Investigation and Control of the Electrode/Electrolyte Interface in Electrochemical Systems

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In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry

CALIFORNIA INSTITUTE OF TECHNOLOGY Pasadena, California

> 2025 Defended February 6th, 2025

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ACKNOWLEDGEMENTS

I have far, far too many people to thank here, truly one of my greatest feats of trickery is convincing all these great people that they should be friends with me. Still not entirely sure how that happened but I'm not going to look a gift horse in the mouth. Truly, every one of you have made such a positive influence in me and I'll carry these memories forever. Thank you all for your presence in my life and I wish you all good tidings.

First and foremost I want to thank my advisor Kim for giving me a chance to work with her. In my cohort, there were a LOT of people who wanted to join the lab, and coming with zero background in electrochemistry, plus I don't exactly come across as the most enthused scientist, I was honestly a little surprised she offered me a position. I think if I did it all over again, I would still choose this lab. You've cultivated truly a wonderful group environment in which everyone feels empowered to support each other and cooperate. I also want to thank you for having such an open dialogue with me, I've always felt like if I had something I needed to talk to you about I could have a fair and honest chat with you, and I think it's been very important for me to have that especially in a PhD filled with lots of outside challenges.

I want to thank Prof. Ken Suslick and Prof. Alison Fout, who gave me my first real forray into research and taught me the beginning of doing scientific research, and also literally directly helping me get into grad school in the first place. Especially Ken, to this day I don't really know what he saw when he took me on as a freshman, but I'm grateful. I also want to thank Jordan Hinman and Joe Nugent, my grad student mentors. Jordan really had to put up with some stuff back then, I was a dumb kid who thought he knew more than he actually did, but he was infinitely patient and really taught me a lot about research. Joe taught me pretty much everything I know about synthesis which was no easy task, and I now realize I probably annoyed him as a research considering my extremely chaotic hood, bench, and box space, whereas Joe is extremely organized, so sorry about that!

My parents, thank you for your support for my career all these years, and it makes me happy to see everyone finally settled. I hope moving forwards we can continue to build towards something good. My brother Eunsol, thank you for being a great little brother, I know it can't have been easy to essentially be the only child at home after I left home so early, but you're doing a great job and I'm proud of who you are now, but I also know that you will continue to find yourself in the future.

I want to thank my grandparents, I really took it for granted back then and I deeply regret it, but your unconditional love and affection have helped me so much all these years. You were the first to believe in me, and while I'm very sorry you couldn't be here to see me graduate and see who I've grown into, I know you're in a better place now. My only regret is that I didn't realize how special it all was back then, but I guess that's how it always is with this kind of stuff. Thank you, I miss you, and I love you.

I want to thank Wendy, honestly when I first met her on my visit weekend I never would've in a million years thought she would become my best friend, but here we are. Grad school's been the first time in my life where I feel even a little bit comfortable being wholly myself, and you've been a huge part of that. I never have to second-guess whether anything I say or do is going to be judged (probably because we're kind of weird in the same way), and that's been so valuable to me. You're more kind than you ever give yourself credit for, you're so capable at your work that it's almost intimidating, and lesser men should indeed be intimidated. It's been such a joy watching you go through grad school and establish your life, it fills me with hope for my own but also both our futures as well. I love you, thank you for being a part of my found family. I'll miss being able to just drive over to your house and talk about whatever weird stuff we talk about, but I'm still so excited to see where life takes our friendship.

Michelle regularly gives me a hard time for telling her within the first few months of knowing each other that I thought her "too bubbly" and us very different people. I think me in first year would be a little surprised at how tight our friendship has become, but now you're one of the most important people in my life. You are so kind, caring, easy to trust, loving and lovable, and so smart and capable, I don't think I can think of many things that I wouldn't trust you to be able to accomplish. You've helped me so much in coming out of my shell, and I know I can always trust you to help me feel better without judgement even in my lowest moments, but also share my joy and happiness as well. I love you very much and I couldn't have done it without your support and friendship. I'll miss being able to simply turn around and talk to you in the office and laugh (you have a 10/10 smile, it always cheers me up even if my experiments go horrifically wrong), but I'm also excited for us to leave the shadowed realm that is grad school and see our friendship evolve.

I want to thank Steven for being in the trenches with me for those years where it was really not ideal. The breakfasts and lunches where we could commiserate really helped me get through it. I definitely couldn't have made it through those days without you. You've also inspired me to get out there and explore and develop hobbies which I think has been very good for my own personal growth. I'm so happy that we're both able to graduate but also that you found Tony. I'm cautiously optimistic and excited about what life's going to look like after graduation for both of us!

Nick, I think back on those days in the Cats apartment in deep COVID fondly. The shenanigans everyone got up to in that apartment, the impromptu lunches you took me to in LA, the complaining about grad school, etc. I appreciate your disarming and frank demeanor, and deeply appreciate your perspective on things. Thank you for hosting me on my numerous visits up to Santa Barbara, they've helped me be both physically and mentally remove myself from work a little bit and just hang out with you guys and Claudia. Thank you for letting me share in your family, you guys telling me about Claudia is still one of my all-time favorite memories.

Chandler and Ana, it was serendipidous but I'm glad I met you guys and became friends, this past year of more active friendship has been a great joy of mine. I sort of regret not warming up sooner but I promise I'm working on that! Chandler, I very much appreciate your dad humor but also your emotional awareness, I feel like the more I learn about you the more I relate and think we have quite a bit in common (it's so damn hard to find people who watch sports in our circle...). Ana your relentless happiness and joy is infectious, and it always makes me feel better. I will miss you both very much, and I hope even after I graduate we can all do more road trips and movies and such together.

Robert, thank you very much for your years of friendship, I still think back to those days in first year when we'd play tennis and you'd talk to be about Pd coupling and I'd pretend to understand while trying not to sky the ball into those parrots, or those times of Trouble back in the Cats when we'd get beer drunk and lament.

Kim, thank you for being office mates, Ch 3x co-TA, encouraging chats in the office, and Ada time! I appreciate your good humor but also relentless drive towards work and DEI!

Jake, thank you for all those DND and geek-outs, all the XPS help, and just being an overall good and positive presence in my life. Sarah, thank you for the hikes, lunches, all the commiserating about bowels and other stuff, and the cat time.

Laura, thank you for being my teammate in wrangling in those kids in Ch 3x, and the Powerpoint parties.

Eshaan, thank you for your relentless optimism in science and academia, your group meetings were always sparks of inspiration in my excitement for the future, however brief.

Skyler and Sam, thank you for being great friends, introducing me to a lifelong hobby in DND, hosting me in Cincinnati. I still miss you Skyler in the office and in group meetings, I could always trust you to be a grounding presence, and Sam for your kindness and good humor. I'm so excited you guys have bought and made a home for yourselves!

Zak and Skyler, thank you for being the "adult" presence in my life. Sorry Zak for some of the shenanigans... I appreciate all the cooking, the brewery hangouts, and the Overcooked nights, watching Skyler yell at my brother was honestly one of the highlights.

Colin, thank you for being my roommate for the last year or so, I'll miss the impromptu deep conversations we'd have and I promise things will get better!

Andreas, thank you for the random light-hearted conversations we'd have, the Magic nights. I appreciate your easy joking manners.

I want to thank everyone in the See group past and present, truly you've been the best coworkers I could've asked for. I'm so very fortunate to have coworkers become friends, it helped so much to look forward to go into lab even when work didn't do that. You all are some of the best scientists I know, and I'm excited to see where you all end up in the future.

I want to thank the boys back in Woodbury, apparently it isn't common to stay friends with such a large group of high school friends all these years. You're the oldest friends I have, and it's so easy to slide back and pick up where we left off, it's a very comfortable friendship. You've helped me stay grounded through grad school and take my mind off of work when I needed it, and it's been so great to see how everyone changed for the better from high school as well.

I want to thank all the friends I made back in Champaign, college was really the first time in my life where I could start to figure out who I was by myself and I'm

sure that transition state was quite clumsy and awkward, but you kept me company through those years. I think back to those fond memories sometimes, the PAR late nights, the DKH Smash sessions, cramming for finals at Grainger.

I need to thank Hazel, my favorite, truly she's such a unique, loving puppy. Thank you for the years of love and comfort and being willing to be my cuddle-buddy (sometimes even when she doesn't really feel like it). Even on my worst days, hearing her bark and run up to shove her entire body into my legs makes it impossible to be sad. In my lowest and darkest moments, it's still impossible to doubt her affection.

Ada, thank you for being such a smart cat and so loving. Not going to lie there were some days when I was cat-sitting that were pretty rough and Ada always knew and would be extra cuddly and purring. I distinctly remember one day involving Taco Bell and Field of Dreams.

Kiki, thank you for being such a bundle of excitement and joy. It's still a 50/50 on whether she pees or not if I pet her the first thing I see her. She's really not that bright but boy does she love enough to more than make up for it. It's always a pleasure and a serotonin-boost to hang out with Kiki, even if her breath stinks.

Finally, I want to thank all the Caltech staff that helped me get to this point. Joe Drew, Alison Ross, Dave Vander Velde, Nate Siladke, Nate Dalleska, Mike Takase, Larry Henling, Chi Ma, Armando and Greg, Aracely, Sadie, Elizabeth, Alex Wertheim, Kitty and Mitch, and Victor Rivera, thank you all.

ABSTRACT

In electrochemical reactions, the electrode/electrolyte interface is of vital importance, as no reactivity occurs in the bulk electrode or the electrolyte. Often, the interface can be the difference between a successful reaction and a failure. In this thesis, we present three works wherein the electrode/electrolyte interface is studied and controlled to drive desired electrochemical reactivity. A Mg-In alloy is employed for Mg metal batteries to prevent Mg dendrite growth, which can cause cell shorting and failure. By coating the surface of Mg metal electrodes with the Mg-In alloy, the nucleation of Mg dendrites is suppressed and instead the Mg electroalloys into the surface alloy upon reduction, significantly increasing the cell life time. Next, the Li-intercalation material LiTiS₂ is studied for use in organic reductive electrosynthesis as counter anodes. Traditional metal sacrificial counter anodes are known to cause issues such as surface passivation, chemical reactivity, and cross-plating at the working electrode, which is deleterious to the desired organic reactivity. It is found that LiTiS2 surface is less reactive in organic electrolytes, reducing both passivation and chemical reactivity. Further, Li⁺ de-intercalated from LiTiS₂ oxidation is found to be less susceptible to cross-plating than Zn, a common sacrificial anode. Finally, the effect of electrode material on the electrochemical reduction of t BuI is studied. Using electrochemical characterization, it is found that the reduction is catalyzed on Au and Ag through adsorption of the initial substrate, as well as the adsorption of the reactive intermediate ^tBu radical. The catalysis of ^tBuI reduction can have meaningful consequences for organic reactivity, driving the desirable generation of the carbanion nucleophile from alkyl halide reactants.

PUBLISHED CONTENT AND CONTRIBUTIONS

Lee, B. C.; See, K. A. A Mg-In Alloy Interphase for Mg Dendrite Suppression. J. *Electrochem. Soc.* 2024, 171 (1), 010513.
B.C.L participated in the conception of the project, collected and analyzed the data, and participated in the writing of the manuscript.

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Chapter 1

INTRODUCTION

1.1 Motivation and background

Electrochemistry is broadly defined as the branch of chemistry concerned with the intersection between electrical and chemical reactions.¹ Simply put, electrochemical reactions use electrons from direct electricity rather than from chemical reagents to perform chemical reactions. Electrochemistry is omnipresent in life, from our very nervous system, to the handheld devices that everyone is now addicted to. While electrochemistry is an ancient field, recently an increased focused has been placed on the field due to the relevance of electrochemistry in addressing climate change and reducing carbon emissions.^{2,3} Technologies such as batteries,^{4,5} electroreduction of CO_2 ,^{3,6–8} hydrogen fuel cells,^{9,10} *etc.* are all such examples of energy-relevant technologies that are electrochemical in nature.

The simplest electrochemical cell consists of two conducting materials called electrodes an electrolyte separating the two. One electrode is referred to as a cathode and the other an anode. At an anode, a chemical species loses an electron to become oxidized. The electron that has been freed then flows through the circuit that connects the two electrodes and arrives at the cathode, where the electron is added to a chemical species to reduce it. Due to the negative charge of an electron, this directed motion of the electron causes a net movement in charge. The balancing of this net charge is the main role of the electrolyte, through which mobile ions can move to counteract the charge build-up.

