Au roughness increases proportionally with deposition thickness and has been reported to be 0.5 to 1 nm (Ra) for thicknesses of 5-20 nm on a glass substrate.\textsuperscript{29} The electroless process used here, yields Au thickness and roughness factors similar to those reported on other substrates using alternative electroless methods.
Figure 2.13: AFM measurements of a glass slide with a PDMS mask coated with Au. AFM image (a) and line scan across the removed PDMS interface (b) show height and roughness information.

2.3.3.2 Mn Dissolution Studies

Table 2.3 shows the results of Mn dissolution studies from bare and Au-coated particles following 72 h immersion into electrolyte-containing solution at two different temperatures. Without the Au coating, the Mn concentration in the electrolyte ranged from 50 ppm at room temperature to over 100 ppm at 65°C. By way of comparison, Mn concentration values in the literature for particles exposed to similar conditions ranged from 20 to 55 ppm at room temperature to 53 to 170 ppm at elevated temperature. The elevated temperature is thought to increase Mn dissolution because the disproportionation reaction of Mn$^{3+}$ to Mn$^{2+}$ and Mn$^{4+}$ is accelerated with heat.
Table 2.3: Mn concentration in electrolyte from untreated and pre-leached LMO and LMO@Au exposure over 72 hours at room temperature and 65 °C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mn conc. from LMO (ppm)</th>
<th>Mn conc. from LMO@Au (ppm)</th>
<th>% less Mn with Au shell</th>
<th>Mn conc. from pre-leached LMO (ppm)</th>
<th>Mn conc. from pre-leached LMO@Au (ppm)</th>
<th>% less Mn with Au shell, pre-leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp</td>
<td>49 ± 1</td>
<td>9 ± 2</td>
<td>82 %</td>
<td>43 ± 4</td>
<td>4 ± 2</td>
<td>91 %</td>
</tr>
<tr>
<td>65 ºC</td>
<td>113 ± 2</td>
<td>14 ± 2</td>
<td>88 %</td>
<td>102 ± 9</td>
<td>8 ± 3</td>
<td>92 %</td>
</tr>
</tbody>
</table>

After coating the particles with Au, the amount of Mn in solution was found to decrease significantly. Table 2.3 shows that the Mn concentration was only 9 ppm following 72 h immersion at room temperature and 14 ppm at elevated temperature. Both of these values represent a decrease of ca. a factor of 5-10 relative to the uncoated case. In comparison, coating with LaF$_3$ provided a decrease in the Mn concentration in the electrolyte of a factor of 2-3 relative to the uncoated study.$^{20}$ AlF$_3$ coating and CeO$_2$ coatings had decreases in the Mn concentration in the electrolyte of a factor 1.5 and 2.5, respectively, relative to the uncoated material.$^{21, 37}$

There are two different ways in which the presence of Au might decrease Mn dissolution from the LMO particle. First, the Au might restrict exposure of LMO to the byproduct HF formed by hydrolysis of PF$_6^−$. The HF is thought to accelerate Mn dissolution.$^9$ Alternatively, the Au coating may function as a diffusion barrier, preventing surface Mn from diffusing into solution and reducing on the anode.
While the Au coating reduced the amount of Mn that dissolves into the electrolyte, there is some adventitious Mn found even with the coated particles. This adventitious Mn could be from incomplete Au coating coverage or from well-coated LMO@Au particles that were damaged during processing, exposing uncoated LMO. In order to evaluate these effects the LMO@Au particles were ‘pre-leached’ by immersing them in electrolyte for 4 d followed by emersion and rinsing before immersion into clean electrolyte again. Pre-leaching of the LMO@Au resulted in even further reduced Mn dissolution in a 72 hour period. Table 2.3 shows that while exposure of the bare LMO particles to solution yielded a solution containing 43 ppm Mn, the LMO@Au particles yielded a solution containing only 4 ppm Mn, following pre-leaching. This indicates that while there is less Mn dissolved from the LMO after a pre-leach, there is significantly less Mn dissolved from the LMO@Au after a pre-leach.

Interestingly, pre-leached bare LMO particles still dissolved to yield Mn concentrations similar to those found from LMO particles that were not pre-leached. Alternatively, the pre-leached LMO@Au particles yielded solutions exhibiting Mn concentrations only half of those from the unpre-leached LMO@Au particles. This indicates that adventitious Mn can be removed from the LMO@Au particles, but not from the bare material.

2.3.3.3 Electrochemical Performance

The electrochemical performance of the bare and coated particles was then evaluated. Figure 2.14 shows cyclic voltammetry of LMO@Au cathodes compared with that from LMO. The voltammograms exhibit peaks at 4.17 and 4.31 V on the anodic scan (associated with
discharging the cell) and 3.83 and 4.02 V on the cathodic scan (associated with charging). These peaks are associated with the reversible, two-step intercalation of Li to form LMO from $\lambda$-MnO$_2$. Both the coated and uncoated particles exhibit these voltammetric features at similar potentials, suggesting the presence of the thin Au coat has little or no influence on the ability of Li to intercalate into the LMO@Au particle.

The voltammogram in figure 2.14 shows that while the peak at 4.13 (anodic scan) and 4.02 (cathodic scan) are similar between the coated and uncoated material, the second intercalation feature at 4.31 V is shifted cathodically by 50 mV in the anodic scan.

![Voltammogram of LMO and LMO@Au](image)

*Figure 2.14: Cyclic voltammagram of the second cycle of LMO and LMO@Au.*

Figure 2.15 shows the discharge capacity obtained from 400 cycles from a half-cell in coin cells charged and discharged at 1C. The figure shows results from the LMO@Au core-shell cathodes, LMO control, and a commercial LMO. While all three materials exhibit near-theoretical gravimetric capacity at the first cycle, this capacity decreases through the first
ca. 50 cycles due to SEI formation and other processes.\textsuperscript{3,4} However, figure 2.15 shows that after this initial drop, LMO@Au maintains a nearly 40% greater capacity over 400 cycles than either bare LMO cathode. The discharge capacity of the LMO@Au half-cell stabilizes at 110 mA·hr·g\textsuperscript{-1} while that of both bare LMO materials occurs at 78 and 85 mA·hr·g\textsuperscript{-1}. Interestingly, the discharge capacity for the LMO@Au stabilizes following the 50\textsuperscript{th} cycles, while both the bare materials exhibit capacity fade continuing through the 400\textsuperscript{th} cycle. The performance of the bare LMO materials is consistent with that reported previously for LMO with capacities stabilizing at 60 to 100 mA·hr·g\textsuperscript{-1} after the first 50 to 150 cycles.\textsuperscript{27,46-48} Thus, the half-cell performance of the LMO@Au material is substantially better than that reported from LMO coated using other methods.

\textit{Figure 2.15: Discharge capacity over 400 cycles for LMO, LMO@Au, and commercial LMO at 1C rate.}
Figure 2.16 shows the discharge curves obtained from the 1st, 100th, and 400th cycle of a LMO/graphite full cell charged and discharged at 1C. The figure shows the potential versus state of charge relative to the first cycle for cathodes made with LMO@Au, LMO control, and commercial LMO. The LMO control shows a decrease in discharge capacity to 64 % after 100 cycles and to 45 % after 400 cycles. The commercial LMO shows a decrease in discharge capacity to 80 % after 100 cycles and to 69 % after 400 cycles. Alternatively, the LMO@Au shows a decrease in discharge capacity to 90 % after 100 cycles and to 86 % after 400 cycles. It is well documented\textsuperscript{3,4} that the discharge capacity will fade with the cycling of LMO batteries; however figure 2.16 shows that the LMO@Au cathodes experience significantly less capacity fade over the 400 cycles. This could be due to a reduced amount of Mn ions dissolving into the electrolyte, reducing the effect of the Mn on the anode.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.16.png}
\caption{Discharge curves for cycles 1, 100, and 400 for LMO/graphite full cell cycling data.}
\end{figure}
Figure 2.17 shows the Coulombic efficiency versus the number of cycles for a LMO/graphite cell charged and discharged at 1C for the LMO@Au cathodes, LMO control, and the commercial LMO. The efficiency is the ratio of the discharge capacity to the charge capacity. The average efficiency for cycles 100 through 400 for the LMO control is 99.7 %, for the LMO@Au is 99.8 %, and for the commercial LMO 99.4 %. All efficiencies are fairly high; however the LMO@Au has the highest average efficiency. Figure 2.17 shows that the Coulombic efficiency of the LMO@Au cathodes is as good or better than that found with either the bare or commercial LMO materials. Thus, the LMO@Au is a conductive, stable material highly suitable for Li battery cathode applications.

*Figure 2.17: Efficiency versus number of cycles for LMO/graphite full cell cycling data.*
2.3.4 Conclusions

Presented here is a general method to coat battery materials with a metal using electroless deposition, a very simple and scalable method. While this paper focuses on Au deposition, electroless plating extends to many other metals and alloys. For example, LMO was successfully coated with Ag as well, however Ag is not stable at the higher potentials utilized here with LMO cathodes.

The LMO@Au particles have demonstrated electrochemical performance greater than prior reported coated LMO particles. It is expected that the Au coating preventing Mn dissolution significantly decreases the capacity fade seen in LMO control cathodes. This Au coating on LMO provides a high voltage, stable cathode material for a Li-ion battery.

2.4 References


Chapter 3

Dimensionally Controlled Lithiation
of Thin Film and Multilayer Conversion Li-ion Battery Anodes

3.1 Introduction

The structural and chemical changes associated with the reversible insertion and extraction of Li in a Li-ion battery electrode are generally categorized as conversion or intercalation reactions.\(^1\) Intercalation materials have long been the foundation for commercial Li-ion batteries.\(^2\) These materials, including graphite or layered Li metal oxides,\(^2\) maintain the crystalline-like phase of their host structure during Li\(^+\) insertion and extraction; this provides the electrode with structural reversibility but intrinsically limits the Li insertion capacity (see figure 1.14). In contrast, conversion materials alloy with Li either homogeneously (e.g., Si, Sn)\(^3\) or heterogeneously (e.g., metal oxides, fluorides, sulfides),\(^4\) the latter leading to phase separation into a Li-rich compound and a reduced parent species (see figure 1.14).\(^5\) The lithiated phases have distinct, thermodynamically stable, crystallographic phases\(^6\) that are not, however, kinetically accessible near room temperature. As a result, the lithiated products of conversion reactions tend to be amorphous.\(^7\)

Conversion reactions of MX compounds (M = metal and X = O\(^{2-}\), S\(^{2-}\), F\(^-\), P\(^{3-}\), etc.) such as the well-known phase separation of a metal oxide into Li\(_2\)O and reduced metal species (e.g., MO\(_x\) + 2xLi\(^+\) ↔ M + xLi\(_2\)O),\(^5\) provide an alternative storage mechanism that is not limited by the electrode crystal structure. As a result, conversion reactions are capable of multiple electron transfers with higher specific capacity than intercalation materials.\(^4,8\) However, these reactions typically have multiple challenges, including reduced discharge plateaus well below Nernstian behavior, significant overpotentials, sluggish kinetics, and large volume changes that...
can reduce particle cohesion, much like intermetallic reactions found in Si and Sn electrodes.\textsuperscript{9,10} Each of these factors has been attributed to competition between interfacial and bulk thermodynamics\textsuperscript{11} and is highly dependent on electrode morphology.\textsuperscript{12}

During lithiation, conversion leads to phase-separated Li-rich and reduced metal species, as depicted in figure 3.1a. Ideally, this phase separation occurs at the nanoscale, providing a high concentration of interfaces and short inter-particle diffusion lengths that would enable reversibility.\textsuperscript{13} As illustrated in figure 3.1a, the metal species typically nucleate as 2-5 nm particles embedded in an amorphous Li-rich matrix.\textsuperscript{5} This nanophase morphology plays a significant role in these reactions: both (1) at the onset, where partial oxidation (and reoxidation) of the metal species impedes both charge and mass transport, leading to substantial irreversibility and overpotentials during the first cycle and (2) over time, where particle ripening can gradually slow mass transfer at the Li\textsubscript{n}X-M interface.\textsuperscript{14} The interface itself is also thought to play a significant role for electronic transport across and electrocatalysis at the metal-Li interface and for ionic transport (of both Li\textsuperscript{+} and O\textsuperscript{2-}). Additional charge storage mechanisms have been attributed to this region as well; however, a fundamental understanding of electrochemical processes at these interfaces has been hindered by the difficulties of accessing the extreme environment of a Li-ion battery and the inherent, three-dimensional complexity of a reacting conversion material.

To better understand the role of interfaces in conversion reactions, we study a model electrode consisting of well-defined, vertically-aligned layers of Cr and CrO\textsubscript{x}, like those depicted in Figure 3.1b. This type of heterostructure is ideal for x-ray reflectivity (XR) which is directly sensitive to interfacial structure and reactivity and can be measured in situ with Ångstrom vertical resolution. Remarkably, we show that the initial nanoscale layering in the electrode provides a
template for guiding the subsequent conversion reaction, in that the metal layers act as a pre-existing nucleation sites for the reduction of the metal oxide lowering the barrier for reaction. This effectively confines the Li$_2$O and Cr products, providing a well-defined architecture for delithiation. The stability of the architecture is suggested by the observation that the internal electrode layering becomes even more pronounced during subsequent cycling and is amenable to aggressive charge/discharge conditions. These results point to a possible new strategy for controlling the morphology of conversion materials during electrochemical cycling.

Figure 3.1: Illustration of phase separation for (a) bulk and (b) layered conversion reactions. The nucleated metal species (M), lithiated phase (Li-X), and their interfaces are indicated by the blue, yellow, and green components respectively with arrows indicating the growth direction of the metal species.

