MECHANISTIC STUDIES OF MAGNESIUM ELECTRODEPOSITION AND OXYGEN REDUCTION FOR ENERGY STORAGE APPLICATIONS

BY
DAVID JOSEPH WETZEL

DISSEYATION
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Doctoral Committee:
Professor Ralph G. Nuzzo, Chair
Professor Andrew A. Gewirth
Professor Ryan C. Bailey
Professor Paul J.A. Kenis
Abstract

Energy storage research is critical for advancing the world’s energy storage technologies in order to meet the needs of the future generations. Global warming due to CO₂ production and diminishing reserves of fossil fuels necessitate a transition to intermittent renewable energy production. Renewable energy will require the storage of energy for load leveling and energy usage off the grid. Towards this goal there are two chemical means of energy storage that are ideal: batteries and fuel cells. This work describes advances in fundamental understandings of important, rate limiting reactions for both batteries and fuel cells. The oxygen reduction reaction can be catalyzed to undergo reduction via two pathways. Oxygen binding energy to the catalyst has previously been shown to determine the activity of the catalyst. Here we use a novel set of comparative experiments to measure the strain in the platinum catalyst due to oxygen binding in in situ measurements over a wide potential range. Reduction is also a concern for magnesium battery anodes, as is re-oxidation of deposited thin films. This work describes fundamental studies of passivation, corrosion, and rate limiting reactions within two magnesium battery electrolytes: ethylmagnesium bromide and magnesium borohydride. These studies provide further insight into reaction rates in these complex systems and can be further used in computational studies or the design of future technologies.
To my mother and father for their constant dedication and faith
Acknowledgments

Such a large undertaking is never without help from others. I would like to acknowledge the help of so many people that have made this dissertation a reality, to whom I am forever indebted. First I would like to mention all my committee members who have helped me in ways they may never realize. Ralph, of course, has been instrumental in guiding me. Repeatedly I have found myself in awe at his ability to both seem aloof, yet grasp a concept more thoroughly than anyone in the room who comports themselves as an expert. His graciousness and understanding as a boss and manager is something I have learned to appreciate as it, unfortunately, is quite rare. Andy similarly has been like a second advisor to me and has taught me an immense amount about how to both manage a team and (through several patient, yet I’m certain quite painful hours for him) how to expertly craft a scientific paper. Paul and Ryan may not have been regular advisors to me, but they were both steady influences in my education and provided an education in other ‘soft’ skills.

I was so fortunate to be a part of several published papers and all of them required consistent collaboration, as can be seen from the author lists of the papers. To abbreviate the messages of gratitude I’ll confine them to quick comments for everyone:

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very cool (and sometimes very large!) projects. Yifei Meng can wield an FIB like Jimi Hendrix wielded a guitar (minus the flames). Thao Hoang does all the work, with a smile. Matt Small is probably still running. Enes Oruc might not know I stole his chair.

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Finally, words of wisdom to those who seek the ivory tower: I used to think creativity was found in hiding one’s sources, but somewhere along my graduate career I came across a similar yet distinctly different adage: It’s not what you do, it’s how you do it. I do not mean to disparage any of my colleague’s accomplishments, but rather to highlight that sometimes it is approaching the same problem from a new direction that gives life to something entirely unexpected.
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1.1 The Emerging Problem of Energy Storage

Lithium burns when it reacts with water in the presence of oxygen. When the goal is to store as much energy in as little space as possible, it is almost inevitable that the consequence will be reactivity of the constituent materials. That is the nature of chemical energy storage. The reason why it is necessary to explore such dangerous materials for mass consumption can be trivially attributed to the drive of continual improvement, but the problem of energy storage cannot be appreciated without first considering the true complexities of both the material limitations and the socio-economic forces driving innovation.

1.1.1 The CO\textsubscript{2} Problem

When the topic of CO\textsubscript{2} arises, it is almost inevitable that global warming follows in the next thought. The media pumps a diluted story to the public that mixes scientific fact with casual observation that results in something with a false causal argument at best and completely illogical at worst. The diluted truth is partly why politicians deny climate change (the other part does not fit in a chemistry dissertation). It is also why there is so much confusion over the correlation between the increase in CO\textsubscript{2} levels and the modest rise in mean global temperature. A rise in sea levels of a few feet seems similarly modest in comparison to the size of the globe, so what, then, is the true impact of the rise in the concentration of CO\textsubscript{2} in the atmosphere?

There is near perfect scientific consensus on the idea that ‘humans are the primary cause of recent global warming’.\textsuperscript{1} It is important to note that the consensus lies in the anthropogenic global warming (AGW), not the future result or extent of the warming. As the famed quantum
physicist Niels Bohr once quipped, “Prediction is very difficult, especially about the future”. In order to even hint at what the future global climate may be, it is helpful to understand what is agreed upon when it comes to the idea of AGW and what is agreed upon in terms of natural temperature cycles.

The first and most widely known study of AGW was the long-term study of the CO₂ concentration in the air in the relatively isolated location on the top of the Mauna Loa mountain in Hawaii, providing a good estimation of the average atmosphere above the Pacific ocean. The results of the Mauna Loa Observatory have been widely disseminated in what is known as the Keeling Curve, named after Charles D. Keeling. The results show a yearly concentration oscillation attributed to the CO₂ uptake by plants as most forests are located in the northern hemisphere. Superimposed on these oscillations is a steep, steady increase in the CO₂ concentration every year since the study’s inception in 1958. The steady increase was eventually attributed to roughly 50% of the annual production of CO₂ through the burning of fossil fuels. CO₂ production has been increasing linearly since 1960 and globally forests only absorb about 30% of the CO₂ produced annually.

Alone the Keeling curve does not completely confirm the human impact on the CO₂ concentration, but further studies of ice cores from Antarctica provide a much deeper insight into both global temperatures over long periods of time (thousands of years) and the effect of humans on global temperature. The ice cores from Antarctica use trapped CO₂ in the ice to track concentration with time based upon depth of the ice probed. Ice cores from different locations (Vostok vs Law Dome) have different resolution based upon snowfall and depth of the ice sheet. Figure 1.1a shows that dating back 400,000 years the highest CO₂ concentration was about 300 ppm. The concentration is now over 400 ppm. As Figure 1.1b shows, the ice core data from the
Law Dome shows a steady level of CO₂ in the ice going back about 2000 years. Interestingly the graph changes in the mid-eighteenth century CE and begins an exponential increase. This change in concentration coincides with the most important anthropogenic CO₂ production event: the Industrial Revolution.

Humans, therefore, have unambiguously caused the uptick in CO₂ concentration in the atmosphere, but the question remains: what are the long-term effects of increased CO₂ levels and have these levels of CO₂ ever been present on Earth? Again, dating back 400,000 years the concentration is much higher than it has ever been. From sediment cores it is possible to observe the relative isotopic abundance of ¹⁸O and ¹³C (which correspond to ocean temperature and organic material respectively) dating back millions of years. The data from such studies shows that the global average temperature is affected by many events including minute oscillations in Earth’s orbit of the Sun and geological transformations like the movement of tectonic plates and corresponds to large, ecological events. CO₂ concentrations cannot be extracted from deep sea sediment cores, but the global average temperature can be extracted and was significantly higher than it is today.

Current human actions will likely have little impact upon geological and astrophysical events, but the rise in CO₂ levels could cause drastic ecological changes as sea levels rise and the ocean acidifies (absorbing CO₂ from the air). It is the ecological implications of climate change that are not easily predictable and are of serious concern for the entire Earth. Even a slight rise in global average temperature could merely mean socio-economic shifts, but massive extinctions pose an entirely different level of issues. Extinctions have ripple effects that extend from foliage to predator (i.e. humans) and can cause entire populations to collapse, sometimes while another species increases in what is known as a trophic cascade. The truth is that no one knows
what will happen if the temperatures continue to rise, but the very real threat of population collapse through unpredictable extinctions is not easily solved with our current understanding of science or even amenable without a sizable investment of resources.

Strategies towards decreasing the concentration of CO\textsubscript{2} in the atmosphere revolve around the two general ideas of sequestration or conversion. CO\textsubscript{2} is known to be a greenhouse gas, but its properties are far different from other greenhouse gases such as water. The difference comes from the chemical and physical characteristics of the individual molecules and the nature of the planet itself. Water is quickly and efficiently cycled through the atmosphere through the formation of clouds and subsequent condensation of water in the form of rain. The similar sequestration of CO\textsubscript{2} is accomplished by nature through two mechanisms: CO\textsubscript{2} solubilizing in the ocean and the formation of new plants. Even with the efficient CO\textsubscript{2} storage mechanisms of plants, biological sequestration is impractical if not impossible for solving the problem of increasing CO\textsubscript{2} levels.\textsuperscript{6} A significant scientific effort has been made in chemical and mechanical methods of CO\textsubscript{2} sequestration, but socio-economic conditions have not brought any such systems into mass production. The topic is very interesting, but is not within the scope of this dissertation and is treated elsewhere.\textsuperscript{12} Suffice it to say there is a lot of energy loss in both concentration of CO\textsubscript{2} (it is still only 400 ppm) and electrical overpotential for conversion to liquid fuels. With sequestration a difficult if not very energy intensive endeavor, the only way to decrease the concentration of CO\textsubscript{2} in the atmosphere is through decreasing the production of CO\textsubscript{2}.

1.1.2 The Fossil Fuel Problem

Concurrently with the rise of CO\textsubscript{2} the world has seen a decrease in the amount of fossil fuels available in the world. Formed through thousands of years of immense pressure on organic matter left by thousands of generations of prehistoric plants and animals, fossil fuels are
inherently a finite resource that once depleted cannot be renewed. As shown in Figure 1.2 the population of the U.S.A. is projected to continue to grow steadily, similar to the rest of the world. Figure 1.3 shows that energy use per capita decreased from 1997 to 2013, but total energy usage is expected to continue to increase. The decrease was due to several factors including the economic recession as well as increased oil prices that gave rise to increased fuel efficiency at both the automobile and the grid level. CO$_2$ levels will continue to rise for some time, but even moderate estimates predict world oil reserves to be depleted within the next 50 years.

Figure 1.4 shows that currently about 70% of the U.S. energy infrastructure uses inexpensive carbon energy sources like coal and gas. The ideal solution, however, lies in renewable energy that produces little to no CO$_2$. The CO$_2$ produced in creating a battery is on par with that for producing gasoline fuel, regardless of the chemistry of the battery, but a battery can utilize high efficiency or even renewable energy from the grid. It is therefore even more important that the world focus immediately on building the systems and infrastructure to support such a transition.

With an inevitable transition to renewable energy sources looming on the horizon due to the combined impact of AGW and diminishing supplies of fossil fuels, the importance of energy storage becomes apparent: Renewable energy systems all suffer from significant fluctuations in the production energy, whether it is a cloud covering a solar cell or a gust of wind pushing a turbine. In order to combat these fluctuations, the energy must be stored so that it can be used both in a controlled manner and when no energy is being produced at the source. The problem for energy storage is that all methods of energy storage are lacking, *vide infra*. 
The capacity of energy storage required at the power grid level is the largest in terms of capacity, but mobile energy storage may be gaining importance. Although significant gains in efficiency are possible, if the entire country shifted to electric vehicles the grid level power would have to increase about 29% in capacity.\textsuperscript{18} This enormous change in resources would subsequently increase the amount of energy storage capacity at both the grid level and the individual vehicle level. Such fanciful ideas as charging roads have been proposed, but the cost of infrastructure in adoption remains a hurdle towards widespread adoption of the technology.\textsuperscript{19} The long-term cost may be higher, but the flexible infrastructure adoption of the battery powered electric vehicle has already shown significant strides in the form of Tesla Motor company. Energy storage will therefore be critical across all levels of energy usage, from small mobile devices to the power grid itself.

1.2 Physical Systems of Energy Storage: Potential to Kinetic Energy

Physical systems of energy storage (PSES) have a variety of distinct benefits over chemical systems of energy storage (CSES) but their primary benefit lies in their ability to store and release energy over thousands of cycles with high power. The primary methods of physical energy storage can be divided into three areas: gravitational force, centripetal force, and thermal energy. Several of these technologies date back thousands of years, but advances in technology have made them quite efficient. Some chemical methods of energy storage can also achieve long cycle life and high efficiency so the real difference comes down to the balance between energy density and power. Often PSES can achieve higher power than CSES, but CSES achieve higher energy density. Figure 1.5 describes the energy density portion of this problem but relative cost and absolute power is described in detail elsewhere.\textsuperscript{20} The appropriate technology often becomes a question of available space. In areas where few people live and land is cheap, physical methods
are often the preferred method of energy storage. However, when space or weight becomes important, CSES are often more attractive. Note that petro-chemical means of energy storage are ignored in this dissertation as viable means of energy storage due to the issue of AGW, otherwise petro-chemical energy storage has many favorable attributes.

1.2.1 Gravity

Perhaps the oldest and most well-known method of energy storage is that of pumped hydro. The paradigm of gravitational storage, a pumped hydro storage facility uses very efficient pumps to essentially transfer a volume of water up a hill. The energy stored is very simply stated as:

\[
W = F \times \Delta x
\]  

(1.1)

Where \(W\), \(F\), and \(\Delta x\) are work, force, and distance respectively. The force is defined by the gravitational force exerted by Earth on an object, which is for most intents and purposes constant on the surface of the Earth at 9.8 m·s\(^{-2}\) multiplied by the weight of the object. Therefore a 2L bottle of water pumped 100 meters up a tower would have a potential energy of 1.96 kJ, which as will be described later, is less than half the energy stored in one, standard alkaline AA size battery. As a method of storing energy it is quickly apparent that a lot of water is necessary to store small amounts of energy.

Often discussions of energy are lopsided to promote the benefits of a specific technology, but the truth is not so simple. The difference arises in rates. The above argument is based upon a relatively slow rate of discharge and at higher rates the amount of energy stored is relatively close between the two. Although there are some limitations, generally the rate at which pumped hydro energy is used can be varied to accommodate a wide range of power requirements. Batteries, however, are limited to relatively low power situations as explained more fully later.
In order to increase the energy stored, the density of the material used has been increased in several systems. One such technology uses a rail system with very dense materials such as concrete (which provides a very low cost to weight ratio) to afford higher energy density while also decreasing the response time towards load leveling at the grid operator level. Similar methods have also been developed that use underground silos in order to minimize the footprint of the technology while increasing the maximum energy density possible.

1.2.2 Compressed Air Energy Storage

Compressed air energy storage (CAES) is a great alternative to pumped hydro. CAES is slightly more energy dense yet retains the high power capabilities of pumped hydro. The fundamental equation governing CAES energy is that of the ideal gas law:

$$PV = nRT$$  \hspace{1cm} (1.2)

where $P$, $V$, $n$, $R$, and $T$ correspond to pressure, volume, moles of molecules, the gas constant, and temperature, respectively. When expansion takes place adiabatically:

$$W = p_f v_f \ln \left( \frac{p_i}{p_f} \right)$$  \hspace{1cm} (1.3)

where $p_i$, $p_f$, and $v_f$ correspond to the initial pressure, final pressure, and final volume respectively. One of the limitations is the cost, but also space can be of a concern.\textsuperscript{20-21}

1.2.3 Centripetal Force

One of the other most popular PSES uses centripetal force in the form of flywheels. Flywheels in a very simple sense are springs that are twisted to very high levels of tension. The energy stored in tension can be very quickly released, affording this technology with very high power densities. The highest power density, however, comes from using carbon fiber composites that can get quite expensive and therefore limit some of the applications. Carbon fiber composites have great strength-density ratios that maximize the speed possible in the rotor:
where $\sigma$, $\rho$, and $v$ correspond to the tensile stress, the density of the material, and the velocity, respectively. Higher the velocities mean higher possible energy storage according to the equation:

\[
\frac{\sigma \varepsilon}{\rho} = v^2 \tag{1.4}
\]

where $E$, $I$, and $\omega$ correspond to the energy, the moment of inertia and the angular velocity, respectively. Research is ongoing and further attributes and are elaborated elsewhere.\textsuperscript{20, 22}

1.2.4 Thermal

The other most popular and general form of energy storage uses thermal energy.\textsuperscript{20} Thermal energy can be stored in a variety of ways, but the most popular system for grid level storage where electricity must be produced (rather than using the heat to warm buildings in cold climates) is a molten salt thermal energy storage system. Molten salts can achieve stable temperatures much higher than water, but are typically coupled to existing steam turbines in power plants. Otherwise the principle of energy storage is similar to CAES, using temperature and salts rather than air and pressure.

1.3 Chemical Systems for Energy Storage

Chemical energy storage is an intriguing alternative to physical methods of energy storage. Their main benefits include high energy density (sometimes rivaling that of gasoline), renewable or recyclable materials, and the ability to circumvent the Carnot cycle efficiency limit of gasoline engines. CSES can generally be subdivided into three groups that will be briefly discussed in this section: fuel cells, batteries, and capacitors.
1.3.1 Electrochemical Potential Energy

In a very general sense, electrical potential energy is like a dam where all the water is exchanged with electrons. In a dam water is stored as potential energy until the dam is opened at which point the water flows out and becomes kinetic energy. If there is still water left in the dam when it is closed, then there is likely still some potential energy in the dam. Electrical potential is created when electrons or charged particles are separated within a system. The “dam” is really a set of charges necessary to maintain an equal number of opposite charges in place. As electrons flow through a circuit the charges equalize and the potential is lost. This potential is also referred to as a voltage and is represented as $V$. It is comprised of the charge per unit area or:

$$V = \frac{q}{A}$$

(1.6)

where $q$ and $A$ are charge and area respectively. Although this analogy obfuscates the incredible intricacies of the underlying physics and chemistry involved, it works surprisingly well for describing how batteries function and comparing to potential energy from macroscopic, physical sources.

1.3.2 Hot Spots for Highly Energy Dense Materials

When considering potential candidates for chemical energy storage it is useful to start with perhaps the most fundamental representation of chemical relationships: The Periodic Table. Within the periodic table are a variety of interesting and useful trends for evaluating favorable energetic characteristics. First and foremost is the general consideration of energy density. Energy density can be described in terms of volumetric or gravimetric terms and in order to simplify comparisons across materials often the metric chosen reflects only the charge, not the actual energy, and is referred to as gravimetric capacity or volumetric capacity. The units used for capacity for batteries are mAh g$^{-1}$ or mAh cm$^{-3}$. From the description of the unit it is possible
to ascertain that it is beneficial when more charge can be stored in a smaller area or a smaller weight. The typical equations for calculating energy density are:

\[
G_c = \frac{(\frac{F}{3.6}n)}{MW}
\]

and

\[
V_c = G_c \ast \rho
\]

where \(F\), \(n\), \(MW\), \(\rho\), \(G_c\), and \(V_c\) correspond to Faraday’s constant, the charge stored in one atom or molecule, the molecular weight, the density, the gravimetric capacity, and the volumetric capacity respectively. Although there are some exceptions, these relationships lead to trends that can be visualized in the following figure.

Figure 1.6 shows two periodic tables colorized according to the gravimetric and volumetric capacities of the elements. Only selected elements were colorized in order to emphasize trends and limit the scope to commercially viable technologies. Generally it can be seen that elements at the top of the periodic table are more favorable when it comes to selecting energy dense materials. In Figure 1.6a, there is a general trend towards the top left of the table where there are light elements capable of holding a high charge. Interestingly, the highest volumetric capacities can be achieved only through using the lightest transition metal elements due to their highly dense solid phases and ability to exist in multiple, stable charge states. Also interestingly most if not all of the best candidates are currently used in commercially available batteries, including the relatively expensive and low energy density element silver. One of the more subtle points of interest is the relative use of elements in chemical energy storage technologies. Batteries use Li, Mg, and Al as anodes in conjunction with transition metal elements, in effect averaging the gravimetric and volumetric properties of the two constituents.
It is important to note that the values obtained for Figure 1.6 omit several important factors. Toxicity is a serious concern and is one of the greatest reasons that Be is not pursued as a candidate for the next generation of energy storage materials. Price and commercial availability also limit several of these elements to merely academic pursuits. The subtlest factor not easily garnered from the figure is the idea of the standard redox potential of the electrochemical reaction. Figure 1.6 only accounts for capacity and ignores voltage concerns such as electrolyte potential windows, electrochemical couples, and reduction potential. Potential is very important for CSES because electrical power is defined as:

\[ P = I \times V \]  

(1.9)

where P, I, and V are power, current and voltage, respectively. In the future chemical energy storage will likely utilize elements highlighted in Figure 1.6, but truly novel chemistries may be still undiscovered that could open up innovative uses of the other parts of the periodic table.

1.3.3 Fuel Cells

Fuel cells have immense prospects and have been thoroughly studied for the greater part of the last century. They are intrinsically different than other methods of chemical energy storage in the design element of physically separated reactants. The two fuels are brought together only when a reaction (i.e. power) is desired. Fuel cells probably have the widest variety of chemistries and designs due to the sheer number of molecules that can be considered as a fuel.

Figure 1.7 shows a diagram of one of the most typical fuel cells, a hydrogen fuel cell. One half of the cell consists of the anode where hydrogen is oxidized and the other half of the cell contains oxygen which is reduced. When the hydrogen is oxidized a proton and an electron are formed that move through the electrolyte and an external circuit, respectively. The two recombine with oxygen at the cathode to form water as the product for the overall reaction:
The specific type of fuel cell depicted in Figure 1.7 is that of a proton exchange membrane fuel cell (PEMFC). The operating temperature of about 70°C for a PEMFC is relatively low compared to that of other fuel cells that range from 200-1000°C. Other components of a PEMFC are similar to other fuel cells in that there is usually a current collector-catalyst assembly at the anode and cathode as well as an electrolyte separating the two. PEMFCs classically use Nafion, a perfluorinated sulfonic acid polymer, as their electrolyte, but other fuel cells use liquids or oxide materials, as is the case for solid oxide fuel cells.