One interesting detail about electrochemical cells that is not immediately obvious is that all electron transfer from the electrode to the redox-active species occurs at the electrode/electrolyte interface, an infinitesimally small fraction of the electrode. As a result, electrochemical systems are highly surface-sensitive.^{11,12} In the vast majority of electrochemical cells, the surface is dynamic during operation of the cell, resulting in adsorption^{13,14} or the evolution of a surface layer, which is called the solid-electrolyte interphase (SEI) in battery systems.^{15–17} The SEI is formed as a result of either chemical or electrochemical reactions at the surface which results in an insoluble product that deposits at the surface of the electrode.^{18,19} The properties of the SEI are often critical to the performance of the electrochemical cell.

In Li-intercalation graphite anodes, a widely used anode material in Li-ion batteries, the SEI is formed through the reduction of the electrolyte salt lithium hexafluorophosphate (LiPF₆) and the organic carbonate solvent.²⁰ The SEI on Li-graphite is known to be self-terminating, electronically insulating, and conducting towards Li-ion. The self-terminating and electronically insulating nature of the SEI prevents its infinite growth and electrolyte consumption, while Li-ion conductivity reduces the impedance across the SEI, enabling stable battery operation.²⁰

However, in metal batteries, the SEI is much more problematic. In Li metal anodes, while the SEI retains properties such as the electronic insulation and ionic conduction, the SEI is prone to mechanical cracking during battery operation due to the large volume change in Li metal upon redox. When the SEI cracks, fresh Li is exposed to the electrolyte, generating more SEI. Thus, the SEI on Li metal is not self-terminating, resulting in Li metal loss, increased cell impedance, and dendrite growth which pose a safety issue.^{21,22}

In Mg metal anodes, the SEI is ionically insulating towards Mg²⁺. As such, the impedance across the SEI is extremely high, resulting in polarization of the cell. SEIs with a high impedance are known as passivation layers, due to the ionically and electronically insulating nature of the SEI passivating the metal to further reactions.^{23,24} The passivation of Mg restricts the available scope of electrolytes for Mg metal batteries drastically, hindering further development of the technology.

In electrocatalysis applications such as CO_2 reduction or hydrogen fuel cells, the SEI is typically less of an issue due to the milder potentials catalysis typically occurs at, as well as the lower chemical potential of the electrode material.²⁵ Nonetheless, the electrode/electrolyte interface plays a key role in electrocatalysis due to the adsorption of the reactant at the electrode surface. In the hydrogen evolution reaction (HER), Pt is the state-of-the-art catalyst. The good catalytic performance of Pt towards HER is due to the ideal binding energy of H⁺ to the surface of Pt.²⁶ In CO₂ reduction, Cu is a unique electrocatalyst due to the C–C coupling on Cu resulting in multi-carbon products. The C–C coupling-ability of Cu was revealed to be due to the ideal distance between the intermediates adsorbed on the Cu surface as well as the ideal energy landscape for C–C coupling to occur.²⁷

As such, the electrode/electrolyte interface is vitally important to the performance of several energy-relevant electrochemical systems. For further development of existing and future systems to improve the energy economy, a better understanding and control of the electrode/electrolyte interface is crucial. Here in this thesis, three electrochemical systems and the respective electrode/electrolyte interfaces are studied.

1.2 Thesis outline

We explore the effects of the electrolyte/electrode interface in three different electrochemical systems, and the attempts at controlling the interface to either promote desired redox reactions, or prevent deleterious ones. Techniques such as direct modification of metal surfaces using alloys and design of entirely new electrode materials are employed to this end, and characterization techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) are used to characterize the electrode surface.

In Chapter 2, the development of Mg-In alloy interphases for suppression of Mg dendrites in Mg metal anodes is described. By modifying the surface of Mg metal, the electrolyte/electrode interface is modified to prevent the nucleation of Mg dendrites and instead promoting the electroalloying of the interphase and the subsequent deposition of Mg underneath. The mechanism of the Mg-In alloy is investigated using SEM and XRD as well as electrochemical techniques.

In Chapter 3, a Li-ion intercalation material is adapted for a counter anode in reductive electrosynthesis. Traditional counter anodes in reductive synthesis are typical metal anodes such as Mg, Zn, and Al, which all suffer from deleterious surface reactions such as passivation, chemical reactions, and cross-plating at the working electrode. By using a Li-ion intercalation material, the undesirable surface reactions are curbed.

In Chapter 4, the effect of electrode material on the electrochemical reduction of t BuI is investigated. Through electrochemical characterization, we hypothesize that Ag and Au have an enhancing effect on the t BuI reduction to generate the synthetically-relevant carbanion through adsorption at the electrode surface, by activating the C–I bond initially, and then adsorbing the intermediate radical to prevent deleterious homogeneous reactions in solution.

Finally, in Chapter 5, the findings are summarized, and the future outlook for the control and modification of the electrode/electrolyte interface is discussed.

Chapter 2

A MG-IN ALLOY INTERPHASE FOR MG DENDRITE SUPPRESSION

Lee, B. C., See. K. A. A Mg-In Alloy Interphase for Mg Dendrite Suppression. J. *Electrochem. Soc* 2024, 171 (1), 010513.
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2.1 Abstract

Mg metal batteries have attracted much attention as an alternative to Li-ion technology due to the high abundance and volumetric capacity of Mg metal. Further, early reports show that Mg is less prone to dendritic growth compared to Li, thereby improving the safety and long-term reversibility of Mg metal anodes. However, dendritic growth of Mg can be observed in various conditions, causing cell shorting and capacity loss. Herein, we report a chemically-formed Mg-In alloy interphase that suppresses nonuniform Mg growth during electrochemical reduction. *Ex-situ* X-ray diffraction shows that upon reduction, Mg alloys into the Mg-In interphase with no evidence of Mg deposition on top of the surface during initial cycles. Interestingly, further reduction results in Mg depositing underneath the interphase, which confirms Mg mobility through the interphase. However, the alloying reaction is kinetically limited, leading to significant Mg deposition on top of the interphase at high current densities. Thus, alloys on Mg can affect deposition morphologies, but are limited by the kinetics of Mg conduction through the alloy.

2.2 Introduction

Mg batteries have been studied as a promising alternative to current Li-ion battery technology due to high natural abundance and well-dispersed deposits of Mg-containing precursors.²⁸ However, Mg batteries are only competitive from a performance perspective if a Mg metal anode is used. Mg metal anodes have a very high volumetric capacity of 3833 mAh/cm³ and a reasonable gravimetric capacity of 2295 mAh/g, but face a host of challenges that prevent commercialization. One of the biggest challenges facing Mg metal is the tendency for Mg metal to passivate by reaction with water, oxygen, and other electrolyte components to form an insulating layer, shutting down deposition and stripping of the metal.^{23,29–32} As such, research into Mg metal anodes initially consisted primarily of investigation into electrolytes to control the interface and prevent the passivation of the Mg metal surface. To that end, several classes of electrolytes, such as those based on Grignard reagents, ^{32–38} halide-containing electrolytes, ^{39–44} trifluoromethanesulfonimide (TFSI) salts, ^{45–47} fluorinated weakly coordinating anions, ^{48,49} and boron hydride-based anions^{50,51} were developed to varying degrees of success.

A potential attractive feature of Mg metal anodes is the smooth deposition morphology compard to Li metal. Matsui observed that at the same current densities (2.0 mA/cm²), Li forms dendrites while Mg deposits in plate-like morphologies.⁵² The lower self-diffusion barrier of Mg compared to Li was hypothesized to result in smoother morphologies.⁵³ Control over metal deposition morphology is crucial as dendrites can have many detrimental effects, such as capacity fade as a result of dead metal or shorting of the cell when the dendrites pierce through the separators, posing safety hazards associated with thermal ruanway in the presence of a flammable electrolyte.⁵⁴ However, despite the low self-diffusion barrier inherent to Mg metal, the kinetics of the electron transfer coupled with mass transport limitations can outpace the self-diffusion at high enough current density. During deposition, the metal cations nucleate and deposit until the ions at the surface of the negatively charged electrode deplete. 55–57 The anions are repelled from the cathode, while the cations are consumed, causing a large space charge region at the electrode. As a result of the space charge region, the cations deposit in such a way to maximize growth towards the anode to minimize the space charge build up, causing dendritic morphologies.⁵⁶ As such, dendritic growth of Mg has been reported in literature. Davidson et al. observed Mg dendrites at 0.921 mA/cm², which is a lower current density than Matsui reported.⁵⁸ However, the growth was mostly observed at the edges of a Mg ribbon, where higher local flux would occur. Eaves-Rathert et al. also observed nonuniform growth of Mg at 0.2 mA/cm² in a coin cell geometry using a polymer separator. While the Mg deposits are not dendritic in the classic sense that the deposits do not form classic branching structures, hemispherical islands form using the separator as scaffolding and stack on top of each other to form deposits that cause shorts through the polymer separator.⁵⁹ The deposits are referred to as 3D growth but cause the same harmful effects as a classic dendrite would. The separator scaffolding effect is also observed by Hebié et al. and Ding et al.^{60–62}

A strategy to suppress Mg dendrites is through modification of the electrode surface. The formation of artificial interphases on Mg surfaces has been commonly employed to improve Mg cycling by protecting the anode from passivation.^{63,64} However, some interphases, particularly alloy-based systems, have been noted in literature to minimize dendrites as well. Several different mechanistic explanations have been given for the dendrite-reducing ability of alloy interphases. In many alloy interphase systems, the alloy interphase decreases insulating passivation with the electrolyte, which prevents preferential deposition at localized points with low electrical resistance. As such, a smoother Mg morphology on the electrode is observed.^{65–68}

Of particular interest are two alloy interphase systems where the Mg is hypothesized to conduct through the alloy interphase and deposit underneath. A Mg|Mg-Sn electrode was shown to decrease Mg stripping and deposition overpotential while maintaining fast kinetics, exhibiting <1 V overpotentials at a very high current density of 6 mA/cm² in symmetric cells. The Mg deposits at the Mg|Mg-Sn interface is observed by cross-section SEM. The bulk composition of the alloy remains unchanged through cycling by XPS, indicating mobility of Mg through the Mg-Sn interface. However, the study focused mainly on cycling stability, and the mechanism of the electroreduction process in the interphase was not determined.⁶⁹

In a Mg-Ga alloy interphase system, shorts when cycling in a symmetric cell were prevented when using the alloy interphase. Calculations suggest Mg thermodynamicaly prefers plating at the Mg|Mg-Ga interface rather than the Mg-Ga|electrolyte interface. Experimentally, Mg metal deposition on top of the interface is not observed by XRD or XPS and the interphase composition experiences minimal changes. However, kinetic limitations are present in the system, with the symmetric cell galvanostatic cycling at a relatively low current density of 0.1 mA/cm² with a concentrated electrolyte (0.8 M Mg(TFSI)₂ in glyme) at moderately elevated temperatures (40 °C). In addition, the Mg deposition underneath the interphase was not confirmed by cross-section SEM.⁷⁰ Meng *et al.* evaluated a Mg-Bi interphase, but its impact on Mg morphology was not discussed.⁷¹

Inspired by the initial work on alloy interphases, here we show an artificial interphase based on In metal and its alloys with Mg to reduce Mg dendrites and cell shorting. We then investigate the mechanism of the alloy interphase during reduction. The alloy-based interphase is prepared by a simple chemical redox reaction of Mg metal with InBr₃ in solution. The Mg-In interphase suppresses Mg dendrites, as observed by SEM. In a symmetric cell with glassy fiber separators, the Mg-In interphase

results in a significant increase in the cycling lifetime before shorting. *Ex-situ* XRD shows the Mg content in the interphase increases as Mg^{2+} is reduced, indicating that magnesiation of the alloy phases occurs upon reduction instead of Mg metal plating. Cross-section SEM images show Mg deposition underneath the interphase, confirming Mg mobility through the interphase. Electrochemical characterization reveals that the electroalloying of Mg into the Mg-In interphase is kinetically slow, resulting in a low threshold current density where exceeding said current density results in Mg deposition on top of the Mg-In interphase. The kinetic limitation is an important consideration to understand the behavior and benefits of the alloy interphase.



2.3 Results and discussion

Figure 2.1: SEM image of the Mg metal foil (a) before and (b) after reaction with $InBr_3$ in THF for 2 hr. A rough surface film is observed after reaction across the foil. (c) XRD pattern of the Mg foil after reaction with $InBr_3$ with a four phase Rietveld refinement to Mg, In, and the Mg-In alloys β and β'' , collected in a Bragg-Brentano geometry.