We further study this stable architecture with Si which has the highest known gravimetric capacity at 4400 mAh/g, but expands by nearly 400% at Li$_{4.4}$Si. Generally, repeated cycling pulverizes the electrode, rapidly reducing its overall charge capacity as Si delaminates from its current collector. Numerous strategies have been introduced to improve the reversibility of conversion materials, particularly Si.$^{9,15}$ Most prominent is the use of nanostructured Si
electrodes, such as nanoparticles or ‘conditioned’ particles,\textsuperscript{16} thin films, or nanowires/tubes.\textsuperscript{17} These systems are found to reduce overall strain and associated electrode delamination by tailoring the direction of expansion and suppressing crystallization of Li\textsubscript{15}Si\textsubscript{4} found in more bulk-like electrodes.\textsuperscript{18} Si-based composites with conductive media, such as carbon binders, can also preserve electrical conductivity and cushion volume changes.\textsuperscript{19} Much like particle size in laminates, the cycle lifetime of Si thin films correlates inversely with their thickness or degree of discharge\textsuperscript{20} which complicates scale-up. Nanostructured Si electrodes, such as wires\textsuperscript{17} or patterned crystals,\textsuperscript{21} have shown promising reversibility in half-cells, but often require incomplete lithiation to maintain internal stability during cycling and tend to have low Coulombic efficiency resulting from secondary reactions occurring at the electrode surface.

To date, only a few studies have explored the electrochemical behavior of Si/metal multilayers,\textsuperscript{22,23} notably with Co and Fe. Our recent work with Si/Cr bilayers revealed preferential lithiation at the intermixed silicide interfaces leading to a stratified heterostructure with an unexpected stability to lithiation/delithiation reactions.\textsuperscript{24} This observation suggested that the synergistic use of architectures that combine the energy density of conversion materials with the stability found in layered structures might lead to substantially improved behavior.

Here, we demonstrate that multilayers consisting of alternating amorphous Si thin films and planar, conducting “adhesive layers” of Cr\textsubscript{x}Si (x ~ 3) combine the intrinsically high Li-capacity of Si, the reversibility of ultrathin Si films, and the conductivity of a composite material. Real-time XR measurements reveal that the internal layering in the Si/Cr\textsubscript{x}Si multilayers is preserved during lithiation and delithiation, strongly enhancing its
reversibility. During these reactions, the overall electrode reversibly expands and contracts by a factor of 330 %, but solely in the vertical direction. Extended charging and discharging confirms that the multilayer provides superior reversibility over comparable Si thin films with potential for high power applications. We discuss the effect of overall thickness and pitch on the reversibility and rate capabilities of silicide multilayers under both voltammetric and galvanostatic cycling conditions. These results suggest that the multilayer architecture is a novel strategy for addressing the extreme challenges associated with Si and related materials in Li-ion battery materials.

3.2 Dimensionally Controlled Lithiation of Chromium Oxide


3.2.1 Summary

Oxide conversion reactions are an alternative approach for high capacity Li ion batteries, but are known to suffer from structural irreversibility associated with the phase separation and reconstitution of reduced metal species and Li$_2$O. In particular, the morphology of the reduced metal species is thought to play a critical role in the electrochemical properties of a conversion material. Here we use a model electrode with alternating layers of Cr and CrO$_x$ to better understand and control these phase changes in real-time and at molecular length scales. Despite lacking crystallinity at the atomic scale, this superstructure is observed (with XR) to lithiate and delithiate in a purely one-dimensional manner, preserving the layered structure. The XR data
show that the metal layers act as nucleation sites for the reduction of chromium in the conversion reaction. Irreversibility during delithiation is due to the formation of a ternary phase, LiCrO$_2$, which can be further delithiated at higher potentials. The results reveal that the combination of confining lithiation to nanoscale sheets of Li$_2$O and the availability of reaction sites in the metal layers in the layered structure is a strategy for improving the reversibility and mass transport properties that can be used in a wide range of conversion materials.

3.2.2 Experimental

The thin film samples were grown by DC magnetron sputtering at room temperature as a Si/Cr bilayer on R-plane sapphire. For in situ measurements, the 10 x 3 mm$^2$ sample was immersed in an electrolyte composed of 1 M LiPF$_6$ in 1:1 ethylene carbonate:dimethyl carbonate during the in situ measurements. Chronoamperometric measurements were performed using the sample as the working electrode and separate Li counter and reference electrodes. We additionally characterized the as-grown samples using XR, TEM, and depth-resolved XPS. XR was measured at the Advanced Photon Source, sector 33BM at 20 keV ($\lambda = 0.6198 \text{ Å}$) using a four-circle diffractometer and area detector (Pilatus 100k).$^{25}$ The beam was focused and collimated to 1.5 x 0.2 mm$^2$ at the sample and illuminates a 1.5 x 3 mm$^2$ area on the electrode surface. The scattered x-rays showed no signs of broadening or diffuse scattering throughout the measurement, indicating that changes to the vertical structure of the sample were laterally uniform within the footprint of the beam.

As shown in Figure 3.2, the Si/Cr bilayer was found to have significant structural density modulations within the buried metal layer. The XR data were fit to a layered slab model using a
Figure 3.2: Characterization of the initial film by (a) XR confirms the underlying layered structure. The fit to the reflectivity shown in (a) corresponds to the layered slab model shown in (b). The electron density in the multilayer region is between the bulk Cr and Cr$_2$O$_3$ values.

The electrode structure, was determined by optimizing the overall quality of fit (reduced $\chi^2$) and the propagated errors in the final density profile are shown, as previously discussed. All parameters (thickness, density, and interfacial roughness) were allowed to vary except for the known densities of the sapphire substrate and electrolyte). As seen in Figure 3.2b, fits to the reflectivity indicated that the buried chromium film actually consisted of alternating 10.2 Å-thick layers with densities ranging from 1.5-1.8 e$^{-}\cdot$Å$^{-3}$ ($\pm$ 0.05 e$^{-}\cdot$Å$^{-3}$), buried beneath a Si capping layer. These range from the density of bulk Cr$_2$O$_3$ up to densities approaching Cr metal. This type of layering gives rise to weak multilayer diffraction peak in the XR data (see figure 3.2a). This broad feature is centered
Figure 3.3: Characterization of the initial film by TEM confirmed the underlying layered structure. TEM confirm this overall structure and the lack of crystallinity in each layer.

at $q = 0.28$ Å$^{-1}$ with a full-width $\Delta q = 0.046$ Å$^{-1}$ and is indicative of a repeated multilayer structure with “$d$-spacing” of $2\pi/(q - q_c) \approx 20.4$ Å and six repeated bilayers, in close agreement with the extracted density profile. This multilayer likely formed as a result of the growth process of the Cr film with the Si capping layer.

TEM results (Figure 3.3) confirmed the layering in the underlying Cr layer. The sample was found to be amorphous apart from weak crystalline CrSi$_2$ electron diffraction found at the Si/Cr interface. From the XR and TEM measurements, which are only sensitive to the total electron density, it was unclear whether the initial modulated density was due to Si/Cr intermixing or the presence of an oxide or other impurity.
Closer inspection of the Cr and O lines at the Si/Cr interface and within the Cr layer are shown in figure 3.5. The strong peak at 530.5 eV is consistent with chromium oxide (specifically Cr$_2$O$_3$). The Cr 2p lines appear to a mixture of Cr metal and Cr$_2$O$_3$ contributions, consistent with the modulated Cr/CrO$_x$ composition identified by XR. The atomic ratio of O/Cr in this region is 0.7 ± 0.1, also consistent with the equal atomic fraction of Cr metal and Cr$_2$O$_3$, although higher Cr oxidation states could be present due to the reducing nature of the Ar plasma.
Figure 3.5: (a-b) O 1s spectra from the Si/Cr interfacial region and within the Cr layer. The strongest 530.5 eV feature (b) matches previously measured Cr$_2$O$_3$. The 531.5 eV (a-b) feature is likely related to Al$_2$O$_3$ and the 532.6 eV (a) feature could result from residual SiO$_2$ content from the Si layer. (c-d) The Cr L3 lines appear to be split between sharp metallic states at 574.5 eV and broader contribution from the oxide at 576.5 eV agreeing with known lines of Cr and Cr$_2$O$_3$, respectively.

X-ray absorption near edge structure data was also consistent with this result and appeared to be an admixture of Cr$_2$O$_3$ and Cr metal. No pre-edge feature was found (which indicated that there was no Cr$^{6+}$ present initially).

3.2.3 Results

Having delineated the structure and components present in the film using ex-situ methods, we proceeded to observe the thin-film structure with in-situ XR as a function of
electrochemical potential ($E$, reported as V vs. Li/Li$^+$) during lithiation/delithiation reactions using a custom x-ray-compatible electrochemical cell (described in appendix 1).

We compared structural changes during a gradual potential sweep ($\Delta E = 0.2$ mV/s) and in response to a large potential steps between 3 and 0.02 V. Changes in the normalized reflectivity in both cases are shown in the color plot versus time in figure 3.6. The dominant feature throughout the reaction is the multilayer Bragg peak, which shifts to lower and higher $q$ as the multilayer expands and contracts during lithiation and delithiation, respectively. In figure 3.6, the position of the peak’s maximum (and its second order diffraction peak) are tracked with blue dots as a guide. The persistence and intensification of the diffraction peak at all conditions indicates that the layering is preserved throughout the lithiation and delithiation reactions, despite vertical expansion and contraction by up to 50%.

Much like ‘bulk’ conversion reactions, the structural changes of multilayer are most pronounced during the first lithiation cycle and are highly reversible thereafter. This initial conditioning can be seen during the CV in figure 3.6a, where there is a discontinuity in the reflectivity at 0.3 V. This is partially due to the dampening of the highest frequency oscillations corresponding to the overall thickness of the electrode from the interference of x-rays scattering from the substrate and the top Si surface. As the Si expands and roughens, these oscillations are diminished. Immediately following this transition at 0.3 V, the multilayer (ML) diffraction peak shifts to lower $q$ indicating the coherent expansion of the multilayer by ~50%. Likewise, oxidative current (primarily from the delithiation of the Si capping layer at 0.1 - 0.5 V) precedes the positive shift of the ML Bragg peak as the structure contracts. The increase in the ML diffraction peak intensity after the first discharge is caused by stronger contrast between the lower-density lithiated layers and the higher-density metallic layers, but the persistence of
Figure 3.6: Real-time, normalized XR plotted during (a) CV and (b) potential step measurements. In each case the electrochemical data are shown on the left and the reflectivity intensity is indicated by a logarithmic color scale (shown on the right). Note that the applied potential, $E$, and the measured current, $I$, are overlaid and have different axis ranges, as noted. The color scale on the reflectivity scales logarithmically from $q^2R(q) = 0.01 - 50$. A subset of the reflectivity marked by a box in (a) is shown in figure 3.7.
this first order Bragg peak and the emergence of the higher order diffraction peaks during cycling indicates unequivocally that the ML structure remains intact throughout the conversion reaction.

Beyond the wholescale changes seen at low potential, a smaller, reversible change in the multilayer $d$-spacing can also be seen near the upper voltage limit (3.5 V). A portion of this region is shown in figure 3.7. Such a high voltage reaction could possibly involve O or the decomposition of residual Li$_2$O; however, closer examination of the CV reveals weak, reversible redox features at 3.3 and 1.8 V (see figure 3.7b) that correspond well to finer shifts in the multilayer Bragg peak corresponding to a 5% change in bilayer $d$-spacing. As discussed below, these changes are consistent with a new Li$_x$CrO$_2$ phase that forms after the initial discharge. The lower density of this phase (compared to Cr$_2$O$_3$) is largely responsible for the increased Bragg peak intensity and expansion of the multilayer after one full cycle.

The XR data clearly indicates the structural stability of the multilayer structure during the conversion reaction, but the alignment of the Cr layers could inhibit Li transport. The role of Li transport in such a layered structure was measured with real-time observations of the structural and electrochemical response to potential steps between 3 and 0.02 V. The current response to the step is largely exponential, but with fast (30-60 s) and slower (130-480 s) decay constants (see table 3.1), likely related to the lithiation of the Si and CrO$_x$ layers, respectively (see figure 3.8 for fits used to obtain these relaxation times). In support of this conclusion is the observation that the slower time constant coincides with the response time of the layered oxide’s shifting XR Bragg peak ($t_{XR}$). Note that this time scale in combination with the 20 nm thickness of the Si buffer layer gives an estimated diffusion constant of $\sim 10^{-12}$ cm$^2$·s$^{-1}$, in line with reported literature values for Si, indicating that the rate of lithiation of the Cr$_2$O$_3$ is limited by diffusion
Figure 3.7: Redox changes at high potential from figure 3.6a can be seen clearly both in the cyclic voltammetry (a) and in the reflectivity (b). The electrochemical data in (a) is plotted as a function of time. The background subtracted CV is shown in the inset to emphasize the reversibility of the reaction. The dashed white lines in the XR data are times corresponding to the redox voltages. (b) The shift of the second order Bragg peak indicates contraction of the multilayer structure at at 3.3 V by 5%, followed by a more gradual expansion near 1.8 V.

through the entire heterostructure. This also implies that Li transport occurs vertically through the entire thin film heterostructure, fully consistent with the lack of x-ray diffuse scattering that would otherwise indicate the presence of lateral heterogeneity (e.g., cracks for fast diffusion paths, or random nucleation events). For each cycle, the positive current (corresponding to delithiation) typically has a faster time constant, most likely due to the larger applied overpotential at 3 V.
Table 3.1: Kinetics of potential step measurement.

<table>
<thead>
<tr>
<th></th>
<th>$Q_{tot}$ (mAh)</th>
<th>$t_1$ (s)</th>
<th>$t_2$ (s)</th>
<th>$t_{XR}$ (s)</th>
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</thead>
<tbody>
<tr>
<td>First lithiation</td>
<td>-0.00421</td>
<td>36.8</td>
<td>296</td>
<td>310</td>
</tr>
<tr>
<td>First delithiation</td>
<td>+.00237</td>
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<td>200</td>
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<td>64.1</td>
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<td>470</td>
</tr>
<tr>
<td>Second delithiation</td>
<td>.00200</td>
<td>28.6</td>
<td>130</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 3.1 shows the electrochemical response and shift in XR diffraction peak during the potential step measurements shown in Figure 3.6b. The response was fit to two exponentials plus an overall constant (see figure 3.8). The integrated charge of the combined exponential response ($Q_{tot}$) and its two time scales ($t_1$ and $t_2$) are shown with the time scale of the shift in the reflectivity for comparison. For reference, the theoretical charge of 20 nm Si + 5 nm Cr$_2$O$_3$ is 0.00573 mA·h·g$^{-1}$.