Reports on fuel cells often contain what is known as a polarization curve. There are three regions that are important to interpret when analyzing a polarization curve: the activation region, the ohmic region, and mass transport region. Catalyst development is mainly concerned with the activation polarization because activation is based upon the underlying kinetics of the catalysts. The other regions are important, but mainly for cell engineering purposes in order to reduce internal resistances and maximize mass flow (while maintaining hydration of the electrolyte for H₂/O₂ PEMFCs). A further description of current research in Fuel Cells is presented in Chapter 3 and other reviews give even more detailed descriptions of the different types of fuel cells.²³-²⁵

1.3.4 Batteries

Batteries fill a happy medium in the continuum of chemical energy storage technologies. Generally batteries provide a balance between energy density and power density. The technology is quite old, dating back all the way to Volta who created the ‘Voltaic pile’ which consisted of alternating layers of copper and zinc in an acidic electrolyte. The word for battery in some languages is actually a derivative of this original technology such as the Spanish pila. Battery technology has advanced considerably since then, but the operating principles remain the same.

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O
\]
Figure 1.8 depicts the basic schematic of a battery. The process of electron removal and ionic shuttling across an electrolyte is very similar to a fuel cell, but the similarities stop there. Batteries are self-contained systems where the fuels must be ‘recycled’ as in rechargeable batteries (also known as secondary batteries) or completely replaced as in non-rechargeable batteries (also known as primary batteries). The most energy dense batteries are therefore ones that can utilize only the charge carrier and limit the elements that stabilize the two energy states of the charge carrier. The best way to maximize the energy density then is to use the condensed phases of the materials in the hot spots of Figure 1.6. Various other parameters become important for the properties of each individual element, but this is why batteries are made of elements such as Li, Na, and more recently Mg. Similar reasoning justifies the use of Ag, Zn, Cd, and Ni, but the charge carrier is often OH\(^{-}\) rather than the ion itself. The electrolyte is usually a liquid with a high concentration of the ionic version of the charge carrier and a supporting ion. Figure 1.8 depicts the electrolyte as the common Li-ion electrolyte, LiPF\(_6\), that uses non-aqueous solvents to widen the potential window compared to that of water that limits the potential of traditional batteries. Figure 1.8 also depicts a unique feature of low reduction potential batteries such as Li-ion: the solid electrolyte interphase (SEI). The SEI is a thin, complex layer formed at the electrode interface, but mainly studied at the anode.\(^{26}\) It is created by irreversible decomposition of the electrolyte to produce an ionically conducting yet electrically insulating layer that allows lithium to reversibly insert and remove itself from the electrode. The SEI is a critical component that can determines the stability and longevity of a secondary battery. The importance of the SEI is further outlined in Chapter 4 with an added focus on Mg batteries. Finally, unlike a fuel cell the reactants for each electrochemical half-cell reaction in a battery are always in intimate contact. The intimacy of the reactants and products can be beneficial, but it is
also cause for what is known as self-discharge or deleterious, irreversible side reactions that consume the reactants or electrolyte.

Battery research has many important characterization plots, but generally all batteries are defined by their discharge curves and cycle efficiencies. The ideal discharge curve would be L-shaped, corresponding to an electrochemical reaction that occurs at a specific voltage that ends after all reactants have been consumed. In reality the cell voltage is a superposition of several individual resistances that result in a slight slope in the voltage plateau and internal resistance, like that of fuel cells, leads to further drop of the voltage. Multiple redox reactions can also be present that will result in multiple plateaus as is the case for sulfur cathodes in Li-S batteries. Battery cell charge densities are reported according to the rate applied, which is defined in terms of ‘C-rate’. A C-rate of 1 C is the rate at which it takes to discharge the amount of active material according to the theoretical capacity in 1 hour. Faster rates (>1C) result in lower capacities due to various sources of internal resistance. Further characterization of Mg battery chemistries are discussed in Chapters 4 and 5 of this dissertation, but there are several good reviews and books available to learn more about batteries.27-32

1.3.5 Supercapacitors

Supercapacitors (sometimes ultracapacitors) are very similar to batteries, but they do not undergo faradaic processes to produce current flow.33 They typically maximize surface area and minimize the separation between electrodes in order to maximize the capacitance according to the equation:

\[ C = \varepsilon \frac{A}{d} \]  

(1.10)
where $C$, $\varepsilon$, $A$, and $d$ correspond to capacitance, permittivity, electrode area, and distance between electrodes, respectively. The power is similarly dependent upon the capacitance, but also the maximum voltage according to the equation:

$$W = \frac{1}{2} C \times V^2$$ \hspace{1cm} (1.11)

where $W$, $C$, and $V$ correspond to work, capacitance and voltage, respectively. The extreme limitation of utilizing only surface area rather than bulk material renders supercapacitors less useful for high energy density storage. The high power still makes them useful in conjunction with batteries for load leveling and quick bursts of energy in electric vehicles.

1.4 Conclusion

There are a wide variety of options for energy storage, each representing unique attributes but there is no single, best method of storing energy. With the threat of CO$_2$ levels only increasing, it is likely that all the currently used technologies will continue to be used in order to maximize the possible usage of renewable energy sources and minimize the possible problems of AGW. Figure 1.5 outlines a general comparison across all methods of energy storage and a more detailed analysis of the differences between the methods of energy storage can be found elsewhere. As figure 1.5 shows, the highest energy density and power density can be achieved with advanced batteries and fuel cells, hence the rest of this dissertation describes efforts to improve those technologies.
1.5 Figures

Figure 1.1: (a) Vostok ice core data of the CO$_2$ concentration going back 400,000 years with data closer to 400,000 being representative of present day. (b) Law Dome Ice core data of the CO$_2$ concentration starting at about the year 1 C.E. $^{7-8, 34-35}$
Figure 1.2: U.S.A. energy consumption (blue) and U.S.A. population from 1960 to 2005 with a projection to 2040.\textsuperscript{13}
Figure 1.3: CO₂ emissions in the US according from 1997 to 2013 with important components plotted as percent changes from the values in 1997. Labeled factors are total emissions (black), consumption volume (red), population (yellow), fuel mix (orange), consumption patterns (green), energy intensity (purple), and production structure (blue). Figure used under the creative commons license from source 14.
Figure 1.4: Energy production in the U.S.A. divided into the energy source used as a percentage of the total energy produced per year: coal (red), gas (yellow), oil (orange), nuclear (green), and renewables (blue). Figure adapted and used under the creative commons license from source 14.
Figure 1.5: Comparison of the different energy storage technologies plotted according to power density vs energy density. Used under the creative commons license.
**Figure 1.6:** Periodic tables with colors ranging from low (purple-blue) to medium (green-yellow) to high (orange-red) according to the gravimetric capacity (a) and volumetric capacity (b).
**Figure 1.7:** Schematic of a fuel cell with hydrogen atoms (blue) oxidizing at the highly porous carbon anode (grey, left) and crossing the polymer electrolyte (green) to combine with reduced oxygen atoms (black) at a highly porous carbon cathode (grey, right) to produce water.
Figure 1.8: Schematic of a Li-ion intercalation battery with a graphite anode (grey) covered with a SEI (blue), which the Li$^+$ ions diffuse through along with the electrolyte (green) to insert into the transition metal oxide cathode upon discharge.
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Chapter 2: Techniques for Surface Analysis of Electrochemical Systems

2.1 Preface

This chapter is meant to be an overview rather than an exhaustive review of all the techniques that can be used for the analysis of electrochemical systems. It is broad in focus but consistently revisits applied phenomena specific to energy storage applications. There are immense volumes dedicated to surface analysis so this chapter only explains the basics of the techniques used for analysis throughout this dissertation. In each subsection of this chapter there are references to more comprehensive examinations of each individual topic.

2.2 Electrochemistry Techniques for Energy Storage

This section could easily expand into a dissertation in and of itself, so it will be limited to those techniques that were used in this dissertation. More specifically this section will focus on the traditional chemistry laws governing reactions (thermodynamics and kinetics) while encompassing the description in an applied battery context. There are many great electrochemistry texts available that provide a simple introduction and a reasonably thorough mathematical treatment of the the underlying physics.¹ There are also a few good books for surface electrochemistry and specifically electrodeposition.² Battery specific texts can be found by Aurbach, Linden, Scrosati, and others.³-⁵ The main differences between all the texts are the emphases on mathematical definitions of specific reaction conditions versus activity trends in materials. Most of the fundamentals of electrochemistry were based upon aqueous electrochemistry and spherical, mercury hanging-drop electrodes. Modern battery chemistry, needless to say, relies on rough, often non-ideal electrodes in non-aqueous solutions, sometimes
rendering routine analyses as rather challenging affairs. It is always important to remember how the theories used in electrochemistry were developed and what assumptions are made when applying each equation.

Inherent to every electrochemical process is the idea of potential measured in volts. The potential is a measurement of the fundamental thermodynamics of a reaction but can also contain information regarding many other processes as will be explained later. The ideal or theoretical potential of a reaction is defined by whether or not a reaction can occur by the underlying thermodynamics of a reaction:

$$
\Delta G = \Delta G^\circ + RT \ln(K)
$$

(2.1)

where $\Delta G$, $\Delta G^\circ$, R, T, and K correspond to the free energy of the reaction, the standard free energy of a reaction, the gas constant, the temperature, and the ratio of the reactants and products, respectively. A reaction is spontaneous when the value of $\Delta G$ is negative, corresponding to a net release of energy and the relaxation of the system to a lower energy state. $\Delta G$ and electrochemical potential are related by the equation:

$$
\Delta G = -nFE
$$

(2.2)

where n, F, and E correspond to the number of electrons transferred in the reaction, the Faraday constant, and the cell potential, respectively. Combining the two equations:

$$
E = E^\circ + \frac{RT}{nF} \ln(K)
$$

(2.3)

which is known as the Nernst equation.

Cell potentials are always defined according to a reference potential, which is often the standard hydrogen electrode (SHE):
Commonly the potentials are referred to as the reduction reaction:

\[ O^+ + e^- \rightleftharpoons R^0 \]  

or

\[ Li^+ + e^- \rightleftharpoons Li^0 \]  

One of the reasons that Li, Na, and Mg are of interest for CSES is that they have the lowest reduction potentials (~ -3V vs SHE). Battery or cell voltage, when described chemically, corresponds to the difference in energy between two reactions. For a Li-ion battery the cell voltage is defined by two redox couples, \( Li^{+/0} \) at the anode and \( Co^{4+/3+} \) at the cathode or similarly, whatever transition state metal is present in the cathode intercalation host material. Described explicitly in chemical reactions:

\[ Li^+ + e^- \rightleftharpoons Li^0 \quad (-3.04 \text{ V}) \]  

\[ LiCoO_2 \rightleftharpoons CoO_2 + Li^+ + e^- \quad (-0.72 \text{ V}) \]  

\[ LiCoO_2 \rightleftharpoons CoO_2 + Li^0 \quad (-3.76 \text{ V}) \]  

where

\[ E_{cell}^0 = E_{reduction}^0 + E_{oxidation}^0 \]  

In practice irreversible phase transformations limit the extent of the final reaction products, but the voltage and principles are the same. As mentioned in the previous chapter, the cell voltage is incredibly important because it defines power along with the current applied. According to equation 1.9 for the same chemical reaction rate (or electron flux) a higher voltage will correspond to more power.
Similarly increasing the overpotential will increase rates of a reaction according to the Tafel equation, which is a re-statement of the Arrhenius equation:

\[ i = a e^{\eta} \]  

(2.5)

where \( i \), \( a \), \( \eta \), and \( b \) are the current density, activation energy, overpotential applied, and another constant partially comprised of something called the transfer coefficient, respectively. The Tafel equation applies only when mass transport is not an issue (i.e. for relatively slow reaction kinetics). For reactions with fast kinetics, moving to high overpotential obfuscates the true effect of the overpotential. Overpotential for electrodeposition (the topic of Chapters 4 and 5 of this work) is actually a combination of several components:

\[ \eta = \eta_D + \eta_R + \eta_{Ad} + \eta_{CT} \]  

(2.6)

where \( \eta_D \), \( \eta_R \), \( \eta_{Ad} \), and \( \eta_{CT} \) are overpotentials for diffusion, chemical reactions, adatom diffusion barriers, and charge transfer, respectively. Under certain conditions different variables can be eliminated or ignored from equation 2.6, but the addition of different surface analysis techniques can also be used to gain in situ observations to help determine the rate limiting step.

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2.3 Surface Analysis Techniques

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) and the techniques that derive from its fundamental physics provide an amazing range of useful methods for probing sample characteristics from elemental composition to multi-layer film thicknesses. In this dissertation XRD was used in two of its simplest forms: 2theta-omega scans for thin film analysis and pole figures for
texture analysis. Before describing what those two techniques entail, it is best to start with the fundamentals of XRD.

XRD operates on the fundamental idea of constructive and deconstructive interference of waves in the form of monochromatic x-ray light. Similar to the wave patterns made when two balls are dropped in a calm lake, the monochromatic x-rays will couple to become more intense when the spacing between waves is the same. In a crystalline solid the regular arrangement of atoms results in repeating, characteristic spacings in different directions. The spacing between atoms acts as both a diffraction grating and a reflecting plane, allowing only x-rays with a specific angle of incidence to produce constructive interference. As shown in Error! Reference source not found., the x-rays passing through one plane of atoms will specularly reflect from the subsequent layer of atoms and the resulting beam of x-rays will maintain a strong intensity only at a specific angle of incidence. Other angles of incidence will result in the crystal producing deconstructive interference. The combined effect of these the two interference conditions results in the characteristic diffraction pattern of a specific material. These conditions are defined in Bragg's law:

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

(2.7)

where \( d \) is the spacing between equivalent planes of atoms, \( \theta \) is the reflecting angle, \( n \) is an integer, and \( \lambda \) is the wavelength of the incident x-ray beam. As can be readily seen from this equation, small errors in \( \lambda \) lead to a larger experimental error, hence monochromatic x-rays are desirable.

Error! Reference source not found. depicts a standard set up for a thin film XRD experimental configuration. X-rays are generated from a Cu source, chosen for its
abundance, x-ray emission intensity, and frequency, although other elements have benefits for specific applications. After the x-rays diffract from the sample the beam divergency increases so the beam is passed through a collimator and graphite monochromator to increase resolution before reaching the detector. A typical powder XRD instrument will have the source and detector move in relationship to a stationary sample, but in this thin film configuration the sample and the detector assembly move to satisfy the 2θ condition for coherent diffraction. Sample movement is necessary for thin film texture analysis because an accurate measurement of orientation requires a near hemisphere of measurement points.

Thin film texture is the measurement of the degree of orientation of the individual grains that comprise the analyzed material. Grains, or crystallites, can align themselves along specific axes for several reasons from epitaxial growth on an underlying substrate to preferential slip planes when a material undergoes strain. In electrochemistry (electroplating, corrosion, and electrocatalysis) it is very common to have reaction anisotropies due to underlying reaction kinetics or thermodynamics. It is also common to use additives such as surfactants to change the direction of the anisotropy or even create a random, or isotropic reaction based upon the preferential adsorption of reactants vs. blocking agents towards specific atomic planes.

Figure 3 shows a representation of a pole figure in three dimensions (3a), its two dimensional projection (3b). A pole figure is method of visualizing orientations of individual planes within a crystal and can be used to understand the orientation of a thin film or even a single crystal such as silicon wafers used for microchip production. Typically pole figures are represented simply as a two dimensional projection as shown in Figure 3b.
Each individual point in the two dimensional projection represents an equivalent plane of a crystal. The location of each point (depicted in red) is derived from first extending a line normal to the plane of interest (depicted in green) to the surface of an imaginary sphere that surrounds the crystal, then a line is drawn from each pole of the sphere to intersect with the first line where it touches the surface of the sphere. Where the lines from the poles cross the x-y plane located at the center of the sphere (depicted in grey) are where the planes are noted in the two dimensional projection, but any points lying outside the sphere are discarded, hence the need to draw lines from both poles.

Crystals with high symmetry will contain several points for one pole figure as is represented in Figure 4. The \{10-10\} plane of Mg has six-fold symmetry as Mg crystalizes in hexagonal close packing form and the \{10-10\} plane is the vertical extension of each side of a hexagon as is depicted by the orange side in Figure 4a. Figure 4b shows a model Mg \{10-10\} pole figure with the basal \{0001\} orientation (the \{0001\} plane parallel to the x-y axis). When the crystal is rotated so that it is said to be \{10-10\} oriented, the pole figure will show a single point in the center and two points to the left and right of the center point at 60° from the center, as is shown in Figure 4c. The previous examples are only for single crystals or perfectly oriented crystals, but more often crystals have only one axis of orientation, resulting in a superposition of pole figures with distinct 3 axis orientations. A fiber texture of Figure 4c with only 2 axes of orientation would show a ring at 60° as the \{10-10\} pole figure in Figure 4c is rotated about its z-axis.

Batteries benefit from x-ray diffraction analyses in several ways. First as previously mentioned, there are many electrochemical reactions that are anisotropic. Second, the basis of cathodic materials is that of insertion of Li⁺ into the crystal lattice of transition
metal oxide materials. All of the cathode materials used commercially have either diffusion planes or diffusion channels that can be anisotropic, leading to orientation effects on battery performance. In addition to Li$^+$ diffusion, many cathodes have different crystal structures depending upon process history or depth of discharge. Finally the SEI is a thin surface that can benefit from grazing incidence studies. X-rays are a very useful probe to analyze battery materials, but the information gleaned from x-rays is rather limited to phase and composition, so morphology and nanomaterials can be better probed using other techniques.

2.3.2 Charged Particle Microscopy

Charged particle microscopy techniques provide a wealth of information about the spatial and morphological features of a sample. The high resolutions (<1 nm in certain cases) allow visualization of ultra-thin membranes and accurate measurements of nanometer features. In addition to imaging, elemental information can be extracted from the sample using techniques such as backscatter imaging and energy dispersive x-ray spectroscopy (EDS). The largest benefit (and drawback) to using an ion instead of an electron as the charged particle is the ability to remove layers of the sample surface via ion milling, a technique frequently used in the preparation of cross-sections of thin films.

The basis for charged particle microscopy and why it was developed can be readily understood through understanding the basics of light microscopy. In a typical light microscope light is either reflected from or transmitted through a sample and the signal of light after it has interacted with the sample is guided and focused through a series of lenses. The maximum magnification using visible light is about 1000x and is limited by the equation:
\[ R.P. = \frac{0.61\lambda}{N.A.} \]  

(2.8)

where R.P., \( \lambda \), and N.A. correspond to resolution power, the wavelength of light, and numerical aperture, respectively. Equation (2.8) defines the limit of resolution of a microscope in practical terms as the type of light used or the optics used, further defined by the N.A. In order to increase the R.P. either the wavelength must decrease or the N.A. must increase. The wavelength of light is limited by the materials that can interact with the light to act as a focusing lens to a practical limit of about 400 nm, or the lower limit of the visible spectrum. The numerical aperture is further defined by the equation:

\[ N.A. = n \sin(\alpha) \]  

(2.9)

where \( n \) and \( \alpha \) are the index of refraction and half angle of illumination, respectively. Both the \( n \) and \( \alpha \) limit the N.A. to \( \sim 1 \) meaning that the resolution of a light microscope reaches a lower limit of resolution of about \( \frac{1}{2} \) of 400 nm or 200nm. That is sufficient to see a single mitochondrion as five pixels. Without the development of electron microscopy we might not understand as much about how life as we now know it!

The way that charged particle microscopes achieve higher resolution is by decreasing \( \lambda \) much past the 400 nm limit of light microscopy down to \( \sim 0.007 \) nm for a scanning electron microscope (SEM) and \( \sim 0.003 \) nm or a resolution of \( \sim 0.004 \) nm and \( \sim 0.002 \) nm, respectively. The theoretical limits of resolution are not realized due to several factors, primarily focusing aberrations, sample charging and even sample ablation. The often quoted statement is that the environment at the interface of an electron microscope beam and the surface is like that of an atomic bomb. The atom bomb comparison was meant only to emphasize radiative dosage when analyzing biomaterials or polymers, not necessarily the ablation rate.\(^6\) This dissertation used
SEM, transmission electron microscopy (TEM), focused ion beam (FIB), and helium ion microscopy (HIM). TEM and FIB analyses performed were rather routine and can be effectively treated within specific chapters of this dissertation or elsewhere.\textsuperscript{7-9} The one thing to note (and is briefly discussed in Chapter 5) is that FIB milling of large depths can cause re-deposition on the sidewall that was intended to be milled, effectively changing the morphology or elemental composition if quantitative elemental analysis is attempted.

SEM and HIM were used for important phenomena in this dissertation, but the questions arise: what is the difference between the two analyses and why use one over the other? The probe is the root of all differences. SEM uses electrons accelerated from a tungsten wire (or other materials depending upon application) and HIM uses helium ions that are ionized and accelerated from the tip of what is essentially a Field Ion Microscope (FIM). The difference in resolution is somewhat complicated because it is a mix of differences in wavelengths of the probe (see equation 2.8) while also increasing the mass and a difference in excitation of secondary electrons.