First we discuss the preparation of the Mg-In alloy interphase. The modified electrode is prepared by a chemical reaction of Mg metal with 50 mM InBr_3 in tetrahydrofuran (THF). Mg is a stronger reducing agent compared to In with an E⁰ of -2.36 V vs. the standard hydrogen electrode (SHE)¹ compared to -0.34 V⁷² vs. SHE for In. The Mg metal can therefore chemically reduce the In³⁺ in solution. To determine the fate of the Br⁻, the energy dispersive X-ray spectroscopy (EDS) map is collected on the Mg metal surface after reaction (Figure S2.3). Negligible quantities of Br are detected in the interphase via EDS (roughly estimated at <1%)

by weight), which suggests the $MgBr_2$ precipitates out into solution rather than on the interface. After reaction with $InBr_3$, the foil turns gray. If the foil is allowed to react for a longer period, on the order of 20 hr, then the surface layer flakes off revealing reactive Mg metal. Thus, the reaction is not self-limiting. To evaluate the morphology of the solid reaction product on the Mg surface, SEM images are taken of the Mg metal surface before and after a 2 hr reaction with $InBr_3$. The SEM images is shown in Figure 2.1a,b. The Mg foil before the reaction with $InBr_3$ is smooth with some grooves from the polishing process with sandpaper. After the reaction, the surface layer is rough and uneven, but covers the entire exposed Mg surface.

The XRD pattern measured in Bragg-Brentano geometry of the Mg foil after the reaction with InBr₃ is shown in Figure 2.1c. The (002) reflection of Mg metal is the strongest peak, suggesting that the X-rays can penetrate through the surface film to the Mg metal substrate (Figure S2.1). However, additional peaks are observed suggesting the surface layer has crystalline domains. The additional peaks can be assigned via a four phase Rietveld refinement to In metal and two different Mg-In compounds in the binary phase space: β and β'' .⁷³ The β phase is a disordered fcc structure that forms at high In content at lower temperatures, and <50% In content at higher temperatures.⁷⁴ The β'' phase is an ordered tetragonal structure that forms near 50% In content. The β'' phase forms upon slow cooling between In contents of 35 to 50%, suggesting the phase is thermodynamically favorable at the specificed In contents.⁷⁵ Both the alloys have a moderately wide solid-solubility window near room temperature (approx. 10% in composition), which may enable the electroalloying of Mg upon reduction. Both In and Mg metals have some degree of solubility as well. From the quality of the diffraction pattern collected, we were unable to determine the exact Mg-In contents within each phase. We can estimate the phase fractions of each crystalline phase within the Mg-In interphase from the Rietveld refinement by excluding the Mg fraction due to the visible contributions from the Mg foil substrate. The phase fractions of the phases given in weight percent are 62% In, 15% β'' , and 23% β . Because multiple phases are formed after reaction with InBr₃, we will refer to the surface film as the Mg-In interphase hereafter. Mg foil electrodes with the Mg-In interphase will be referred to as Mg|Mg-In electrodes.

To investigate the effects of the Mg-In interphase on the electrochemical stripping and deposition of Mg^{2+} , the Mg|Mg-In electrode is galvanostatically cycled in a symmetric cell and compared to a bare Mg control. The galvanostatic cycling



Figure 2.2: Galvanostatic cycling of Mg metal and Mg|Mg-In electrodes at (a) 0.025 mA/cm^2 and (b) 0.5 mA/cm^2 using MACC + Mg(HMDS)₂ electrolyte with a glassy fiber separator. Each half-cycle is 1 hr. A higher overpotential and faster shorting behavior is observed with bare Mg metal electrodes when compared to Mg|Mg-In electrodes at low current densities. When cycling at 0.5 mA/cm^2 , there are no meaningful differences between the galvanostatic behavior of bare Mg and Mg|Mg-In electrodes.

data are shown in Figure 2.2. The electrolyte of choice for the electrochemical characterization of the electrode is a magnesium aluminum chloride complex (MACC) electrolyte chemically conditioned with magnesium hexamethyldisilazide (Mg(HMDS)₂).⁷⁶ MACC + Mg(HMDS)₂ is chosen for its high anodic stability compared to Grignard-based electrolytes and its potential susceptibility for dendrites due to its low Mg²⁺ concentration (60 mM) that causes low conductivity. A polytetrafluoroethylene (PTFE) Swagelok union cell with Mo current collectors are used to avoid stainless steel corrosion with the chloride-containing electrolyte. At a current density of 0.025 mA/cm^2 , bare Mg metal electrodes show a rapid increase in the plating and stripping overpotential until erratic spikes are observed after about 9 cycles, which is attributed to electrical soft shorts in the cell (Figure 2.2a). Upon disassembly of the cell, black deposits are observed on both sides of the porous glassy fiber separator which we assume to be Mg. In contrast, the Mg|Mg-In electrodes exhibit a much slower and gradual increase in overpotential, and cell shorting is not observed until after 144 cycles (Figure 2.2a). The increasing overpotentials upon galvanostatic cycling suggests an instability in the Mg|Mg-In electrode upon extended cycling, likely the result of an insulating interphase forming on top of the Mg-In alloy, or a mechanical breakdown of the Mg-In alloy. However, compared to galvanostatic cycling results of bare Mg electrodes, the overpotential increase is much slower, suggesting an improvement in the electrode stability. The galvanostatic cycling behavior at 0.05 mA/cm² is shown in Figure S2.4, and similar trends hold. However, 0.05 mA/cm² is not a commercially relevant current density. As such, the symmetric cells were cycled at elevated current densities to study the kinetic limitations of the Mg|Mg-In electrodes. The galvanostatic cycling performance of the bare Mg and Mg|Mg-In electrodes at a current density of 0.5 mA/cm² are shown in Figure 2.2b. No meaningful differences in electrochemical performance between bare Mg and the Mg|Mg-In electrode are observed, suggesting a possible kinetic limitation with the interphase.



Figure 2.3: SEM images of the (a,b) bare Mg and (c,d) Mg|Mg-In electrode after applying -0.05 mA/cm² for 10 h. A PTFE donut separator is used to prevent the separator from affecting the morphology. A heterogeneous deposit is clearly observed in (a,b) while absent in (c,d).

First, we probe the low current reduction behavior to investigate the changes to morphology. SEM images of the electrode surfaces are taken after applying - 0.05 mA/cm² for 10 h. To eliminate the effect of the separator scaffolding on the deposition morphology, a donut PTFE separator is used in a Swagelok cell. The well of the separator is filled with the electrolyte solution, thus providing a planar electrode surface with no scaffolding to seed nucleation or affect growth morphology. The SEM image of the bare Mg electrode after reduction is shown in Figures 2.3a and b. Small spherical Mg clusters are found scattered across the electrode. This morphology is similar to the Mg deposits observed by Eaves-Rathert and coworkers, arising from hemispherical deposition of Mg under moderate overpotentials.⁵⁹ The SEM of the Mg|Mg-In electrode after reduction is shown in

Figure 2.3c and d. In contrast to the bare Mg electrode, the Mg|Mg-In electrode morphology changes minimally with the rough surface becoming marginally less fractal. No hemispherical growths are observed suggesting Mg is not plated on the surface. To determine if the Mg-In alloy remains intact following an oxidation, the Mg|Mg-In electrode is oxidized at 0.05 mA/cm² and imaged. The SEM and corresponding EDS maps are found in the SI in Figure S2.18. In is still present homogenously dispersed on the electrode surface following oxidation, suggesting that at least for short term cycling, the Mg-In alloy remains intact.



Figure 2.4: (a) SEM image, (b) Mg EDS map, and (c) In EDS map of the Mg|Mg-In electrode after a deposition of 1.25 mAh/cm^2 at a current density of 0.5 mA/cm^2 . Large Mg deposits are observed on the surface. (d) Cyclic voltammograms of the Mg|Mg-In electrode swept at 5 mV/s after a deposition of 3 mC, at a current density of either 0.025 mA/cm^2 or 0.5 mA/cm^2 . The small anodic peak observed after higher current density deposition is an indicator of Mg deposits on top of the Mg|Mg-In electrode.

However, the significantly different galvanostatic cycling behavior of the Mg|Mg-In electrode at a higher current density suggests different processes are occuring at high current densities. To study the surface morphology after a high current reduction step, SEM images of the Mg|Mg-In electrode surface after a reduction at -0.5 mA/cm² are collected. The SEM image and the EDS elemental maps of the Mg|Mg-In electrode surface after the reduction are shown in Figures 2.4a-c. Contrary to the morphology at low current density, deposits are observed on top of the electrode with no In present in the deposits, indicating the deposits are Mg metal. Thus, there appears to be a rate at which Mg will deposit on top of the interphase.

To electrochemically probe if Mg is deposited at the electrode surface, i.e. on top

of the Mg-In surface, a two-stage electrochemical experiment is devised. First, the Mg|Mg-In electrode is reduced at a constant current density. Then, a positive sweep cyclic voltammogram (CV) is collected. The experiment is repeated with increasing current densities. Two CVs from the experiment are presented in Figure 2.4d, one after a deposition at 0.025 mA/cm² and another at 0.5 mA/cm². The CV after reduction at 0.5 mA/cm^2 exhibits a depletion effect where the current density decreases as the potential is swept positively. This depletion effect in the CV is attributed to stripping of freshly-deposited surface Mg on top of the Mg-In interphase, such as the deposit imaged in Figure 2.4a. Once all the freshly-deposited Mg is stripped off, the current density decreases. A similar phenomenon was observed by Melemed *et al.* where a depletion effect was observed via CVs after a deposition of fresh Ca on top of a passivation layer.⁷⁷ However, no such depletion effect is observed in the CV after reduction at 0.025 mA/cm², which indicates no such deposited Mg is available on the surface of the electrode. A clear kinetic limitation in the Mg-In interphase is therefore observed where past a critical current density, the Mg-In interphase acts as a deposition substrate instead of suppressing dendrites.



Figure 2.5: XRD patterns of the Mg|Mg-In electrode in a (a) pristine condition and (b) after a 0.025 mA/cm² reduction for 100 hours. The patterns are fit with a fourphase Rietveld refinement that includes In, Mg, and two Mg-In phases β and β'' . Upon reduction, a growth of the Mg-rich β'' phase is observed with a corresponding decrease in In metal.

To gain more insights into the reduction process in the MgMg-In electrode, we investigate the mechanism by characterizing the MgMg-In electrode after reduction *ex-situ*. First, the XRD pattern of the MgMg-In electrodes are collected after

phases ^a	pristine (wt%)	reduced (wt%)
In	62%	16%
$\beta^{\prime\prime}$	15%	64%
eta	23%	20%
^a The Mg	phase is excluded	as the X-ray penetrates

through the alloy layer into the Mg substrate. The remaining three phases are renormalized.

Table 2.1: Phase fractions of the In-related phases present in the interphase layer, as calculated from the Rietveld refinement.

reduction at low current densities to observe the changes in the crystalline domains in the interphase. In Figure 2.5, the XRD patterns of the Mg|Mg-In electrode before and after reduction are shown. The patterns can be fit via a Rietveld refinement to the four phases identified in Figure 2.1c: Mg, In, and the binary Mg-In alloys β and β'' . The largest peak is the Mg(002) reflection with a preferential orientation for the (002) plane, which suggest that the X-rays penetrate through the entire Mg-In interphase to the Mg foil substrate. Therefore, we assume that all the crystalline phases of the Mg-In interphase are captured by XRD. All the In-containing phases can be fit well due to isolated peaks. The intensities of the two XRD patterns are normalized to the Mg(101) reflection to better compare the relative intensities of the reflections of different phases. After reduction of the Mg|Mg-In electrode, an increase in the intensity of the reflections attributed to the β'' phase is observed. The increase in intensity is most evident in the $\beta''(100)$ reflection near 27° 2 θ . A corresponding decrease in the intensity in the In reflections is observed, easily observable in the In(101) and In(002) reflections near 33° 2θ and 36° 2θ , respectively. The calculated phase fractions from the Rietveld refinement are shown in Table 1. Upon reduction of the Mg|Mg-In electrode, a clear decrease in the In phase fraction is observed, as well as a slight decrease in the In-rich β phase alloy. A significant increase in the Mg-rich β'' phase is observed. The XRD patterns thusly indicate that the crystalline domains of the Mg-In interphase magnesiates upon reduction. Based on the diffraction patterns, two possible mechanisms can be posed. The Mg-In alloy could act essentially as an alloy electrode deposited on a conductive substrate (Mg), where the redox occurs only on the deposited alloys. Indeed, In and the β'' phase alloy have been shown in literature to be capable of acting as Mg bulk alloy electrodes with changing Mg contents as the electrode reduces and oxidizes.⁷⁸ A similar phenomenon is observed in the Mg-Hg amalgam surface system, where upon reduction of the surface modified electrode, an increase in magnesiation in the Mg-Hg alloy on the surface of the electrode is observed. Based on the increase in magnesiation upon reduction in the alloy interphase, the authors suggest that the amalgam surface is not active as a protective surface, but rather as a simple Mg-Hg alloy electrode deposited on top of an inert Mg metal substrate.⁷⁹ However, an alternate mechanism can be hypothesized, wherein Mg mobility through the interphase can occur alongside alloying into the interphase, allowing Mg to plate underneath the interphase.