The current response of the thin film was measured during the XR measurement and is plotted in figure 3.8. The negative step (3 to 0.01 V, giving negative current) and positive step (0.01 to 3 V positive current) curves are shown for the first (figure 3.8a) and second (figure 3.8b) cycles. These data were fit to the sum of three decaying exponentials. The two with the slower components are associated with Faradaic processes and the fast response is assumed to be related to a capacitive response. The latter response has negligible integrated charge and is much faster than the temporal resolution of an XR scan.

The current response was compared to the average position of the first order Bragg peak, as shown in figure 3.9 for the first discharge, charge, and second discharge cycles. As shown in table 3.1, the slow response of the multilayer Bragg peaks is statistically the same as the slowest
current response measured electrochemically. This is unsurprising since the multilayers structure is buried by the 20 nm Si layer.

![Graphs](image1)

*Figure 3.8: Three exponential fits to data for the (a) first and (b) second cycles. The 1/e time constant and amplitude of the exponential were allowed to vary for each curve.*

Fitting was using a Parratt calculation of reflectivity from a layered sample using a standard analysis package. Each layer had a density, interfacial roughness, and thickness that were allowed to vary, apart from the substrate and electrolyte densities. While constraints were

![Graphs](image2)

*Figure 3.9: Single exponential fit to the average position of the first order multilayer Bragg peak during (a) first discharge, (b) first charge, and (c) second discharge.*
used in initial fitting, every parameter was allowed to vary in the final model to test the robustness of the model (i.e. the overall covariance). Genetic fitting was used to find a global fit, followed by traditional nonlinear regression (Levenberg-Marquardt) to obtain best fit values and error-bars for each parameter and an overall covariance matrix. These values were used to propagate errors to the density profile itself. The errors in the overall profile and the goodness of fit (reduced to $\chi^2$) were evaluated to determine the most accurate model.

Choosing the best model depends on the number of layers. For instance, $\chi^2$ will be reduced with an increasing number of layers; however, having too many layers can result in layers with impossibly small thicknesses or layers with similar parameters, resulting in systematic covariance in the extracted density profile. As an example, figure 3.10 shows three different fits to the CrO$_x$ heterostructure. Fit1, fit7, and fit8 have $\chi^2$ values of 5.07, 1.64, and 1.45 respectively due to small variation in the high-q data largely influenced by structural variation at the Cr/Si interface. Fit1 used only 12 layers, whereas fit7 included 15 layers and fit8 had 17 layers. Despite having a better $\chi^2$ value, the additional 2 layers in fit8 covary significantly with the underlying structure. Hence, fit7 was used as the best fit in the main text. Other features such as consistency in fits throughout the charge/discharge process, the full-width of the multilayer Bragg peak, and the information from the data’s Patterson function, were also used to evaluate fits to the dataset as a whole.

The number of layers increases from (3.10a) 12 to (3.10b) 15 to (3.10c) 17 and the $\chi^2$ improves from 5.07 to 1.45. However, the increasing number of layers leads to covariance between parameters at the Si/Cr interface. This covariance is especially apparent in the overdetermined system (fit8) where the addition of a final modulation in the electron density leads to significant errors in the propagated electron density for the entire model.
3.2.4 Discussion

The high degree of complexity that is resolved in the XR observations of conversion reactions in this model structure raise multiple points for discussion.

3.2.4.1 CrO$_x$ Phase Identification and Nucleation

Changes in the species and size of each layer are obtained by quantitatively fitting the XR data over the entire first cycle CV (figure 3.6a) in a manner similar to the ex-situ sample shown in figure 3.2. The resulting electron density profiles (EDPs) at the extreme conditions (i.e., at the

Figure 3.10: Three fits from XR data during the discharge of the CrO$_x$/Cr multilayer with varying number of layers: (a) 12, (b) 15, and (c) 17.
open circuit and following lithiation and delithiation over the first cycle and lithiation during the second cycle) are shown in figure 3.11a-d. The data confirm that the multilayer structure persists throughout the reaction, as suggested by the shifting Bragg peak in figure 3.6. Moreover, the thickness of both the oxide and metal layers increases during the first lithiation cycle, indicating that the preexisting Cr layers act as nucleation sites for the metal reduction during the conversion reaction. Figure 3.11e shows the vertically staggered EDPs at intermediate conditions during the first lithiation cycle.

The extracted electron densities can be used to identify the species present in the reaction. Based on a comparison of the observed densities with the values of known Cr and Li oxides (labeled in each panel of figure 3.11) and the changes in each layer’s thickness, we propose the following reactions:

(i) \[ \text{Cr}_2\text{O}_3 + 6\text{Li}^+ + 0.2 \text{V} \rightarrow 2\text{Cr} + 3\text{Li}_2\text{O} \]

(ii) \[ 2\text{Cr} + 3\text{Li}_2\text{O} \xrightleftharpoons{\sim 1.0 \text{ V}}^{0.2 \text{ V}} 1.5\text{LiCrO}_2 + 0.5\text{Cr} + 4.5\text{Li}^+ \]

(iii) \[ 1.5\text{LiCrO}_2 + 0.5\text{Cr} \xrightleftharpoons{3.3 \text{ V}}^{1.8 \text{ V}} \text{CrO}_2 + 0.5\text{Cr} + 1.5\text{Li}^+ \]

Reaction (i) occurs during the first discharge. As seen in figure 3.11b, Li insertion begins to lower the oxide layer’s electron density while the nominal metal layers densify and increase in thickness from the displacement reaction. Note that the phase separation of low density Li$_2$O and the Cr species is most pronounced near the surface of the oxide multilayer, as might be expected with vertical transport through the ML structure. The theoretical volume change of reaction (i) is 92 %, which is in line with the measured volume changes since roughly half of the heterostructure reacts with Li.
Figure 3.11: Extracted electron density profiles from the XR data in Figure 3.6a at (a) the open circuit condition, (b) at 0.035 V during the first lithiation (c) 3 and 3.5 V during the first delithiation, and (d) 0.035 V during the second lithiation. EDPs at intermediate conditions during the first lithiation cycle are vertically staggered in (e) to highlight the evolution of the multilayer structure and the changing density of the Si overlayer. Note that each reflectivity curve was measured over a 0.07 V (350 s) interval, which can broaden features in the EDP during abrupt structural changes. In (a)-(d), bulk electron densities for CrO₅ and Li₂O, the individual layers, and the overall size of the multilayer are provided for reference. To highlight the changing thickness of both oxide and metal layers, the individual metal, metal oxide, and lithiated phases are colored gray, blue, and red respectively. In (e), the electron density is also defined by the color scale provided at the bottom of the plot.
Reaction (ii) connects the profiles seen in figure 3.11b and 3.11c. Conversion reactions are, with few exceptions, irreversible during the first cycle, often stopping at the first stable oxidation state during delithiation. Along these lines, previous authors suggested that divalent CrO was the delithiated phase, in analogy to the lithiation of Co and iron oxides, i.e.

$$2\text{Cr} + 3\text{Li}_2\text{O} \rightleftharpoons 4\text{Li} + 2\text{CrO} + \text{Li}_2\text{O}$$

instead of reaction (ii). Based solely on the extracted electron density alone, we cannot identify which phase is present since CrO and LiCrO$_2$ have similar densities that are both in line with our results; however, such a reaction would lead to some residual Li$_2$O and the metal layers would return to their original thicknesses or even smaller if adjacent metal layers became partially oxidized. Instead, we find that the oxide layers are nearly the same thickness and that the metal layers are thicker than at the start. This finding is summarized in table 3.2 and is highlighted by the marked layers in figure 3.11. Also, we see no evidence for any residual, lower density Li$_2$O phase in the delithiated structures. Furthermore, LiCrO$_2$ is also the most stable phase in the Li/Cr/O phase diagram, whereas CrO is thermodynamically unstable and is likely to decompose to more stable Cr and Cr$_2$O$_3$ phases.

These numbers do not include the top metal layer which includes contributions from the adjacent CrSi$_2$ phase. Oxide and metal layers included in table 3.2 are labeled 1-10 in figure 3.11a-b. The increase in thickness of the oxide layer during lithiation is due to the insertion of up to six Li per Cr$_2$O$_3$ molecule. The change in thickness of the metal layer confirms that the chemically neutral Cr plays a key role in reducing the CrO$_x$ layer during lithiation.
Table 3.2: Changes in average thickness for the oxide and metal layers at each condition shown in figure 3.11.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Average Oxide Layer Thickness (Å)</th>
<th>Average Metal Layer Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>10.44</td>
<td>11.12</td>
</tr>
<tr>
<td>First lith. (0.05 V)</td>
<td>15.63</td>
<td>15.58</td>
</tr>
<tr>
<td>First delith. (3.0V)</td>
<td>10.98</td>
<td>14.58</td>
</tr>
<tr>
<td>First delith. (3.5 V)</td>
<td>10.88</td>
<td>13.54</td>
</tr>
<tr>
<td>Second lith. (0.05 V)</td>
<td>18.20</td>
<td>19.02</td>
</tr>
</tbody>
</table>

The 3.3 V delithiation event is described by reaction (iii) and both endmembers are shown in figure 3.11c. We believe this reaction is similar to the intercalation reaction between LiCrO$_2$ and CrO$_2$ that has been reported at similar potentials with a comparable 5.5% volume change. However, the species found in this reaction are likely amorphous, and the large 1.5 V hysteresis found between the redox peaks in figure 3.7 could result from diffusion limitations and overpotentials associated with conversion. In this conditioned state, the multilayer expands even further during the second lithiation reaction, as seen in figure 3.11d. Both the metal and oxide layers expand by ~75% from their initial thicknesses with the oxide layers reaching the theoretical density of Li$_2$O and the metal layers maintaining their original density. Compared to the first lithiation event (figure 3.11b), the lithiated layers are more
uniform in density suggesting that lithiation proceeds more uniformly, perhaps owing to lateral defects created by the significant volume changes during the first cycle. Such porosity may also explain the lower overall density in the metal layers than seen in the first cycle (figure 3.11b). Nonetheless, the vertical modulation of the ML structure is even more ordered after the second lithiation reaction than at the start suggesting that the multilayer architecture may be beneficial for balancing strain, mass transport, and charge transfer in a conversion reaction.

3.2.4.2 Li Stoichiometry and Excess Charge

The electron density profiles also provide a complementary route for measuring the Li concentrations within the layered electrode structure. By comparing the integrated electron density in the multilayer region \( Q_{XR} \) to the initial condition, the number of additional charge species in the lithiated structure can be determined using equation 3.1.

\[
\Delta Q_{XR} = \frac{\int_0^{Z_{ML}} \rho_{\text{lithiated}}(z) dz}{\int_0^{Z_{ML}} \rho_{\text{initial}}(z) dz} \quad \text{equation 3.1}
\]

This quantity can be related to the conversion process itself using the additional charge from each Li atom and the atomic number \( Z \) of each species in the reaction. This quantity can be directly converted to stoichiometry, assuming that the initial reactive species is \( \text{Cr}_2\text{O}_3 \). Using the atomic number \( Z \) of each species, we obtain the following relation for \( \Delta Q_{XR} \) (equation 3.2).

\[
\Delta Q_{XR} = \frac{Z_{\text{Cr}_2\text{O}_3} + x_{\text{Li}}Z_{\text{Li}}}{Z_{\text{Cr}_2\text{O}_3}} \rightarrow x_{\text{Li}} = 24(\Delta Q_{XR} - 1) \quad \text{equation 3.2}
\]
For complete conversion, $x = 6$. Table 3.3 lists $\Delta Q_{XR}$ obtained using equation 3.2 for each condition shown in figure 3.11. As expected from the volume changes given in table 3.3, the additional electron density present after a complete cycle of lithiation and delithiation indicates that the process is somewhat irreversible at 3 V, nominally consistent with LiCrO$_2$, which would leave 1.5 Li per Cr$_2$O$_3$ molecular species. At 3.5 V, the structure contracts further, and the integrated electron density reaches the same value as the initial open circuit structure, indicating that complete delithiation can be achieved with sufficiently large overpotentials.

Table 3.3 shows the change in integrated charge density ($\Delta Q_{XR}$) from the profiles in figure 3.11b-d relative to the open circuit condition (figure 3.11a) were used to calculate the additional Li stoichiometry using equation 2. For reference, the fractional volume change is also shown for each case.