The benefit, then, of using HM instead of SEM is to achieve greater depth of field to visualize large, possibly high aspect ratio, materials in high resolution. Less intuitively there is an added benefit of visualizing very thin, non-conductive membranes such as the SEI in batteries. Ideally one day HIM will achieve an added, unique analysis which is \textit{in situ} mass spectrometry to achieve high-resolution microscopy coupled with surface sensitive elemental analysis that could rival AES and be used with non-conducting materials.\textsuperscript{10}

2.3.2 Auger Electron and X-ray Photoelectron Spectroscopy

HIM-MS is regrettably still in its nascent development stage and it was therefore necessary to employ other surface analyses including X-ray photoelectron spectroscopy (XPS)
and Auger electron spectroscopy (AES) in order to fully understand the reaction dynamics studied in this dissertation. AES and XPS present very unique analyses in this dissertation. Both methods utilize similar physics for excitation and each provides quantitative elemental analysis that is limited to about 5 nm of the surface of the sample due to the mean free path of an electron in a solid. XPS uses an x-ray to excite an electron from the core level that has a characteristic loss in binding energy for each element whereas AES has a subsequent step where the core hole is filled with an outer-shell electron, giving rise to a characteristic energy that is the difference between the two levels.11 Both provide chemical bonding information via slight shifts in electron core levels, but in practice AES peaks are too weak to accurately determine the differences, hence XPS is used for chemical bonding information. They differ in spatial resolution of tens of nanometers for AES to hundreds of microns for XPS, which is limited by the excitation source.

Plasmon peaks are less often discussed, but are of critical importance for XPS of battery materials. Plasmons are essentially oscillations or waves in the metal electron cloud that result in changes in the apparent binding energy of the effected electrons. XPS works better for higher Z elements, so the signal intensity of Li is quite low in any XPS analysis. When Mg metal is present, the plasmon peaks of Mg, even though they are small relative to the primary Mg peak, overlap with the Li peak resulting in very difficult quantitation or even qualitative analysis of the presence of Li. Auger has similar problems, making it important for any analysis of the two elements to use a different technique like secondary ion mass spectrometry (SIMS). Further reading is available from thorough surface analysis books.12-14

2.3.3 Surface Stress via the Cantilever Bending Method

Originally developed as a means to measure stress development in electrodeposited thin films15, the method has expanded considerably to measure monolayer arrangements of molecules
and even antibody based sensors.\textsuperscript{16-17} Stoney’s equation calculates stress, $\sigma$, according to the equation:

$$\sigma = \frac{Y_s t_s^2 C}{6(1-v_s)}$$  \hfill (2.9)

where $Y_s$, $t_s$, $C$, and $v_s$ are the Young’s modulus of the substrate, the thickness of the substrate, the curvature of the cantilever, and the Poisson ratio of the substrate, respectively. There are certain, specific design elements that make this measurement possible, briefly, that the substrate be thin yet much larger than the thin film, the substrate must be long and thin (hence cantilever), and the stress must be uniform and isotropic. These are rather strict assumptions that can be easily overlooked when designing an experiment. Figure 5 depicts a very basic version of the principle and dimensions required for analysis and is representative of experiments performed in this work. The method was used in this work to determine the strain induced by oxygen binding and reducing on platinum \textit{in situ} and is further elaborated upon in Chapter 3.

\textbf{2.3.4 Synchrotron X-ray Measurements}

The physical process of X-ray absorption is actually quite similar to that of AES and XPS (i.e. the photoelectric effect), but routine measurement can be quite difficult due to low signal intensities and difficulties in focusing x-rays. It is therefore useful to apply for experiment time at government operated synchrotrons that yield tunable frequency and polarization with very high intensity. Synchrotrons achieve these x-ray beam properties by confining electrons to a circular ‘storage ring’ where x-rays are continually lost as the electrons change momentum by moving in a circle. The high intensity of the x-ray beams available allows for analysis of very small samples and therefore is uniquely suited to the analysis of nanoparticle samples, especially for \textit{in situ} measurements.
Of the many possible experiments at a synchrotron, the two analyzed in this work are x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS). Both XANES and EXAFS are derive from the same data, the x-ray absorption edge for a specific element where the energy of the incident x-ray is close to that of the binding energy of a core electron. Oxidation state changes are readily qualitatively analyzed from XANES data due to the change in binding energy of the ejected core electron. The EXAFS data, however, is quite a bit more complicated. EXAFS data is comprised of small oscillations in the absorption just after the intense increase in absorption intensity that is XANES. The oscillations are due to interference waves as the ejected electron leaves the atom of interest and interacts with the electron clouds of the surrounding atoms due to the wave-particle duality of electrons. EXAFS enraptures the mind due to the elegance of the phenomenon, but EXAFS also causes many headaches due to its incredibly complex fitting calculations. FEFF and IFFEFFIT were developed to simplify the calculations and were eventually wrapped into a user friendly graphical interface called Demeter. Demeter was developed by Bruce Ravel and Mathew Newville and for further understanding of both the equations as well as working with actual data it is suggested that the reader explore their publications and Github resources.

2.4 Conclusions

There is an immense number of techniques and methods available for surface analysis but ideally this chapter provided a sufficient introduction to the techniques used in this dissertation and why they might be useful. Battery and fuel cell materials present unique challenges that can only be solved using increasingly more innovative uses of the probes available. As will be shown in further chapters, these techniques provided unique insight into the complex reaction equilibria present in fuel cells and batteries.
Figure 2.1: Depiction of coherent x-ray waves (red lines) diffracting from planes of atoms (blue circles).\textsuperscript{20}
Figure 2.2: Experimental setup for thin film texture measurements.
Figure 2.3: Pole figure showing a tilted crystal plane (green) and a line normal to the titled plane that has two lines from the poles of the sphere crossing the center plane of the sphere.
Figure 2.4: (a) Depiction of a hexagonal crystal with the \{10-10\} plane colored dark orange. (b) Model pole figure of the \{10-10\} diffraction peak with a sample orientation of \{0001\}. (c) Model pole figure of the \{10-10\} diffraction peak with a \{10-10\} sample orientation.
Figure 2.5: An exaggerated depiction of the bending of a thin, long cantilever used for stress measurements of an adsorbed molecule on a catalyst. Copyright by American Chemical Society.
2.6 References

Chapter 3: A Comparison of Atomistic and Continuum Approaches to the Study Of Bonding Dynamics in Electrocatalysis: Microcantilever Stress and in situ EXAFS Observations of Platinum Bond Expansion Due to Oxygen Adsorption During the Oxygen Reduction Reaction


3.1 Abstract

Microcantilever stress measurements are examined to contrast and compare their attributes with those from in-situ X-ray absorption spectroscopy (XAS) to elucidate bonding dynamics during the oxygen reduction reaction (ORR) on a Pt catalyst. The present work explores multiple atomistic catalyst properties that notably include features of the Pt-Pt bonding and changes in bond strains that occur upon exposure to O₂ in the electrochemical environment. The alteration of the Pt electronic and physical structure due to O₂ exposure occurs over a wide potential range (1.2 to 0.4 V vs normal hydrogen electrode vs. NHE), a range spanning potentials where Pt catalyzes the ORR to those where Pt-oxide forms and all ORR activity ceases. We show that Pt-Pt surface bond strains due to oxygen interactions with Pt-Pt bonds are discernible at macroscopic scales in cantilever-based bending measurements of Pt thin films under O₂ and Ar.
Complementary extended X-ray absorption fine structure (EXAFS) measurements of nanoscale Pt clusters supported on carbon provide an estimate of the magnitude and direction of the in-operando bond strains. The data show that under O₂ the M-M bonds elongate as compared to an N₂ atmosphere across a broad range of potentials and ORR rates, an interfacial bond expansion that falls within a range of 0.23 (±0.15) % to 0.40 (±0.20) %. The EXAFS – measured Pt-Pt bond strains correspond to a stress thickness and magnitude that is well matched to the predictions of a mechanics mode applied to experimentally determined data obtained via the cantilever bending method. The data provide new quantitative understandings of bonding dynamics that will need to be considered in theoretical treatments of ORR catalysis and substantiate the sub-picometer resolution of electrochemically mediated bond strains detected at the macro-scale.

3.2 Introduction

Pt is a superior catalyst for the ORR but its high cost presents a major barrier to the commercial viability of technologies, such as polymer electrolyte membrane fuel cells, that require it.³ The ORR has a large overpotential (ca. 0.4 V) in these cells and high mass loadings are often needed to provide useful rates.⁴-⁵ While work in finding non-noble-metal-based catalysts has led to considerable advances,⁶-⁹ Platinum group metal (PGM) electrocatalysts remain the best ORR catalyst to date and notable for utilizing the high efficiency, direct 4-electron reduction pathway.¹⁰⁻¹² Increase in Pt mass activity through increased surface area has lowered overall catalyst cost considerably, but edge effects reduce ORR site-specific activity in PGM catalysts, resulting in a nanoparticle size vs. activity limit at 3 - 4 nm.³,⁵,¹³⁻¹⁶ Alloying techniques can further
maximize active surface area by exposing a larger ratio of the more active Pt (111) plane, and also affect the electronic character of the catalyst.\textsuperscript{12,17-23}

Catalytic activity balances on interrelated properties such as $d$-band occupancy, Pt-O bond strengths and distances, and $O_2$ adsorption activation barriers.\textsuperscript{24-33} In particular, the $d$-band model, relating the energy difference between the $d$-band center and the Fermi level to the binding energy of the adsorbates, has been successfully applied to catalyst design.\textsuperscript{34-35} These studies, both \textit{ab initio} and experimental, have focused on the Pt-O bond, while presuming a static Pt-Pt bond character during ORR.\textsuperscript{24-33} However, it is understood that there are significant reasons, and data,\textsuperscript{36-37} that suggest such static models are too simplistic and a need exists for better information as to the real nature of the bonding dynamics.

There exist means that can be used, in principle, to measure such effects. Electrochemical surface stress measurements have long been used to investigate the lattice strain effects that result from electrodeposition, and the technique has recently been applied to the study of oxygen reduction.\textsuperscript{38-39} Previously, Heaton and Friesen studied the stress-potential behavior of Pt and Au electrodes using electrocapillarity. More specifically, they described features in the surface stress behavior of Pt in oxygen saturated environments as they related to the onset of oxygen reduction.\textsuperscript{40} Seo and Serizawa investigated the changes in surface stress of Pt electrodes in acidic and alkaline sulfate and alkaline fluoride solutions by a bending-beam method, one similar to the one we employ here.\textsuperscript{41} Stafford utilized a dynamic stress analysis, probing the capacitive response of Pt films in order to further understand the surface charge effects in the double
layer region and the multiple stress generating effects caused by adsorbate interactions with the Pt surface.$^{42}$

The present work addresses and compares quantitative measurement protocols that provide insights into the \textit{in-operando} structural dynamics of electrocatalysts, using the oxygen reduction reaction (ORR), carried out using a Pt catalyst, as an exemplary model system. Of specific concern in this work is the critical comparison of an in-situ local probe of atomistic structure, X-ray absorption spectroscopy (XAS), and a continuum-level/macroscopic probe of interfacial dynamics, cantilever strain measurements, that embed these same atomistic features within the more macroscopic characteristics of the mechanics involved. The question addressed is the degree to which fully quantitative analyses of the atomistic features of the dynamics of electrocatalysis can be derived from such data.

In \textit{situ} electrochemical surface stress measurements on Pt films track the macroscopic tensile and compressive responses (Fig. 3.1a) to applied potentials under inert gas and O$_2$ sparged environments. In principle, this measurement can report on the Pt-Pt bond length change as a function of O$_2$ exposure, albeit at the macroscopic level. The mechanics are more complex than this, however, and other features of the interfaces involved can be (and are expected to be) important contributors to measured strain data.

X-ray absorption spectroscopy (XAS) is a direct atomistic probe that provides an experimental method for measuring \textit{d}-band model properties directly.$^{43-50}$ In an earlier report, \textit{in-situ} XAS studies of the ORR showed that the platinum catalyst oxidation state changes significantly with potential.$^{45-46}$ More recent \textit{in-situ} XAS studies of the ORR on Pt, ones benefitting from advances in XAS instrumentation and \textit{in-situ} cell designs, have
made it possible to extend these insights and to quantitatively study more complex phenomena such as platinum oxide growth and potential-dependent bond disorder that results from perturbations due to interfacial bonding.\textsuperscript{46,51-52} Our previous work used in-situ electrochemical X-ray absorption near-edge structure (E-chem XANES) to show that the electronic structure of a Pt electrocatalyst is strongly influenced when exposed to O\textsubscript{2} under potentiostatic control, exhibiting larger $d$-band vacancies than exist at the same potential under N\textsubscript{2}.\textsuperscript{53} Additionally, the largest difference between the O\textsubscript{2} and N\textsubscript{2} integrated $\Delta\mu(E)$ L\textsubscript{3}-edge XANES data occurs at cathodic potentials. The change in $\Delta\mu$ between O\textsubscript{2} and N\textsubscript{2} exposure is associated with charge transfer between the Pt and the oxygen adsorbate. These results, obtained using 3 nm Pt nanoparticles, have been reproduced on the 1.2 nm particles used in the present work (\textit{vide infra}). Fig. 3.1b shows an atomic resolution scanning transmission electron microscopy (STEM) micrograph of a typical Pt/C supported nanoparticle in the 1.2 nm size range, comprised of Pt atoms well described by a truncated cuboctahedral shape.

A particular consequence of the charge transfer process – developed in our XANES work and in other studies referenced above – is that Pt-Pt bond distances should also exhibit dependences due to the O\textsubscript{2} exposure and potential. The nature of these structural changes have yet to be fully characterized—their study being complicated by the fact that they are likely to be local to the surface atoms of a supported electrocatalytic metal cluster. As the EXAFS reports on ensemble averages, the surface bonding information will be convolved with the more-bulk-like atomic bonding that is also present in a cluster. Very small clusters, however, can be used to more heavily weight (and thus better detect) changes due to surface bonding—dynamic bond strains that may
be small and thus challenging to characterize *in-operando*. It therefore remains an opportunity for progress in research to establish how bonding dynamics evolve quantitatively during the electrocatalysis of the ORR by Pt. The current work addresses this interest.

In this study, we explore the complimentary attributes of two independent means through which bond strains manifested in an *in-operando* electrochemical environment can be explored. We specifically highlight the similarities that exist between macroscale mechanical stresses manifested in thin film cantilever measurements and the atomic-scale structural perturbations evidenced by EXAFS measurements made on small supported electrocatalytic Pt clusters—specifically, the surface localized bond strains evidenced in each system in the presence of O₂. The measurements reported in the current work demonstrate that these electrochemically-mediated bond strains are in fact small, being manifested as an expansion that varies weakly over the range of potentials investigated. We demonstrate that the EXAFS and cantilever measurements (when analyzed via a suitable model) agree in terms relative magnitude and direction of the Pt-Pt bond strain (expansion) evidenced under O₂ during the ORR. Of particular note is the finding that the cantilever-based measurement reveals the nature of a generally weak potential dependence of the Pt-Pt bond strains with a higher analytical certainty.

3.3 Experimental Details

In-situ stress data was collected using an optical stress measurement setup and cell described previously⁵⁴-⁵⁵ while the electrochemistry was monitored with a CV-27 potentiostat (BASi West Lafayette, IN). Surface stress was measured using cantilever
curvature as previously described\(^{56-57}\) and was calculated using Stoney’s equation.\(^{58}\)

Cyclic voltammetry was conducted using a modified glass cover-slip as the working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. Cyclic voltammograms were measured at room temperature in Ar or O\(_2\) saturated 0.1 M HClO\(_4\) at a scan rate of 10 mVs\(^{-1}\) from 1.6 V to 0.0 V (vs. NHE). We note that the scan rate used is sufficiently low to ensure the stress response reflective of a steady state regime, as further affirmed by estimates of the same as are predicted by the Cottrell equation.\(^{59}\) Both the surface stress changes and the electrochemical data were recorded using a home-built program written using LabVIEW (National Instruments, Austin, TX).

Glass coverslips coated on one side with a 20 nm Ti adhesion layer and 200 nm of Pt were prepared from borosilicate glass microscope cover-slips (Gold Seal No. 1, 150 \(\mu\)m thick, Young’s modulus = 75.9 GPa). Cantilever-electrodes approximately 25 mm \(\times\) 1.5 mm were then cut from the cover-slips using a diamond-tipped pen in accordance with cantilever dimensions for accurate stress values.\(^{54}\) The cantilever-electrodes were rinsed with Milli-Q water (>18 M\(\Omega\) cm\(^{-1}\)) and annealed with a H\(_2\) flame prior to use.

The Pt/C electrocatalyst used in this study was prepared using the incipient wetness technique followed by heating under a H\(_2\) atmosphere, as described in section 3.8. The particle size distribution, obtained by using STEM was 1.20 ± 0.60 nm (Fig. 3.2). The catalyst loading on the gas diffusion electrode was measured against a standard using X-ray micro tomography (MicroCT) (Fig. 3.3). The particle size distribution (1.23 ± 0.37 nm) and catalyst loading of the electrode were measured following XAS data acquisition, and are given in section 3.8, showing the electrode and catalyst structures changed little during data acquisition (Fig. 3.4 – 3.5).
The electrochemical in-situ XAS cell featured oxygen permeable PDMS windows as described previously.\textsuperscript{53} Electrochemical measurements with the XAS cell were performed using a CH Instruments potentiostat. All potentials are referred versus the normal hydrogen electrode (NHE), which was calibrated by exposing the Pt electrocatalyst to H\textsubscript{2} prior to experiments. The XAS experiments were obtained with the Pt catalyst operating in three potential regions: the double layer region, (400, 500 and 600 mV); at the onset potential for ORR (900 mV), and at a potential where the Pt is electrochemically oxidized to PtO\textsubscript{x} (1 < x < 2), (1200 mV). Electrochemical data for the XAS experiments can be found in the Supplementary Information (Fig. 3.6).

The XAS experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory, beamline X18B. The beamline utilizes a Si (111) double-crystal monochromator, which was detuned 25\% to minimize higher harmonics. Experiments were performed in fluorescence mode, using an Ar-filled Lytle detector for measuring fluorescence intensity from the sample. X-ray absorption through bulk Pt foil positioned downstream from the sample between the two Ar-filled ionization chambers, was measured in the same energy scan with the electrochemical XAS data for energy calibration and alignment. Incident beam intensity was measured using a N\textsubscript{2}-filled ionization chamber positioned upstream from the sample. Typical acquisition times were 20 min per scan with a typical potential point requiring up to 20 scans. Due to time constraints, only 4 XAS scans were performed at 1200 and 900 mV, which is the origin of the relatively large experimental uncertainties at these potentials compared to the data obtained at other potentials. EXAFS data were extracted from the raw absorption coefficient data using Autobk method\textsuperscript{60} implemented in the IFEFFIT data analysis
The data were Fourier transformed from k-space, where k is the photoelectron wave number, to R space and the fitting ranges for quantitative analysis in both k-space and R-space were determined. The data were fit in R-space with FEFF6 theory. For analyzing the structural changes obtained at different potentials, only the nearest neighbor Pt-O and Pt-Pt contributions to EXAFS were included in the theory. Since EXAFS cannot distinguish between O and C as the scattering atom, "Pt-O" refers to any pair of Pt and O or C as the 1NN. For 3D structure determination of a representative particle from the ensemble we applied a multiple scattering analysis method that takes into account five nearest Pt-Pt coordinations, including multi-atom linkages, as described in greater detail below.

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3.4 Results and Discussion

3.4.1 Electrochemical Stress Measurements

Figure 3.7 shows representative results of macroscopic electrochemical stress measurements made on a thin film Pt electrocatalyst during the ORR. Fig. 3.7A shows voltammetry (vs NHE) obtained from the polycrystalline Pt/glass cantilever in an Ar purged electrochemical stress cell showing oxygen evolution at 1.4V, oxide stripping between 0.7 to 0.5 V, hydrogen associated features below 0.2 V, and oxide formation at 0.8 V during the anodic sweep. The data in Fig. 3.7B, obtained under O2, show that the ORR is operative on this surface, with an onset of ca. 0.8 V. The voltammetry presented here agrees with previous reports.

Fig. 3.7C shows electrochemical surface stress-thickness changes occurring on the cathodic sweep with and without the presence of O2. Absent O2, the Pt surface
exhibits three regions of activity as the potential becomes more negative from 1.5 V to ca. 0.1 V. First, the surface stress becomes more tensile as the potential is swept to more negative values. Second, the tensile slope increases between 0.8 and 0.1 V, but abruptly becomes more compressive between 0.1 V to the negative potential limit of 0.0 V. The form of the potential-stress profile is consistent with the results of prior reports. The tensile stress observed between 0.8 V to 0.4 V is assigned to surface contraction resulting from oxygen removal during reduction of the surface oxide. The surface stress remains tensile as surface potential becomes more negative (0.5 to 0.2 V), which has been explained in the past as being a consequence of the increasing surface charge density in the double layer region. In general, increasing surface charge results in more attractive interactions between surface atoms, which cause tensile stress. Nevertheless, Stafford’s investigations show that isolating the contributions of adsorption using a macroscopic cantilever measurement, particularly within the double layer region, is not trivial. Importantly, Figure 3.7C shows that while surface stress-thickness curves from Ar and O\textsubscript{2} saturated solutions exhibit similar patterns, the curve from the O\textsubscript{2}-exposed sample is displaced in a more compressive direction over the entire potential window interrogated. The $\Delta$stress (Ar minus O\textsubscript{2}) responses of Pt under O\textsubscript{2} and Ar behave as predicted by Feibelman’s ab initio calculations, which predict a lengthening of M-M surface bonds, that is a reduction in tensile surface stress of the Pt surface, in the presence of adsorbed oxygen. As discussed in sections that follow, the quantitative aspects of these noted differences can be related to precise aspects of the M-M bonding dynamics, ones that EXAFS data help constrain and validate.
3.4.2 EXAFS Data Modeling

Data from XAS, here using small 1.2 nm average-sized clusters supported on C, help establish the magnitude of the structural relaxations that occur on Pt surfaces more similar to fuel cell catalysts, while simultaneously monitoring the electronic state of the d-band. The EXAFS region in XAS refers to the oscillatory part of X-ray absorption coefficient that begins at about 40 eV past the absorption edge. The oscillations originate from the interference of the outgoing and backscattered photoelectron waves. These fine structure oscillations are analyzed quantitatively by fitting a theoretical EXAFS equation that takes into account multiple scattering contributions of photoelectron paths, to the experimental data. From such fits, the bond distances of the metal-metal and metal-adsorbate pairs, their coordination numbers, as well as the values of mean square bond length disorder, $\sigma^2$ can be obtained.