Figure 2.6: (a) Cross-section SEM image of the pristine Mg|Mg-In electrodes and corresponding EDS maps for (b) Mg, (c) In, and (d) O. (e) Cross-section SEM images of the Mg|Mg-In electrode after a 100 hour deposition at 0.025 mA/cm² and corresponding EDS maps for (f) Mg, (g) In, and (h) O. Compared to the pristine Mg|Mg-In electrode, the Mg underneath the Mg-In layer is clearly heterogeneous, with freshly deposited veins of Mg visible in the Mg and O maps.

To determine whether Mg mobility through the Mg-In interphase is possible, *ex-situ* cross-section SEM images of the Mg|Mg-In electrodes before and after reduction are collected. The cross-section SEM image of the Mg|Mg-In electrode before reduction with the corresponding EDS map is shown in Figures 2.6a-d. The EDS map shows a mix of both Mg and In in the interphase layer, which is *approx*. 5 µm thick. Some O is found on the surface layer, likely due to air exposure during sample preparation and transfer.

The cross-section SEM image of the Mg|Mg-In electrode after reduction is shown in Figures 2.6e-h. Mg deposits of a different morphology from the Mg foil substrate are observed beneath the Mg-In interphase. Interestingly, the deposits do not form a uniform layer underneath, instead forming localized veins. We hypothesize that Mg nucleation occurs preferentially underneath the interphase where the interphase is the thinnest, due to the kinetic limitations of the interphase. Upon nucleation, further Mg deposition preferentially occurs at these sites. The deposited Mg also exhibits more oxidation during sample preparation compared to the Mg substrate as evidenced by the O EDS map (Figures 2.6d and h). The increased surface area of the deposited Mg compared to the densely packed commercial Mg foil likely causes faster oxidation in the deposited Mg. Some Mg deposits are also observed on top of the interphase, which is attributed to the depletion effects associated with the extreme length of the reduction necessary to deposit enough Mg underneath the interphase to observe with an SEM (100 hours at 0.025 mA/cm²) (Figure S2.17). No Mg deposits are observed when a shorter reduction time was used, as seen above in Figures 2.3c-d.



Figure 2.7: Cartoon illustrations of the Mg^{2+} reduction process at (a) bare Mg and (b) Mg|Mg-In electrode surfaces. In bare Mg, the rate of self-diffusion (k_s) of Mg across the surface is in competition with the rate of deposition (k_{dep}), while in Mg|Mg-In electrodes, the rate of alloying (k_{alloy}) competes against the rate of reduction (k_{red}) to determine the morphology.

Next we discuss the results in the context of metal deposition models. Chazalviel and coworkers described a model in which the dendritic growth of metals is caused by the formation of a space charge region at the surface of the cathode, due to repulsion of anions and consumption of cations^{55,80}. The model is used to describe the diffusion-limited aggregation (DLA) that causes the classic branching dendritic morphology. However, the deposits observed in Figures 2.3a and b do not resemble a DLA morphology. Instead, the deposits observed on a bare Mg electrode are better described as hemispherical growth. Hemispherical growth occurs under

mixed diffusion and kinetic control at intermediate current densities. Unlike a DLA regime, full mass transport limitation is not yet achieved⁸¹. A cartoon of the reduction process with a bare Mg electrode is shown in Figure 2.7a. The kinetics of the deposition overtake the kinetics of the self-diffusion of Mg across the surface. As such, instead of forming a smooth surface and minimizing the surface energy, the cations reduce as soon as they arrive on the surface.

Based on our experimental observations, we theorize that the electroreduction process at the Mg|Mg-In electrode is different. Processes occurring on the Mg|Mg-In electrode are governed by different rates. In Figure 2.7b, the same reduction process is shown instead with an alloy interphase. In the Mg|Mg-In electrode, upon reduction of the Mg²⁺ cation at the surface of the electrode, the cation alloys into the Mg-In interphase. The alloying process appears more facile than the self-diffusion of Mg, indicated by the suppression of dendrites at same current densities. As such, even at moderate current densities, the alloying process can kinetically keep up with the cation flux. The concentration gradient in the interphase then causes Mg to diffuse, depositing underneath the interphase at the Mg|Mg-In interface. At elevated current densities however, the diffusion through the Mg-In interphase.

The kinetic limitation of the alloy interphase controlling the deposition location of the metal is also observed in literature in Li alloy interphase systems. In a Li-Sn interphase system, Li plates underneath the interphase below the exchange current density of the Li|Li-Sn electrode. However, upon increasing the deposition current density past the exchange current density, Li begins plating on top of the Li-Sn interphase⁸². In another study investigating a Li-Sn interphase system, computed surface energies of the electrode surface suggest that at low current densities, plating underneath the interphase is energetically favorable, but at high current densities Li accumulates at the surface and delaminates⁸³.

2.4 Conclusion

Herein, we demonstrate more uniform reduction with a Mg electrode with a Mg-In alloy interphase compared to Mg metal. The Mg|Mg-In electrode is easily prepared by a chemical reaction of a Mg foil with a solution of $InBr_3$ in THF. The Mg|Mg-In electrode is capable of undergoing more deposition and stripping cycles before evidence of soft shorts are observed compared to Mg metal. While Mg electrodes grow heterogeneous Mg deposits upon reduction, the Mg|Mg-In electrodes do not under the same conditions and instead undergo alloying reactions followed by Mg deposition occurring below the alloy. However, the Mg|Mg-In electrode is kinetically limited by the alloying process. At higher current densities, the alloying kinetics cannot keep up with the rate of Mg²⁺ reduction and Mg deposits on top of the Mg-In interphase. Improved alloy interphases thus must have higher Mg mobility, again highlighting the crucial role of divalent solid-state ion conductivity in Mg-based electrochemical cells. Higher mobility could be achieved by targeting a new phase or leveraging defect engineering strategies. Nevertheless, the Mg-In system serves as a proof-of-concept system for the use of alloy interphases to leverage alloy solid solubility to reduce Mg deposition and cell shorting, an issue that is likely to impact commercial cells due to the use of separators.

2.5 Experimental

General considerations All manipulations were performed in a N₂-filled glovebox (MBraun, <1 ppm H₂O and O₂) unless otherwise stated. Tetrahydrofuran (THF, Fisher Scientific) was dried on a solvent purification system then dried over 4 Å sieves before use. Anhydrous MgCl₂ (99.9%, Fisher Scientific), anhydrous AlCl₃ (99.999%, Sigma Aldrich), anhydrous InBr₃ (99.999%, Thermo Scientific), and anhydrous hexanes (99%, mixed isomers, Sigma Aldrich) were used as received. Magnesium hexamethyldisilazide (Mg(HMDS)₂, 97%, Sigma Aldrich) was recrystallized in hexanes at -20 °C before use. Magnesium foil (99.9%, MTI Corporation, 0.1 mm thick) was cleaned with 0.1 M acetic acid in air, then brought inside the glovebox, where it was further polished with 320 then 1500 grit silicon carbide sanding paper (3M).

Mg-In electrode and electrolyte preparation A 20 mL scintillation vial was charged with 17.8 mg of InBr₃, which was then dissolved in 5 mL of THF. The Mg foil was punched with a 6 mm hammer-driven punch or cut into appropriate pieces, then placed in the reaction vessel for *approx*. 2 hour. The foil was then washed thoroughly in THF before use. The MACC electrolyte was prepared in an N₂-filled glovebox according to Barile *et al.* with the addition of Mg(HMDS)₂ as in Kim *et al.* in 5 mL batches.^{41,43} Solutions of MACC+Mg(HMDS)₂ (30 mM AlCl₃ + 60 mM MgCl₂ + 10 mM Mg(HMDS)₂) were prepared by adding 2.5 mL of chilled THF (cooled to approximately 0 °C on a Peltier plate) dropwise to anhydrous AlCl₃ (20 mg). THF (2.5 mL) was added to anyhdrous MgCl₂ (28.5 mg) and allowed to stir for 1 min. The AlCl₃ was completely dissolved in THF to yield a colorless solution. The AlCl₃ and MgCl₂ solutions were combined, and the resulting solution was

stirred at 420 rpm until it turned clear and colorless (*approx.* 6 h). The electrolyte was subsequently conditioned by adding $Mg(HMDS)_2$ (17.5 mg) and allowed to stir until the solution turned clear.

Electrochemical measurements The galvanostatic cycling and long term deposition experiments were conducted on a VMP3 potentiostat (Bio-Logic) in a two-electrode geometry with the reference and the counter electrodes shorted. Cells were assembled in a 0.25 in inner diameter polytetrafluoroethylene (PTFE) Swagelok cells with Mo current collectors. GF/D (Whatman) filters were used as separators for the symmetric cell galvanostatic cycling experiments with 0.1 mL of Mg(HMDS)₂ electrolyte, at 0.025, 0.05, and 0.5 mA/cm², with 1 hour half-cycles. The GF/D filters were punched with a 0.25 in diameter hammer-driven punch and dried at 80°C under reduced pressures before use. The long-term deposition experiments for *ex-situ* characterizations were done using a Mg|Mg-In working electrode and a Mg foil counter electrode. PTFE donut separator (0.25 in outer diameter., 0.125 in inner diameter) to eliminate scaffolding effects of a physical separator. The wells of the separator were filled with 0.05 mL of MACC+Mg(HMDS)₂ electrolyte.

Tandem deposition-cyclic voltammogram experiments for kinetics The experiments were concuted on a VMP3 potentiostat (Bio-Logic) in a three-electrode geometry. A Ag/Ag_2S reference was used,⁸⁴ which is well-characterized in the MACC+Mg(HMDS)₂ system⁸⁵. Cells were assembled in a glass four-neck heart cell using electrode holders (Gamry Li BMC 1.5 mm substrate holder). The experiment consists of an initial deposition step for *approx*. 4 μ Ah/cm², then a 5 s open circuit hold, then a cyclic voltammetry (CV) scan from open circuit potential to -1 V then back to -1.7 V vs. Ag/Ag₂S at 5 mV/s. This sequence is repeated for different current densities, at 0.01, 0.025, 0.05, 0.075, 0.1, and 0.5 mA/cm².

Physical characterizations All characterization was completed on working electrodes after rinsing with 1 mL of THF and drying in a N_2 glovebox. SEM images were taken with a ZEISS 1150 variable pressure field emission scanning electron microscope with a 15 kV accelerating voltage and an in-lens secondary electron detector. Energy dispersive X-ray spectroscopy (EDS) data were collected using an Oxford X-Max Silicon Drift Detectors X-ray energy dispersive spectrometer with a 15 kV accelerating voltage. Samples were briefly exposed to air during transfer into the instrument. Cross sections of electrode samples were taken by cooling the electrode with liquid nitrogen, then cutting with a scalpel. XRD patterns of the Mg-In electrodes were collected using the Rigaku SmartLab diffractometer equipped

with a HyPix-3000 detector and a Cu K α x-ray source with a 20 kV accelerating voltage, using a Rigaku airtight sample holder. The patterns were collected from 10 to 50° 2 θ at 3° per minute in a Bragg-Brentano geometry. The grazing incidence XRD pattern of the pristine Mg|Mg-In electrode was collected in a parallel beam geometry with an ω of 0.3°.

2.6 Funding acknowledgement

This research was supported by the Packard Fellowship for Science and Engineering. X-ray diffraction data were collected at the X-ray Crystallography Facility in the Beckman Institute of the California Institute of Technology. SEM and EDS data were collected at the GPS Division Analytical Facility of the California Institute of Technology.

2.7 Supplemental information



Figure S2.1: XRD pattern of the Mg foil substrate before reaction with $InBr_3$ in a Bragg-Brentano geometry.



Figure S2.2: Low-magnification SEM image of the surface of the pristine Mg|Mg-In electrode.



Figure S2.3: EDS map of the surface of the Mg|Mg-In electrode (a) In, (b) Mg, (c) O, (d) Br. (e) SEM image of the Mg|Mg-In electrode. (f) EDS spectrum with approximate weight percentages assigned to the elemental species. Trace amounts of Br are observed, likely contamination from the $InBr_3$ solution after the preparation step.



Figure S2.4: Symmetric cell galvanostatic cycling of Mg|Mg-In electrodes at 0.05 mA/cm².



Figure S2.5: Low-magnification cross-section SEM image of the pristine Mg|Mg-In electrode.



Figure S2.6: EDS map of the Mg deposits on bare Mg after deposition at 0.05 mA/cm^2 (a) SEM image, (b) Mg, (c) C, (d) O.