Table 3.3: Change in charge, stoichiometry and volume in the CrO$_x$ regions using XR data.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta Q_{XR}$</th>
<th>$x_{Li}$ (eq. 2)</th>
<th>$\Delta z$ (total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First lithiation</td>
<td>1.407</td>
<td>9.77</td>
<td>46.3%</td>
</tr>
<tr>
<td>First delith. (3 V)</td>
<td>1.080</td>
<td>1.92</td>
<td>15.6%</td>
</tr>
<tr>
<td>First delith. (3.5 V)</td>
<td>0.991</td>
<td>-0.22</td>
<td>9.8%</td>
</tr>
<tr>
<td>Second lithiation</td>
<td>1.285</td>
<td>6.84</td>
<td>54.9%</td>
</tr>
</tbody>
</table>
The amount of Li inserted during each discharge (using equations 2 or 3) is actually larger than theoretically expected, consistent with the integrated charge measured during cyclic voltammetry (-0.0077 and -0.071 mAh for the first two cycles, well beyond the expected -0.057 mAh for 20 nm of Si and 5 nm of Cr$_2$O$_3$). The observation of lithiation capacities that go beyond theoretical expectations is a well-known phenomenon in conversion materials and has been ascribed to a variety of mechanisms, including: (i) electrolyte decomposition;\textsuperscript{35} (ii) a pseudocapacitive “polymeric/gel” species forming at low potentials;\textsuperscript{36} (iii) the reduction of LiOH forming additional, active Li$_2$O species;\textsuperscript{37} and (iv) a space-charge layer at the interface between the charged metal products and the Li-conducting Li$_2$O.\textsuperscript{38} The results in table 3.3 are derived from the buried electron density profiles of the CrO$_x$ layers. Hence, mechanisms (i), (ii), and (iii) which occur at the electrode surface likely do not play a significant role in these results (although they would contribute to the electrochemical signal). A final explanation involves a buildup of Li$^+$ in response to charge accumulation at the metal under anodic potentials which could explain the additional charge (and expansion) measured by both the XR and electrochemical data, especially given the high concentration of buried interfaces in the model heterostructure. However, the 4 Å vertical resolution from the XR data is not sufficient to resolve these individual layers. The interfacial accumulation of Li at the buried interfaces may explain the unexpectedly high density in the Cr-rich layers in figure 3.7b, since XR is sensitive to the change in density across each interface. Higher resolution data (i.e., taken to higher momentum transfers) could provide a definitive answer to this mechanism.
3.2.4.3 Changes Related to Si and Sapphire

Beyond the pronounced structural changes found in the CrO$_x$ conversion reaction, other components of the electrode also respond to lithiation. These changes can be seen in figure 3.11e, which shows the changes in ML electron density profiles from fits to the reflectivity during the first CV cycle. For example, the density of the Si layer reduced by a factor of two at low potentials, in agreement with the reduced electron density of fully lithiated Si (Li$_{22}$Si$_5$) (the thickness of the lithiated Si layer was, however, difficult to identify due to its large surface roughness following lithiation and the similar electron densities of Li$_{22}$Si$_5$ and the electrolyte). The CrSi$_2$ layer at the Si/Cr interface, identified by TEM in figure 3.3c, also undergoes a sudden reduction in density (starting at $E = 0.17$ V) associated with a conversion reaction,

$$\text{CrSi}_2 \rightarrow \text{Cr} + 2\text{Li}_x\text{Si}$$

Upon lithiation, this region also shows a modulated structure, corresponding to phase-separated Li$_x$Si-rich and Cr-rich layers. Eventually the reduced Cr from this reaction coalesces with the top metal layer from the underlying ML structure (from 0.27 to 0.7 V).

While insulating sapphire is not typically considered an active material for Li-ion batteries, electron density at the interface between the substrate and the bottom Cr layer was found to reversibly decrease in density at low potentials. This could involve Li reacting with the oxygen-terminated surface of R-plane Al$_2$O$_3$ or possibly a ternary Li aluminate phase as seen in studies involving amorphous alumina coatings on anodes using atomic layer deposition.$^{39-41}$
3.2.5 Conclusions

By combining electrochemistry with the interfacial sensitivity of operando XR, we tracked the molecular-scale processes in a Li-conversion reaction of a model layered Cr/CrO\textsubscript{x} thin film. In such a heterostructure, the electrochemically-driven phase separation and recombination of the oxide into reduced Cr and lithiated Li\textsubscript{2}O species is confined to one-dimension, preserving its layering throughout the subsequent electrochemical cycles. This structure enables a detailed view of reactions and processes that are present at the interfaces between nanoscale species formed in bulk oxide electrodes. Such an intentionally layered structure provides a new strategy toward improving the structural and electrochemical reversibility of oxide conversion reactions by providing a pre-existing template (i.e., nucleation sites) for the reactions and controlling overpotentials. These in-situ measurements provide new insights into the interplay between structural kinetics, volume changes, and chemical species of conversion reactions at the molecular scale.

3.3 Li Intercalation Behavior in Multilayer Si Electrodes


3.3.1 Summary

Next generation Li battery materials will require a fundamental shift from those based on intercalation to elements or compounds that alloy directly with Li. Intermetallics, for instance, can electrochemically alloy to Li\textsubscript{4.4}M (M = Si, Ge, Sn, etc.), providing order-of-magnitude
increases in energy density. Unlike the stable crystal structure of intercalation materials, intermetallic-based electrodes undergo dramatic volume changes that rapidly degrade the performance of the battery. Here, we combine the energy density of Si with the structural reversibility of an intercalation material using a Si/metal silicide multilayer (ML). In operando XR confirms the ML’s structural reversibility during Li insertion and extraction, despite an overall 3.3-fold vertical expansion. The ML electrodes also show enhanced long-term cyclability and rate capabilities relative to a comparable Si thin film electrode. This intercalation behavior found by dimensionally constraining Si’s lithiation promises applicability to a wide range of conversion reactions.

3.3.2 Experimental

MLs were grown at room temperature using DC magnetron sputtering by alternating between Cr and Si deposition to form 20 periodic bilayers. Depositions were carried out at ambient temperatures under an argon pressure of 2.3 mTorr over 3 in. diameter planar sputter guns at constant speed. Uniform masks were placed on top of the sputter guns. Cr was chosen for its adhesion properties, electronic conductivity, and because it does not alloy with Li. The MLs were grown on Cu electrodes for electrochemical characterization in coin cells and on atomically-flat R-plane sapphire substrates for synchrotron x-ray characterization.

XR was used to characterize the thickness and density of each layer. Growth rates were calibrated by fitting lab-source XR from test growths on Si substrates, as seen in figure 3.12. Note that the interlayer roughness is greater for these samples due to the roughness of the Si substrate. Using a standard reflectivity fitting package, in all samples grown this way the 2 nm-thick Cr layer was found to have a density much lower than Cr metal due to intermixing
with the adjacent Si layer which agrees with previous work. Chromium silicides are known to form even at room temperature,\textsuperscript{42,43} and the reflectivity indicates an amorphous layer with density near that of Cr\textsubscript{3}Si. Like Cr metal, Cr\textsubscript{3}Si is a metallic alloy\textsuperscript{44} that does not alloy with Li.\textsuperscript{45} The mass used to normalize Li capacity in the coin cell measurements resulted from these growth rate calibrations.

The ML structure provides a nano-scale periodicity that can be followed directly using x-ray diffraction even though the individual materials are intrinsically amorphous. XR measurements were performed at 20 keV (\(\lambda\)) at sector 33BM at the Advanced Photon Source.\textsuperscript{46} The x-ray beam (with cross-section of 2 x 0.2 mm\textsuperscript{2} and divergence of 40 \(\mu\)rad = 0.0005 Å\textsuperscript{-1} along the 20 direction) illuminated a 2 x 3 mm\textsuperscript{2} area on the sample. Data was collected at fine intervals (\(\Delta q = 0.0005\ \text{Å}^{-1}\)) using an area detector (Pilatus 100k), allowing for a full 3D reciprocal space measurement of the specular truncation rod. Samples were probed in a specially-designed spectroelectrochemical cell (using a ‘transmission-geometry’, see appendix 1) with a Li counter/reference electrode and controlled using a CHI760d potentiostat. Both x-ray and coin cell measurements were performed using Li half-cells and all potentials are reported versus the Li/Li\textsuperscript{+} redox couple. Reflectivity scans typically took 15 minutes (1600 data points) and were measured repeatedly during (i) voltammetric (\(\Delta E = 0.2 \text{ mV} \cdot \text{s}^{-1}\)) and (ii) galvanostatic cycling (\(I = 60 \mu\text{A} \cdot \text{cm}^{-2}\)) between 0.01 and 3.5 V. The samples were held for 2-4 hours at the extreme potentials to establish a stable structure in both cases.

Using the area detector, we were able to integrate the background-subtracted reflectivity intensity in real-time (rather than relying on offset specular scans or rocking scans). The area detector also was useful for monitoring for powder lines from surface decomposition phases or other weakly crystalline phases arising from the Si or Cr layers or possible metastable lithiated
Figure 3.12: (a) Lab source reflectivity from calibration sample. Fitting results are given in the caption. (b) ML electron density profile from the fit to run 284. Note that the Cr layer has density lower than Cr metal and matches Cr$_3$Si within statistical error. The profile without interfacial roughness is shown by the dotted line.

phases, such as Li$_{15}$Si$_4$. Apart from strong Bragg peaks from the underlying R-plane sapphire and diffuse rings from the polyimide windows, no other crystalline features were detected. This indicates that the samples were amorphous within our detection limits (apart from the ML films). The area detector also allowed us to monitor the diffuse scatter perpendicular to the rod (e.g. along the $\chi$-direction); however, there was negligible diffuse scattering perpendicular to the specular rod (e.g. along the $\chi$-direction) before and after lithiation. The large horizontal beam
size (1.5 mm at the sample and the detector) smeared out diffuse scattering from features greater than $2\pi/\Delta q_\parallel = 400$ nm in size.

Figure 3.13 shows the detector images taken at the beginning, after lithiation, and after delithiation for potentiostatic and galvanostatic measurements. Diffuse scattering from the crystal truncation rod and nearby Bragg peaks can be seen in all cases. Note the finer spacing of the diffraction peaks when lithiated and the increase in overall diffuse scatter for the galvanostatic case. The shadow of the anti-scattering slit can be seen to the right of pixel 80 in all cases.

![Detector images taken at the beginning, after lithiation, and after delithiation for potentiostatic and galvanostatic measurements. Color is on a logarithmic scale. The specular rod cuts through pixel 52 in the $2\theta$ direction and pixels 12-25 in the $\chi$-direction.](image)

Change in diffuse scattering was seen during lithiation or delithiation of the sample during potentiostatic lithiation. In fact, there was negligible diffuse scattering, which indicates
that: (1) the lateral domain size of the sample was smaller than we could resolve with our relatively large horizontal beam or (2) the domain size was small enough that diffuse was spread out beyond our detection limit. Since the latter scenario would significantly reduce the specular rod signal, it appears that the sample remains coherent over length scales larger than we can measure.

3.3 Results
3.3.1 Structural Changes Under Potentiostatic Conditions

XR data from a Si/Cr$_3$Si ML (20 bilayers) under potentiostatic control are shown in figure 3.14a-b and are stacked sequentially, starting at the top of figure 3.14a. The first through $n^{th}$-order ML Bragg peaks (seen clearly at the extreme potentials) appear periodically in momentum transfer $q$ due to the repeated bilayer d-spacing. For the as-grown ML, $d_{\text{Si+Cr}_3\text{Si}} = 2\pi/\Delta q = 8.1$ nm based on the higher-order consecutive Bragg peaks that are least affected by refraction. The finer fringes between the Bragg peaks in the as-grown film result from the overall thickness of the film and are directly related to electron density changes at the surface. These surface fringes initially grow in amplitude (at 0.4 V) due to Li$^+$ surface accumulation that increases the change in surface electron density.$^{24}$ As seen in the subsequent reflectivity curves in figure 3.14a, the surface fringes rapidly diminish below 0.4 V as the surface roughens in response to lithiation. At the same time, the ML Bragg peaks from the starting 8.1-nm periodicity decrease in intensity and new Bragg peaks begin to appear, especially at lower $q$. As the potential is held at 0.01 V, Bragg peaks corresponding to a bilayer d-spacing of 26.7 nm grow in intensity as the layering becomes more coherent. In all cases, the reflectivity
data are modulated by a long period oscillatory background corresponding to the unlithiated Cr$_3$Si layers which remain 1.9 nm thick.

Figure 3.14: Selected reflectivity curves during (a) lithiation and (b) delithiation. Reflectivity has been scaled by $q^4$ to remove the sloping Fresnel background and offset for clarity. The average potential during each scan is labeled on the right side of the plot. Two intermediate conditions are highlighted in purple and orange during lithiation and delithiation. (c) Cyclic voltammogram taken during the measurement at 0.2 mV·s$^{-1}$. The sample was also held at 0.01 V for 4.5 hours. (d) Schematic highlighting the ML’s extreme height change during lithiation and delithiation.

Upon delithiation (figure 3.14b), the Bragg peak amplitude of the lithiated structure rapidly decreases in height and $d$-spacing, indicating contraction of the lattice with a variable
layer thickness. From 2-3 V, the reflectivity continues to exhibit very little structural order except for a broad oscillation (corresponding to the thickness of the unaffected Cr$_3$Si layers) and several low-$q$ ML peaks, indicating that the Si layers still lack a consistent $d$-spacing. After increasing the voltage above the open circuit condition to 3.5 V, sharper Bragg peaks immediately reappear near their original position with a spacing corresponding to a 9.3 nm thick bilayer with a surprisingly coherent layered structure.

The CV taken simultaneously with the reflectivity data, shown in figure 3.14c, has features characteristic of Si electrochemistry.\textsuperscript{47} Figure 3.14d depicts the overall expansion and contraction of the ML by 330\% at the extreme potentials. These results reveal a process, under potentiostatic conditions, in which individual layers delithiate at varying potentials, but that the vertical structure becomes laterally homogeneous once it is equilibrated at extreme potentials.

### 3.3.3.2 Structural Changes under Galvanostatic Conditions

Similar measurements taken at constant current (i.e., galvanostatic conditions) reveal a laterally heterogeneous lithiation process. Reflectivity curves taken in real-time at 60 $\mu$A·cm$^{-2}$ (corresponding to a two hour charge rate) are shown in figure 3.15a. These reflectivity data show a coexistence of Bragg peaks corresponding to both lithiated and unlithiated phases throughout the cycling. At the onset of lithiation (delithiation), the new set of Bragg peaks shift rapidly in $q$ indicating a fast, coherent expansion (contraction). Galvanostatic measurements were performed at 15 $\mu$A and held at 0.01 V and are shown in figure 3.15c.
Figure 3.15: (a) Data taken continuously during the discharge/charge is shown as a 2D density plot. Solid curves follow the path of the 3rd order Bragg peak during lithiation and delithiation; a dashed, gray line highlights the unlithiated 3rd order peak. (b) Selected curves from (a) are shown for comparison to the potentiostatic conditions shown in Figure 3.14. Curves are offset for clarity. Note the coexistence of unlithiated and lithiated phases in each case. (c) Galvanostatic measurements corresponding to figure 3.15a. Measurements were performed at 60 μA·cm$^{-2}$ and held at 0.01 V and 3.5 V to establish equilibrium.