Multiple scattering analysis of a representative nanoparticle sample, for the size/shape determination purpose, was performed using an approach reported in previous work. Figure 3.8 depicts the EXAFS data in k-space (Fig. 3.8A) and R-space (Fig. 3.8B) obtained with the sample held at a potential of 400 mV under N$_2$. The k-space range used in the Fourier transform was from 2.8 to 17.6 Å$^{-1}$ and the R-range used in the fit was from 1.4 to 6.3 Å. The k-space data obtained at other potentials are shown in Fig. 3.9. The $k^2$-weighting was applied to all the data. The most prominent peak at ca. 2.6 Å, uncorrected for the photoelectron phase shift, is due to the Pt-Pt contribution. The fitting region in k-space and r-space are indicated by arrows. The fitting model included the Pt-O contribution for the first nearest neighbor to a Pt atom as well as Pt-Pt contributions corresponding to the first five nearest coordination spheres around Pt absorbers in the
face centered structure. Multiple scattering paths were included in the theoretical
calculation as well, as described in greater detail in section 3.8. The best fit results for the
average coordination numbers of Pt-Pt neighbors in the coordination spheres of 1 through
4 around a Pt atom present in the cluster are presented in Table 3.1. The entire list of fit
results is reported in Table 3.2 in section 3.8.

The electrochemical structural sensitivities at all potentials were analyzed for the
nearest neighbor Pt-O and Pt-Pt contributions. The Pt-Pt bond distances obtained from
EXAFS fits (Fig. 3.10 – 3.12) of the R-space data are plotted versus potential in Figure
3.13A. The figure shows an increase in Pt-Pt bond distance, \( \langle R \rangle \), upon exposure to
oxygen at all potentials relative to \( \text{N}_2 \). Figure 3.13B shows the average bond expansion,
\( \Delta \langle R \rangle \). It is defined as the difference between the average bond distances under \( \text{O}_2 \),
\( \langle R \rangle_{\text{O}_2} \) and \( \text{N}_2 \), \( \langle R \rangle_{\text{N}_2} \), according to Eq. 3.1:

\[
\Delta \langle R \rangle = \langle R \rangle_{\text{O}_2} - \langle R \rangle_{\text{N}_2}
\] (3.1)

Fig. 3.13A shows that Pt-Pt distance under \( \text{O}_2 \) exposure is systematically longer
compared to the \( \text{N}_2 \) exposure, despite a partial overlap of the Pt-Pt distance error bars at
potentials greater than 500 mV. This expansion is more clearly observed in the
differential potential-dependent distances \( \Delta \langle R \rangle \) (Fig. 3.13B). The trends seen here show
that the \( \text{O}_2 \) environment, across a range of potentials that include the double layer region,
lead to small, but measurable, bond length elongation. These modest trends are ones that
are also inferred by mechanics models applied to the cantilever data, a point discussed
below.
3.4.3 Pt Nanoparticle Modeling

The measured bond length expansion is intrinsically averaged over all bonds sampled in the EXAFS experiment. The bonds averaged include those on the surface and in the interior of the Pt nanoparticle. Surface relaxations figure very prominently for supported Pt clusters of this size. In order to estimate the surface contribution to the overall bond length expansion, we modeled the Pt nanoparticle by constructing it to be consistent with the EXAFS derived coordination numbers and TEM-determined size range as described below. 69

In order to obtain the effective coordination number and thus particle size to estimate the surface contribution to the EXAFS we utilized results of the multiple-scattering fit to the data, described above (Fig. 3.8) and tabulated in Table 3.1. The relevant structural parameters for modeling the particle size and shape are the coordination numbers ranging from the first coordination shell (N1) to the fourth (N4). The coordination numbers and the STEM-determined average particle diameter (1.2 ± 0.6 nm, Fig. 3.2) were compared against their respective theoretical values calculated for three models of the perfect truncated (with 111 plane) cuboctahedron (T-CO) series to determine the best size that fits both EXAFS and STEM sets of results. The T-CO nanoparticles are thought to be a good model for supported Pt nanoparticles at the length scale considered here. 69 71 Table 3.1 shows that the T-CO most closely related to the combination of the experimental data (EXAFS and STEM) is that of a 1.1 nm, 37 atom particle. This average cluster structure is depicted schematically in Fig. 3.14. Figure 3.4 shows that minimal particle size changes occur during the course of the EXAFS measurement.
Figure 3.14 shows the cuboctahedral model used to define a surface-restricted expansion. In this surface-restricted model, the basal plane atoms are coordinated with the carbon support, and are therefore considered static atoms (blue). Surface atoms are represented in green. There are 129 total bonds ($N_{total}$) in this model, 75 of which involve at least one surface atom ($N_{surface}$) and 54 of which involve only static atoms ($N_{static}$) (Figure 3.15).

Using the 37 atom T-CO model, maximum and minimum values of the surface Pt-Pt bond expansion can be calculated from the ensemble-average EXAFS results, as the ORR is a surface phenomenon, it seems reasonable to assume that primarily the surface bonds will change during a reaction while the subsurface bonds and those surface bonds involving the carbon support will remain relatively unperturbed. Averaging over only the surface atoms results in the estimated maximum surface bond expansion value (vide infra). The opposite extreme is uniform bond expansion over the whole nanoparticle, resulting in the estimated minimum surface bond expansion value.

Fig. 3.16 reports these minimum and maximum oxygen-induced expansion values as a function of potential, using the modeling described above and in section 3.8 (Fig. 3.15). The figure shows there is a clear Pt-Pt surface bond expansion in the presence of O$_2$ at 400 mV, regardless of the model chosen. The expansion at this potential ranges from 0.006 ($\pm$0.004) Å for the ensemble minimum expansion to 0.011 ($\pm$0.006) Å for surface-restricted maximum expansion. These data correspond to a 0.23 ($\pm$0.15) % to 0.40 ($\pm$0.2) % relative expansions of the Pt-Pt bonds under O$_2$ over the Pt-Pt bonds present under N$_2$. Fig. 3.16 also shows the magnitudes of the Pt-Pt expansion occurring
in the presence of O$_2$ at other more positive potentials using the same limiting cases of the model. These data and calculations are detailed in section 3.8 (Table 3.3 and 3.4).

Adsorbate induced surface relaxation is a commonly observed phenomena,\textsuperscript{72-75} with lattice constant changes of about a few tenths of Å being common for Pt.\textsuperscript{37, 76-78} For example, hydrogen adsorption has been shown to expand the Pt-Pt near-surface bonds by 0.05 Å or less.\textsuperscript{79} Such values are important and theoretical modeling suggests that the surface lattice constant is linearly related to the energy of the d-band center.\textsuperscript{78} As the lattice expands, the d-band contracts, raising the energy of electrons near the Fermi level that can be donated to adsorbates. The XAS experiment probes both these bond length changes (via EXAFS) and the perturbations in the electronic structure (via XANES) in the same in-situ experiment. To this end, we repeated the XANES white line intensity measurements performed on 3 nm Pt/C particles in previous work\textsuperscript{53}, with the 1.2 nm Pt/C particles employed here, with similar trends being observed (Figure 3.17-3.19). The increased potential-dependent $\Delta$XANES intensify differences seen between O$_2$ and N$_2$ sparged environments, especially at more cathodic potentials, corresponds to an increase in electron density at or near the Fermi level and thus to an increase in the stability of O$_2$ and O adsorbates. At the same time, the unoccupied orbitals directly above the Fermi level are lowered in energy, reducing anti-bonding repulsion present in O adsorption.\textsuperscript{78}

### 3.4.4 Comparison of Cantilever and EXAFS Results

The data in Fig. 3.20 shows the differences between potential-dependent stress data for the Ar and O$_2$ cases more directly, with the O$_2$ displacement being evidenced lying between 0.05 and 0.2 N/m. Interestingly, we see in the cantilever measurement that the compressive displacement observed in the presence of O$_2$ is larger at more cathodic
potentials. Though this trend appears to be in qualitative agreement with the increased Pt-Pt bond expansion found in the EXAFS measurements reported above, the magnitude of the errors in the EXAFS data given the exceedingly small bond length changes being measured make it impossible to state with certainty what the functional form of the potential dependence might be other than that it must be weak over the potential range examined.

In order to compare the relative magnitudes of Δstress observed in the two measurements, we next use the EXAFS-derived Pt-Pt bond expansion to calculate a limiting magnitude for a M-M bond stress in order to compare this value with experiment. In cantilever-based measurements the stress is calculated using Stoney’s equation:

$$\Delta \sigma = \sigma^t - \sigma^0 = \frac{Y_s t^2 C}{6(1 - \nu_s)}$$  \hspace{1cm} (3.2)

Here $\Delta \sigma$ is the change in stress, $Y_s$ is the Young’s modulus of the substrate, $t_s$ is the substrate thickness, $C$ is the curvature of the cantilever, and $\nu_s$ is the Poisson ratio of the substrate. Stoney’s equation is valid in the limit where stress is proportional to the (elastic) strain via the Young’s modulus of the material:

$$\sigma_f = \varepsilon_f Y_f$$  \hspace{1cm} (3.3)

where $\sigma_f$ is the stress in the film, $\varepsilon_f$ is the strain in the film, and $Y_f$ is the Young’s modulus of the film. The Young’s modulus for Pt thin films has been reported in literature to have some variation, typically having values slightly less than that of bulk Pt.\textsuperscript{80-81} A value
of 147 GPa was taken from the literature and used as a reasonable approximation for this calculation.

The bond expansion is used to calculate the strain via:

\[ \epsilon_f = \frac{\Delta D}{a} \]  

(3.4)

where \( \Delta D \) is the change in bond distance and \( a \) is the Pt-Pt bond distance. From the 400 mV data from EXAFS, \( \epsilon_f \) ranges between 0.0023 and 0.0040 (using the minimum and maximum expansion models described above). Assuming the stress to be manifested over one atomic layer, i.e. using data from the maximum expansion model, an estimated stress thickness can be calculated, as is reported in Fig. 3.20.

Fig. 3.20 shows the stress-thickness derived from the EXAFS measurements overlaid with the change in stress due to \( O_2 \) exposure obtained from the cantilever method. Strikingly, the EXAFS derived stress-thickness nearly exactly overlaps the data from the cantilever-based measurement. As the potential decreases, compressive stress increases in the oxygenated system. It is interesting to note that the uncertainties in the EXAFS measurement give rise to error bars in the stress calculation that are larger than those found with the cantilever method. The nearly quantitative agreement in magnitude between the two techniques nonetheless means that other putative sources of stress change upon \( O_2 \) exposure – such as defects, surface roughness, and impurities – are likely insignificant contributors in this case and that cantilever measurements, via atomistic models of the mechanics, can yield information relevant to bond dynamics manifested at sub-picometer length scales.
3.5 Conclusions

This work shows that adsorbed O$_2$ results in Pt-Pt bond expansion relative to Pt absent this gas. The Pt-Pt bond length increases at more negative potentials as oxides are removed from the Pt surface. Electrochemical surface stress measurements obtained from Pt films shows that the presence of O$_2$ leads to compressive stress relative to the O$_2$-free case, the magnitude of which is nearly identical to that predicted using the Pt-Pt bond expansion obtained from the EXAFS. Our observation of oxygen induced Pt-Pt bond expansion provides additional input for computational studies examining the dynamic Pt-Pt bond during the ORR. It is shown here that the underlying atomistic bond dynamics manifest in macroscopic, measureable stress changes in a benchtop, microcantilever experiment.

The current results suggest that cantilever-based surface stress measurements, when conjoined with mechanics modeling, can provide a simple and quantitative means through which one can explore surface-localized bond-dynamics of metal electrocatalysts, doing so in ways that compliment in-operando data provided by XAS. We believe the current results suggest an important role that these methods can play in mechanistic studies of electrocatalysis. Our future work will explore this possibility, specifically for cases involving multimetallic compositions.

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3.7 Supplemental Information for Experimental Design and Analysis

3.7.1 Electrocatalyst Synthesis and Characterization Before XAS Data Acquisition

The Pt/C catalyst was prepared using the incipient wetness technique followed by heating under a H₂ atmosphere. Briefly, (NH₃)₄Pt(OH)₂ (Strem Chemicals, Inc.) was dissolved in a 0.1 M solution of NH₄OH (BDH Chemicals Ltd.) and mixed with enough carbon black (Cabot Corp.) to yield a 5% wt. loading of Pt. After allowing the solvent to evaporate, the impregnated C was reduced in a tube furnace at room temperature with 100% H₂ for 30 minutes. After this reduction step, the temperature was raised to and held at 300°C, for an additional one hour. Finally, the sample was cooled to room temperature under H₂ and flushed with Ar for 10 minutes prior to removal from the furnace. An ethanol suspension of the Pt/C sample was dropcast onto a carbon coated, 200 mesh Cu grid (Ted Pella, Inc.) and characterized using a JEOL model 2010-F scanning transmission electron microscope (STEM).
3.7.2 Nanoparticle Size Distribution

The STEM micrograph of the electrocatalyst is presented in Figure 3.2a. The corresponding size distribution is presented in Figure 3.2b. The particle size is 1.20 ± 0.6 nm (with one standard deviation).

3.7.3 Catalyst Deposition and MicroCT

The catalyst deposition is described in our previous paper. Briefly a slurry of the electrocatalyst with Nafion binder (1 mg catalyst : 1000 mg IPA : 4 µL 5 % NafionTM resin (510211, Sigma-Aldrich)) is sonicated for 1 hr. The catalyst suspension was airbrush deposited (Iwata High Performance Plus HP-B Plus, TCP Global) onto the carbon cloth electrode (CC6, Fuel Cell Earth) with high purity Ar carrier gas. The level of catalyst overspray was calculated utilizing X-ray microtomography (MicroCT). The grayscale signal, $S$, is proportional to the total catalyst mass, $m$, divided by area, $A$:

$$S \propto \frac{m}{A} \quad (3.5)$$

The catalyst was loading was found to be 2.5 mg Pt cm$^{-2}$, before and after XAS data acquisition. The standard utilized for MicroCT was a 1.3 cm diameter pellet containing 159.7 mg of 20 % Pt/C (E-tek) catalyst. The signal to loading ratios were utilized to calculate the amount Pt present in the sample, possible due to the much higher X-ray absorption by Pt than by C. The MicroCT image used for the loading calculation, prior to XAS acquisition, is presented in Figure 3.3.
3.7.4 Electrocatalyst Characterization After XAS Acquisition

The STEM micrograph of the electrocatalyst after XAS data acquisition is represented in Figure 3.4a. The corresponding size distribution plot is represented in Figure 3.4b. Particle ripening is null or minimal; the particle size after acquisition is 1.23 ± 0.37 nm vs. 1.20 ± 0.60 nm before data acquisition.

The MicroCT image of the electrode after XAS data acquisition, with the same standard used previously, is depicted in Figure 3.5. The loading calculated using is the same as before XAS acquisition (2.5 mg Pt/cm²).

3.7.5 Electrochemical Behavior of the Cell

Figure 3.6 depicts the electrochemical behavior of the cell. A CV of the electrode at 50 mVs⁻¹ is depicted in Figure 3.6a. The cell has low Pt loading (~5 % wt Pt/C), so the main CV peaks under N₂ are lacking; the charging current obfuscates the hydrogen under potential deposition (H-UPD) region observed with larger loading electrodes. The main Pt-oxide reduction peak is observed and when the electrode is exposed to O₂ the large cathodic ORR current associated with Pt is evident. The oxidation peak on the anodic sweep at 0.8 V in N₂ indicates that the Pt is at least partially oxidized above this potential.

The electrochemical behavior during XAS data acquisition is depicted in Figure 3.6b-c. Chronoamperometric data from Figure 3.6b shows that steady-state current conditions occur shortly after potential is applied, resulting in very small standard deviations of the current at each potential presented in Figure 3.6c.

The electrode loading, calculated by MicroCT (vide supra), was found to be 2.5 mg cm⁻² before and after data acquisition. The geometric area was 0.46 cm².
Electrochemical surface area was not calculated from the CV in Figure 3.6a due to the large charging current contribution.

3.7.6 EXAFS Fits

The multiple-scattering fits of the sample under N₂ at 400 mV shown in Figure 3.8 were performed as follows. The fitting model included the Pt-O contribution for the first nearest neighbor to a Pt atom as well as Pt-Pt contributions corresponding to the first five nearest coordination spheres around Pt absorbers in the face centered structure. Multiple scattering paths were included in the theoretical calculation as well. The basics of this fitting strategy were described in earlier works.69-70

The bond lengths between Pt atoms and their nearest Pt neighbors, up to the fifth neighbor, were constrained to follow the fcc structure, with the possibility to uniformly expand or contract, compared to the distances in bulk Pt. The Pt-O distance and the first nearest neighbor (1NN) Pt-Pt distance were varied independently. In addition, an anharmonic correction, or third cumulant, was added in the fit to the 1NN Pt-Pt path (its effect turned out to be negligible on the fit). The coordination numbers (CNs) and bond length disorder parameters (σ²) of all neighbors were varied independently, whereas the CNs and most of the σ² values of multiple-scattering paths were constrained. The triangular path (denoted as T1) between the first shell Pt atoms had its CN constrained to be 8 times larger than the CN of the first nearest Pt neighbor (1NN), as in the bulk. The next important triangular path, T2, between the central Pt and its 1st shell and 3rd shell neighbors, had its CN constrained to be 4 times larger than the CN of the 3NN. The CNs of the collinear paths connecting the central Pt, its 1NN and its 4NN were constrained as
follows: the double scattering (focusing) path DSF had the CN equal twice the CN of the path connecting the central Pt and its 4NN (to account for another, time-reversal, path through the same group of atoms) and the triple-scattering path TS had the CN equal to the Pt-4NN CN. In addition, the double scattering DS path between the central Pt atom and its 1NNs on the opposite sides was included in the fit as well. The single-scattering paths between Pt and its five nearest Pt neighbors are denoted P1-P5. The $\sigma^2$ values of the non-collinear paths were varied independently, while those of collinear paths, DSF and TS, were constrained to be equal to the $\sigma^2$ value of the P4 path. Some of the constraints used in the fit are also apparent from Table 3.2.

The amplitude factor was found from fitting the bulk Pt foil and fixed to be 0.867 in the fits of nanoparticle EXAFS data. The isotropic bond expansion factor was obtained to be $\varepsilon = \Delta R/R = -0.16\pm0.13\%$. The rest of the fitting results are given in Table 3.2.

The fits for Pt-Pt bond expansion measurements were done using the first nearest neighbor, single-scattering contributions only. The k-space data (red/solid) and fits (blue/dashed) are presented in Figures 3.9 and 3.10. The data was fit to R-space using Artemis software (Figures 3.11 and 3.12). EXAFS data were extracted from the raw absorption coefficient data using Autobk method that is implemented in the IFEFFIT data analysis package. The data were fit in R-space with FEFF6 theory using the nearest neighbor Pt-O and Pt-Pt contributions only. Since EXAFS cannot distinguish between O and N as the scattering atom, "Pt-O" refers to any pair of Pt and O or N as the 1NN. Fit windows are indicated with black arrows in Figures 3.11 and 3.12.
3.7.7 The 37-Atom Model of the Pt Bond Length Expansion

The nanoparticle used for the calculating the surface-restricted expansion contains 37 total atoms with 129 total bonds (Fig. 3.14 and Table 3.1). Atoms in Fig. 3.15 are indicated by large green and blue circles, later designated as surface, expanding atoms (green) and subsurface, static, non-expanding atoms (blue). The model 37 atom, perfect truncated cuboctahedral (PTCH) nanoparticle contains three rows of atoms; there are 6 atoms in the upper plane, 12 in the middle plane, and 19 basal atoms. The atom positions above each plane are indicated by the red dots in the lower planes.

There are 129 total bonds in this model nanoparticle. Each atom in the upper plane has three bonds to the lower plane for a total of 54 interplane bonds. There are 9 in-plane bonds in the first layer, 24 bonds in middle plane and the basal plane contains 42 in-plane bonds.

For the surface restricted expansion, the expanding atoms are indicated in green (15 total), and the static atoms are blue (22 total) (Fig. 3.14). All bonds connected to expanding atoms will lengthen (75 dynamic surface bonds). Each expanding atom has 3 inter-plane bonds connecting it to the lower plane, totaling 45 bonds. The in-plane bonds that expand are indicated in orange; the top plane contains 9 lengthening in-plane bonds, the middle 21 lengthening in-plane bonds.

The average bond distance, $\langle R \rangle$, is a combination of the total number of surface and static bonds, $N_{surface}$ and $N_{static}$ as well as the average surface and static bond distances, $\langle R \rangle_{surface}$ and $\langle R \rangle_{static}$. 

70
\[
\langle R \rangle = \frac{\langle R \rangle_{\text{Surface}} + \langle R \rangle_{\text{Static}}}{N_{\text{total}}}
\] (3.6)

For the purposes of this derivation, surface-surface and surface-static bonds are averaged due to the relatively small expansion observed experimentally.