Figure S2.7: EDS map of the Mg|Mg-In electrode after deposition at 0.05 mA/cm^2 (a) SEM image, (b) Mg, (c) In, (d) O, (e) Al, (f) C. Trace amounts of Al are observed, likely contamination from the electrolyte or minor codeposition of Al.



Figure S2.8: Cyclic voltammograms of the Mg|Mg-In electrodes after reduction at different current densities, as seen in Fig. 4d in the main text. (a) 0.01, (b) 0.05, (c) 0.075, (d) 0.1 mA/cm².



Figure S2.9: Chronopotentiogram of the 10 hour reduction of bare Mg and the Mg|Mg-In electrode at low current density (0.05 mA/cm^2) .



Figure S2.10: Full EDS map of the Mg deposit on top of the Mg|Mg-In electrode after deposition at high current density (0.5 mA/cm^2) . (a) SEM image, (b) Mg, (c) In, (d) Cl, (e) O.



Figure S2.11: Chronopotentiogram of a 2.5 hour reduction of the Mg|Mg-In electrode at high current density (0.5 mA/cm^2) .



Figure S2.12: Full Bragg-Brentano XRD pattern of the Mg|Mg-In electrode (a) before and (b) after reduction at 0.025 mA/cm^2 .



Figure S2.13: Grazing incidence x-ray diffraction pattern of the pristine Mg|Mg-In electrode, with an ω of 0.3°.



Figure S2.14: Low-magnification cross-section SEM image of the Mg|Mg-In electrode after reduction at 0.025 mA/cm².



Figure S2.15: Full EDS map of the cross-section image of the Mg|Mg-In electrode after deposition at 0.025 mA/cm^2 . (a) SEM image, (b) Mg, (c) O, (d) C, (e) In.



Figure S2.16: Chronopotentiogram of a 100-hour reduction at 0.025 mA/cm² of the Mg|Mg-In electrode as the WE, and Mg foil as CE. The WE was analyzed with X-ray diffraction and cross-section SEM.



Figure S2.17: SEM image of the surface of the Mg|Mg-In electrode after a 100-hour reduction at 0.025 mA/cm².



Figure S2.18: (a) SEM image and corresponding EDS maps showing (b) In, (c) O, and (d) Mg of the Mg|Mg-In electrode after oxidation at 0.05 mA/cm^2 for 30 minutes. Both In and Mg remain homogeneous across the surface of the electrode suggesting that the Mg-In alloy remains intact following oxidation.

Chapter 3

LI-INTERCALATION ELECTRODE LITIS₂ AS A COUNTER ANODE IN REDUCTIVE ORGANIC ELECTROSYNTHESIS

3.1 Abstract

The application of a Li-intercalation electrode LiTiS_2 as a counter anode in reductive electrolysis is reported. The electrode features decreased passivation, eliminates competitive metal reduction, and reduces deleterious chemical reactivity with alkyl bromide substrates compared to traditional metal sacrificial anodes like Zn and Mg.

3.2 Introduction

Electrochemistry in organic synthesis enables unique reactivity compared to thermochemical redox reactions by introducing different site selectivity and/or allowing modulation between one- versus two-electron pathways.^{86,87} In addition, the redox strength of the electron can be tuned via the electrode potential unlike chemical redox agents, resulting in improved selectivity.

Generally, electrochemical organic syntheses focus on half-reactions in which the desired transformation is either an oxidation or a reduction. In reductive electrolyses, the desired reduction reaction occurs at the working electrode (WE) while the counter electrode (CE) provides those electrons by oxidizing the electrode material itself or a species in solution. The most commonly used CE used for reductive synthesis is a sacrificial metal anode at which the bulk metal is oxidized to its cationic form, which often dissolves into solution. Sacrificial metal anodes are useful because of their ease of preparation and low relative cost.

However, a sacrificial metal anode can interfere with the desired reactivity at the WE, adding additional variables that must be optimized.⁸⁸ The performance of sacrificial anodes is dependent on the electrolyte formulation. In certain electrolytes, the sacrificial anode forms a passivation layer through a reaction with the electrolyte causing a significant increase in the oxidation overpotential.^{23,32,89} High overpotentials cause a decrease in the energy efficiency of the electrolysis as the cell voltage increases. In extreme cases, especially upon scale-up, the overpotential can increase enough to reach the compliance limit of potentiostats, thus preventing reaction completion.⁹⁰

Metal sacrificial anodes can also damagingly react with species in solution. Many commonly used metal anodes such as Mg and Zn are strong reducing agents that are frequently used in chemical syntheses, and can chemically reduce substrates or products in solution.^{91,92} The side reactivity can lead to a decrease in selectivity or desired product formation.^{93–97}

While many commonly used sacrificial metal anodes (*e.g.* Mg, Al, Zn) have negative reduction potentials, cross-plating of the metal cation generated from the sacrificial anode at the WE is still readily observed, resulting in decreased yield of the desired transformation.^{98,99} One way to address the issue of metal cross-plating is by using a metal with an even more negative reduction potential, such as Li (-3.0 V vs. SHE compared to -2.4 V for Mg and -0.76 V for Zn),⁷² which makes it thermodynamically more difficult to reduce the resulting cation. However, the more negative the reduction potential of a metal is, the more chemically reducing it is. As such, Li metal reacts with many solvents commonly used such as tetrahydrofuran (THF),¹⁰⁰ as well as many substrates.

Li-intercalation electrodes can serve as an alternative to metal anodes for sacrificial CEs in reductive electrosyntheses. Li-intercalation electrodes are inorganic materials composed of Li⁺, redox-active transition metals, and anion. Upon oxidation, electrons are extracted essentially from the *d* states of the transition metal and Li⁺ is deintercalated and solvated in the electrolyte causing minimal changes to the crystal lattice.¹⁰¹ Li⁺ is thermodynamically much more difficult to reduce than Mg^{2+} or Zn^{2+} , thus suppressing issues associated with cross-plating. In addition, Li-intercalation electrodes have a much milder reduction potential than Li, thus preventing the chemical reactivity with substrates and solvent. The milder reduction potential also decreases the formation of passivation layers as a result of reactivity with trace impurities and solvent. Finally, Li⁺ is highly soluble in organic solvents compared to most other metal cations, which minimizes salt precipitation on the CE surface and passivation.

In this work, we investigate LiTiS_2 as a model material to interrogate intercalationbased counter anodes. LiTiS_2 is the earliest example of electrochemical Li intercalation. ^{101,102} The crystal structure of LiTiS_2 consists of layers of edge-sharing TiS_6 octahedra with Li⁺ occupying octahedral sites between the TiS_2 layers. The intercalation of Li⁺ into TiS_2 is a reversible process, with no phase change of the TiS_2 structure observed. ¹⁰¹ In addition, TiS_2 is a semi-metal with a high electronic conductivity compared to other commonly used oxide-based cathode materials, which increases the limiting current density of LiTiS_2 . The average redox potential of LiTiS_2 is approx. 2.3 V vs. Li/Li^+ , or -0.7 V vs. SHE, significantly higher than Li, Mg, or Al metal.

3.3 Results and discussion

The electrochemical behavior of LiTiS_2 is well-documented in common battery electrolytes, which are typically LiPF_6 dissolved in carbonates. LiTiS_2 typically undergoes a single-phase electrooxidation that is identified by a sloping curve in the constant current oxidation.¹⁰² However, organic electrosynthetic conditions require electrolyte conditions that can vary significantly, resulting in different interfacial chemistries. In addition, the cell geometry differs significantly from battery applications to electrolysis setups. As such, we examine the electrosynthesis:⁸⁷ tetrabutylammonium hexafluorophosphate (TBAPF₆),⁹⁹ perchlorate (TBAClO₄),⁹⁰ and bis(trifluoromethane) sulfonimide (TBATFSI) salts with THF,⁹⁰ acetonitrile (MeCN), and *N*,*N*-dimethylformamide (DMF)^{98,99} as solvents. The constant current oxidation of LiTiS₂ in the electrolytes is shown in Figure 3.1.



Figure 3.1: The potential traces from constant current oxidation of LiTiS_2 electrodes in (a) THF, (b) MeCN, and (c) DMF with 0.5 M solutions of various supporting electrolytes commonly used in organic electrosynthesis. A $\text{Li}_{0.5}\text{FePO}_4$ reference and a carbon cloth capacitive CEs are used with a current density of 56.3 mA/g (C/4). The maximum theoretical capacity of LiTiS_2 assuming complete delithiation is 225 mAh/g (8.4 mF/g).

Under constant current electrolysis, the LiTiS_2 oxidation proceeds as expected with a single sloping region in most of the electrolytes we examine. A small hump near 10–20% capacity is observed in the beginning of the oxidation that we attribute to

the oxidation of some impurities in the electrolyte. Interestingly, the initial oxidation is not seen when using $LiPF_6$ in a mixture of carbonates (LP100) (Figure S3.6) or LiOTf (Figure S3.13), suggesting that the impurity could be inherent to the TBA⁺. For TBAClO_4 in both THF and MeCN, the potential of the sloping oxidation is 500 mV higher than other electrolyte salts in the same solvent. In addition, erratic jumps in potential are observed throughout oxidation with TBAClO₄ in THF, which suggests incompatibilities with LiTiS₂ in TBAClO₄/THF. In addition, a general trend is observed with the solvent and anion effects on LiTiS₂ oxidation. The highest capacity is observed in MeCN, followed by THF and then DMF. Among anions, TFSI⁻ supports the most capacity, followed by PF_6^- and ClO_4^- . However, in DMF, ClO_4^- supports a higher capacity than PF_6^- . The accessible capacity behavior with solvent and anion effects can loosely be explained by ionic conductivity; TBATFSI in THF has the highest ionic conductivity due to the high dissociation of TBATFSI compared to TBAPF₆ and TBAClO₄, resulting in the higher overpotentials for the sloping region with TBACIO₄.¹⁰³ The poor capacity in DMF is hypothesized to be the result of chemical instability of LiTiS₂ in DMF, likely due to the tendency of DMF to exfoliate layered materials such as LiTiS₂.^{104,105} MeCN exhibits higher capacities compared to THF due to the higher dielectric constant for MeCN. 106 As such, at a given cutoff voltage, the accessible capacity is higher with electrolytes with higher conductivity. Nevertheless, in all electrolytes examined, the electrochemical oxidation of $LiTiS_2$ is stable albeit at differing capacities, meaning $LiTiS_2$ can be utilized as a potential counter anode in a wide breadth of electrolytes.

To evaluate the utility of a LiTiS₂ CE compared to a CE known to passivate, we study the electrochemical reduction of benzhydryl bromide (Ph₂MeBr) in TBAPF₆ as a model system with either a LiTiS₂ or Mg CE. Upon reduction, Ph₂MeBr will dehalogenate to either form the hydrogenated or the homocoupled product.¹⁰⁷ The potential during electrolysis of Ph₂MeBr in a TBAPF₆ in THF electrolyte at both the WE (E_{WE}) and the CE (E_{CE}) are shown in Figure 3.2a and b, respectively. We observe that when using a Mg CE, E_{WE} stays around -1.5 V vs. Li_{0.5}FePO₄ before the cell fails. However, E_{CE} polarizes to 10 V vs. Li_{0.5}FePO₄ within a minute, stopping the electrolysis as the potentiostat compliance limit is reached. Thus, the reaction is halted due to cell voltage rise that is driven by the passivation of the Mg anode. Due to the premature cell failure, no yield of the reduced products of Ph₂MeBr is observed. In contrast, when using LiTiS₂ as the CE, E_{WE} reaches a plateau of -3.7 V vs. Li_{0.5}FePO₄ and the E_{CE} stays below 1.5 V vs. Li_{0.5}FePO₄ for the course of the entire electrolysis. The reaction proceeds to completion, resulting in a 76% yield



Figure 3.2: The potential at the (a) WE and (b) CE during galvanostatic reduction of Ph_2MeBr using a graphite WE and either a Mg or $LiTiS_2$ CE in 0.25 M TBAPF₆ in THF at a current density of -1 mA/cm². When using Mg as a CE, the CE potential polarizes within minutes, leading to cell failure. On the other hand, $LiTiS_2$ CE maintains a stable anodic profile through electrolysis and the reaction proceeds to completion (2 e⁻ supplied per Ph₂MeBr).

for the dehalogenated products of Ph_2MeBr (Table 3.1). The different electrolytic behaviors indicate that while $LiTiS_2$ oxidation is facile and low overpotential in $TBAPF_6$ and THF, Mg oxidation is unable to occur due to passivation, enabling a wider scope of electrolyte compositions for reaction screening.



Figure 3.3: Nyquist plots of Mg|C and LiTiS₂|C cells with (a) 0.25 M TBAPF₆/THF electrolyte and (b) with added Ph₂MeBr. The equivalent circuits used to fit the Nyquist plots are shown in the ESI (Figure S3.14). The inset shows the high frequency features in (a). EIS is measured with a sinus amplitude of 50 mV from 1 MHz to 100 mHz. A much larger semicircle indicating a higher interfacial impedance is observed for Mg compared to LiTiS₂.