### 3.3.4 Discussion

The differences in reflectivity between figure 3.14 and figure 3.15 suggest two distinct routes for lithiation and delithiation under potentiostatic and galvanostatic conditions. Under
controlled potential, the lack of diffraction peaks at intermediate lithiation or delithiation indicates a structure with varied Si layer thicknesses. Since layer thickness corresponds to the degree of lithiation, these incoherent intermediate structures indicate that Li is transported vertically through the ML. In contrast, the persistent diffraction peaks from partially lithiated and delithiated phases are clearly visible during intermediate conditions in figure 3.15, indicating that these layers expand and contract with uniform lattice spacing under galvanostatic conditions. The aforementioned heterogeneity under constant current suggests that defects separating the lithiated and unlithiated phases provide access to the ML’s edge-plane, leading to vertically uniform domains. This effect is most visible during delithiation in figure 3.15, i.e. following defect formation. These two scenarios are illustrated in figure 3.16.

![Figure 3.16](image)

**Figure 3.16**: Structural differences between potentiostatic and galvanostatic lithiation are illustrated in (a) and (b) respectively. The mechanism is based on the position and distribution of ML diffraction peaks during lithiation and delithiation. The color and height of the individual Si layers in the illustration indicates the degree of lithiation and arrows indicate the direction of Li transport.

To quantify changes in the ML structure upon lithiation, we analyze the Fourier transform of the Fresnel-normalized reflectivity. Essentially a 1D Patterson function, this
quantity is the autocorrelation function for the derivative of the electron density $\rho(z)$ within the kinematic limit for reflectivity. As discussed at length in appendix 2, 

$$\frac{R(q)}{R_F(q)} = \left| \int e^{-iqz} \frac{\partial \rho}{\partial z} dz \right|^2 \Rightarrow \langle \rho'(z)\rho'(z') \rangle = \left| \int e^{iqz} \frac{R(q)}{R_F(q)} dq \right|^2$$

For step-wise density profiles, this quantity directly reveals internal spacings in the ML structure. As depicted in figure 3.17a, the correlation associated with the thickness of an individual layer in a series of alternating layers is negative since it results from the product of a positive and negative change in density at its boundaries. Similarly, the bilayer thickness is indicated by a positive. In such a ML, these three peaks are repeated in the Patterson function and decay in intensity as a function of the overall coherency of the layer spacing.

Patterson functions for the five highlighted conditions in figure 3.14 are shown in figure 3.17b. In the starting case (the open circuit condition), the repeated three peak pattern can be attributed to the Cr$_3$Si, Si, and bilayer thicknesses of 19, 62, and 81 Å respectively. After potentiostatic lithiation, the bilayer consists of Cr$_3$Si, Li$_x$Si, and bilayer layers of 19, 248, and 267 Å thicknesses, respectively. The Si layers’ four-fold expansion is consistent with full lithiation to Li$_{4.4}$Si. The galvanostatic case is more complicated. Lithiation only consumes part of the sample, as Patterson features from the original structure persist. The amplitude of the peaks during lithiation and delithiation is also comparatively muted and decays faster, indicating vertical disorder. As discussed in appendix 2, the FWHM of the lithiated ML’s Bragg peaks also grows quadratically in $q$, indicating weak paracrystalline order.
Figure 3.17: (a) Example of Patterson function for a ML. From top to bottom: the electron density for the repeated bilayer, its derivative, and the autocorrelation function for the derivative. (b) Patterson functions for the initial, lithiated, and delithiated ML structures (3, 0.01, and 3.5 V respectively). The curves have been offset for clarity and the first three peaks are labeled according to the lower right key. The curves’ colors correspond to the conditions shown in figure 3.14. The galvanostatic correlation functions overlay the extreme conditions lithiation.

3.3.5 Extended Electrochemical Characterization

The high structural reversibility observed by XR when these Si-rich MLs undergo an overall 3.3-fold vertical expansion and contraction during lithiation suggests that this architecture bypasses the known mechanical instabilities of lithiated Si anodes. We evaluated the electrochemical stability of these MLs by lithiation/delithiation cycling in a half-cell battery (i.e. versus a Li metal counter electrode). For these tests, MLs were deposited on Cu foil and compared to thin Si films with the same overall Si thickness (figure 3.18a). Both the 100 nm-thick Si film and the 5/2x20 ML (5 nm Si on 2 nm Cr3Si repeated 20 times) initially
show stable 2000 mAh·g\(^{-1}\) capacity (cycled at 80 \(\mu\)A·cm\(^{-2}\)), although with a systematic loss of capacity between cycles 40-300. During this period, the Coulombic efficiency decreases to ~99.5%. While the thin film eventually loses nearly all of its lithiation capacity, the ML retains ~750 mAh·g\(^{-1}\) Si capacity with consistent charge/discharge density in this region.

Furthermore, at this applied current, the electrode has an extremely fast charging time of 700 s. Diffusion limitations appear to be limiting the capacity in this regime. When cycled at 4 \(\mu\)A·cm\(^{-2}\), a ML with the same d-spacing showed nearly the full theoretical capacity (~4000 mAh·g\(^{-1}\) Si). One of the most attractive features of the ML is that it has an extremely high Coulombic efficiency: 99.78\% over the whole cycle range and 99.89\% over the last 1000 cycles, well beyond efficiencies for most Si electrodes, particularly high surface-area 3D nanostructures.\(^\text{17}\) The efficiency is expected to be higher for thicker MLs structures that have smaller area-to-volume ratios and for MLs cycled at less extreme voltages.

We examined the diffusion limitations of the Si/Cr\(_3\)Si MLs by cycling four types of MLs grown on copper foil at variable rates (doubling the current between 10-320 \(\mu\)A/cm\(^2\)). The ML given in figure 3.18a (5/2x20) was compared to MLs containing thicker Si layers (10 nm, i.e. 10/2x20), thicker Cr\(_3\)Si layers (6 nm, i.e. 6/6x20), and a structure with a larger number of layers (35 layers, i.e. 5/2x35) (see figure 3.18b-c).
Figure 3.18: (a) Cycling data for a 5/2x20 ML compared to a thin film with same overall Si thickness (100 nm). Each sample was cycled at 80 μA/cm² between 3 and 0.01 V. (b,c) Rate studies measuring the capacity and charging time for MLs with varying layer thickness and number of layers. In each case, the naming convention corresponds to (Si thickness in nm)/(Cr₃Si thickness in nm)x(repetitions).
As seen in figure 3.18b-c, each ML shows a power law behavior associated with diffusion limitations of Li in the Si; that is, the capacity decreases linearly as the current is doubled in this regime. With the largest overall amount of Si, the 10/2x20 ML initially has the largest overall capacity since its current/mass ratio is the lowest of all the structures; however, this structure also shows irreversible losses as the structure is returned to slower cycling rates, in particular after cycle 40. In contrast, the 5 nm Si MLs show greater reversibility, even after charge times of only ~100 s at 320 μA·cm⁻². In fact, the 35 layer structure shows a capacity enhancement during the initial cycling and on the return to slower cycling, possible due to the creation of defects over time, as discussed above and in figure 3.16b. The average Coulombic efficiency over the 71 cycles shown was >99% in all cases.

3.3.6 Conclusions

These studies demonstrate that combining a highly Li-reactive material, such as Si, with thin metallic interlayers in a digitized vertical structure is a new route toward achieving the fast kinetics of nanoscale thin films with improved lifetimes and significantly higher capacities (i.e., thicker electrodes). In operando XR reveals that the layered structure remains intact despite a 3.3-fold vertical expansion and contraction during lithiation. Thus, it retains its 1D ‘meta-crystal’ structure, much like a layered intercalation material, but with amorphous components. We conclude that this ML architecture which combines the robust framework with a conversion material (each consisting of amorphous materials) is the key feature that constrains the Si to purely vertical expansion without delamination, thereby improving reversibility. This general architecture greatly expands the range of materials possible for intercalation in Li-ion batteries, including higher power conversion anodes, such as Ge,⁴⁸ or the higher voltage redox couples found in metal fluoride and sulfide cathodes.⁴⁹
3.4 References


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Chapter 4

Improving Electrodeposition of Mg through an Open Circuit Potential Hold


4.1 Introduction

Mg electrodeposition onto an anode surface and Mg ion intercalation into a cathode are the processes that drive Mg batteries.\textsuperscript{1,2} Mg batteries offer promise as an alternative electrical energy storage because of Mg's abundance in the earth's crust, low atomic weight, low cost, and advantageous electrochemical properties.\textsuperscript{1-3} Most Mg compounds are environmentally benign, non-toxic, and biodegradable.\textsuperscript{4} Mg batteries possess a higher theoretical volumetric capacity (3832 mA·h·cm\textsuperscript{-3}) than currently used Li-ion batteries (2062 mA·h·cm\textsuperscript{-3}).\textsuperscript{2,5,6} Additionally, Mg is less water-reactive than Na and Li, so large scale batteries could be simpler to engineer and present fewer safety concerns.\textsuperscript{2,4}

Many issues hinder the commercialization of Mg batteries. Developing a working system with a robust anode, cathode, and electrolyte has proven difficult with challenges in all three areas. The options for cathodes beyond low-voltage Mo\textsubscript{6}S\textsubscript{8} are limited due to the difficulty of Mg intercalation.\textsuperscript{7,8,9} Electrolyte choice is limited due to the limited stability of Mg to a narrow potential window and its insolubility in many common solvents.\textsuperscript{4} Finally, development of a Mg metal anode that possesses high efficiency of plating/stripping is challenging.\textsuperscript{1,2}
The carbonate-based solvents used in commercial Li-ion batteries do not support Mg deposition and stripping due to the growth of passivation layers on the anode surface.\textsuperscript{10,11} Grignard reagents in ethers were the first class of electrolytes discovered to facilitate reversible Mg deposition and stripping,\textsuperscript{12} but due to the reactive nature of these organomagnesium electrolytes, their anodic stability is limited to \(~1\) V.\textsuperscript{13,14} Aurbach and coworkers improved the stability of Grignard-based electrolytes by modulating their reactivity with Al species, resulting in organohaloaluminates, which in some cases possess anodic stability of \(~3\) V with good Coulombic efficiencies.\textsuperscript{15,16} More recently, electrolytes containing inorganic chloride salts in ethers have also been explored.\textsuperscript{17-19} Other studies based on Mg alkoxides, Mg bis-(trifluoromethanesulfonylimide), or carboranes suggest that these electrolytes may be promising.\textsuperscript{20-24}

Despite this progress, the conditions for low overpotential, high rate Mg electrodeposition remain unknown. Mg exhibits a deposition overpotential of ca. 200 mV and a 270 mV·decade\textsuperscript{-1} Tafel slope.\textsuperscript{25} By way of contrast, Ag – the best electrodeposition system – exhibits overpotentials of approximately 2 mV and a strict 120 mV Tafel slope expected for facile electrodeposition.\textsuperscript{26} For electrodeposition of Cu, it has long been known that additives such as Cl\textsuperscript{-} can enhance electrodeposition.\textsuperscript{27} No such deposition enhancer, however, is yet known to improve Mg deposition. Previous studies have suggested that passivation layers containing MgO and products of solvent decomposition develop on the electrode surface in a variety of Mg electrolytes.\textsuperscript{28-31} In situ x-ray absorption spectroscopy has revealed intermediate species of Mg electrodeposition at potentials lower than the deposition potential.\textsuperscript{30}

The central focus of this manuscript is to begin to establish a fundamental understanding of the processes that occur at the electrode surface during Mg deposition and stripping with the
long-term goal of enabling Mg deposition at the anode of a Mg-based battery. In situ synchrotron x-ray diffraction is used in this manuscript to observe Mg electrodeposition at the electrode/electrolyte interface of a model anode. The evolution of Mg coverage and texture as observed by bulk Mg x-ray diffraction during electrodeposition and stripping on Pt is measured with two different electrolytes. x-ray measurements are complemented by additional electrochemical testing, ex situ scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). The results demonstrate that Mg electrodeposition is facilitated by an open circuit pause, which leads to the formation of a Mg-Cl-containing ‘enhancement layer.’

4.2 Summary
We used in situ x-ray diffraction, XPS, SEM and electrochemical methods to interrogate the mechanism of Mg electrodeposition from PhMgCl/AlCl₃ (APC) and EtMgCl electrolytes. An open circuit potential (OCP) pause following Mg deposition led to retained enhancement of Mg deposition and stripping kinetics along with lowered overpotentials for both. In situ x-ray diffraction demonstrated that the OCP pause led to a more polycrystalline deposit relative to that without the pause, while SEM presented micrographs that showed smaller deposits with an OCP hold. The improvement is attributed to an ‘enhancement layer’ that formed on the electrode during the OCP hold. Analysis of XPS data suggests that the ‘enhancement layer’ consists of Mg and Cl retained on the electrode surface, possibly following electrode depassivation.

4.3 Experimental
Chemicals were obtained from Sigma Aldrich unless otherwise specified. Electrolytes were prepared in an Ar-filled glove box, which contained < 4 ppm of O₂ and < 2 ppm of H₂O.
Glassware was flame-dried with a Bunsen burner before introduction into the glove box. THF was distilled over Na and benzophenone under Ar before use. Diglyme was dried over molecular sieves (3 Å) for at least 24 hrs before use. The “all phenyl complex” (APC) was synthesized from PhMgCl and AlCl₃ in THF according to a literature procedure at an Al concentration of 400 mM. EtMgCl in diglyme was synthesized starting from EtMgCl in THF. The THF was subsequently removed by evaporation, and the electrolyte was redissolved in diglyme to give a concentration of 200 mM. EtMgBr, a more common electrolyte, was unstable in the x-ray beam.