Under the maximum, surface-restricted model, O\(_2\) adsorption affects the surface only, so the summations involving static bonds under O\(_2\) and N\(_2\) are identical:

\[
\langle R \rangle_{\text{Static}}^{\text{Surface}} = \langle R \rangle_{\text{Static}}^{\text{Surface}}
\] (3.7)

Combining Eq. 3.6 and 3.7 and examining both the O\(_2\) and N\(_2\) cases gives the difference between \(\langle R \rangle_{N_2}\) and \(\langle R \rangle_{O_2}\)

\[
\left( \langle R \rangle_{O_2} - \langle R \rangle_{N_2} \right) N_{\text{Total}} = \frac{\langle R \rangle_{\text{Surface}}^{\text{Surface}}}{N_{\text{Surface}}}^{O_2} - \frac{\langle R \rangle_{\text{Surface}}^{\text{Surface}}}{N_{\text{Surface}}}^{N_2}
\] (3.8)

By dividing by the total surface atoms, we can find the average bond expansion for surface atoms, simplified as:

\[
\langle R \rangle_{\text{Max}} = \left( \langle R \rangle_{O_2} - \langle R \rangle_{N_2} \right) \frac{N_{\text{Total}}}{N_{\text{Surface}}} = \frac{\langle R \rangle_{\text{Surface}}^{\text{Surface}}}{N_{\text{Surface}}}^{O_2} - \frac{\langle R \rangle_{\text{Surface}}^{\text{Surface}}}{N_{\text{Surface}}}^{N_2}
\] (3.9)

3.7.8 Quantitative Results from in situ Electrochemical EXAFS Experiments

The fit results are presented in Table 3.3. EXAFS derived data are represented in Table 3.3. The bond length changes in the Pt catalyst operated in the presence of O\(_2\) and N\(_2\) are plotted in Fig. 3.13 and 3.16, are presented in Table 3.4. The Pt-Pt expansion
values for the ensemble measurement and for the maximum expansion (Eq. 3.6 – 3.9) are presented in Table 3.4. Table 3.4 contains relative change of Pt-Pt bond distance changes between O₂ and N₂.

3.7.9 XANES Data

The normalized XANES data for all experiments described in this work are depicted in Fig. 3.17. The data under O₂ are depicted in solid lines, while the data under N₂ are depicted in dotted lines. At all potentials, the white line intensity is larger under O₂ than under N₂, as described in section 3.5. The data in Fig. 3.17 is utilized for the ΔXANES data depicted in Fig. 3.18a, normalized against the data at the lowest intensity at 400 mV in N₂.

In Figure 3.18(a), the ΔXANES μ(E) intensity data for XAS experiments normalized by subtraction of the data at 400 mV under N₂. (b) shows the integrated values from (a). Error bars are calculated from the average standard deviation from 11575 to 11585 eV in (a) for all scans (excluding the scan used for normalization, 400 mV under N₂), multiplied by the integration range (10 eV).

The integrated ΔXANES intensity from Fig. 3.18 b (dotted lines), is plotted against data from our previous study (solid lines) in Figure 3.19. Our previous study utilized a larger 3.0 ± 1.0 nm electrocatalyst (solid lines). Fig. 3.19 further illustrates how the trend seen from previous experiments is repeated, but with a much smaller magnitude. This smaller change in d-band vacancy is due to the much smaller particle size, removing much of the possible contribution from bulk oxide formation. The small
increase between 400 and 500 mV in the 1.2 nm particle $\Delta\mu(E)$ data is likely due to precoordination of H$_2$O.

3.8 Figures and Tables

Figure 3.1: (a) The contraction or expansion of surface bonds yield stresses that by convention are described as mediating either tensile or compressive modes of deflection in a macroscale cantilever, respectively. (b) Aberration-corrected STEM image of an exemplary, individual Pt nanoparticle supported on carbon.
Figure 3.2: (a) STEM micrograph of the nanoparticles used in the experiment, 5 % Pt on Vulcan XC-72. (b) The size distribution calculated from the STEM image, resulting in 1.20 nm ± 0.60 nm.
Figure 3.3: MicroCT image used for calculation of the electrode loading, before electrochemical testing and XAS data acquisition occurred.
Figure 3.4: (a) STEM micrograph of the nanoparticles used in the experiment, 5 % Pt on Vulcan XC-72, after XAS data acquisition. (b) The size distribution calculated from the STEM image, resulting in $1.23 \pm 0.37$ nm.
Figure 3.5: MicroCT image of the electrode, after XAS data acquisition, above a standard pellet used to calculate a loading by comparison of Pt content (vide supra).
Figure 3.6: Electrochemical behavior of the cell. (a) The CV of the electrode at 50 mV/s, characteristic of low Pt loading (5% Pt/C) in acidic electrolyte. (b) The operational current densities at varied potentials. (c) Averaged limiting current densities over 30 minutes of acquisition time (error bars = 1 std. dev.)
Figure 3.7: (a) and (b) show characteristic cyclic voltammograms of Pt/glass under Ar and O₂ sparged environments, respectively. (c) Stress data of Pt/glass of both Ar and O₂ conditions.
Figure 3.8: (a) k space and (b) R space plots of the k2-weighted EXAFS data under N2 at 400 mV, with a multiple-scattering fit. Best fit results or coordination numbers for Pt-Pt shells from 1 through 4 are presented in Table 3.1. The k-space and r-space Fourier transform window boundaries used for the fits are marked with black arrows.
Figure 3.9: k-space data (O\textsubscript{2} red, N\textsubscript{2} black) for the electrode at (a) 1200 mV, (b) 900 mV and (c) 600 mV (d) 500 mV and (e) 400 mV vs. NHE.
**Table 3.1:** Coordination numbers from EXAFS derived data from the sample measured under N_2 at 400 mv and the mean particle diameter obtained by STEM, compared to three cuboctahedral models.

<table>
<thead>
<tr>
<th></th>
<th>Total atoms</th>
<th>N_1</th>
<th>N_2</th>
<th>N_3</th>
<th>N_4</th>
<th>Diameter / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td>n/a</td>
<td>6.7 ± 0.4</td>
<td>3.1 ± 1.5</td>
<td>12.3 ± 4.7</td>
<td>4.7 ± 1.4</td>
<td>1.2 ± 0.6</td>
</tr>
<tr>
<td><strong>Models</strong></td>
<td>10</td>
<td>4.8</td>
<td>1.2</td>
<td>2.4</td>
<td>0.6</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>7.0</td>
<td>2.4</td>
<td>7.1</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>92</td>
<td>8.2</td>
<td>3.2</td>
<td>10.4</td>
<td>5.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Table 3.2: Pt-Pt and Pt-O coordination numbers, bond lengths, and $\sigma^2$ values from the multiple-scattering EXAFS fit obtained for the sample at under N=2 at 400 mV. The values shown together with their uncertainties correspond to the independent fitting variables. The rest of the values were constrained in the fits as described above.

<table>
<thead>
<tr>
<th>Path</th>
<th>N</th>
<th>R(Å)</th>
<th>$\sigma^2$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-O</td>
<td>0.7 ± 0.2</td>
<td>2.00 ± 0.02</td>
<td>0.003 ± 0.003</td>
</tr>
<tr>
<td>P1</td>
<td>6.7 ± 0.4</td>
<td>2.751 ± 0.006</td>
<td>0.0052 ± 0.0002</td>
</tr>
<tr>
<td>P2</td>
<td>3.1 ± 1.5</td>
<td>3.91</td>
<td>0.0073 ± 0.0022</td>
</tr>
<tr>
<td>P3</td>
<td>12.3 ± 4.7</td>
<td>4.79</td>
<td>0.0083 ± 0.0015</td>
</tr>
<tr>
<td>P4</td>
<td>4.7 ± 1.4</td>
<td>5.54</td>
<td>0.0049 ± 0.0022</td>
</tr>
<tr>
<td>P5</td>
<td>2.9 ± 3.8</td>
<td>6.19</td>
<td>0.0048 ± 0.0042</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Path</th>
<th>N</th>
<th>R(Å)</th>
<th>$\sigma^2$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>24.6 (=8N_F2)</td>
<td>4.15</td>
<td>0.012 ± 0.019</td>
</tr>
<tr>
<td>T2</td>
<td>49.1 (=4N_F3)</td>
<td>5.16</td>
<td>0.016 ± 0.012</td>
</tr>
<tr>
<td>DSF</td>
<td>9.5 (=2N_F4)</td>
<td>5.54</td>
<td>0.0049 (= $\sigma^2_{F4}$)</td>
</tr>
<tr>
<td>DF</td>
<td>4.7 (=N_F4)</td>
<td>5.54</td>
<td>0.0031 ± 0.0029</td>
</tr>
<tr>
<td>TS</td>
<td>4.7 (=N_F4)</td>
<td>5.54</td>
<td>0.0049 (= $\sigma^2_{F4}$)</td>
</tr>
</tbody>
</table>
Figure 3.10: k-space data and fits for Pt under O$_2$. 
Figure 3.11: R-space data and fits for Pt catalysts in the electrochemical cell under N₂ flow.
Figure 3.12: R-space data and fits for Pt catalysts in the electrochemical cell under $O_2$ flow.
**Figure 3.13:** (a) Pt-Pt bond distances under N\textsubscript{2} and O\textsubscript{2} at three potentials in the double layer region (400 mV, 500 mV and 600 mV) and at the ORR onset potential (900 mV) and at an oxidizing potential (1200 mV). (b) Δ⟨R⟩ at all potentials, showing a distinct expansion at all potentials upon exposure to O\textsubscript{2}.
**Figure 3.14**: Depiction of the 37 atom, perfect truncated cuboctahedral nanoparticle, the best of the three models in terms of their agreement with EXAFS results (Tables 3.1 and 3.2); this T-CO was used for calculating the maximum, surface-restricted expansion. The static atoms in the surface-restricted expansion model (Eq. 3.9) are represented in blue, whereas the dynamic surface Pt atoms are represented in green. This ideal particle has 37 atoms with 129 total Pt-Pt bonds, of which 75 lengthen when the 15 surface atoms expand.
**Figure 3.15:** The 37 atom, perfect hemispherical, truncated cuboctahedron used in calculating the surface-restricted expansion. Surface atoms are in green, whereas the bulk, static atoms are blue. Each expanding planar Pt-Pt bond is marked with orange solid lines. Each surface atom also has 3 expanding bonds to Pt atoms in the lower plane. Small red dots indicate where the Pt atoms in plane above are positioned. The truncated cuboctahedron used for this model has 129 total bonds with 75 surface bonds for the 15 surface atoms.
**Figure 3.16:** The minimum and maximum Pt-Pt surface bond expansion under $O_2$ calculated from the ensemble measurement and surface-restricted expansion. Plotted are both absolute expansions, $\Delta \langle R \rangle_{\text{Min}}$ and $\Delta \langle R \rangle_{\text{Max}}$, and percent expansion. Derivations are included in the supporting information.
Table 3.3: Pt-Pt and Pt-O coordination numbers, bond lengths, and $\sigma^2$ values from the EXAFS fits obtained at under the O$_2$ and N$_2$ at the indicated potentials.

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>N(Pt-Pt)</th>
<th>R(Pt-Pt) / Å</th>
<th>$\sigma^2$(Pt-Pt) / Å$^2$</th>
<th>N(Pt-O)</th>
<th>R(Pt-O) / Å</th>
<th>$\sigma^2$(Pt-O) / Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ 400 mV</td>
<td>6.3 ± 0.4</td>
<td>2.762 ± 0.003</td>
<td>0.0052 ± 0.0002</td>
<td>0.7 ± 0.2</td>
<td>2.00 ± 0.02</td>
<td>0.004 ± 0.004</td>
</tr>
<tr>
<td>N$_2$ 500 mV</td>
<td>6.3 ± 0.6</td>
<td>2.762 ± 0.004</td>
<td>0.0049 ± 0.0003</td>
<td>0.6 ± 0.3</td>
<td>2.00 ± 0.03</td>
<td>0.004 ± 0.006</td>
</tr>
<tr>
<td>N$_2$ 600 mV</td>
<td>6.5 ± 0.4</td>
<td>2.761 ± 0.003</td>
<td>0.0051 ± 0.0002</td>
<td>0.6 ± 0.2</td>
<td>2.02 ± 0.01</td>
<td>0.002 ± 0.002</td>
</tr>
<tr>
<td>N$_2$ 900 mV</td>
<td>6.6 ± 0.7</td>
<td>2.762 ± 0.004</td>
<td>0.0057 ± 0.0004</td>
<td>0.7 ± 0.3</td>
<td>2.00 ± 0.02</td>
<td>0.003 ± 0.004</td>
</tr>
<tr>
<td>N$_2$ 1200 mV</td>
<td>6.2 ± 0.6</td>
<td>2.761 ± 0.004</td>
<td>0.0051 ± 0.0004</td>
<td>0.7 ± 0.3</td>
<td>2.00 ± 0.02</td>
<td>0.003 ± 0.003</td>
</tr>
<tr>
<td>O$_2$ 400 mV</td>
<td>5.9 ± 0.5</td>
<td>2.768 ± 0.003</td>
<td>0.0050 ± 0.0003</td>
<td>1.2 ± 0.5</td>
<td>2.01 ± 0.02</td>
<td>0.006 ± 0.005</td>
</tr>
<tr>
<td>O$_2$ 500 mV</td>
<td>5.8 ± 0.4</td>
<td>2.767 ± 0.003</td>
<td>0.0047 ± 0.0003</td>
<td>0.9 ± 0.3</td>
<td>2.01 ± 0.01</td>
<td>0.003 ± 0.003</td>
</tr>
<tr>
<td>O$_2$ 600 mV</td>
<td>6.3 ± 0.5</td>
<td>2.765 ± 0.003</td>
<td>0.0052 ± 0.0003</td>
<td>0.6 ± 0.2</td>
<td>2.01 ± 0.01</td>
<td>0.000 ± 0.001</td>
</tr>
<tr>
<td>O$_2$ 900 mV</td>
<td>6.2 ± 0.6</td>
<td>2.765 ± 0.004</td>
<td>0.0052 ± 0.0004</td>
<td>0.7 ± 0.2</td>
<td>2.02 ± 0.01</td>
<td>0.000 ± 0.002</td>
</tr>
<tr>
<td>O$_2$ 1200 mV</td>
<td>5.7 ± 0.4</td>
<td>2.766 ± 0.003</td>
<td>0.0048 ± 0.0003</td>
<td>0.7 ± 0.2</td>
<td>2.00 ± 0.01</td>
<td>0.000 ± 0.001</td>
</tr>
</tbody>
</table>

Table 3.4: Bond lengths and expansion of Pt-Pt bonds upon exposure to O$_2$ are shown under uniform expansion of all Pt bonds and when expansion is limited to surface bonds, according to the model described above.

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>$\Delta R$(Pt-Pt) / Å</th>
<th>$\Delta R$(Pt-O) / Å</th>
<th>Surface limited exp. R(Pt-Pt) / Å</th>
<th>Surface limited exp. $\Delta R$(Pt-Pt) / Å</th>
<th>Surface limited exp. %Exp</th>
<th>Surface limited exp. %Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 mV</td>
<td>0.006 ± 0.004</td>
<td>0.00 ± 0.02</td>
<td>2.773 ± 0.006</td>
<td>0.011 ± 0.006</td>
<td>0.2 ± 0.2</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>500 mV</td>
<td>0.005 ± 0.005</td>
<td>0.01 ± 0.03</td>
<td>2.770 ± 0.006</td>
<td>0.008 ± 0.007</td>
<td>0.2 ± 0.2</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>600 mV</td>
<td>0.004 ± 0.004</td>
<td>-0.01 ± 0.02</td>
<td>2.768 ± 0.006</td>
<td>0.007 ± 0.006</td>
<td>0.2 ± 0.1</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>900 mV</td>
<td>0.003 ± 0.006</td>
<td>0.02 ± 0.02</td>
<td>2.767 ± 0.007</td>
<td>0.005 ± 0.008</td>
<td>0.1 ± 0.2</td>
<td>0.2 ± 0.3</td>
</tr>
<tr>
<td>1200 mV</td>
<td>0.005 ± 0.005</td>
<td>-0.00 ± 0.02</td>
<td>2.769 ± 0.005</td>
<td>0.008 ± 0.007</td>
<td>0.2 ± 0.2</td>
<td>0.3 ± 0.2</td>
</tr>
</tbody>
</table>
Figure 3.17: Near-edge region of Pt L3 edge data, obtained under O$_2$ or N$_2$ atmosphere conditions. The inset shows the region near the maximum in the range from X to Y.
Figure 3.18: ΔXANES data, (a), and integrated areas under O$_2$ and N$_2$ atmospheres, (b).
Figure 3.19: Integrated values from Fig. 3.18b (dotted lines) plotted against 3.0 nm particle data from a previous study (solid lines). {Erickson, 2012}
Figure 3.20: Characteristic stress differences obtained from in situ cantilever and EXAFS measurements. The black line shows delta stress of Ar minus O₂ (from Fig. 3.7c) and the blue points indicate the expected delta stress based on the Pt-Pt bond strains obtained via EXAFS.
3.9 References


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Chapter 4: Passivation Dynamics in the Anisotropic Deposition and Stripping of Bulk Magnesium Electrodes During Electrochemical Cycling


4.1 Preface to the 4th Chapter

This chapter focuses primarily on the solid-electrolyte interphase (SEI) and the literature of Mg batteries prior to 2008. The current problems facing Mg batteries and the literature since 2008 will be discussed in further detail in the preface of the following chapter. The division in the discussion of literature is meant to emphasize the recent, immense gain in understanding of non-aqueous Mg chemistry, especially after the advances from 2008-2015. This increase in understanding is reflected in the spike in publications specifically in 2008 and 2013 as can be seen from Figure 4.1. Figure 4.1 is a Scopus search using the terms ‘magnesium’ and ‘battery’. The publications on Mg batteries follow an exponential increase that tentatively can be attributed to the internet journal era and the increased interest in battery research for energy storage, but superimposed on this exponential increase are notable spikes between 2008 and 2013. The research performed in this dissertation reflects this research trend, beginning with a more fundamental study of a traditional electrolyte followed by a study of a newly developed electrolyte that is more representative of the current generation of electrolytes.
4.1.1 An Introduction to Magnesium Battery Anodes and Electrolytes

As outlined in Chapter 1, Mg is in a ‘hot spot’ for energy dense materials. It has a $2^+$ charge yet its ionic radius is nearly identical to that of lithium. If double the charge in the same amount of space sounds too good to be true, that is because it is. Along with the $2^+$ charge comes a completely different chemistry that still is causing difficulties for researchers. The $2^+$ charge state causes issues that span every component of the battery from anode to cathode. Possibly the clearest evidence of this problem is at the cathode where there is really only one material that has been shown to work well with Mg. In 2000, Aurbach’s group showed that the Chevrel phase, $\text{Mg}_2\text{Mo}_6\text{S}_8$ works well as a cathode but has a relatively low energy density compared to Li-ion cathodes (Aurbach, 2000). Over the following decade Aurbach’s group went on to produce some of the seminal research that established the groundwork for the expansive research that followed in the first part of the 2010’s.

The theoretical benefit of Mg anodes still entices researchers, even with the problems associated with the increased charge density. Summarized in Figure 4.2, Mg has more mass which translates to a lower gravimetric capacity than Li. In fact, the gravimetric capacity of Mg is about half that of Li. The real benefit for Mg then is when volume is the limiting critical element because the volumetric capacity of Mg is nearly double that of Li.

In order to realize the full volumetric benefits of Mg, new cathodes needed to be developed that would surpass the Chevrel phase. Oddly enough the limitation was not only in the cathode material, but in the electrolyte to test the materials. The increased charge density has a very challenging effect on the electrolyte: traditional Li-ion electrolytes do not work with Mg. Many Mg salts simply will not dissolve in useful concentrations that yield solutions with high conductivity. Those salts that will dissolve often decompose when in contact with Mg or the salts
undergo side reactions that result in species that react with Mg. Also only a handful of ethers are reductively stable towards Mg at potentials low enough for Mg electrodeposition, further limiting possible electrolyte combinations that are stable at both electrodes. The result is that a thin, non-conductive SEI is often present that passivates the electrode (where X denotes a halide). The SEI is the most important part of Li-ion batteries due to its electrically insulating yet ionically conducting properties that allow Li-ions to insert into an electrode host material without allowing Li electrodeposition. In addition, the SEI in Li-ion batteries is relatively stable, so a well-engineered Li-ion battery loses very little capacity to forming the SEI after the first one or two charge cycles. For Mg batteries the SEI must be completely removed if formed, which causes a serious drop in capacity each cycle.

Even though there have been immense research efforts to understand the SEI in Li-ion batteries, the true nature of its structure and function remains elusive due to the complex, multi-component nature of its formation. Mg SEI formation is similarly complex although far fewer studies have examined it. The importance of the Mg SEI and its relatively unknown nature presented an intriguing research opportunity. We sought to answer questions including: What is the elemental composition of the SEI and what is the primary source of the SEI (i.e. salt vs. solvent)? In the process it was determined that many of the processes that define the SEI are intimately connected to the process of corrosion.