Substrate	CE	Electrolyte	Conv.	Yield	Charged
			(%)	(%)	passed (e ⁻
					per mol of
					substrate)
Ph ₂ MeBr	Mg	TBAPF ₆ /THF	0	0	<0.01
Ph ₂ MeBr	LiTiS ₂	TBAPF ₆ /THF	100	76	2
Ph ₂ MeBr	Zn	TBATFSI/DME	100	59 ± 3	2
Ph ₂ MeBr	LiTiS ₂	TBATFSI/DME	100	78 ± 9	2
PhOBuBr	Mg	TBATFSI/THF	43	24	_
PhOBuBr	LiTiS ₂	TBATFSI/THF	0	0	_

Table 3.1: Conversion and yield of reductive electrolyses of alkyl bromides with metal sacrificial anodes and LiTiS_2 in different electrolyte conditions

To further investigate Mg passivation in TBAPF₆ electrolytes, we use electrochemical impedance spectroscopy (EIS) to measure the impedance of Mg and LiTiS₂ electrodes in the electrolyte. The EIS Nyquist plots of Mg and LiTiS₂ WEs with graphite CEs in the neat TBAPF₆/THF electrolyte are shown in Figure 3.3a. The Mg electrode EIS exhibits a high frequency semicircle with a charge transfer resistance (R_{ct}) of 925 Ω , and a large low frequency tail (660 k Ω). The LiTiS₂ meanwhile exhibits a high frequency semicircle of 567 Ω and a small capacitive tail (1.6 mF). The comparitively large impedance of the Mg electrode suggests the high impedance passivation layer present on Mg electrodes in TBAPF₆ in THF, whereas no passivation is observed with LiTiS₂.

The EIS behavior of Mg and LiTiS₂ WEs upon the addition of the alkyl bromide is shown in Figure 3.3b. The Mg electrode high frequency semicircle remains mostly unchanged with a R_{ct} of 870 Ω , but two more semicircles appear with R_{ct} of 3400 and 3000 Ω , suggesting a change in the interface, likely due to Grignard-type reactivity with the alkyl bromide. On the other hand, the LiTiS₂ EIS spectrum changes very little in the presence of the alkyl bromide, with the same semicircle (677 Ω) and a capacitive tail (12 mF). The EIS spectrum of the LiTiS₂ WE is also measured after electrolysis, to observe changes in the interfacial impedance of the electrode. After electrolysis, the resistance of the semicircle decreases (315 Ω), as does the capacitance of the capacitive tail (5 mF).

To examine the chemical reactivity of LiTiS_2 , we expose LiTiS_2 and Mg to electrolyte solutions containing 4-bromobutoxybenzene (PhOBuBr). After a 5 hour exposure to LiTiS_2 , 100% of the alkyl bromide substrate is recovered with no conversion (Table 3.1). In contrast, PhOBuBr exposed to Mg metal results in 24% yield of the

dehalogenated product with a 43% overall conversion due to a chemical reduction of the alkyl bromide by Mg metal. The other products are unaccounted for via nuclear magnetic resonance spectroscopy (NMR) suggesting that additional side reactions yield insoluble products that cannot be identified by NMR.



Figure 3.4: The potential at the (a) WE and (b) CE during galvnostatic reduction of Ph_2MeBr with a graphite WE and either Zn or $LiTiS_2$ as the CE. The electrolysis is done with a 0.25 M TBATFSI in THF electrolyte at a current density of -1 mA/cm² until 2 e⁻ are supplied per Ph_2MeBr . When using Zn as a CE, the WE potential is 500 mV higher and increases to over 2 V higher compared to the graphite WE with a LiTiS₂ CE. The cell with a Zn CE has a more unstable WE potential, suggesting Zn cross-plating.

One potential method to avoid chemical reactivity of Mg is to use a milder sacrificial anode such as Zn metal. However, a milder sacrificial anode by definition has a more positive reduction potential making it easier to reduce at the WE thereby worsening the cross-plating issue. Figure 3.4a and b shows the potential at the WE and CE, respectively, during reduction of Ph₂MeBr in 1,2-dimethoxyethane (DME) with a TBATFSI supporting electrolyte. DME is chosen as the solvent to enable Zn oxidation, which does not occur readily in THF (Figure S3.12). One cell is run with a Zn sacrificial anode and a second cell with a LiTiS₂ anode. In the cell with a Zn anode, the graphite WE potential proceeds to a pseudo-plateau at -2.6 V vs. $\text{Li}_{0.5}\text{FePO}_4$ — a significantly higher potential is unstable with peaks and blips in the voltage curve occasionally observed. The peaks can be attributed to an unstable surface of the graphite electrode. Near the end of the electrolysis, the reduction potential increases to an even higher potential of -1.5 V vs. $\text{Li}_{0.5}\text{FePO}_4$. We hypothesize that the higher and unstable WE potential with a Zn CE is a result

of Zn cross-plating. Upon completion, $59 \pm 3\%$ yield of the reduced products are observed by NMR. The Zn CE potential is shown in Figure 3.4b, and the oxidation potential remains stable at -0.4 V vs. $\text{Li}_{0.5}\text{FePO}_4$ throughout electrolysis.

However, when a LiTiS₂ CE is used instead, the graphite WE potential in Figure 3.4a results in a plateau at -3.4 V vs. $Li_{0.5}FePO_4$, in good agreement with the Ph₂MeBr reduction observed in Figure 3.2a. In addition, the potential curve is very stable unlike the graphite potential when using a Zn anode, suggesting a stable graphite surface. An increased yield and Faradaic efficiency in the reduced products were observed (78 ± 9%), which suggests that the competitive reduction of the metal cation is decreased in LiTiS₂. Competitive Zn reduction has been previously shown in literature to drastically lower the yield of reductive transformations.^{98,99}



Figure 3.5: (a) Photograph of the graphite electrode after electrolysis of Ph_2MeBr using a (a) LiTiS₂ CE and a (b) Zn CE. SEM image of the graphite electrode after electrolysis using (c) LiTiS₂ CE and (d) Zn CE. All electrolyses were done at -1 mA/cm² using a 0.25 M TBATFSI in DME electrolyte.

To determine if cross-plating is the culprit, the surface of the graphite electrodes after the electrolysis are imaged. In Figures 3.5a and b, a photograph of the graphite surface is shown after reduction of Ph_2MeBr using either a LiTiS₂ or Zn CE, respectively. When a LiTiS₂ CE is used, the surface is relatively clean with some salt crusts forming on the surface of the graphite. However, when using a Zn CE, clear heterogeneous gray deposits form on the graphite electrode, as well as shiny metallic deposits consistent with Zn deposition. In Figures 3.5c and d, the scanning electron microscopy (SEM) images of the same graphite electrodes are shown. The graphite electrode used with the LiTiS₂ CE shows a roughened surface compared to

the pristine graphite electrode (see Figure S3.1 for a pristine graphite electrode for reference). The surface roughening is likely due to residual electrolyte precipitates as the surface visibly cleans up upon washing with acetone, supported by energy dispersive X-ray spectroscopy (EDS) which indicates significant presence of S and F from the TFSI⁻ anion (Figure S3.3). However, the graphite electrode used against the Zn CE shows different, heterogeneous deposits and the EDS map shows the heterogeneous constructs are Zn (Figure S3.2). The EDS detector is unable to detect characteristic Li X-rays, and as such EDS maps cannot determine Li crossplating. However, based on the differences in the electrode surface morphology after electrolysis as well as the difference in yield, we conclude that LiTiS₂ reduces competitive metal reduction.

3.4 Conclusion

In conclusion, Li-intercalation electrodes are useful sacrificial anodes for reductive electrosyntheses and we have demonstrated LiTiS_2 as a model electrode. Compared to conventional sacrificial anodes such as Mg and Zn, LiTiS_2 shows reduced passivation, reduced chemical reactivity with substrate, and limited cross-plating issues. As such, higher yield of the desired transformation is observed. Li-intercalation sacrificial anodes will be a useful tool for synthetic organic electrochemists when discovering new reactivity, serving as a relatively inert sacrificial anode option that reduces the effects of the CE on desired reactivity.

3.5 Experimental

General considerations All manipulations were performed in a N₂-filled glovebox (MBraun, <1 ppm H₂O and O₂) unless otherwise stated. Tetrahydrofuran (THF, Fisher Scientific), acetonitrile (MeCN, Fisher Scientific), and 1,2-dimethoxyethane (DME, Honeywell) were dried on a solvent purification system then stored over 4 Å sieves before use. Anhydrous *N*,*N*-dimethylformamide (DMF, Sure-Seal, Sigma Aldrich) was stored in a glove box before use. Ti powder (Beantown Chemical, 99.9%), sulfur (Acros Organics, 99.5%), *n*-butyllithium (*n*-BuLi, Sigma Aldrich, 1.6 M in hexanes), tetrabutylammonium bis(trifluoromethanesulfonimide) (TBATFSI, Supelco, 99%), tetrabutylammonium perchlorate (TBAClO₄, Supelco, 99%), 4-bromobutoxybenzene (PhOBuBr, Ambeed, 97%), benzhydryl bromide (Ph₂MeBr, TCI America, 97%) and lithium triflate (LiOTf, Sigma Aldrich, 99.99%), were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 99%, Sigma Aldrich) was recrystallized in ethyl acetate before use. Magnesium foil (99.9%,

MTI Corporation, 0.1 mm thick) and Zn foil (Sigma Aldrich, 99.9%, 0.25 mm thick) were brought inside the glovebox and polished with 320 then 1500 grit silicon carbide sanding paper (3M).

Synthesis of TiS₂ Ti and S₈ powder were combined in a 1:2.2 molar ratio in a mortar and pestle, then pressed into a pellet and sealed under reduced pressures in a quartz ampoule. The pellet was then heated at 2 °C per minute to 650 °C and held for 24 hours, then quickly cooled in room temperature water, resulting in a dark olive-green pellet that was ground into a powder before use.

Lithiation of TiS₂ to LiTiS₂ The lithiation of TiS₂ was adapted from literature.¹⁰⁸ The TiS₂ powder was added to a reaction vessel with 0.2 M *n*-BuLi in hexanes added slowly, with 1.5 equivalents of *n*-BuLi, and allowed to stir for 1 week. The resulting black powder was then filtered through a glass frit and washed with 20 mL of hexanes before drying under reduced pressures.

Electrochemical testing All electrochemical tests were performed in a four-neck glass heartcell with a Li BMC large foil holder (Gamry) for the sacrificial anode, with 2 mL of electrolyte. All electrochemical measurements were made on the VMP3 potentiostat (Bio-Logic). The LiTiS₂ powder, Super P carbon (Thermo Scientific, 99%), and poly-tetrafluoroethylene (PTFE, Sigma Aldrich) were mixed in a 53:27:20 ratio by weight in a mortar and pestle and pressed into a 10 mm pellet under 6 tons of force for 5 minutes in a hydraulic press. The graphite plate electrode (IKA) was cleaned with acetone and then polished with 320 grit silicon carbide sand paper. The metal foils were polished with 320 then 1500 grit silicon carbide sand paper in a glove box before use. The carbon cloth electrode (Fuel Cell Store) was cleaned with ethanol then dried in a vacuum oven before use. The $Li_{0.5}FePO_4$ (MTI) reference electrode was prepared according to literature.¹⁰⁹ The electrolyte was prepared by dissolving the appropriate electrolyte salt in the desired solvent, and 0.1 mmol of the alkyl bromide substrate where applicable. EIS experiments were performed at frequencies of 1 MHz to 100 mHz with a sinus amplitude of 50 mV, using a Li_{0.5}FePO₄ reference electrode and a graphite CE.

Sample characterizations All characterizations of *ex-situ* electrodes were completed after rinsing with 10 mL of acetone and air drying. SEM images were taken with a ZEISS 1150 variable pressure field emission scanning electron microscope with a 15 kV accelerating voltage and an in-lens secondary electron detector. Energy dispersive X-ray spectroscopy (EDS) data were collected using an Oxford X-Max Silicon Drift Detectors X-ray energy dispersive spectrometer with a 15 kV

accelerating voltage. Samples were briefly exposed to air during transfer into the instrument.

XRD patterns of the LiTiS₂ powder were collected using the Rigaku SmartLab diffractometer equipped with a HyPix-3000 detector and a Cu K α X-ray source with a 20 kV accelerating voltage, using Kapton tape to keep the sample air-free.