Potentiostatic electrochemical measurements were performed using a CH Instruments Electrochemical Workstation (Model 760D, Austin, TX) or Biologic potentiostat (Model SP-150, France) and a three-electrode cell under an Ar atmosphere. Pt working electrodes were fabricated from Pyrex glass slides modified on one side by DC magnetron sputter deposition of 20 nm Ti followed by 200 nm Pt.

Mg metal was used for the counter and reference electrodes (GalliumSource, LLC). All potentials are reported with respect to Mg/Mg²⁺. The surface morphology of the electrodes was analyzed using SEM (JEOL, JSM-7000F). The surface composition of the electrodes was analyzed using XPS (Kratos Axis ULTRA). Electrochemistry for SEM and XPS measurements was performed using electrochemical cells that were assembled in the glove box, sealed prior to use, and contained ~1.5 mL of electrolyte and ~0.5 cm³ of head space. For initial electrochemical experiments with APC, samples were cycled between -1 V and 2 V. For initial electrochemical experiments with EtMgCl, samples were cycled between -1 V and 1.2 V. For all further experiments with APC (EtMgCl), one full deposition and stripping sweep were performed (open circuit potential (OCP, ca. 0.8 V) from -1 V to 2 (1.2) V), followed by a deposition sweep and
then a pause at OCP. The samples were then cycled by repeating a linear sweep voltammogram (LSV) from -1 V to 2 (1.2), a 10 min potential hold at 2 (1.2) V, a LSV from 2 (1.2) V to -1 V, and a 10 min potential hold at -1 V. The potential holds were necessary to obtain enough material to see changes in the relative concentrations of Mg on the electrode surface with the x-ray measurements. Pauses at OCP were 0 min, 1 min, or 1 hr for the electrochemical measurements and SEM. Pauses were either 0 mins or 5 mins for the x-ray measurements. For cyclic voltammograms (CVs), Coulombic efficiencies were calculated by dividing the integrated anodic current by the integrated cathodic current.

X-ray measurements were conducted in a spectroelectrochemical cell using a “transmission-geometry” previously described. In situ x-ray diffraction measurements were performed at 20 keV (λ = 0.062 nm) at sector 33BM at the Advanced Photon Source. The x-ray beam illuminated a 2 × 3 mm area on the sample with an incident angle of 7.15°, with a vertical scattering geometry, and with the detector centered at 2θ = 14.3°. Data was collected continuously for 30 s exposures for EtMgCl samples, while data was collected for 10 s exposures every 10 mins for APC samples to avoid electrolyte degradation. An area detector (Pilatus 100k) was used, allowing for a 34°-wide sector of the powder rings to be observed.

4.4 Results

4.4.1 Mg Electrodeposition using APC in THF

Figure 4.1 shows the cyclic voltammogram obtained from a Pt working electrode in a solution consisting of 400 mM APC in THF. The voltammogram displays reductive current associated with Mg deposition commencing at ca. -200 mV vs. Mg/Mg

2+ and oxidative current associated with Mg stripping. As previously reported by Aurbach and coworkers, the APC in
THF electrolyte possesses a Coulombic efficiency of ~100% and an electrochemical window greater than 3 V.

Figure 4.1: Cyclic voltammogram of the first cycle of APC in THF on a Pt working electrode at a scan rate of 10 mV·s⁻¹.

Figure 4.2a shows a sample potential program for the experiments in APC in THF. The top graph shows the program for the no-pause condition while the lower graph shows an example of a 5 min pause condition. During the pause, the circuit is opened. Some variation from the initial 1 V OCP will occur during the pause, depending on the length of the pause and the applied potential just prior. Figure 4.2b-c shows LSVs obtained for deposition (figure 4.2b) and stripping (figure 4.2c) between 2 V and -1 V during the second cycle following the potential pauses at OCP for each condition tested (0 min pause, 1 min pause, 1 hr pause, and a fresh electrode). Figure 4.2b shows a decrease in deposition overpotential (250 mV to 160 mV) occurs with the increase in pause time. Similarly, figure 4.2c shows that Mg stripping becomes more facile with an increase in pause time. The corresponding Tafel slope changes from
Figure 4.2: (a) Sample potential programs with and without a pause. Linear sweep voltammograms during (b) deposition and (c) stripping after no pause, a 1 min pause, a 1 hr pause and for a fresh electrode in APC in THF, showing differences in deposition overpotentials. (d) Stripping sweep for no-pause and 1 hr pause conditions for 1<sup>st</sup> cycle and 40<sup>th</sup> cycle following the pause.

77 mV·dec<sup>-1</sup> for the no-pause condition to 58 mV·dec<sup>-1</sup> following a 1 hr pause. The more facile deposition and stripping following a 1 hr pause relative to the no-pause condition suggests the presence of structural or compositional changes in the Mg deposit.
To evaluate the origin of this behavior (e.g., electrode vs. electrolyte), we replaced the electrode utilized after a 1 hr pause with a fresh electrode. Figure 4.2b-c shows that this fresh electrode showed deposition and stripping behavior similar to that found with the no-pause condition. This result suggests that the electrode itself is affected by the pause. Figure 4.2d shows the stripping sweep on the first cycle and the 40th cycle. The figure shows that while the deposition and stripping exhibits improved Tafel slopes following 40 cycles for both the pause (58 mV·dec\(^{-1}\) on cycle 1 to 47 mV·dec\(^{-1}\) on cycle 40) and no-pause conditions (77 mV·dec\(^{-1}\) on cycle 1 to 59 mV·dec\(^{-1}\) on cycle 40), the enhancement from the pause at OCP still provides improved electrochemistry over the no-pause condition. This enhancement even after 40 cycles following the pause suggests that the change to the electrode surface exhibits some permanence.

Table 4.1 reports deposition overpotentials, exchange current densities, and Tafel slopes for Mg stripping and deposition for each of the pause conditions examined obtained for the second cycle following the OCP hold. The table shows that with a pause, the overpotential for deposition decreases, the exchange current density increases, and the Coulombic efficiency increases. Interestingly, while the Coulombic efficiency for the APC using triangle wave voltammetry (figure 4.1) approaches 100%, such is not the case when using either voltage program shown in figure 4.2a. Rather, the efficiency is substantially lower as has been found previously.\(^{15}\)
Table 4.1: Deposition overpotentials, exchange current densities, and Tafel slopes for Mg stripping and deposition for each of the pause conditions examined.

<table>
<thead>
<tr>
<th></th>
<th>Deposition Overpotentials (mV)</th>
<th>Tafel Slope (mV·decade(^{-1}))</th>
<th>Exchange current density (mA·cm(^{-2}))</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deposit</td>
<td>Strip</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APC</td>
<td>No pause</td>
<td>250</td>
<td>109</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>210</td>
<td>107</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
<td>160</td>
<td>83</td>
<td>58</td>
</tr>
<tr>
<td>EtMgCl</td>
<td>No pause</td>
<td>362</td>
<td>136</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
<td>329</td>
<td>87</td>
<td>61</td>
</tr>
</tbody>
</table>

Figure 4.3a shows the x-ray diffractogram obtained at a potential of -1 V after 3 cycles of deposition and stripping of Mg with the no-pause condition. At -1 V, Mg is present on the electrode surface, and from the Coulometry, we estimate the deposit has an equivalent thickness of ca. 290 nm. The diffractogram shows features associated with reflections from the 100, 002, and 101 orientations of Mg. Interestingly, the disproportionately intense 002 reflection suggests the presence of oriented growth in this direction. The inset to figure 4.3a shows that the 002 powder ring is strongly peaked at the specular condition, indicating that the growth is highly textured along the c-lattice direction, but also with a non-textured deposit leading to the diffuse ring.
Figure 4.3: X-ray diffractograms (linear scale) after Mg deposition with (a) no pause and (b) a 5 min pause in APC in THF. The insets show the view of the image detector with approximately 34 degrees of the powder rings visible. (c) Representations of the Bragg diffraction planes of interest in the HCP Mg crystal structure. Miller indices are indicated as well as the representation of the atoms on the plane.

For reference, figure 4.3c shows representations of the (002), (100), and (101) reflection planes of an HCP (hexagonal close packed) crystal structure. Below each is a schematic of the atoms on the planes. The (002) plane is a close packed plane while the (100) and (101) planes are not close packed. Figure 4.3b shows the x-ray diffractogram obtained at -1 V after three cycles with the 5 min pause condition. The diffractogram again shows the 100, 002, and 101
peaks, but with an integrated intensity ratio of 1.02:1.00:2.03, consistent with the 1:1:2 ratio expected from a polycrystalline deposit. By way of contrast in figure 4.3a only ca. 21% of the integrated intensity of the 002 reflection is due to the small amount of polycrystalline deposits while the remaining 79% of the integrated intensity is due to the oriented deposits. Thus, a pause in electrochemical cycling at OCP changes the habit of Mg electrodeposition from one exhibiting more textured, oriented growth of large crystallites (and less polycrystalline character) to one where the Mg deposit is finer-grained and more polycrystalline.

Figure 4.4a shows the relative integrated intensity obtained from the 34 degrees of powder ring diffraction for each reflection as a function of time alongside the integration of the current over time as the electrochemical cycling occurs for the no-pause condition. APC is a light-sensitive electrolyte, thus, we obtain a 30 s exposure following which the x-rays were blocked with a shutter for 10 min to minimize any x-ray perturbation to the electrolyte. Figure 4.4a shows there is a good correlation between increase in x-ray intensity and charge on deposition. Yet this correlation is not maintained during stripping, with the x-ray intensity decrease lagging behind the charge. This lag in the decrease of the x-ray intensity is particularly noticeable for the 002 reflection.

We also evaluated the ratio of deposition and stripping integrated intensity for the 002 reflection and find that this ratio is 2.2 for the second cycle. The corresponding ratio of charge for deposition and stripping for the same cycle is 2.0. The difference between these values demonstrates a dissonance in the relationship between the x-ray scattering intensity and the volume of Mg on the surface or indicates that there may be additional side reactions occurring.
Figure 4.4 shows the relative integrated intensity obtained from the diffraction for each reflection as a function of time alongside the integration of the current over time as the electrochemical cycling occurs for the 5 min pause condition. The figure shows that the increase and decrease in Mg diffraction intensity match well with the charge for both deposition and stripping. We evaluated the ratio of deposition and stripping intensity for the 101 reflection and find that this ratio is 2.0 for the second cycle. By way of comparison, the corresponding ratio of charge for deposition and stripping for the same cycle is also 2.0. The close correspondence of these numbers suggests that the charge utilized for deposition and stripping is expressed fully in plating and stripping Mg from the electrode. However, the increase in x-ray intensity with cycle number suggests that Mg is retained on the working electrode following each stripping cycle, a conclusion that is supported by the observed 51% Coulombic efficiency.

To further probe the effect of a cycle pause on the Mg deposit, we obtained SEM images of the working electrode following the different deposition conditions. Figure 4.5a is an image of the electrode with the no-pause condition obtained after five deposition and stripping cycles.
followed by a deposition. The electrode was emersed in the glove box and rinsed with THF prior to SEM imaging. This image shows a few large agglomerated deposits, possibly associated with the oriented and textured material seen in the x-ray data. Figure 4.5b is an image of the electrode with the 1 min pause condition following 5 cycles, Mg deposition, emersion, and rinsing. This image shows more and smaller deposits than seen in figure 4.5a. Finally, figure 4.5c is an image of the electrode with the 1 hr pause condition following 5 cycles, Mg deposition, emersion, and rinsing. This image shows even smaller and more dispersed deposits on the surface of the electrode. We associate these smaller, dispersed deposits with the polycrystalline deposition observed directly in the x-ray data.

*Figure 4.5: SEM images of the electrodes after 5 cycles and rinsing for (a) no pause, (b) 1 min pause, and (c) 1 hr pause conditions in APC in THF.*

There are a number of mechanisms that enhance deposition as a consequence of an OCP hold state being inserted into the potential cycling program for the Mg electrode. The impact is postulated to be due to an ‘enhancement layer’ and the question thus naturally follows as to whether this in turn is underpinned mechanistically via attributes that are either structural or
compositional in character. The SEM and x-ray data discussed above clearly establish that differences in structure are correlated with the experimentally observed improvement in deposition and stripping. The question of compositional correlations are ones we further investigated, examining the surface compositions of electrodes that were cycled 5 times, rinsed, and analyzed with XPS under either the pause (1 hr) or no-pause conditions. Additionally, we examined a control electrode which was exposed to the electrolyte for the same amount of time without electrochemical cycling. The XPS spectra obtained for Mg, Al, O, C, and Cl are shown in figure 4.6.

The integrated peaks from the XPS in figure 4.6 were normalized to the integrated intensity of the Mg peak and the ratios were compared for each element analyzed (table 4.2).\textsuperscript{35} For Al, O, and C, the ratios were similar for both the paused and no-pause samples indicating that the relative amount of Al, O, and C does not change between samples. In contrast, the Cl:Mg ratio for the paused sample is 23% larger than that found for the no-pause condition. This difference between the no-pause and pause conditions for Cl demonstrates that there is much more Cl on the surface relative to the Mg with the pause condition, suggesting that the Cl may be a major component of the ‘enhancement layer’ that forms on the electrode when paused at OCP.
Figure 4.6: XPS spectra for a no pause sample and a 1 hr pause sample, zoomed in on peaks for (a) Mg, (b) Al, (c) O, (d) C, and (e) Cl.
Table 4.2: Ratio of integrated peak areas of each element relative to the Mg peak area from XPS of emersed electrode surfaces.