4.2 Abstract

Although rechargeable magnesium (Mg) batteries show promise for use as a next generation technology for high-density energy storage, little is known about the Mg anode solid electrolyte interphase and its implications for the performance and durability of a Mg-based
battery. We explore in this report passivation effects engendered during the electrochemical cycling of a bulk Mg anode, characterizing their influences during metal deposition and dissolution in a simple, non-aqueous, Grignard electrolyte solution (ethylmagnesium bromide, EtMgBr, in tetrahydrofuran). Scanning electron microscopy images of Mg foil working electrodes after electrochemical polarization to dissolution potentials show the formation of corrosion pits. The pit densities so evidenced are markedly potential dependent. When the Mg working electrode is cycled both potentiostatically and galvanostatically in EtMgBr these pits, formed due to passive layer breakdown, act as the foci for subsequent electrochemical activity. Detailed microscopy, diffraction, and spectroscopic data show that further passivation and corrosion results in the anisotropic stripping of the Mg {0001} plane, leaving thin oxide-comprising passivated side wall structures that demark the {0001} fiber texture of the etched Mg grains. Upon long term cycling, oxide side walls formed due to the pronounced crystallographic anisotropy of the anodic stripping processes, leading to complex overlay anisotropic, columnar structures, exceeding 50 µm in height. The passive responses mediating the growth of these structures appear to be an intrinsic feature of the electrochemical growth and dissolution of Mg using this electrolyte.

4.3 Introduction

Recently there has been an accelerated push toward the development of rechargeable batteries that use bulk metal anodes. The use of metal anodes in energy storage devices is seen as being advantageous due in part to their high theoretical energy densities and capacities. Various performance-related issues, however, have limited the development of market-ready, bulk metal-anode-based rechargeable batteries. Lithium (Li) metal, for instance, has received significant attention in research, but to date viable technologies have yet to emerge due to battery
failures that occur from the formation of Li dendrites that grow out from the metal anode surface as a result of repetitive charging and discharging.\textsuperscript{12} Research into the causes and strategies for the elimination of Li metal dendrites is a subject of ongoing work in the field.\textsuperscript{13-17}

Due to its physical and chemical properties, magnesium (Mg) has been considered as an alternative anode to Li metal, especially for the case of rechargeable batteries for electric vehicles. Compared to Li, Mg is divalent (with a theoretical volumetric capacity of 3832 versus 2062 mAh cm\textsuperscript{-3}), more abundant, less toxic and, most importantly, less susceptible to dendritic growth. Metallic Mg is highly reactive, however and is thus susceptible to passivation, which is problematic for its use as an electrode. When exposed to air, Mg forms a surface layer consisting of atmospheric contaminants, most notably oxide and hydroxide, although with proper surface preparation this surface film can be reduced or eliminated.\textsuperscript{1} Nevertheless, even if the initial oxide layer is removed, Mg still can be passivated from species developed as a consequence of electrochemical activity. The current literature suggests the reactivity of the electrolyte solvent plays a central role to this end. Such features of the reactivity of Mg have limited the use of non-aqueous solvents to primarily ethers.\textsuperscript{18}

Such issues notwithstanding, there has been a marked increase in work focused on the study of Mg rechargeable batteries.\textsuperscript{19-31} The majority of this work has been focused on the discovery and characterization of novel non-aqueous electrolytes with large electrochemical windows. Notable non-aqueous magnesium battery corrosion work has focused on current collector corrosion and has shown that Mo is stable to high potentials whereas stainless steel is not, implying stainless steel components high in Mo content may yield stable Mg battery current collectors and casings.\textsuperscript{23, 32} Although the stability of non-active components towards corrosion is important for Mg batteries, the study of passivation and corrosion of Mg itself is also important
for understanding Mg self-discharge and losses in coulombic efficiency. Hardly any work related to Mg rechargeable batteries has examined the morphology of bulk Mg anodes as result from extended electrochemical processing in non-aqueous solutions, except to note that Mg tends to form strongly passivated surfaces using electrolyte mimics of traditional Li-ion batteries.\textsuperscript{1}

In this paper we examine the morphologies of Mg anodes after polarization to dissolution potentials, as well as cyclic potential steps, in order to develop insights into the passivation dynamics and electrochemically-mediated corrosion processes of Mg as occur in Grignard-based electrolytes and how these processes might impact the viability of Mg as an energy storage material. Even though it has shown increased solvent stability towards noble metals, we do not explore the effects of lewis acid addition due to the complex equilibria of species affected by electrolyte synthesis procedures that are in stark contrast to the highly reproducible, widely studied ethylmagnesium bromide in THF. We show that upon extensive cycling the inherent dynamics of the processes involved are distinguished by strong crystallographic anisotropies and passive film formation, particularly during Mg stripping, that lead to the growth of anisotropic columns of Mg that could lead to battery failures not unlike those that result from Li dendrites.

\section*{4.4 Experimental Details}

Ethylmagnesium bromide, 1.0 M in tetrahydrofuran (EtMgBr-THF), the electrolyte used for all electrochemical experiments, was purchased from Sigma-Aldrich and used with no further preparation. All electrochemical experiments were carried out in an Argon-filled MBRAUN LABstar glovebox. Electrochemical experiments were performed using either a CH Instrument 650 B or 660 D analyzer/workstation. Electrochemical cell components were acid washed, rinsed with Milli-Q water, and oven dried before each use. Magnesium foil (GalliumSource,
LLC), 99.95% and 0.05 mm thick, was used as the working electrode for most experiments. Immediately prior to each experiment a new piece of Mg foil was polished with 421 polishing compound, a felt pad, and rotary tool (all purchased from Dremel) inside the glovebox, then washed with THF and wiped with a cloth to remove excess polishing compound. Although several chemical polishing methods were attempted, mechanical polishing inside the glovebox resulted in the best finish and thinnest oxide layer on Mg (as confirmed by electrochemical and microscopy measurements). For all experiments the counter and reference electrodes used were similarly polished strips of Mg ribbon.

The scanning electron microscope (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and focused ion beam (FIB) instrumentation used in this work are located at the Frederick Seitz Materials Research Laboratory (FS-MRL) on the campus of the University of Illinois at Urbana-Champaign and described at mrl.illinois.edu. The helium ion microscope (HIM) images were taken at Bielefeld University in Bielefeld, Germany (see below).

A Hitachi S4700 high resolution SEM and a JEOL 7000F analytical SEM were used in the collection of SEM images. After the completion of each experiment, the Mg foil was rinsed with THF and allowed to dry inside the glovebox after which it was transferred to the SEM. During transfer to the SEM the Mg foil is exposed to air therefore, in order to limit this exposure, Mg foils were transferred immediately before analysis.

A PANalytical Philips X’pert MRD system equipped with a Cu K-α source at 0.15418 nm was used for x-ray diffraction experiments. A polycrystalline Mg substrate was purchased from MTI Corporation and used as a reference. XRD 2-theta scans were taken at a scan rate of 2° min⁻¹ for both the Mg foil and polycrystalline substrate. Pole figures of the (002) diffraction
line were also obtained for both samples of Mg. XRD results were analyzed using JADE XRD analysis software.

A Physical Electronics PHI 5400 equipped with a Mg source and a pass energy of 35.75 eV, was used to obtain high resolution XPS results for polished, stripped, and cycled Mg foils. Electrochemical experiments were conducted inside the glovebox after which, the foils were rinsed with THF and then immediately placed within an XPS transfer vessel. The XPS vessel was then doubly sealed in resealable bags and transported directly from the glovebox to the XPS instrument, where the vessel works as a load lock. The transfer procedure was done to keep the samples from being exposed to air. The samples were electrically grounded, and binding energies were calibrated using the Ag 3d5/2 peak at 368.06 eV (+0.24 eV) measured from a reference foil within the vacuum chamber.

A FEI Helios 600i focused ion beam (FIB) with a gallium ion source was used to mill structures in preparation for helium ion microscope imaging. The HIM images were taken with a Carl Zeiss Orion Plus helium ion microscope operating with an accelerating voltage of about 39.5 kV and a current of about 0.4 pA. Sample distance was 11 mm with a spot size of 10 µm and each image used averaging of 32 lines with a dwell time of 1 µs per pixel.

4.5 Results and Discussion

Figure 4.3a shows the current-time transients (solid traces) obtained from three Mg foil working electrodes stepped from open circuit potential (approximately 50 mV vs. Mg) to potentials held at 500, 700, and 900 mV in a 1.0 M solution of EtMgBr in THF for 1800 seconds. The potentiostatic stripping experiments highlight the initial state characteristics of the anode surface and maintain a surface at constant potential in order to evaluate the relative contribution
of thermodynamic and kinetic contributions to stripping. Current-time transients of
electrochemically-mediated metal dissolution have been used previously to elucidate the relative
kinetic and thermodynamic contributions to such processes for Cu in an aqueous electrolyte
system. In a similar vein, Souto et al. used nucleation and growth models to characterize the
potentiostatically controlled dissolution of a Cu electrode, including above the potential at which
the passive film breaks down, $E_b$, where contributions to the current density are controlled by a
mixture of kinetics and diffusion. The most important point for the discussions that follow is
that above $E_b$, Souto et al. observe a Cu corrosion process dominated by pit corrosion. It is
observed, based on an inspection of the data presented in Figure 4.4, that a freshly polished Mg
foil in EtMgBr-THF has an apparent $E_b$ of about 250 mV (1st cycle electrodissolution
overpotential due to the initial oxide layer); since we are above this potential for the applied
potentials used for Figure 4.3a, it is likely that the currents seen there are ones lying in the mixed
kinetic and diffusion controlled regime. Although the Cu-aqueous system is not analogous to
our system we fit the experimental data in Figure 4.3a (dashed traces) using the following
general current equations established for dissolution nucleation and growth:

$$j_t = j_c + j_d'$$  \hspace{1cm} (4.1)

$$j_c = P_4 [1 - \exp(-P_5 t^2)]$$  \hspace{1cm} (4.2)

$$j_d' = P_6 t^{-1/2} [1 - \exp(-P_7 t)]$$  \hspace{1cm} (4.3)

The current response is related to the kinetic term, $j_c$, and the diffusion term, $j_d'$. The parameters
$P_4$ and $P_5$ contain apparent rate constants for the pit growth. The parameters $P_6$ and $P_7$ contain
the term for the diffusion coefficient of Mg ions in solution. These parameters also contain
constants and properties of Mg and are fully addressed in section 4.8 and reference 30. As shown
in the work done by Souto et al., the kinetic term models the pit growth and nucleation and the diffusion term models the metal dissolution through a passive film, which suggests that the response of the Mg metal to the potentials applied in Figure 4.3 is the formation of pits with Mg dissolution through a passive film, so evidenced with experimental results shown below. The fit parameters for the transient models are provided in Table 4.1. The best fits were achieved when the total contribution to the current included both the kinetic and diffusion controlled transient models. Though the fact remains that Mg dissolution behaviors are not entirely understood, the goodness of fit of these models to our experimental data may supply a fundamental understanding of the dynamics involved in the dissolution of Mg in a non-aqueous electrolyte.

The data in Figure 4.3b presents an expanded view of the current density measured from 0 – 100 seconds for each of the three applied potentials examined. These data show that, during each potential hold, there appears to be a period of quiescence — a time before substantial current begins flowing. This period appears to be greatest for the lowest magnitude potential step (500 mV) and approximately the same for the two higher overpotentials. These features have the functional form of a pitting corrosion process, where the initial induction time arises as an inherently stochastic process. The fact that the initial current flow at the first potential step is not linearly correlated with the applied potential is indicative of attributes of compositional/structural complexity present in the residual oxide film left on the Mg surface by the polishing step used to activate it. The data taken together suggest that polarization of the Mg foil working electrode toward dissolution potentials leads to local failures of the surface layer, leading to dissolution at sites exposed on the Mg surface. The microscopy data presented and discussed below affirms this latter point and the suitability of the functional form of the models used to quantify the potential step data of Figure 4.3.
The micrographs shown in Figure 4.5 are SEM images of three exemplary Mg metal foils following emersion during potential step experiments at three increasing potentials in a manner similar to that described for Figure 4.3. These images show that numerous and widely dispersed pits are present on each of the Mg foils. More importantly, a quantitative analysis of the data shows that the magnitude of the anodic potential step correlates with both the areal density of pits formed and the magnitude of the currents that flow. These features, as well as the relatively comparable dimensions of the pits, supports a model of pitting dynamics emphasizing the strong impacts of potential upon pit nucleation, yet diffusion control of their growth (Figure 4.6). When taken together, these data clearly reveal pitting dynamics mediate the metal dissolution and highlights a morphological embodiment for the induction time effects seen in Figure 4.3. It can also be seen in Figure 4.5 that the pits are weakly aligned with the grooves created by the polishing process. An exemplary sample with pits even more strongly aligned with the polishing defects is shown in Figure S3, along with the Fast Fourier Transform of the corresponding micrograph that shows a high intensity line perpendicular to the grooves in the original micrograph, a result strongly indicating that the pits are both parallel to the grooves and have irregular spacings. We also found at the macro scale that pits can be formed clustered in regions of higher mechanical stress, such as the area near the O-ring or regions where the foil was buckled. This suggests that a more favorable path to film breakdown occurs in regions of thinner, or less-protecting films (e.g. as due to surface defects), or where strain induced failures may exist. It has been noted in the literature that other magnesium electrolyte systems show localized regions of breakdown that increase with the anodic current density.\textsuperscript{35} The potentiostatic stripping experiments highlight the initial state characteristics of the anode surface and maintain a constant potential surface when passivation breakdown occurs. As we show below, repeated
potentiostatic stripping and deposition cycles can mitigate such sample-preparation history
dependences but with the caveat that crystallographic dependences are enhanced by the inherent
electrochemical reaction dynamics of this system.

The temporal evolution of the electrochemical cycling behavior of bulk Mg electrodes is
illustrated in the data presented in Figure 4.8. Figure 4.8a gives plots of the electrochemical data
obtained from cycling at three different limiting potential ranges: a) slightly past $E_b$; b)
moderately into the mixed control region; and c) at a high overpotential. The dash trace is for an
electrode cycled between $-/+ 300$ mV, in which the potential was first held at $-300$ mV for 15
minutes and then switched to $+300$ mV for 15 minutes, repeating for 10 cycles. The same
cycling procedure was used for the $-/+ 500$ mV (solid trace) and $-/+ 700$ mV (dash dot trace)
cases shown in the figure. In a manner similar to what is observed in Figure 4.3, the current
density seen in both the anodic and cathodic potential steps increases with the magnitude of the
potential applied (versus a Mg reference). The data in Figure 4.8b plots the ratio of the
integrated area for the deposition to that of dissolution step for each of the 10 cycles (presented
as a percentage). It should be noted that for all but one cycle, dissolution is favored. In fact, for
the $-/+ 300$ mV and $-/+ 700$ mV cases, dissolution is moderately more dominant than deposition
for the first few cycles. The origin of this asymmetric current scaling is not completely
understood. It has been observed by others that, unless the Mg metal surface is activated in the
electrolyte, it will be covered in a passivating film composed of environmental contaminants$^1$
and though deposition is not completely blocked, it is hindered by this film. It is also known that
in aqueous systems electropositive metal impurities within the Mg metal can greatly perturb the
behavior of the Mg electrode, but it is also true that this is not completely understood$^{36}$. Even so,
in the present case it remains true that the time-based measure always (with one exception) more
efficiently removes Mg from the bulk anode than the deposition step adds to it for the initial cycles. The data discussed in the sections that follow suggest an explicit mechanism responsible for the more facile dissolution dynamics this rate/property correlation reveals.

The data presented in Figures 4.9(a-c) are SEM images measured for electrodes cycled at the different potential ranges after the completion of 10 full deposition/dissolution cycles. These data establish that variations in the potential produce different surface morphologies. In each case, albeit with different scales of texturing, the cycling leads to the occurrence of anisotropic Mg structures on the surfaces of the bulk electrodes. Although other structures are formed, many of the structures evidenced suggest an anisotropic pattern of growth/etching of a specific preferred orientation of hexagonal close packed (hcp) Mg grains. This finding has literature precedent in that Hill et al. observed that, under specific conditions in ether solvents containing alkyl halides, a major fraction of the pits formed on Mg metal are anisotropically etched when an \{0001\} oriented single crystal was used.³⁷ The crystallographic texture of the foil samples was examined for this reason; X-ray diffraction studies (Figure 4.10) show that the Mg foils used for our experiments are in fact preferentially oriented along the \{0001\} direction. As the data in Figure 4 illustrate, the anisotropy that occurs after multiple cycles, after ending at the dissolution potential limit, is broadly distributed across the sample surface and comprise mainly the walls of Mg crystallites deposited with a preferred \{0001\} oriented texture. Geometric analysis of the structures seen in Figure 4.9b produces angles of 63.2° ± 4.9 and 121.5° ± 6.9, confirming roughly vertically aligned (and oblately presented) \{0001\} hexagonal crystals typical of an hcp lattice. In fact, the quasi-hexagonal morphology deposits are the only anisotropic texture observed, regardless of the order of the potential holds, galvanostatic vs. potentiostatic cycling, or even substrate texture (Figures 4.11-4.13). Others have observed dissolution differences

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between planes of magnesium. Liu et al. suggested that the activation energy of dissolution increases as the packing density of the plane increases for the hexagonal close-packed (hcp) magnesium. Planes perpendicular to the \{0001\} basal plane, however, have lower packing densities and by this model should have a more favorable dissolution. In point of fact, the literature contains some contradictions regarding the dissolution behaviors of the \{0001\} plane of Mg. Song et al. observed that in 0.01 M NaCl the \{0001\} plane is most resistant to dissolution, yet McCall et al. observed that in 0.01 M NaCl/0.0001 M dichromate solution the \{0001\} plane is the least resistant when compared to low-index prismatic planes (e.g. the \{10-10\} plane). Song et al. proposed that this contrast is due to the fact that growth of surface films can vary markedly on the different planes and also vary in different electrolytes. We believe the current data support this picture of corrosion due to halide species and that the structures observed upon cycling likely result from passive films that vary in structure for the different Mg hcp planes, a factor resulting in both an anisotropic stripping and subsequent replating of the Mg. Logical inferences suggest an oxide speciation is likely for the passive films that mediate this rate-structure correlation.

To test this assumption, the surface speciation of three different Mg foil samples was determined by use of XPS. Plotted in Figure 4.14 are the core level data measured in the O(1s), Br(3d), and the Mg(2p) core-level binding energy regions, here recorded for a polished Mg foil (p), a Mg foil working electrode stripped at +500 mV for 30 minutes (s), and a Mg foil working electrode after 10 cycles at +/- 500 mV with the cycles terminated at the anodic potential limit (c). In order to minimize exposure to air, the Mg foils were transferred to the XPS instrument via a sealed transfer vessel. These data (as tabulated in Table 4.1) show the state of the surface of the Mg after processing by polishing in an inert atmosphere, electrochemical stripping, or
potentiostatic cycling. The data in Figure 4.14a show plots of the oxygen 1s binding energy region. The polished Mg foil sample shows the presence of mostly glovebox related surface contaminants, namely MgO and MgCO₃. The other samples contain lesser amounts of MgO, a result of removal of the initial surface oxide during electrochemical cycling. The increase in the peak around 533 eV observed for the stripped and cycled experiments, is due to an increase in oxygen containing species on the surface of the Mg foil (Mg(O)X) most likely as a result of solvent (THF) decomposition. We note that here X does not refer to a halide but rather to an unknown species. The data in Figure 4.14b are plots in the region of the Br 3d core level binding energy. The results for the stripped and cycled Mg foils show the presence of a distinct MgBr₂ speciation. According to one of the dissolution reactions proposed by Aurbach et al.,⁴³ MgBr₂ is a corrosion product and, since it has low solubility in THF, forms as a precipitate. As corrosion proceeds, corrosion products build up,³⁶ especially in the form of halide salts. Even though MgBr₂ accumulates during both hemispherical pitting and anisotropic pitting, the lack of non-passivated Mg {10-10} planes upon initial stripping precludes the dismissal of MgBr₂ as a species contributing to the anisotropic stripping. We note that the additional peaks present in the spectra given in Figure 5b are likely due to the KLL Auger excitations of Mg and a bulk Mg plasmon (at 67.4, 73.6 and 70.0 eV respectively).⁴⁴-⁴⁵ The data in Figure 5c show plots of the Mg 2p core level binding energy region. The polished Mg foil sample has peaks near where Mg⁰ and MgO binding energies are expected. When the Mg foil is stripped or cycled, the electrolyte decomposition and corrosion products build up on the surface and the Mg⁰ peak is reduced in intensity. Not surprisingly, the surface film formed during electrochemical processes contains mostly decomposition/corrosion products.
To further establish the character and morphology of passive films that likely mediate the anisotropic growth/dissolution behaviors established above, FIB was used in conjunction with HIM to garner a structural understanding of the films from high resolution cross-sectional images. Such images provide mechanistic insights into the process of stripping and deposition of Mg. The data in Figures 4.15a and 4.15c are HIM images taken at normal incidence, each showing the morphologies of typical Mg structures formed during the potentiostatic cycling (at -/+ 500 mV, 20 cycles, for 15 minutes per half cycle) of a Mg foil working electrode. There are several dominant morphologies seen, including smooth areas, quasi-hexagonal symmetry crystals, and, as previously noted regarding the images presented in Figure 4.9, nested hexagonal motifs. The smooth areas represent non-activated regions of the original, passivated surface of the Mg foil. Unlike previous examples, this sample processing was ended on a deposition half-cycle, resulting in many quasi-hexagonal structures with varying degrees of nesting. Two distinct quasi-hexagonal structures are evident, with apparently different degrees of filling by Mg. Each of these morphology types was cross-sectioned via FIB milling and imaged by HIM. The images in Figures 4.15b and 4.15d show views of specific cross-sections from 4.15a and 4.15c representing the nested and non-nested structures, respectively. Figure 4.15b shows that the anisotropic stripping in the Grignard electrolyte often does not completely remove the Mg deposited during the previous half-cycle, as manifested in the lateral discontinuity seen at the top of the structure (combined with the relatively uniform interior) and the very thin (~ 10 nm) films of oxidized material. Most notably, both cross-sections reveal interstices that develop during deposition. The presence of interstices (sometimes referred to as voids or pores in literature) is common in electroplating and results from multiple grains growing into one grain to begin columnar growth. As evidenced by the relatively large, uniform growth of the crystal in Figure
4.15d, deposition is also preferentially oriented to the \{0001\} plane. This deposition orientation has never been observed for EtMgBr-THF and is likely due to a combination of homoepitaxial growth and surface-oxide-limited diffusion of the Mg.