NMR spectra were collected on a Varian 400 MHz spectrometer at room temperature. Chemical shifts for ¹H NMR are reported in parts per million downfield from tetramethylsilane and are referenced to the solvent residual NMR solvent (CDCl₃ at 7.26 ppm, Cambridge Isotope Laboratories, 99.96%). The crude electrolysis mixtures were worked up by concentrating the mixture under reduced pressures then eluting through a silica plug using diethyl ether as the eluent. NMR quantification was performed using 1,3,5-trimethoxybenzene (Sigma Aldrich, 99%) as internal standard.

3.6 Funding acknowledgement

This work was supported by the NSF Center for Synthetic Organic Electrochemistry, CHE-2002158. SEM and EDS data were collected at the GPS Division Analytical Facility of the California Institute of Technology. The NMR spectra were collected at the California Institute of Technology liquid NMR facility, supported by the NIH RR027690 grant. X-ray diffraction data were collected at the X-ray Crystallography Facility in the Beckman Institute of the California Institute of Technology.

3.7 Supplemental information

Table S3.1: Yield distribution between Ph_2CH_2 and the dimer $(Ph_2CH)_2$ of reductive electrolyses of alkyl bromides with metal sacrificial anodes and $LiTiS_2$ in different electrolyte conditions

Substrate	CE	Electrolyte	Yield of	Yield of
			Ph_2CH_2	$(Ph_2CH)_2$
			(%)	(%)
Ph ₂ MeBr	Mg	TBAPF ₆ /THF	0	0
Ph_2MeBr	LiTiS ₂	TBAPF ₆ /THF	26	50
Ph ₂ MeBr	Zn	TBATFSI/DME	12 ±	47 ± 3
_			0.03	
Ph ₂ MeBr	LiTiS ₂	TBATFSI/DME	16 ± 4	62 ± 10



Figure S3.1: SEM image of the graphite electrode surface before any electrolysis



Figure S3.2: EDS map of the graphite electrode after electrolysis of benzhydryl bromide in TBATFSI/DME using a Zn CE, (a) Zn, (b) O, (c) S, (d) F, (e) C, (f) Br. (g) the EDS spectrum.



Figure S3.3: EDS map of the graphite electrode after electrolysis of benzhydryl bromide in TBATFSI/DME using a LiTiS₂ CE, (a) C, (b) O, (c) F, (d) S, (e) Br. (f) the EDS spectrum.

Table S3.2: The calculated fit values of the equivalent circuits for the Nyquist plots of the EIS spectra of Mg and LiTiS_2 in $\text{TBAPF}_6/\text{THF}$ electrolyte

Sample	L1	R1	Q1 (F)	R2	Q2 (F)	R3	Q3 (F)
	(H)	(Ω)		(Ω)		(Ω)	
Mg w/o sub-	_	-	-	831	4.7×10^{-10}	663000	5.0×10^{-6}
strate							
LiTiS ₂ w/o sub-	-	-	-	566	7.8×10^{-10}	-	0.0087
strate							
Mg with sub-	-	3370	2.8×10^{-6}	2960	4.9×10^{-5}	868	4.9×10^{-10}
strate							
LiTiS ₂ with sub-	-	-	-	677	5.7×10^{-10}	-	0.013
strate							
LiTiS ₂ with	-	-	-	315	0.88×10^{-9}	_	0.0053
substrate post-							
oxidation							



Figure S3.4: X-ray diffraction pattern of TiS_2 as-synthesized. The pattern was fit with the March-Dollase ratio for the 001 reflection being allowed to deviate to account for the preferential orientation of the layered TiS_2 . The background fit was subtracted from the data and the fit.



Figure S3.5: X-ray diffraction pattern of LiTiS_2 as-synthesized. The pattern was fit with the March-Dollase ratio for the 001 reflection being allowed to deviate to account for the preferential orientation of the layered LiTiS_2 . The background fit was subtracted from the data and the fit.



Figure S3.6: The chronopotentiogram of LiTiS_2 in 1 M LiPF_6 in a 1:1:3 ratio by volume mixture of ethylene carbonate, propyelen carbonate, and dimethyl carbonate with a Li CE in a two-electrode configuration. A current density of 225.2 mA/g (1C) was applied.



Figure S3.7: Crude ¹H NMR spectrum of the benzhydryl bromide electrolysis using LiTiS₂ CE in TBATFSI/DME electrolyte, with 1,3,5-trimethoxybenzene internal standard in CDCl_3 .



Figure S3.8: Crude ¹H NMR spectrum of the benzhydryl bromide electrolysis using Zn CE in TBATFSI/DME electrolyte, with 1,3,5-trimethoxybenzene internal standard in CDCl_3 .



Figure S3.9: Crude ¹H NMR spectrum after soaking LiTiS₂ in electrolyte containing TBATFSI/THF and PhOBuBr for 5 hours, with 1,3,5-trimethoxybenzene internal standard in CDCl_3 .



Figure S3.10: Crude ¹H NMR spectrum after soaking Mg in electrolyte containing TBATFSI/THF and PhOBuBr for 5 hours, with 1,3,5-trimethoxybenzene internal standard in CDCl₃.



Figure S3.11: Crude ¹H NMR spectrum of the benzhydryl bromide electrolysis using LiTiS₂ CE in TBAPF₆/THF electrolyte, with 1,3,5-trimethoxybenzene internal standard in CDCl₃.



Figure S3.12: Electrode potential at the (a) WE, (b) CE of the reduction of Ph_2MeBr in 0.25 M TBATFSI/THF electrolyte using Zn anode at 1 mA/cm².



Figure S3.13: Chronopotentiogram of LiTiS_2 oxidation in 0.5 M LiOTf/DMF electrolyte, with a carbon cloth CE at a current density of 56.3 mA/g (C/4). The maximum theoretical capacity is 225 mAh/g (8.4 mF/g).



Figure S3.14: The equivalent circuits used in fitting the Nyquist plots of the EIS spectra of (a) Mg without Ph_2MeBr substrate, (b) $LiTiS_2$ without substrate, (c) Mg with substrate, (d) $LiTiS_2$ with substrate, (e) $LiTiS_2$ with substrate after oxidation, in $TBAPF_6/THF$ electrolyte.

Chapter 4

EFFECT OF AG AND AU ON THE ELECTROCHEMICAL REDUCTION OF TERTIARY ALKYL HALIDES

4.1 Abstract

Electroreduction of alkyl halides to generate the carbanion is a powerful tool in organic synthesis to generate C–C bond-forming nucleophiles without a chemical reductant. However, tertiary alkyl halides are difficult to activate electrochemically because the intermediate tertiary carbon radical is difficult to reduce than the starting tertiary alkyl halide. The electrocatalytic ability of Ag and Au towards the reduction of alkyl halides has been well-studied in literature. However, the electrocatalytic effect and the mechanism for the terminal reduction to form the carbanion is not well-understood. Herein, we report a study of the electrochemical reduction of *tert*-butyl iodide on glassy carbon, Ag, and Au. The transfer coefficient α is estimated for each electrode using cyclic voltammetry which show that Au>Ag>glassy carbon in terms of catalytic effect. Bulk electrolysis of a tertiary alkyl iodide confirms the catalytic effect trend observed via α , however the specific catalytic effects on the initial reduction versus the desired terminal reduction cannot be determined. Based on additional voltammetry experiments as well as previous literature, we propose a possible mechanism for the electrocatalysis of *tert*-butyl iodide on Ag and Au.

4.2 Introduction

Alkyl halides are a very useful class of compounds in organic synthesis, as a very versatile electrophile. However, alkyl halides can also be reduced to act as a nucle-ophile, such as a Grignard reagent, ¹¹⁰ lithiated carbanion, ^{111,112} or through transition metal catalysis. ¹¹³ Alkyl nucleophiles generated this way can then be used as a useful method to form C–C bonds. Traditionally, alkyl nucleophiles are generated using a chemical reductant such as Mg⁹¹ and Li. ^{111,112} Recently, electrochemically generated alkyl nucleophiles from alkyl halides have been reported. ^{90,114,115} Electrochemical reduction of alkyl halides can simplify the desired coupling reaction and improve selectivity by eliminating the chemical reductant from the reaction pot, and offering a degree of control over the selective reduction of the desired alkyl halide over other species in solution.

The electrochemical reduction of alkyl halides has been extensively studied in the

literature for the mechanism of reduction and the kinetics involved in the electron transfer.¹¹⁶ The reduction occurs through two one-electron reductions, first a concerted one-electron transfer and the C–X bond cleavage resulting in the halide and an alkyl radical.¹¹⁷ The subsequent one-electron reduction of the radical to the carbanion. However, in most alkyl halides, the resulting radical is thermodynamically easier to reduce than the starting alkyl halide, thus in voltammetry the reduction is observed as a two-electron reduction.

In tertiary alkyl halides however, the two distinct reductions can be resolved.¹¹⁸ The tertiary alkyl radical is more stable than the primary or secondary variant due to stabilization from the neighboring carbons. On the other hand, the tertiary alkyl carbanion is less stable than the secondary or the primary carbanion, because alkyl groups are electron-donating. As a result, the first electron transfer becomes thermodynamically more favorable, while the second electron transfer becomes less so. As a result, by cyclic voltammetry, the two reduction waves can be resolved.¹¹⁷ As a consequence of the separation of the two electron transfer events, it is more difficult to electrochemically generate the nucleophilic carbanion from tertiary alkyl halides, which has been reported to have a limiting effect on the available substrate scope.⁹⁰

The mechanism of the alkyl halide reduction can vary massively based on the electrode material. On glassy carbon (GC), the reduction proceeds as relatively simple two reduction peaks.¹¹⁷ On Hg however, a series of Hg–R and Hg–X species are formed, resulting in a complicated voltammogram.^{119,120} On Ag, it is also hypothesized that the alkyl halide adsorbs onto the surface and forms Ag–X and Ag–R species on the surface.¹²¹ On Au, not only does the halide also adsorb onto the surface, but primary alkyl radicals are known to readily form self-assembled monolayers onto Au electrodes.¹²²

Andrieux *et al.* reported the cyclic voltammograms (CVs) of *tert*-butyl iodide (^tBuI) on GC and Au electrodes in *N*,*N*-dimethylformamide (DMF).¹¹⁷ On GC, two reduction waves are observed, the first reduction as a result of the radical formation, and the second reduction the subsequent carbanion formation. Interestingly, they reported that on Au the CV largely looks identical, with the peaks shifted about 100 mV more negative, which is unexpected given the reported behavior of alkyl halides on Au electrodes. Vieira and Peters reported the reduction of *tert*-butyl bromide on Hg electrodes in DMF, and observed the two separate reduction features for the two one-electron reductions.¹²⁰ In addition, halide-assisted oxidation of Hg was also

observed. Strawsine *et al.* reported the reduction of ^{*t*}BuI on Ag in DMF, observing two separate reduction features with a large separation of 1 V between them.¹⁰⁷

As such, different electrode materials can have an activating effect on the reduction of the tertiary alkyl radical to its carbanion, thus enabling more expansive substrate scope in the electrochemical generation of alkyl nucleophiles from alkyl halides. Herein, we report the investigation of the electrochemical reduction of tertiary alkyl halides on GC, Ag, and Au in tetrahydrofuran (THF). We observe significant differences in the CVs of the reduction of tertiary alkyl halides between GC, Ag, and Au, and suggest that Au is the best catalyst for the reduction of the tertiary alkyl radical, followed by Ag then GC. Constant current electrolysis product distribution also supports Au as the best-performing catalyst, with GC being the worst. The voltammetric experiments we perform suggest a complicated system involving surface reactivity, adsorption, and homogeneous reactions, and we propose a mechanism for each electrode material.

4.3 Results and discussion



Figure 4.1: CVs at 50 mV/s of 10 mM ^tBuI in THF with 0.2 M TBAPF₆, using (a) GC, (b) Ag, and (c) Au WEs.

The cyclic voltammogram (CV) of *tert*-butyl iodide (^tBuI) in 0.2 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in tetrahydrofuran (THF) using different working electrodes (WE) is shown in Figure 4.1. The potential window of -3.5 V vs. Fc/Fc⁺ is chosen due to electrolyte decomposition observed at more negative potentials. On glassy carbon (GC), a reduction peak A is observed at -2.7 V vs. Fc/Fc⁺, with no oxidation on the return wave, suggesting that the reduction is chemically irreversible. A second reduction at -3.3 V vs. Fc/Fc⁺ (B) also appears, also with

no oxidation on the return, and therefore also suggesting chemical irreversibility. In addition, the peak current of B is much lower compared to A, which suggests the product of A chemically decomposes, suggesting either an ECE or a EC' mechanism. The cyclic voltammogram in Figure 4.1a is in good agreement with similar experimental results observed by Andrieux *et al.*¹¹⁷ for the reduction of ^{*t*}BuI on GC. As such, we tentatively assign reduction A to be the concerted reduction and C–X bond cleavage of ^{*t*}BuI to the ^{*t*}Bu radical and I⁻, and reduction B the further reduction of the ^{*t*}Bu radical to its carbanion.