<table>
<thead>
<tr>
<th></th>
<th>No pause</th>
<th>Pause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.7 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>O</td>
<td>200 ± 3</td>
<td>204 ± 5</td>
</tr>
<tr>
<td>C</td>
<td>2.8 ±0.2</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>Cl</td>
<td>6.6 ± 0.3</td>
<td>8.1 ± 0.4</td>
</tr>
</tbody>
</table>

4.4.2 Mg Electrodeposition using EtMgCl in Diglyme

To evaluate the possibly salubrious effect of an open circuit potential hold on a related Mg deposition system, we examined EtMgCl in diglyme. Figure 4.7a shows the cyclic voltammogram obtained from a Pt working electrode in a solution consisting of 200 mM EtMgCl in diglyme. The figure shows reductive current associated with Mg deposition commencing at ca. -300 mV vs. Mg/Mg$^{2+}$ and oxidative current associated with Mg stripping. The substantial overpotentials for both deposition and stripping are similar to those seen in other Grignard-based electrolytes, such as EtMgBr. The voltammograms evolve slightly with cycle number, with minimal change in deposition or stripping overpotential.

Figure 4.7b shows the Coulombic efficiency for the Mg deposition and stripping process. The Coulombic efficiency evolves with cycle, attaining a value of about 54% from cycles 70-150, consistent with the 50% value found for EtMgCl in THF. As with the APC electrolyte described above, the Tafel slope for Mg stripping changes from 98 mV·dec$^{-1}$ for no-pause to 61 mV·dec$^{-1}$ following a 1 hr pause (table 4.1).
Figure 4.7: (a) Cyclic voltammograms of EtMgCl in diglyme at cycle 2, 10, and 100 and (b) the Coulombic efficiencies of the first 150 cycles.

Figure 4.7b shows the Coulombic efficiency for the Mg deposition and stripping process. The Coulombic efficiency evolves with cycle, attaining a value of about 54% from cycles 70-150, consistent with the 50% value found for EtMgCl in THF. As with the APC electrolyte described above, the Tafel slope for Mg stripping changes from 98 mV·dec⁻¹ for no-pause to 61 mV·dec⁻¹ following a 1 hr pause (table 4.1).

Figure 4.8a shows the relative integrated intensity for each reflection obtained over the 34 degrees of powder ring accessible during the measurement along with the charge passed as a function of time for the no-pause condition. The figure shows that the 002 reflection is most intense, particularly following the second cycle at 6500 s. The increased intensity of the 002 reflection relative to 100 and 101 again suggests oriented and textured deposition of Mg on the electrode surface. Figure 4.8a also shows that while the increase in x-ray intensity follows the charge during deposition, the decrease (during stripping), is more prolonged relative to the charge, a result also seen in figure 4.4 for experiments in APC. The ratio of deposition to stripping x-ray intensity for the second cycle is 3.6 while the corresponding charge ratio is 3.0.
The increased Mg intensity following a deposition and stripping cycle again demonstrates retention of Mg on the electrode.

Figure 4.8: Charge passed and the integrated intensities of each powder ring over 3 cycles in EtMgCl for (a) no-pause and (b) a 5 min pause condition.

Figure 4.8b shows the integrated powder ring for each reflection alongside the integration of the current over time as the electrochemical cycling occurs for the condition with a 5 min pause. Similar to the results obtained from the APC electrolyte in figure 4.4b, the increases and decreases in intensity of the Mg diffraction match very well with the charge passed. This correspondence is seen in the ratio of deposition to stripping x-ray intensity, which is 2.2 for the second cycle and the corresponding charge ratio is 2.3. Similarly, polycrystalline powder rings were seen for the paused condition.

Figure 4.9 shows SEM images of electrodes obtained after 5 stripping and deposition cycles in the EtMgCl electrolyte followed by Mg deposition, emersion, and rinsing with diglyme. Figure 4.9a-c are images of the electrodes obtained with a) the no-pause condition, b) the 1 min pause, and c) the 1 hr pause. These images, similar to those obtained from the APC electrolyte
in figure 4.5, show fewer large deposits for the no-pause condition and more and smaller deposits for the paused conditions. This result is consistent with the x-ray results showing more polycrystalline behavior with the pause conditions, but fewer and larger deposits with the textured and oriented growth for the no-pause condition.

Figure 4.9: SEM images of the electrodes after 5 cycles in EtMgCl and rinsing for (a) no-pause, (b) 1 min pause, and (c) 1 hr pause conditions.

Taken together, the data show that the potential program, and most importantly the passage of the Mg electrode through an OCP rest state, leads to marked and facilitating impacts on the electrochemical reaction dynamics. These effects are ones seen in representative classes of the electrolyte systems currently known to sustain efficient and reversible deposition of this divalent metal. In the section that follows, we explore features of the mechanisms that must be operating in consequence here.
4.5 Discussion

We use electrochemistry and x-ray diffraction to examine the effect of specific voltage profiles on the efficacy of Mg deposition and stripping in two different electrolytes. There are two major outcomes from this work.

First, deposition following a pause at OCP gives rise to more facile Mg stripping and deposition behavior. In both electrolytes the exchange current densities change by at least 30 % and the Tafel slopes change by at least 25 %. The Coulombic efficiency increases by 11 % and 18 % with a 1 hr pause for APC and EtMgCl, respectively. Replacing the Pt working electrode with a new one following an OCP hold removed the electrochemical benefit observed. This behavior suggests that some change has occurred on the electrode surface. The above suggests that holding the electrode at OCP leads to an altered surface which enhances both the stripping and deposition of Mg.

Second, deposition following a pause at OCP gives rise to a deposit without any preferential orientation along the surface normal as seen with x-ray diffraction. This behavior is maintained over at least three cycles. Perhaps it is the polycrystalline deposit that lends to more facile deposition and stripping. We suggest that the polycrystalline deposit is due to an ‘enhancement layer’ that forms during the pause at OCP, while a more oriented growth occurs without a pause (and presumably without an ‘enhancement layer’).

We next ask: what does this ‘enhancing deposit’ actually consist of and do other features of mesoscopic structure play a putative role within the chemistry seen? Some insight comes from the x-ray diffraction, which demonstrates that Mg is retained on the electrode surface following stripping. We suggest that this retained Mg is the foundation of the deposition and stripping enhancements seen, albeit possibly via mechanisms that are quite complex.
Furthermore, the XPS obtained from emersed samples shows that the paused samples exhibit higher Cl on the surface relative to those that were not paused. This suggests that the ‘enhancing deposit’ consists of Mg and Cl.

We now consider how the ‘enhancing deposit’ might actually increase deposition and stripping rates relative to surfaces without this material. There are two possibilities. First, the ‘enhancing deposit’ might facilitate electron transfer to solution species. Indeed, previous literature shows that Cl on the surface does in fact enhance the electrodeposition of other metals including Cu and Co.\textsuperscript{27,36} In these cases, the Cl-decorated surface is maintained with exposure to Cl-containing solution, possibly similar to what is happening with Mg. An important point to note is that the enhancing effects seen here are ones impacting both the deposition and stripping phases of the electrochemical dynamics. This strongly suggests other aspects of mechanism might also merit consideration. As a second mechanism of operation, the Mg-Cl ‘enhancing deposit’ may actually serve to depassivate the Mg electrode surface in some manner, where it is well known that refractory MgO overlayers formed as passive films can strongly inhibit both electron transfer and metal dissolution processes.\textsuperscript{28} However this might be, we note that the Mg:O ratio from both the pause and no-pause surface are the same within 1%. Perhaps most important here is the varying impacts seen on nucleation in the pause and no-pause potential programs. The weight of the data on this suggests that prolonged exposure of the Mg surface to Cl is necessary to form the facilitating features associated with the Mg-Cl overlayer. An intriguing microstructural model seems to capture most (even all) of the features of the electrochemical/structural dynamics that the current data reveal.

It is now well established that Mg is strongly susceptible to pitting-based corrosion in the presence of halides\textsuperscript{37} and that these sensitivities are also strongly retained in the electrochemical
deposition/stripping of this metal.\textsuperscript{38} In the present case we believe the OCP hold state may render the substrate sensitive to mixed corrosion that leads to localized failures of an otherwise passive surface film. These dispersed/nascent pits might be expected to lead to very efficient nucleation for Mg deposition and subsequent stripping on return to conditions of potential control. A mechanism of this sort, one involving local perturbations of the structure of a passive film, seem to rationalize the dispersed fine scale structures that are seen in the microscopy and account as well for the retention of the Mg with structure and dispersion of grain structure indicated by the diffraction data.

4.6 Conclusions

Electrochemistry and x-ray diffraction demonstrate the effect of a pause at OCP during cycling on the efficiency of Mg deposition and stripping in two different electrolytes. In both electrolytes, deposition following a pause at OCP gives rise to more facile Mg stripping and deposition behavior. The Coulombic efficiency increases 11\% and 18\% with a 1 hr pause for APC and EtMgCl, respectively. The results herein suggest that holding the electrode at OCP leads to deposition of some material – containing both Mg and Cl – onto the electrode which enhances both the stripping and deposition of Mg. This deposition may be facilitated by pitting of the surface during the OCP hold. X-ray diffraction shows that Mg is retained on the electrode surface following stripping. We suggest that the retained Mg, and local structural/compositional features within it, forms the basis of the ‘enhancement layer’ which lends to more facile deposition and stripping. Additionally, Mg electrodeposition on the ‘enhancement layer’ following a pause at OCP shows a more polycrystalline deposit with x-ray diffraction. The nucleation of a polycrystalline deposit may be the basis of the more facile deposition and
stripping. Without the presence of the ‘enhancement layer,’ oriented growth of Mg is seen. Based on these results, a simple pause at OCP during initial cycling could improve the stripping and deposition of Mg batteries using Cl-based electrolytes.

4.7 References


Appendix A

Electrochemical Cells

A.1 Beaker cells

Most electrochemical testing took place in a two electrode or three electrode cell. The three electrode cell has a working electrode, counter electrode, and reference electrode. In a two electrode cell, the counter electrode acts as both the counter and reference electrodes. The electrodes of a beaker cell are immersed in an electrolyte in a beaker with some physical distance between the electrodes (see figure A.1). If the materials are air-sensitive as they are in Li-ion and Mg-ion, these cells must be tested in an inert environment — a glove box or glove bag.

![Figure A.1: Illustration of a beaker cell set up.](image)

A.2 Coin cells

In a coin cell (standard are 2032 cells), the cell materials are layered closely together and sealed with an O-ring between two metal casings (see figure A.2) so that an inert environment is maintained inside the cell even if it is brought into the atmosphere. Because the electrodes are closely layered, a separator is needed between the electrodes to keep them from shorting. This
separator is an ion-permeable polymer that is soaked in electrolyte to facilitate ion transport between the electrodes. Coin cells are industry standards for testing electrochemical performance of battery systems.

![Diagram of materials layered in a 2032 coin cell](image)

*Figure A.2: Illustration of the materials layered in a 2032 coin cell.*

### A.3 Modified beaker cells

Modified beaker cells were designed for ease of use and to reduce electrolyte consumption. Because a modified two electrode cell was commonly used in our electrochemical testing, the modified beaker cells were designed for a two electrode system. This cell was additionally designed to present a specific area of a planar working electrode for easy current density calculations. The dimensions of the cell were chosen to make use in a glove box simple and yet minimize the volume of electrolyte (see figure A.3a). In this cell, a working electrode is pressed to the bottom of the cell onto an O-ring (size 009). A wire is placed either front side or back side (depending on the conductivity of the working electrode substrate) and to the side of the O-ring to allow for complete sealing of the electrode with the O-ring. The working electrode
is held in place by anchoring two steel plates (the bottom one wrapped in Teflon tape to prevent short circuiting) around the base of the cell (see figure A.3b). A counter/reference electrode may then be lowered in from the top of the cell. The cell uses a total of approximately 2-3 mL for each experiment.

Figure A.3: Illustration of (a) the modified beaker cell with dimensions, (b) the cell assembled with the steel plates holding the working electrode in place, and (c) the cross section of the modified beaker cell.
A.4 Spectroelectrochemical cells

*Figure A.4: (a) Fully assembled transmission cell and (b) exploded view of cell with each part labeled A-M. Parts are described in text.*

This cell is referred to as a ‘transmission-geometry’ cell because the x-rays pass through the circular opening in the cell. The sample is fully immersed in the electrolyte, in analogy with a traditional beaker electrochemical cell. At the working energy of 20 keV, the 3.5 mm path length leads to 20% x-ray absorption. The solution also increases the amount of background scatter, which was subtracted by the specular rod peak in each image acquired by the area detector. The individual parts, as labeled in figure A.4 are: (a) kel-f cell body; (b) Al goniometer adaptor; (c) kel-f working electrode clamp; (d) stainless steel working electrode plungers; (e) kel-f plunger shells; (f) 20-30 kfm O-ring (PSI); (g) 0.024 in. OD stainless steel compression
(h) 10x3x1 mm sample; (i) kel-f sample holder; (j) 2-56 stainless steel set screw for sample height adjustment; (k) Al2O3-coated 75 μm Kapton window (the coating prevents air/water permeation through the kapton); (l) Teflon flange; (m) kel-f window clamp. The fluid inlet and outlet (syringe, stopcock and Teflon tubing) are attached via PVDF compression fittings on the cell body’s NPT fittings. The counter/reference electrode may be a piece of Li foil crimped to a Cu wire and laid above the sample or Mg foil folded through a glass capillary, supported on the outside with Cu wire and held in place with Torr Seal. Other electrodes may be used by supporting a wire with epoxy to glass tubing and attached using a compression fitting. The other NPT fittings are capped, but could be used for additional electrodes or a bubbler. The working electrode has a primary O-ring seal at the sample using a custom miniature O-ring and secondary O-ring seals at the working clamp. We found that the working electrode seal is particularly important for samples with low conductivity and nanoscale thicknesses (these x-ray samples grown on sapphire had a surface resistivity of up to 1 kΩ) since leakage currents can become comparable to redox processes. In this case, IR losses appeared to be minimal.