The schematic depiction given in Figure 4.16 illustrates several of the important features that we believe are involved in the complex growth dynamics occurring in this system. Upon initial failure of the relatively thin oxide layer formed after polishing, nucleated pit growth occurs in a relatively stochastic manner due to the localized nature of these sites and the remnants of the relatively passive surface films that remain. Switching to negative potentials initiates homoepitaxial growth on the now activated and generally \{0001\} textured surface planes exposed by the pits, leading to the formation of microcrystalline hexagonal motif deposits (shown here in orange). It is known that even after low potential cycling that solvent decomposition products such as $\gamma$-butyrolactone appear in the electrolyte,\textsuperscript{22} and therefore rapid passivation from the byproducts of the decomposition of THF (along with MgBr\textsubscript{2}) likely occurs on all Mg surfaces. Once the hexagonal passivated structures are formed, these same crystals tend to selectively strip from the substrate (Figure 4.16c). Other passivated surfaces become activated but are primarily localized in these and adjoining areas of the substrate. Subsequent deposition then follows upon the low overpotential, ‘fresh’ surfaces created frequently within the residual structures from past deposition/passivation/stripping sequences. We believe that this co-localization is why we observe a progression toward unity in the ratio of deposition to dissolution in Figure 3. Initially there is a strong overpotential for deposition due to the native passivation layer. As the potentiostatic cycling proceeds, however, stripping cycles reveal more ‘fresh’, weakly passivated magnesium, allowing more rapid deposition. Near 100% coulombic efficiency has been observed with EtMgBr in THF on some electrodes,\textsuperscript{47} emphasizing the
presence of an overpotential for the passivated, prismatic planes of magnesium compared to the basal plane. Extensive cycling exacerbates this effect, and as shown, causes very large 50 micron or taller columns to protrude from the electrode surface even after a relatively short sequence of cycles (Figure 4.17). The concern following from this, similar to issues caused by lithium metal anode dendrites, is that these structures would eventually grow large enough to create an electrically active mode of failure in a full cell.

4.6 Conclusions

Passivation and corrosion processes play a crucial role in the electrochemical behavior of bulk Mg metal anodes using a non-aqueous Grignard electrolyte. Morphological characterization of the Mg working electrode after electrochemical reactions shows the formation of corrosion pits and anisotropically etched hexagonal Mg structures. Observation of the Mg working electrode after extensive deposition and dissolution cycles reveals the formation of isolated columnar structures. Although they do not have as high of an aspect ratio nor are as numerable as the dendrites formed on Li metal anodes, these structures hold the possibility of extending toward the cathode to cause battery failure as well as a potential for the loss of electroactive Mg. These results, if more broadly generalized in the electrochemistry of this metal, suggest that careful consideration of the possible anisotropy of both the deposition and the stripping of Mg is necessary for Mg to be a viable candidate for use as an anode in a rechargeable battery. Avenues of further research exist in understanding discrete mechanisms of passivation layer formation as well as high rate deposition orientation effects on both passivation and corrosion, especially for Mg electrolytes with more complex solution equilibria and different Mg coordination spheres, in order to establish an atomistic understanding of this phenomenon and guide strategies for improving performance.
4.7 Acknowledgements

This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. This work was carried out in part in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois at Urbana-Champaign and in the Department of Physics, Bielefeld University.

4.8 Supplemental Information for Experimental Design and Analysis

The following are further descriptions and parameters of the Eq. 4.1-4.3 that are discussed in section 4.5:

\[
P_4 = zFk
\]

\[
P_5 = \pi M^2 N_0 k' \rho^{-2}
\]

\[
P_6 = zF \pi^{-1/2} D' \frac{1}{\Delta C'}
\]

\[
P_7 = K' \pi D' N_{os}
\]

\[
K = (8\pi M \Delta C')^{1/2} \rho^{-1/2}
\]

\(j_c\) is the current density concerned with the corrosion of metal at the pits and defines the instantaneous nucleation and three-dimensional conical pit growth charge transfer control.

Where,

\(z\) is the charge number and \(F\) is the Faraday constant

\(k\) and \(k'\) are the apparent rate constants for pit growth in the directions perpendicular and parallel to the corroding surface plane, respectively.
M and $\rho$ are the atomic weight and the density of the metal, respectively

$N_0$ is the number of sites available for pit nucleation

$j_{d'}$ represents metal dissolution through a basic metal salt layer formed at certain regions of the electrode

$D'$ is the diffusion coefficient of the metal ions in the solution

$\Delta c'$ is the concentration gradient of the metal ionic species at the salt/solution interface

$N_{os}$ stands for the number of sites for pit growth
Figure 4.1: Results of the number of publications versus the year from a Scopus search for the terms ‘magnesium’ and ‘battery’.
Figure 4.2: Volumetric (purple) and gravimetric (green) capacities of some important anode materials for next generation batteries.
Figure 4.3: Current-time transients of polished Mg foils in EtMgBr-THF at three different dissolution potential holds of (a) 500 mV, 700 mV, and 900 mV for 30 continuous minutes (dashed lines represent fitting results). (b) Magnification of the region between 0 – 100 seconds in (a). Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.4: Cyclic voltammogram of a Mg foil working electrode in EtMgBr-THF after 1 (black), 10 (blue), 40 (pink), and 50 (orange) cycles. Cycles were run at 10 mV s⁻¹ versus a polished Mg ribbon reference electrode.
Table 4.1: Fit parameters for current transient models.

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>$P_4$ (mA cm$^{-2}$) ($10^{-4}$)</th>
<th>$P_5$ (s$^{-2}$) ($10^{-7}$)</th>
<th>$P_6$ (mA s$^{1/2}$ cm$^{-2}$)</th>
<th>$P_7$ (s$^{-1}$) ($10^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>267.6 ± 1.1</td>
<td>19.99 ± 0.13</td>
<td>100 ± 70</td>
<td>8 ± 5</td>
</tr>
<tr>
<td>700</td>
<td>429.0 ± 0.9</td>
<td>2319 ± 10</td>
<td>26.71 ± 0.24</td>
<td>118.2 ± 1.3</td>
</tr>
<tr>
<td>900</td>
<td>895.8 ± 2.6</td>
<td>466.2 ± 1.3</td>
<td>8.963 ± 0.014</td>
<td>567.9 ± 1.9</td>
</tr>
</tbody>
</table>
Figure 4.5: SEM images of Mg foil working electrodes after 30 continuous minutes of stripping in EtMgBr-THF at (a) 500 mV, (b) 700 mV, and (c) 900 mV. Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.6: Plot of charge density versus pit density with a linear fit forced through the origin (a). Calculations of the average pit diameter according to a hemispherical model using fit from (a) (blue line) fall within error of the measured pit diameter from SEM images (b).
Figure 4.7: SEM image (a) and corresponding FFT magnitude spectrum (b) of a Mg foil sample held at 900 mV vs Mg for 1800s.
Figure 4.8: Electrochemical results from potentiostatic deposition/dissolution cycling of polished Mg foils in EtMgBr-THF. (a) deposition/dissolution cycling data for 10 cycles (15 minutes per half cycle) at three different potentials: +/- 300 mV (dash); +/- 500 mV (solid); +/- 700 mV (dash-dot). (b) A plot of the deposition/dissolution ratio presented as a percentage for +/- 300 mV (square); +/- 500 mV (circle); +/- 700 mV (triangle). Counter and reference electrodes were polished strips of Mg ribbon.
**Figure 4.9**: SEM images of each Mg foil working electrode after the completion of the 10 cycles for each of the experiments presented in Fig. 3a; (a) +/- 300 mV, (b) +/- 500 mV, and (c) +/- 700 mV.
Figure 4.10: X-ray characterization of preferred oriented (PO) and randomly oriented (RO) Mg substrates. (a) XRD 2-theta plot of the (PO) and (RO) orientations. X-ray pole figures of the (002) line of the preferred oriented (b) and the random oriented Mg substrates.
Figure 4.11: Electrochemical results from the potentiostatic cycling of Mg foil in EtMgBr-THF starting at a stripping potential and ending at a deposition potential. (a) dissolution/deposition data for 10 cycles (15 minutes per half cycle) at +/- 500 mV. (b) SEM image of Mg foil working electrode at normal incidence after the completion of the 10 cycles. Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.12: Electrochemical results from the Galvanostatic cycling of Mg foil in EtMgBr-THF. (a) dissolution/deposition data for 10 cycles (15 minutes per half cycle) at +/- 0.15 mA cm$^2$. (b) SEM image of Mg foil working electrode at normal incidence after the completion of the 10 cycles. Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.13: Electrochemical results from the potentiostatic cycling of a polished randomly oriented Mg substrate in EtMgBr-THF. (a) deposition/dissolution data for 10 cycles (15 minutes per half cycle) at -/+ 500 mV. (b) SEM image of the Mg substrate working electrode at normal incidence after the completion of the 10 cycles. Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.14: Plots of the XPS results for polished Mg foils after different electrochemical processes: (p) polished, no electrochemistry, (s) stripped at +500 mV for 30 minutes in EtMgBr-THF, and (c) 10 potentiostatic deposition/dissolution cycles at -/+ 500 mV (15 minutes per half cycle) in EtMgBr-THF. Plot of binding energies in the ranges of (a) Oxygen (1s), (b) Bromine (3d), and (c) Magnesium (2p) are presented. For electrochemical processes the counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.15: HIM images of Mg residual structures on the surface of polished Mg foil after 20 potentiostatic deposition/dissolution cycles (15 minutes per half cycle) at -/+ 500 mV. (a/c) Normal incidence view (b/d) cross-section view at 45 degrees in relation to (a/c) respectively. Counter and reference electrodes were polished strips of Mg ribbon.
Figure 4.16: Illustrative representation of the proposed progression of the Mg surface morphology. (a) Initial stripping of the oxide layer (dark grey) leads to pitting into the substrate (light grey). (b) Deposition favors the relatively unpassivated Mg \{0001\} surface resulting in hexagonal crystals (orange) normal to the surface. (c) Anisotropic stripping occurs on the \{0001\} Mg plane of the crystal. (d) Subsequent deposition (blue) occurs within hexagonal structures forming elongated, nested residual structures.
Figure 4.17: SEM images of Mg columnar growth from the surface of polished Mg foil after 200 potentiostatic dissolution/deposition cycles (15 minutes per half cycle) in EtMgBr-THF at +/- 500 mV. (a) Isolated columns. (b) Zoomed-in image of one of the columns from (a), showing the striations on the side. Images were obtained at a 30 degree tilt. Counter and reference electrodes were polished strips of Mg ribbon.
4.10 References


(2) Verma, P.; Maire, P.; Novák, P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. Electrochim. Acta 2010, 55, 6332-6341.


5.1 Preface to the 5th Chapter

5.1.1 Current State of Magnesium Batteries

When it comes to energy density rather than capacity, Mg faces significant challenges. Power is a serious concern because the standard redox potential for magnesium lies ~0.7 V more positive than lithium. It has been calculated that a commercially viable magnesium battery will require a cathode with a voltage greater than 3 V. The 3 V limit is very difficult as it is at the edge of the current knowledge of intercalation cathode material technology. To fully grasp the challenge, the current standard cathode for Mg is still the Chevrel phase Mo₆S₈ identified by Aurbach in 2000 and is only about 1.1 V vs Mg/Mg²⁺, although new cathodes have been examined.

Investigations have been limited by yet another significant challenge of magnesium batteries: the electrolyte window. To date there are only a handful of electrolytes that reversibly deposit magnesium at the anode and have an oxidative stability greater than 3 V. The number of electrolytes that are compatible with cathodes, have a significant exchange current density, and are stable over time drops to only one, perhaps two electrolytes. Even one electrolyte is significant progress and opens the door to advancements in cathodes will follow closely.

An interesting and important difference in the boron containing electrolytes and the TFSI⁻ electrolytes compared to those containing chloride is that of coordination. The μ-Cl complex is widely stated as the necessary component for electrodeposition of Mg. The boron and TFSI⁻
containing electrolytes have no Cl so the \( \mu \)-Cl complex cannot exist, yet electrodeposition occurs. Our group had previously examined a borohydride based electrolyte, so we sought to understand more about coordination and the deposition mechanism through indirect observations of the morphology of the deposited film upon changing the reaction rate.

5.2 Abstract

A highly anisotropic electrodeposition was observed using the hybrid battery electrolyte \( \text{Mg(BH}_4\text{)}_2 \) with \( \text{LiBH}_4 \) in diglyme. At low overpotentials high aspect ratio platelet morphologies are observed with a strong fiber texture composed of a \{10-10\} and a \{11-20\} component, the first evidence of behavior of this kind in magnesium battery electrolytes. At high overpotentials the deposit aspect ratio is indistinguishable but the texture is shown to be primarily composed of a \{11-20\} fiber texture. The kinetic parameters relative to the relevant crystallographic faces are extracted from electron microscopy images and compared with the observed bulk rate extracted from the electrochemical data. The use of polycrystalline Ag foil substrates with little preferred orientation at the surface allowed highly polycrystalline nucleation at lower overpotentials than that of platinum, likely due to Ag alloying with Mg. Characterization using focused ion beam (FIB) cross-sections with Auger Electron Spectroscopy (AES) elemental analysis confirm that the deposits are primarily Mg although Mg-Ag alloys of various compositions were observed. It is proposed that the orientation at slow rates of growth is due to the underlying kinetics of adatom diffusion on Mg and that higher rates diminish the phenomenon due to decreased time for diffusion and instead are governed by the rates of adatom formation or more specifically the adatom vacancy formation on the different low-index planes of Mg.
5.3 Introduction

Magnesium has many of the indicators of a technology to displace Li-ion batteries. Mg compared to Li is less expensive, more environmentally benign, has a higher volumetric capacity (3833 vs 2062 mAh/cm$^3$), and is not plagued by the formation of dendrites. Commercial production of Mg batteries has been limited due to many problems that can generally be categorized as ion mobility within the cathode, anode passivation, and electrolyte oxidative stability, all of which stem from the root, intrinsic property of the high charge density of the Mg$^{2+}$ ion. Electrolyte development has been arguably the most critical challenge because further studies of prospective cathodes depend upon establishing a stable, non-corrosive electrolyte with a 3 V potential window. The problem of electrolyte development has been a Sabatier-like problem of coordination, requiring Cl$^-$ to coordinate and dissolve the Mg$^{2+}$ ion and a µ-Cl complex to release Mg$^{2+}$ for electrodeposition.$^{13-14,17}$ It is only recently that electrolytes have been developed that are considered ‘non-coordinating’,$^{10-11,18}$ but the degree of coordination is debated due to the presence of breakdown products.$^{19}$ When facing the challenge of electrolyte development the characterization of the morphology and texture of electrodeposits at the anode is often overlooked or minimized (although there are notable exceptions$^{20-21}$). As we have previously shown, deposition, stripping, and passivation anisotropies can play a significant role in the final deposit morphology.$^{22}$

Electrodeposition morphology plays an important role in metal anode batteries yet isolating individual contributions to morphology can be challenging. Electrodeposition morphology is defined by overpotential and overpotential is a complex combination of properties including mass diffusion, electrolyte equilibria, charge transfer processes, as well as traditional nucleation and growth concepts like surface energy and adatom diffusion. Rates for charge transfer and
mass diffusion can be extracted from electrochemical data, but nucleation and growth parameters can be much more difficult to analyze. Nucleation can be modeled using electrochemical data, but such treatments rely on hemispherical nuclei and only report on number of nuclei, not crystallographic orientation.\textsuperscript{23-25} In a study of Mg electrodeposition using ethylmagnesium chloride and dimethylaluminum chloride in tetrahydrofuran, Matsui suggested morphology is dominated by surface energy maximization at slow rates and diffusion at high rates.\textsuperscript{20} Surface energy is undoubtedly important, but adatom diffusion on different crystallographic planes also has been found to be critical for deposit morphology for a variety of elements.\textsuperscript{26-28}

The choice of substrate is important when studying deposition morphologies due to factors of underpotential deposition (UPD), epitaxial growth, and alloying. Electrolyte development studies typically use Pt as a substrate due to its stability towards corrosion, but more practical materials show different behavior.\textsuperscript{29} We have previously shown that Pt decreases the overpotential for deposition from a Mg(BH\textsubscript{4})\textsubscript{2} electrolyte with a LiBH\textsubscript{4} additive due to the UPD of Li on Pt.\textsuperscript{30} Silver is an intriguing alternative to Pt. Silver could be a prospective alloying anode material for Mg batteries due to its high theoretical potential, yet no studies have examined it for such a purpose (see Tables 5.1-5.4). Silver also has an unexpected benefit for morphology studies due to an even lower overpotential for deposition than Pt \textit{(vida infra)}, further allowing uniform nucleation and growth at slower rates than Pt.

Herein we describe discovery and analysis of a distinctly different anisotropic growth mode than has previously been seen in Mg electrolytes. The electrolyte used is Mg(BH\textsubscript{4})\textsubscript{2} with LiBH\textsubscript{4} in diglyme (G2), a well-studied electrolyte that has been proven to work well in Li-Mg hybrid batteries.\textsuperscript{31-33} Previous studies have shown that the coulombic efficiency is high and Li plays a significant role in the deposition overpotential, but deposition texture has not been thoroughly
analyzed.\textsuperscript{30,34} In addition to attempting to understand the underlying principles of the observed deposition anisotropy, we discuss the ideas of observed overpotential and alloy anodes in the context of Mg batteries, with a specific emphasis on Ag versus Pt.

\textit{5.4 Experimental}

LiBH\textsubscript{4} and Mg(BH\textsubscript{4})\textsubscript{2} were purchased from Sigma-Aldrich and used without further purification. Anhydrous diglyme was purchased from Sigma-Aldrich and further purified by distilling over calcium hydride and subsequently storing over activated molecular sieves to decrease water content to less than 10 ppm according to Karl-Fischer titration analysis. All electrochemical experiments were performed in an argon-filled MBRAUN LABstar glovebox with O\textsubscript{2} < 2 ppm. Electrochemical experiments were performed using either CH Instrument 650 B or 660 D model instruments. Electrochemical cell components were stored in acid baths of nitric and subsequently sulfuric acid with No-Chromix (>5 hrs each), then rinsed with Milli-Q water, and finally flame-dried before use. Mg foil (99.95%, 0.05 mm thick, GalliumSource, LLC), stainless steel foil (304, 0.1 mm thick, Alfa Aesar), Pt foil (Grade 1, 0.1 mm, thick Johnson Matthey), and Ag foil (99.998%, 0.1 mm thick, Alfa-Aesar), were used as the working electrodes. Roughening of the Ag foil was performed according to a previously established protocol.\textsuperscript{35} Roughening of Ag was performed in order to increase the polycrystalline texture at the surface of the Ag foil since it is textured in the (220) direction as evidenced by the increased relative intensity of the peak at 64° as compared to the peak at 38° (Figure 5.1). For all experiments, the counter and reference electrodes used were Mg ribbon that were freshly scratched. All electrode potentials in this report are referenced to Mg/Mg\textsuperscript{2+}. 
XRD experiments utilized a PANalytical Philips X’pert MRD system equipped with a Cu K-α source at 0.15418 nm located in the Frederick Seitz Materials Research Laboratory (FS-MRL) at the University of Illinois at Urbana-Champaign. XRD 2Θ-Ω scans were taken at a scan rate of 1.2°/min for all samples. Pole figures of the (10-10), (10-11), and (11-20) peaks for depositions at -200 and -500 mV on Ag foil were taken at 5°/s. XRD results were analyzed using JADE XRD analysis software and the MTEX toolbox for Matlab\textsuperscript{36}. SEM experiments used a JEOL 7000F analytical SEM that has an EDS attachment and is housed at the FS-MRL facilities. Samples were rinsed with diglyme and allowed to dry in the glovebox before removing for imaging. All experiments utilized a 15 keV accelerating voltage and working distance of 10 mm.

FIB and AES analysis were performed by Evans Analytical Group. The sample was exposed to atmosphere before FIB and again before AES analysis. AES analysis was performed using a 10 keV accelerating voltage and 29 nA sample current. Sample was tilted 30° with respect to the incoming electron beam. Sputtering was done with a 2kV argon ion beam. Sputter depth for AES was calculated according to the sputter rate of 5.8 nm/min for SiO\textsubscript{2}.