All kel-f and Teflon parts in contact with the electrolyte were soaked overnight in concentrated (97%) sulfuric acid and nochromix and then rinsed repeatedly with DI water until the pH of the effluent was above 6.5. The remaining parts were sonicated in methanol and rinsed with DI water and dried in a vacuum furnace for at least 12 hours. This cell uses a total of approximately 3-4 mL for each experiment.
Appendix B

X-ray Reflectivity

B.1 Principles of x-ray scattering techniques

X-ray diffraction was discovered in 1913 by the William Henry and William Lawrence Bragg. They measured the x-rays being diffracted off a surface at different angles to determine the spacing between layers of atoms (see figure B.1).¹

![Figure B.1: Diagram showing two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms. The lower beam traverses an extra length of 2dsinθ.](image)

The d-spacing may be computed with Bragg’s law:

\[ 2d \sin(\theta) = n\lambda \]  

(B.1)

Using Bragg’s law, a large \( \theta \) would correspond to a small \( d \)-spacing and a smaller \( \theta \) would correspond to a larger \( d \)-spacing. Similar to x-ray diffraction, x-ray reflectivity measures
the x-rays being reflected (or diffracted) of a sharp interface (or surface) at different angles. X-ray reflectivity uses low angles and thus measures larger $d$-spacings, on the order of nanometers, measuring thicknesses of thin films (see figure B.2).

![Diagram](image)

**Figure B.2:** Comparison of (a) x-ray diffraction at higher angles and (b) x-ray reflectivity at lower angles.

Because the $d$-spacing is greater (compared to x-ray diffraction) and the x-rays are travelling through more material, the refractive index of the new material will play a role in the reflectivity. The refractive index of a material depends on the frequency of the light (i.e., blue light is refracted more than red light). For x-rays, most materials have a refractive index, $n$, that is less than one. Because of this, a total reflectance is possible at small incident angles where the photons will not penetrate the material, but will rather all be reflected off (see figure B.3).\(^1\)
At each interface, a portion of the x-rays will be reflected back to the surface and a portion will be absorbed into the next layer. Those reflected back to the surface will be combined with the reflected x-rays and will either constructively or deconstructively interfere, causing changes in the overall intensity which can be measured. During x-ray reflectivity, it is that intensity that is measured to analyze the structure of the films.

B.2 X-ray reflectivity equations and examples

The equation depicting x-ray reflectivity of a smooth thin film is:

\[ R = -i \frac{\lambda \rho r_0 d}{\sin(\alpha)} \]  

\[ (B.2) \]
where $\lambda$ is the wavelength of the incident x-rays, $\rho$ is the electron density, $r_0$ is the scattering length for each electron, $d$ is the thickness of the film, and $\alpha$ is the incident angle. From this, it is clear that the reflectivity is directly proportional to the electron density of the material and the thickness of the film. The distance between two peaks, $\Delta$ is equal to $2\pi/d$. See figures B.4 and B.5 for examples of these relationships.¹

---

**Figure B.4:** A sample x-ray reflectivity for (a) bulk Si and (b) combined bulk Si and a 30 nm thin film of Si on a sapphire substrate. The distance between peaks is $\Delta Q=0.021$ Å⁻¹. The film thickness is $d = 2\pi/\Delta Q = 2\pi/0.021$ Å⁻¹ = 300 Å⁻¹ = 30 nm.
Figure B.5: A sample x-ray reflectivity for (a) varying Si thicknesses and (b) varying film materials. The film thicknesses are (red) $d_{\text{red}} = 2\pi/\Delta Q = 2\pi/0.021 \text{ Å}^{-1} = 300 \text{ Å} = 30 \text{ nm}$ and (blue) $d_{\text{blue}} = 2\pi/\Delta Q = 2\pi/0.063 \text{ Å}^{-1} = 100 \text{ Å} = 10 \text{ nm}$.

When there is more than one film, the effect of the reflectivity of different interfaces may be added together.\(^1\)

When a bilayer or multilayer is being considered, the difference in the electron density between the materials at the interfaces becomes important. The difference must be significant enough compared to the difference at another interface so that neither interface overcomes the amplitude of the peaks, hiding the interface with the smaller difference.\(^1\)

Additionally, the roughness of the surface should be considered. A rougher surface can make the peaks less crisp and easy to identify. Thus a surface must be sufficiently smooth to obtain reasonable signal to noise.\(^1\)
Figure B.6: A Si Cr multilayer (shown in a) showing the various interfaces and the corresponding x-ray reflectivity data (b). Colors match the different interfaces with the matching fringes.
B.3 Patterson function derivation

B.3.1 Patterson function formalism

While reflectivity can be calculated exactly for a discrete number of layers, it can also be evaluated for a continuously varying electron density. In the kinematic regime (e.g. away from total reflection), this relationship is,

\[ \frac{R(q)}{R_F(q)} = \left| \int \frac{d\rho}{dz} e^{iqlz} dz \right|^2 \]  \hspace{1cm} (B.3)

where \( \rho \) is the electron density. In the manuscript, we make use of the Patterson function relationship between the normalized reflectivity and the autocorrelation function for the density derivative, e.g.

\[ \langle \rho'(z)\rho'(z') \rangle = FT \left\{ \frac{R}{R_F} \right\} \]  \hspace{1cm} (B.4)

Using the properties of Fourier transforms, this relationship is straightforward to derive. First, the autocorrelation function can be written as a Fourier transform using Parseval’s equation,

\[ \langle \rho'(z)\rho'(z') \rangle = \int \rho'(z)\rho'(z' - z) dz' \]

\[ = \frac{1}{2\pi} \int FT\{\rho'(z)\} FT\{\rho'(z')\}^* e^{iqlz} dz = \frac{1}{2\pi} \int |FT\{\rho'(z)\}|^2 e^{iqlz} dz \]  \hspace{1cm} (B.5)

Using equation B.3,

\[ \langle \rho'(z)\rho'(z') \rangle = \frac{1}{2\pi} \int \left| \frac{R}{R_F} \right|^2 e^{iqlz} dz = FT \left\{ \frac{R}{R_F} \right\} \]  \hspace{1cm} (B.6)

Note that the Patterson functions shown in figure 3.17 were performed using a full Fourier transform between \( q = 0.1 \) and 0.65 Å\(^{-1}\). The width of the peaks in the Fourier transform are related to the ‘resolution’ of the Patterson function, \( \Delta z = \pi/q_{\text{max}} = 4.8 \) Å convolved with a Gaussian related to the average interfacial roughness in the multilayer (see following section).
The decay in the peak height of the Patterson function is related to the coherency (or crystallinity) of the multilayer. This can be equivalently measured from the dispersion of the diffraction peak width in $q$, as discussed below.

B.3.2 Reflectivity from a multilayer

In the absence of multiple scattering events (e.g. far from the critical angle for total reflection), we can treat diffraction from the multilayer kinematically, i.e. as a one-dimensional sum over bilayer ‘unit cells.’

$$ f = \sum_{j=1}^{N} f_{uc}(q)e^{iq(jc)} \quad (B.7) $$

Where $f$ is the form factor, $f_{bl}$ is the bilayer form factor, $N$ is the number of bilayers, and $c$ is the bilayer thickness. In the kinematic limit, the unit cell form factor is:

$$ f_{uc}(q) = \sum_{k} \frac{\partial \rho(z_k)}{\partial z} e^{iqz_k} \quad (B.8) $$

Which is summed over the unit cell’s $k$ interfaces in $z$.

Low angle reflectivity is typically analyzed in discrete layers, where the interface for each slab is defined by a pair of error functions. For the $n^{th}$ interface, this gives

$$ \rho_n(z) = \frac{1}{4}(\rho_n - \rho_{n-1}) \left( \text{erf} \left( \frac{z - z_{n,n-1}}{\sigma_{n,n-1}} \right) + 1 \right) $$

$$ + \frac{1}{4}(\rho_{n+1} - \rho_n) \left( \text{erf} \left( \frac{z - z_{n+1,n}}{\sigma_{n+1,n}} \right) + 1 \right) \quad (B.9) $$

where $z_{n,n-1}$ and $z_{n+1,n}$ are the top and bottom interfaces and $\sigma_{n,n-1}$ and $\sigma_{n+1,n}$ are the top and bottom roughnesses.
For the N-layer system, this gives:

\[
\frac{\partial \rho}{\partial z} = \sum_{n=0}^{N+1} \frac{(\rho_{n+1} - \rho_n)}{\sqrt{\pi} \sigma_{n+1,n}} \exp \left[ -\frac{z - z_n}{\sqrt{\pi} \sigma_{n+1,n}} \right]
\]  
(B.10)

where \( n = 0 \) is the substrate and \( n = N+1 \) is the superstrate (in this case the electrolyte). The form factor is then just:

\[
f(q) = \sum_{n=0}^{N+1} \frac{(\rho_{n+1} - \rho_n)}{\sqrt{\pi} \sigma_{n+1,n}} \exp \left[ -\frac{z - z_n}{\sqrt{\pi} \sigma_{n+1,n}} \right] \exp[iqz]
\]  
(B.11)

Recall that the Fourier transform of Gaussian is a Gaussian. Hence the Patterson function consists of Gaussian shaped peaks at the multilayer’s length scales.

\[
F(z) \equiv FT\{f(q)\} = \sum_{n=0}^{N+1} \frac{(\rho_{n+1} - \rho_n)}{\sqrt{\pi} \sigma_{n+1,n}} \exp \left[ -\frac{z - z_n}{\sqrt{\pi} \sigma_{n+1,n}} \right] \exp[iqz]
\]  
(B.12)

Generally speaking, the electron density derivative term is similar to an atomic form factor in classic diffraction, and is increased for larger density changes or small interfacial roughness. For a bilayer, there are only two terms in this sum. For the following analysis, we will only be considering a small range in \( q \) near the multilayer Bragg peak. If the interfacial roughness is the same at each interface, the bilayer form factor is simply,

\[
f_{uc}(q) \propto e^{iqz_1} - e^{iqz_2}
\]  
(B.13)

And if we choose the origin at \( z = z_1 \), we simply have

\[
f_{uc}(q) = 1 - e^{iqz_2} \propto \cos \frac{qz_2}{2}
\]  
(B.14)

The amplitude of the Bragg peaks will be modulated by this structure factor, as seen in the data, which shows a broad oscillation from the sharp Cr interfaces, confirming the overall modulation from \( f_{uc} \) given in equation B.14.
B.3.3 Peak width analysis

Ignoring unit cell modulation of the Bragg peak intensity (e.g. letting \( f_{uc} = 1 \)), the sum in equation B.8 reduces to

\[
f = e^{iqc} \frac{1-e^{Niqc}}{1-e^{iqc}} \quad \text{(B.15)}
\]

The measured intensity, \(|f|^2\) gives the familiar sine function

\[
I = |f|^2 = \frac{\sin^2(Ncq/2)}{\sin^2(cq/2)} \quad \text{(B.16)}
\]

Which has Bragg peaks in \( q \) at integer multiples of \( 2\pi/c \). The first order Bragg peak is shown in figure B.7, where \( c \) has been set to \( 2\pi \) and \( N = 20 \).

![Figure B.7: 20 layer diffraction peak given by equation B.14. The c-lattice parameter was set to 2\pi, so that the first-order Bragg peaks appears at q =1.](image)

Note that the intensity equals \( N^2 \) at the Bragg peak. The full width at half maximum (FWHM) of the \( n^{th} \) Bragg peak (FWHM = 2\( \epsilon \)) is given by:

\[
\frac{\sin^2[N\pi(k+\epsilon)]}{\sin^2[\pi(k+\epsilon)]} = \frac{N^2}{2} \quad \text{(B.17)}
\]

This can be easily solved by Taylor expanding each sine function to second order,
\[ \sin^2\left(\pi(n + \epsilon)\right) = \pi^2 \epsilon^2 - \frac{\pi^4}{3} \epsilon^4 + O(\epsilon^6) \]  

which gives

\[ 2\epsilon = \frac{1}{\pi} \sqrt{\frac{3(2N^2-1)}{2N^4-1}} \]  

This full width is plotted in figure B.8 as a function of N and matches the FWHM seen in experiment.

When factoring in disorder, the FWHM will increase in width with \( q \). The dispersion of the FWHM with \( q \) depends on the type of disorder present:

1) Zero dispersion: a perfect crystal.

2) Linear dispersion: a strained crystal. In this regime, the Bragg peak can be considered a distribution of Bragg peaks for the different c-lattice parameter for each layer. If a particular layer is strained by \( \Delta c \), the \( N^{th} \) order Bragg peak shifts in \( q \) by:

\[ \frac{2\pi N}{c+\Delta c} = \frac{2\pi N \Delta c}{c^2} + O\left(\frac{\Delta c^2}{c^2}\right) \]
For small strains, this leads to a linear dispersion in $q$ with an average strain given by the slope of this trend scaled by $c/2\pi$.

3) Quadratic dispersion: a paracrystal. Paracrystalline order is the intermediate state between amorphous and crystalline materials and are characterized by the $g$-factor defined by:

$$g = \left( \frac{c^2}{\bar{c}^2} - 1 \right)^{1/2}$$

$g = 0$ is a perfect, crystal; $g = 0.05$-0.1 for graphite crystals; $g = 0.03$ for polymers; $g = 0.12$ has been found for nearly amorphous quartz; $g = 1$ would be a Boltzmann gas.$^2$

\[\text{Figure B.9: Dispersion of the diffraction peak FWHM as a function of } q \text{ for the starting, lithiated, and delithiated cases, as discussed in the text. A polynomial fit is given in red and 90% confidence intervals given by the gray dashed curves.}\]
Initially, the sample shows no dispersion in $q$, in agreement with a perfect multilayer. When fully lithiated, the lowest-$q$ Bragg peaks shift to lower FWHM (due to the increased $d$-spacing), and show a small, quadratic dispersion. The dispersion is consistent with a $g$-factor of 0.3%. While higher-order Bragg peaks are difficult to resolve at intermediate conditions, the second-to-last scan during delithiation shows a linear behavior consistent with a 1% overall strain in the structure. In the last scan, the multilayer appears to show little dispersion at all before delamination halfway through the scan (discussed above). Both the lithiated and delithiated Bragg peaks are consistent with a well-ordered one-dimensional crystal.

**B.4 References**