\section*{5.5 Results and Discussion}

The data presented in Figure 5.2 are cyclic voltammograms (CV) of 0.1 M Mg(BH\textsubscript{4})\textsubscript{2} + 1.5 M LiBH\textsubscript{4} in diglyme on Pt and Ag substrates. The CVs in Figure 5.2a start from +1500 mV and switch direction at -500 mV. Mg deposition has an overpotential on Pt of about 230 mV whereas there is almost no overpotential on Ag. Crossover of the forward and reverse sweeps is evident in the Mg deposition region on Pt whereas on Ag the crossover is almost non-existent and +100mV of that on Pt. The evidence of crossover in the CV during electrodeposition has been attributed to
the nucleation process.\textsuperscript{37} The more positive crossover potential in the Ag substrate is an indication that nucleation is facile on Ag compared to Pt, either through underpotential deposition (UPD) of a thin layer of Mg or through Mg-Ag alloying. Previously our group showed that Li UPD is important to the low overpotential and high current density with this electrolyte on Pt.\textsuperscript{30} Li undergoes UPD on Ag at -280 mV and Li-Ag alloying begins at -430 mV, both significantly lower than the onset of reductive current observed here.\textsuperscript{38-39} As seen in Figure 5.2b (a magnification of 5.2a), there are no distinct underpotential features in the CV on Pt, but Ag has a distinctive redox couple at +300 to +400 mV, indicating an alloying event. In addition the reduction peak correlates well with the highest theoretical potential for a Mg-Ag alloy as calculated from DFT calculations from the Materials Project\textsuperscript{40} and experimental values\textsuperscript{41} as shown in Table 5.5 according to the equation:

\[ V = \frac{\Delta G}{eF} \]  

(5.1)

Where V, \( \Delta G \), e, and F are the voltage, free energy of formation, number of electrons, and Faraday’s constant, respectively. The lower overpotential for deposition due to alloying that is achievable on Ag allowed us to obtain uniform, dense nucleation at very low overpotentials characteristic of homoepitaxial growth without the use of a Mg substrate that would otherwise obfuscate texture analysis.

SEM images of potentiostatic depositions at low and high overpotentials are presented in Figure 5.3. Figure 5.3a shows that when a -200 mV potential is applied to the working electrode, hexagonal platelets grow perpendicular to the Ag substrate. The sharp, high aspect ratio crystals appear in stark contrast to the smaller, roughly hemispherical morphology that dominates at the more reducing potential of -500 mV shown in Figure 5.3b. Potentiostatic measurements were chosen for emphasis of features, but amperostatic measurements show similar behavior as seen...
on Pt surfaces in Figure 5.4. This morphological phenomenon is unusual for Mg electrodeposition at low rates as the texture is usually random or \{0001\} oriented$^{20,22}$, so we sought to understand this behavior in more detail using XRD and AES to understand the texture and elemental composition of the deposits.

XRD patterns of Mg deposited for 16 hours are presented in Figure 5.5. 2Θ-Ω scans for the -200 mV and -500 mV deposit are presented in Figure 5.5a. Full patterns can be found in Figure 5.6. Individual peaks are labeled according to their material assignments: Ag (black squares), Mg (blue diamonds), and Ag$_x$Mg$_y$ (green circles). The fact that Mg peaks appear in both cases of Mg deposition examined here provides direct evidence that even at slow rates, the deposition of Mg yields elemental Mg metal and not simply an alloy. Our results, however, with time show that initial peak splitting characteristic of two separate alloy phases eventually transitions to one peak at about 38.5° as depicted in Figure 5.7. The change with time has been seen in literature experiments of age-hardening and highly anisotropic Guinier-Preston zones that develop at low temperatures in high Mg content Ag-Mg alloys, eventually resulting in stable AgMg$_3$ phases.$^{42-43}$ Figure 5.5b shows the 38° region in more detail with comparisons to literature patterns extracted from various powder diffraction file databases. The peak splitting in the -200 mV sample in Figure 5.5b is indicative of a mixture of highly anisotropic Ag$_3$Mg and Ag$_{17}$Mg$_{54}$ phases corresponding to peaks at 37.8° and 38.8° whereas the -500 mV sample overlays almost perfectly with the AgMg peak at 38.5°. Cross sectioning and elemental analysis using FIB and AES was used to better understand the extent of alloying and clarify the morphological effects of alloying in relation to the observed platelets.

A FIB cross-section and AES spectra of the -200 mV sample are presented in Figure 5.8. Figure 5.8a is a false color SEM image of the FIB cross-section of the sample. The bottom of Figure
5.8a shows the Ag substrate depicted in orange. Different contrast regions in the Ag substrate are indicative of different grain textures and the particles at the interface are due to the roughening procedure pre-deposition of Mg. The blue, Mg region extends from the Ag all the way to the Pt-C protection layer (depicted in grey) added for FIB milling. AES spectra were taken in at increasing depths in both the Ag substrate and the Mg thin film deposit until signals stabilized. AES data of the final depth probed are shown in Figure 5.8b and resulted in Ag:Mg ratios of about 9:1 in the Ag substrate and 1:3 in the Mg deposit. Full data, sampling locations, depths and elemental mapping are outlined further in Figures 5.9-5.12 and Table 5.6. From the AES results it is evident that most of the alloying that occurs in the sample is restricted to the Mg deposit and can be explained by the rapid diffusion of Ag in Mg. The minimal diffusion of Mg into Ag then precludes the use of Ag as an alloy anode with Mg. Also the asymmetrical diffusion of Ag into Mg indicates that the platelet morphology observed at the relatively low overpotential of -200 mV is due to Mg and not alloying but over time the elemental composition changes towards a stable Mg-Ag concentration as Ag diffuses into Mg. With the understanding of the effects of nucleation and alloying, it is now possible to begin to analyze the Mg deposition morphology at low and high overpotentials.

The evolution of texture in the electrodeposition of Mg is depicted in Figure 5.13. Magnified SEM images of the platelets formed at -200 mV are shown in Figures 5.13a and 5.13b. Both Figure 5.12a and 5.13b contain platelets with information about shape and crystal size that appear to be rotated relative to each other. The true crystallographic orientation of the individual crystals in Figures 5.13a and 5.13b is not discernable from the SEM images because the probable orientation planes of \{10\text{-}10\} and \{11\text{-}20\} form identical angles with the hexagonal \{0001\} plane. A quantitative interpretation of the orientation of the Mg deposits can be obtained from
the texture coefficients outlined in Figure 5.13c. Only the low index planes of \{10-10\}, \{0001\}, \{10-11\}, and \{11-20\} corresponding to the XRD peaks at 32.2°, 34.4°, 36.6° and 57.4° were analyzed because they are the most important for crystal growth. Texture coefficients are numerical values of the observed XRD peak intensities normalized to the standard diffraction pattern of Mg via the equation:

\[
TC_{(hkl)} = \frac{\frac{I_{(hkl)}}{I_{0(hkl)}}}{\frac{1}{n} \sum \frac{I_{(hkl)}}{I_{0(hkl)}}} \tag{5.2}
\]

where \(TC\), \(I_{(hkl)}\), \(I_{0(hkl)}\), and \(n\) are the texture coefficient, the experimental peak intensity, the standard diffraction peak intensity, and the number of peaks used for the calculation, respectively. A texture coefficient of 1 corresponds to a random orientation whereas a texture coefficient above 1 corresponds to a preferred orientation. Pole figures were also performed but the results are less obvious to the untrained eye and are more difficult to analyze due to the overlapping textures and polycrystalline nature of the deposits. The pole figures appear to show one or more fiber textures and justifies the use of peak intensities from a 2\(\Theta\)-\(\Omega\) scan for analysis of the texture (Figure 5.14). The very low texture coefficient of the basal \{0001\} plane indicates an orientation of the Mg crystals away from the \{0001\} plane, as was evident from Figures 5.13a and 5.13b. The other texture coefficients indicate data that would otherwise not be interpreted from SEM images. The -200 mV sample is oriented away from the \{10-11\} plane but is oriented towards both the \{10-10\} and the \{11-20\} planes. The -500 mV sample is oriented only slightly away from the \{10-11\} plane yet maintains its orientation towards the \{11-20\} plane. Together the texture information indicates that at low overpotential there is a \{10-10\} and \{11-20\} combined texture but high overpotentials change to primarily a \{11-20\} texture. The exchange of
preferred orientations could be due to a multitude of factors, but as we will show this is actually indicative of the underlying kinetics of the reaction.

The platelet dimensions of the low overpotential case of Mg electrodeposition can be readily extracted from SEM images as is outlined in Figure 5.15. Only platelets with distinct edges and nearly vertical orientations were used for analysis as indicated by Figure 5.15a (further examples in Figure 5.16). The average aspect ratio remains nearly identical at about 5.3 for both 30 min and 120 min depositions (actual step edges from cross-sections can be found in Figure 5.17). The constant rate of growth can therefore be used to obtain the observed rates of growth of 0.33 nm/s in the \(<10\overline{1}0>\) and \(<11\overline{2}0>\) directions and 0.062 nm/s in the \(<0001>\) direction. The electrochemical growth rate (derived from the charge passed, the geometric surface area, and the total time of deposition) falls between the observed values at 0.26 nm/s. The macroscopic dimensions in principle reflect the intrinsic atomic level growth dynamics of step edges and terraces that develop due to adatom formation, diffusion and incorporation into kink sites during nucleation and growth. Calculated Mg adatom activation energies have been previously calculated and provide a good estimate of the actual diffusion energy according to the Arrhenius like equation:

\[
D = D_0 e^{E_a/kT}
\]

(5.3)

where \(D, D_0, E_a, k,\) and \(T\) correspond to the diffusion constant, the pre-exponential factor, the activation energy, the Boltzmann constant, and the temperature, respectively.\(^45\) The pre-exponential factor has been determined to be roughly identical for many metal atoms, often varying by only a factor of 2 for different crystallographic planes of the same element.\(^46\) The ratio of the diffusion constants for different planes of Mg can therefore be interpreted as just the ratio of the exponential factor as summarized in Figure 5.18 and Table 5.7.
The important results of the analysis of the ratios of the diffusion energy barriers in the context of this work are summarized in Figure 5.19. A diffusion anisotropy exists on both the preferred texture planes observed in the Mg electrodeposition experiments, namely the \{10-10\} and \{11-20\} planes. On the \{10-10\} plane the diffusion rates parallel to the basal plane are \(~800\times\) faster than those in the perpendicular direction, depicted in Figure 5.19a. On the \{11-20\} plane the diffusion rates perpendicular to the basal plane are \(~100\times\) faster than those in the parallel direction, depicted in Figure 5.19b. Combined the surface diffusion anisotropies due to the channels in both planes lead to a ratio of anisotropies of \(~8\) compared to the measured aspect ratio of \(5.3\). Two factors could be bringing down the observed ratio. First, the pre-exponential factor is assumed to be negligible, but may be contributing to the observed ratio. Second, the vacancy diffusion rate anisotropy is opposite that of the surface diffusion anisotropy and is about \(1:4\). At high overpotentials the difference in rate is due to the relatively fast diffusion on the \{11-20\} plane. Average surface diffusion rates are faster on the \{11-20\} plane than \{10-10\} plane. The minimum diffusion rate for both surface diffusion and vacancy diffusion are also faster for the \{11-20\} plane compared to the \{10-10\} plane, making the \{11-20\} plane the preferred plane at high overpotentials or fast deposition rates.

Further proof of that it is the adatom diffusion rates that are defining the deposition texture can be found from Cl\(^-\) additive experiments. Outlined in Figure 5.20, we observed that the distinct anisotropy seen in this report changes to a \{0001\} orientation parallel to the substrate when a chloride additive is present. Grignard reagents contain a significant amount of halides and achieve similar results of random to \{0001\} orientation according to our previous results and the results of Matsui.\(^{20,22}\) Schmickler has shown via DFT calculations that Au-Cl complexes diffuse much faster than Au adatoms alone.\(^{47}\) The change in morphology due to addition of Cl\(^-\) indicates
that either adsorbed Cl\(^-\) is inhibiting Mg adatom diffusion or Cl\(^-\) complexes Mg\(^{2+}\) to form adsorbed complexes compared to a relatively non-coordinating environment provided by the borohydride anion.

\[ C_G = \frac{q}{n \Delta} \ast Q \] (5.4)

5.6 Conclusion

In a relatively non-coordinating electrolyte, the borohydride anion in diglyme, we have shown that the morphology and texture of Mg deposits are strongly \{11-20\} and \{10-10\} oriented due to the underlying rate anisotropies in adatom surface diffusion and adatom vacancy diffusion on the low index planes of Mg. Analysis of the texture was facilitated by Ag-Mg alloys contributing to the low overpotential for deposition and uniform, dense nucleation. Chloride additive studies further support the adatom surface diffusion hypothesis through distinctly different textures compared to the non-chloride electrolytes.

5.7 Acknowledgements

The authors would like to thank the United States Department of Energy, Office of Science, Basic Energy Sciences for funding this research through the Joint Center for Energy Storage Research (JCESR). The authors would also like to thank Dr. Brad Burrow and Dr. Hyung Lee of Evans Analytical Group for their rapid and skillful analysis that helped complete this report. The authors would also like to thank Marvin Malone for his useful discussions and editing of this work. Also the authors would like to thank Mauro Sardela and Elvan Ekiz-Stumphy for their helpful discussions regarding the XRD and pole figures.

5.8 Supplemental Information for Experimental Details and Analysis
\[ C_V = C_G \cdot \rho_A \]  \hspace{1cm} (5.5)

\[ C_{G*} = \frac{q}{MW_{AMg}} \cdot Q \]  \hspace{1cm} (5.6)

\[ C_{V*} = C_{G*} \cdot \rho_{AMg} \]  \hspace{1cm} (5.7)

\( C_G \) is the conventional gravimetric capacity equation

\( C_V \) is the conventional volumetric capacity equation

\( C_{G*} \) is the gravimetric capacity equation in the charged state

\( C_{V*} \) is the volumetric capacity equation in the charged state

Where,

\( q \) is the charge per unit cell

\( \rho_A \) and \( \rho_{AMg} \) are the densities of Mg and the alloy phase, respectively

\( AW_A \) and \( MW_{AMg} \) are the atomic weight of the alloying element and molecular weight of the alloy phase, respectively

\( Q \) is the coulomb to mAh conversion factor

\( n \) is the number of atoms of the alloying element in the unit cell
5.9 Figures and Tables

Table 5.1: Calculated Gravimetric Capacities in the Charged State for Mg Alloy Anodes.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fully Magnesiated Phase</th>
<th>Charged Gravimetric Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Li</td>
<td>3862</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg</td>
<td>2206</td>
</tr>
<tr>
<td>Si</td>
<td>Li1.4Si</td>
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<td>Ga</td>
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Table 5.2: Calculated Conventional Gravimetric Capacities for Mg Alloy Anodes.

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<th>Element</th>
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<tr>
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**Table 5.3:** Calculated Volumetric Capacities in the Charged State for Mg Alloy Anodes.

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<th>Fully Magnesiated Phase</th>
<th>Charged Volumetric Capacity (mAh/cm³)</th>
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**Table 5.4:** Calculated Conventional Volumetric Capacities for Mg Alloy Anodes.

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Figure 5.1: X-ray diffraction pattern of textured Ag foil after electrochemical roughening (solid red), a glancing angle measurement of the same foil (dashed red), and a silver standard diffraction pattern (solid blue).
Figure 5.2: (a) CV data comparing Pt (black) and Ag (red) substrates at 20 mV/s. (b) Magnification of the positive potential region of (a) showing a redox couple positive of bulk Mg deposition on Ag but not Pt.
Table 5.5: Calculated Alloy Formation Potentials.

<table>
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<tr>
<th>Materials Project</th>
<th>Alloy</th>
<th>Formation Energy (eV)</th>
<th>Calculated Voltage (mV vs Mg/Mg²⁺)</th>
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<tbody>
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<td>MgAg₃</td>
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<td>MgAg</td>
<td>-0.252</td>
<td>250</td>
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<td>Mg₅₄Ag₁₇</td>
<td>-0.14</td>
<td>90</td>
<td></td>
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<td>Experiment from Nayeb-Hashemi Review</td>
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<tr>
<td>10 at. % Mg</td>
<td>-0.074</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>20 at. % Mg</td>
<td>-0.132</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>28 at. % Mg</td>
<td>-0.166</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>40 at. % Mg</td>
<td>-0.234</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>50 at. % Mg</td>
<td>-0.245</td>
<td>240</td>
<td></td>
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Figure 5.3: SEM images of Mg deposits at -200 mV (a) or -500 mV (b) for 2 hr on a roughened Ag foil.
Figure 5.4: SEM images of Mg deposits on stainless steel (SS), Mg, and Pt at low current densities.
Figure 5.5: (a) XRD patterns of -200 mV (red), -500 mV (blue), and the Ag substrate (black). Peaks are labeled according to Mg (◊), Ag (□), and Mg-Ag alloy (●). (b) Standard diffraction pattern overlays of discrete, possible Mg-Ag alloys (dotted lines) on top of -200 and -500 mV deposit XRD patterns (solid lines).
Figure 5.6: Full XRD pattern of the 16 hour Mg deposits on roughened Ag foil at -200 mV (middle, red), -500 mV (top, blue), and Ag substrate (bottom, black).
Figure 5.7: XRD patterns of the 16 hour Mg deposit at -500 mV one day after depositing on a roughened Ag foil (black) and 6 weeks later testing the same sample (cyan). (a) Contains the 2Θ range of 30-50°. (b) Contains the 2Θ range of 50-85°.
Figure 5.8: (a) FIB-SEM cross-section image of Mg deposited on Ag at -200 mV for 2 hr with elemental compositions colored for Mg$_3$Ag (blue), Ag (orange), and Pt-C (gray). (b) AES spectra corresponding to the elemental mapping in (a).
**Figure 5.9:** AES spectra of the Mg deposit (a) and Ag substrate (b). Colors in both graphs correspond to milling depths in the spectrometer of 0 nm (black), 10 nm (red), and 40 nm (blue).
Figure 5.10: AES spectrum of the Mg deposit top surface after milling through the surface layer 100 nm. Residual Pt is from the FIB protection layer.
**Figure 5.11:** FIB cross-section of Mg deposited on roughened Ag for 2 hr at -200 mV showing areas used for AES elemental analysis.
Figure 5.12. AES elemental mapping of the initial state after FIB cross-sectioning. Lighter areas indicate higher concentration.
Table 5.6: Quantified AES Results.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Depth (nm)</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Magnesium</th>
<th>Sulfur</th>
<th>Gallium</th>
<th>Silver</th>
<th>Platinum</th>
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<tbody>
<tr>
<td>Mg</td>
<td>0</td>
<td>--</td>
<td>53</td>
<td>40</td>
<td>--</td>
<td>2</td>
<td>5</td>
<td>--</td>
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<tr>
<td></td>
<td>10</td>
<td>--</td>
<td>35</td>
<td>44</td>
<td>--</td>
<td>--</td>
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<td>--</td>
<td>11</td>
<td>67</td>
<td>--</td>
<td>--</td>
<td>23</td>
<td>--</td>
</tr>
<tr>
<td>Ag</td>
<td>0</td>
<td>--</td>
<td>36</td>
<td>7</td>
<td>6</td>
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</tr>
<tr>
<td></td>
<td>40</td>
<td>--</td>
<td>6</td>
<td>8</td>
<td>--</td>
<td>--</td>
<td>86</td>
<td>--</td>
</tr>
<tr>
<td>Mg Surface</td>
<td>&gt; 100</td>
<td>6</td>
<td>12</td>
<td>73</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>9</td>
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</table>
Figure 5.13: SEM images of a -200 mV sample showing a \{11-20\} (a) and a \{10-10\} (b) oriented crystal. (c) Texture coefficients of the 16 hr depositions with the standard diffraction pattern coefficients equal to 1.
Figure 5.14: XRD pole figures of the \{10\-10\}, \{10\-11\}, and \{11\-20\} peaks for both the -200 mV and -500 mV samples as well as model pole figures of a \{11\-20\} and a \{10\-10\} oriented crystal calculated with MTEX software.
Figure 5.15: SEM image depicting the method of measurement for aspect ratios (a). Histograms of AR (b) and length (c) after 30 min (black) and 120 minutes (red) of deposition at -200 mV on silver.
Figure 5.16: SEM image showing particles used for analyzing the average aspect ratio. Particles selected for analysis were limited to those particles that were vertically aligned and all edges were discernible with very few overlapping particles.
Figure 5.17: SEM cross-sectional images after FIB milling into a -200 mV deposit.

Measurements of step edges are noted in white text and the average step height ratio is noted on the right side of the figure.
Figure 5.18. Depiction of the different diffusion planes calculated by the Lu group at the Rensselaer Polytechnic Institute (Reference 33 in the main text). Faster diffusion directions are depicted with colored arrows corresponding to the diffusion plane.
Table 5.7: Summarized Adatom Properties on Mg Low Index Planes.

<table>
<thead>
<tr>
<th>Crystallographic plane</th>
<th>Adatom Formation Energy (eV)</th>
<th>Adatom Diffusion Anisotropy (at 273 K)</th>
<th>Adatom Vacancy Formation Energy (eV)</th>
<th>Adatom Vacancy Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>{10-10}A</td>
<td>0.34</td>
<td>1600</td>
<td>0.26</td>
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<tr>
<td>{11-20}</td>
<td>0.28</td>
<td>100</td>
<td>0.20</td>
<td>2000</td>
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<tr>
<td>{10-11}</td>
<td>0.46</td>
<td>37</td>
<td>0.32</td>
<td>55</td>
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<tr>
<td>{10-10}B</td>
<td>0.06</td>
<td>11</td>
<td>0.08</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>{0001}</td>
<td>0.61</td>
<td>1.2</td>
<td>0.42</td>
<td>1</td>
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</tbody>
</table>
Figure 5.19: Schematic of adatom diffusion anisotropies on the relevant planes. Red arrows indicate the preferred diffusion direction and blue arrows indicate the slower diffusion direction.
Figure 5.20: Comparing borohydride results to that of a chloride additive. (a) Compares an electrolyte with 1.5 M LiBH$_4$ + 0.1 M Mg(BH$_4$)$_2$ (black) to an electrolyte with 1.5 M LiBH$_4$ + 0.1 M MgCl$_2$ (red) on Pt wire. (b) Compares XRD patterns of the Cl additive (blue) and the normal electrolyte (red) on a roughened Ag substrate. (c) SEM image of the deposit at -200 mV for 16 hours. (d) Magnified SEM image of the center of (c).
5.10 References

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