In Figure 4.1b, the CV of ^{*t*}BuI on Ag electrode is shown. On Ag, peak A appears at a much higher voltage of -1.9 V vs. Fc/Fc⁺, suggesting a strong activation of the initial reduction of ^{*t*}BuI. The catalyzing effect of Ag for the electrochemical reduction of alkyl halides has been documented extensively in literature. ^{121,123} An oxidation peak is not observed for peak A on the reverse scan, but a small oxidation that decreases rapidly is observed on the reverse scan at -1.8 V vs. Fc/Fc⁺. We attribute the oxidation to surface reactivity, likely the corrosion of Ag in the presence of I⁻. ¹²⁴ Peak B shifts 200 mV positively relative to the same peak on GC. The shift can be attributed to a catalysis of the carbanion formation by Ag. Compared to the CV on GC, the relative ratio of the peak currents of peak B and A is lower on Ag, due to the reactive nature of the ^{*t*}Bu radical ¹²⁵ and the larger *E* gap between A and B and thus longer *t*. As with GC, no oxidation is observed for peak B on the reverse sweep.

On Au, peak A appears at -1.7 V vs. Fc/Fc^+ , the most positive among the three electrodes examined, suggesting Au is the strongest catalyst for the initial reduction of ^{*t*}BuI. Au is also known to be a strong catalyst for the reduction of alkyl halides.¹²² Peak B appears at -3.3 V vs. Fc/Fc^+ , which is unexpectedly 200 mV negative of the same peak on Ag, despite peak A being shifted further positive compared to Ag on Au. Additionally, another peak is observed at -2.7 V vs. Fc/Fc^+ , which appears chemically reversible. This anomalous additional peak will be discussed further later.

The scan rate-dependence of CVs can be used to determine several important information about an electrochemical system, such as possible adsorption and the transfer coefficient α . The CVs of ^tBuI at different scan rates (ν) are shown in Figure 4.2a–c. On all electrodes, peak current density j_p grows more negative as a function of ν , as does peak potential E_p . In addition, no anodic peak is observed even at the fastest ν , which suggests that neither electron transfer undergoes an



Figure 4.2: CVs of 10 mM ^tBuI at different scan rates on (a) GC, (b) Ag, and (c) Au as working electrodes. Scan rates of 500, 400, 300, 200, 100, 70, 50, 30, and 10 mV/s are used. (d) Plot of ν versus j_p . (e) Plot of $\nu^{1/2}$ versus j_p . (f) Plot of $log(\nu)$ versus E_p . The slope of the linear fits of (f) are used to calculate α .

EC' mechanism. A significant shift negative in E_p with increasing ν indicates the electrochemical irreversibility of the reduction of ^tBuI, which is corroborated by previous reports.¹¹⁸ To determine whether the substrates are freely-diffusing or adsorbing, j_p is plotted against ν and $\nu^{1/2}$, as shown in Figures 4.2d and e, respectively. The plots clearly show that j_p is not linear with ν , whereas a linear trend is observed with $\nu^{1/2}$. However, we note that the linear fit of j_p against $\nu^{1/2}$ does not intercept at the origin as would be expected for an ideal electron transfer of freely-diffusing substrates, suggesting that other processes such as further surface or homogeneous reactions could be occurring. Nevertheless, the linear trend with $\nu^{1/2}$ suggests that the reduction features observed are not a result of pure monolayer adsorption.¹

This result is somewhat surprising due to the tendency for dissolved halide anions to adsorb onto Ag and Au.^{126,127} With regards to alkyl halides, Rondinini *et al.* concluded based on a systematic structure-property study of a broad scope of organic halides that both the first and second reduction steps go through an intermediate in which Ag…X interactions contribute.¹²¹ Simonet and Jouikov invoked initial adsorption and partial charge transfer from Au to the alkyl iodide, in addition to the adsorption of the carbon radical.¹²² As such, the result from Figure 4.2 that j_p does not trend linearly with v is contradictory, as CVs of adsorbing substrates generally show linear trends in j_p versus v. However, if the adsorption of the reactant to the electrode surface is relatively weak, j_p is known to be proportional to $v^{1/2}$ at low v, while being proportional to v at large v.^{1,107} As such, we hypothesize that on Ag and Au, adsorption may contribute to the reduction of ^{*t*}BuI.

To calculate the transfer coefficient α , E_p is plotted against log(v), as shown in Figure 4.2f. For a totally electrochemically irreversible system, E_p changes as a function of v, and is given by

$$E_p = E^{0'} - \frac{RT}{\alpha F} \left(0.780 + ln \frac{D_0^{1/2}}{k^0} + ln \left(\frac{\alpha F \nu}{RT} \right)^{1/2} \right)$$
(4.1)

assuming semi-infinite linear diffusion, which is accurate for the disk electrodes that are used for the above CVs.¹ Equation 4.1 can be rearranged as a function of v:

$$E_{p} = E^{0'} - \frac{RT}{\alpha F} \left(0.780 + ln \frac{D_{0}^{1/2}}{k^{0}} \right) - \frac{RT}{2log(e)\alpha F} log(\nu)$$
(4.2)

Thus, from the slope of the plot of E_p versus log(v), α can be calculated, shown in Table 4.1. Note however that Equation 4.1 is assuming a simple one-electron transfer with free diffusion of the substrate and no coupled reactions. As a result, the α calculated here are mere estimates, doubly so for the calculated α for B, as B is coupled to A as well as other homogeneous reactions. As such, the relative trends of the calculated α are more significant than the absolute values. The measured α suggests a clear trend of GC<Ag<Au in terms of catalytic effect for the reduction of ^tBuI. Importantly, the terminal reduction of the ^tBu radical to the carbanion is also catalyzed by Au and to a lesser extent Ag, corroborating literature invocations of carbon radical intermediate adsorption to Au and Ag electrodes.^{121,122}

Table 4.1: Measured transfer coefficient α for the reduction of ^{*t*}BuI A and B on GC, Au, and Ag electrodes

α	GC	Ag	Au
α_A	0.10	0.12	0.15
α_B	0.12	0.14	0.22

To investigate the effects of the catalysis in bulk electrolysis, we reduce a tertiary alkyl iodide with the three electrodes at a constant current of -2 mA/cm^2 and quantify the products using GC-MS. The reduction and subsequent protonation of ^{*t*}BuI results in isobutane, which is a gas at room temperature and requires a gas-tight electrolysis cell. As such, 2-iodo-2-methyl-4-phenyl butane is used as a proxy. The

electrolysis is performed in a divided cell with two equivalents of electrons per molecule of the alkyl iodide in the presence of diethyl malonate-d₂ in 50% excess as an acid to capture the final carbanion. The observed product distribution from the electrolysis is shown in Table 4.2. Three major products are observed by GC-MS, one corresponding to the dehalogenated alkane isoamyl benzene, and two isomers of the olefin product, 2-methyl-4-phenyl-1-butene and 2-methyl-4-phenyl-2-butene.

Minimal yield of total product is observed on a glassy carbon WE, but Ag and Au both lead to a significant increase in the overall yield of the reduced products, supporting the electrocatalytic ability of Ag and Au. In particular, the yield for the alkane product is observed for a glassy carbon WE at 1.8%, while a significant catalytic effect is observed for both Ag and Au, 23.6% and 31.8% respectively.

The alkane can be the result the protonation of the electrochemically-generated carbanion by unreacted starting material, the TBA⁺ cation, or trace water in the electrolyte. The alkane could also arise from H-atom abstraction by the intermediate tertiary carbon radical, or a bimolecular radical disproportionation resulting in one molecule of the alkane and one molecule of the olefin.¹²⁸ In addition to the radical disproportionation, the olefin could also be the result of the deprotonation and β elimination of the iodide starting material due to the lability of iodides. The two isomers of the olefin may arise as a result of the β -elimination at the methyl or the internal β position.

Interestingly, neither the alkane nor the olefins are deuterium-labelled despite the deuterated acid present, with the pK_a of diethyl malonate being 16.5 in dimethyl sulfoxide.¹²⁹ The lack of deuterium-labelled product suggests the presence of proton donors in solution that are more acidic than diethyl malonate. The unreacted starting material has β -protons to the iodide that are very acidic, due to the high stability of the I⁻ leaving group.

Table 4.2:	Product	distribution	of	the	electrolysis	of	2-iodo-2-methyl-4-
phenylbutane	with GC,	Ag, and Au					

Electrode	Alkane	Olefin 1	Olefin 2
	yield (%)	yield (%)	yield (%)
glassy carbon	1.8	7.6	6.9
Ag	23.6	13.1	33.1
Au	31.8	17.3	25.4

Based on the lack of deuteration and the multiple pathways of forming the observed products, conclusions about the specific catalytic effect of Ag and Au on the terminal reduction to the carbanion cannot be drawn. As such, a stronger acid that is more selective towards reactions with the carbanion, MeOD, is used as the deuterated acid (Table S4.12). However, no deuteration is observed. To determine the relative pK_a of the iodide, the tertiary iodide is reacted with sodium methoxide, the conjugate base of methanol (Table S4.10). Only the β -elimination products, olefins, are observed by GC-MS, suggesting that the pK_a of the iodide is lower than methanol. A stronger deuterium source in D_2O is used, but no deuteration and significant olefin products are observed (Table S4.11). As such, the electrolysis is performed with the bromide variant of the starting substrate, using MeOD as the deuterium source (Table S4.13). Yet still no deuteration is observed, with significant yields of the olefin observed.

Direct electrochemical $S_N 2$ using 3-phenoxypropyl bromide is attempted instead of deuteration, as $S_N 2$ reactions are selective towards the carbanion rather than the radical intermediate.⁹⁰ However, no coupled $S_N 2$ products are observed for both the iodide and bromide tertiary halide starting materials (Tables S4.14 and S4.15). As such, further optimization of the electrolysis system is required to drawn specific conclusions about the electrocatalysis of the first reduction versus the terminal reduction.

In diagnosing the electrolysis to optimize the experiment, the relative yields of the alkane product versus the olefin warrants a closer look. Both radical disproportionation and β -elimination via the carbanion of the starting material results in a 1:1 ratio of the alkane to the olefin. However, in all electrolyses, the yield of the olefin is higher, in many cases significantly so, than the alkane. As such, another reaction must be responsible for generating some of the olefin during the electrolysis. One possible hypothesis is the direct deprotonation of the halide starting material by the electrode to form metal hydrides in the case of Ag and Au to form H₂, thus generating an olefin molecule by itself.^{130,131} The use of different metal electrodes such as Ti, V, or Zn that are known to be poor metal hydride formers may lead to a suppression of the hypothetical direct deprotonation of the starting halide, thus leading to successful deuteration.¹³² Another possible approach may be in optimizing the electrolyte, such as the supporting electrolyte salt or the solvent, such as TBACIO₄ or acetonitrile.

To further elucidate the origin of the catalytic effect of Au and Ag and the reduction mechanism, a concentration series of CVs are collected. The concentrationdependent CVs of t BuI on Ag and Au are shown in Figure 4.3. Both peaks A and B are present at both low and high concentrations, which suggest neither are pure



Figure 4.3: CVs of ^{*t*}BuI on Ag electrodes at (a) 0.5 mM, (b) 10 mM, and (c) 50 mM substrate. CVs of ^{*t*}BuI on Au electrodes at (d) 0.5 mM, (e) 10 mM, and (f) 50 mM substrate. A scan rate of 50 mV/s and 0.2 M TBAPF₆ electrolyte in THF are used.

adsorption-mediated reductions. Interestingly, the anomalous peak on Au seems to nearly disappear into the baseline at 0.5 mM, and grow faster with concentration than A or B. On both Ag and Au, the peak current density increases with increasing concentration, as expected. However, the peak potential also shifts further negative, which is unexpected for conventional electrochemical systems. The peak shifting is observed for both peaks A and B, as well as the anomalous reduction peak on Au. At 50 mM ^{*t*}BuI, the peak shifting causes peak B to disappear out of the electrochemical window alltogether. In systems where the electrogenerated species undergoes a bimolecular dimerization, $E^0 - E_p$ increases as a function of reactant concentration due to the second-order dimerization.¹³³ Assuming that properties inherent to the electron transfer transition state do not change (such as k^0 , α , $E^{0'}$), the only other explanation for a shifting peak potential is a change in the diffusion coefficient *D* in simple diffusion-based electrochemical systems.

Thus, to test the hypotheses we collect a scan rate series of CVs at each concentration to estimate D using the equation for the peak current of a CV for an electrochemically irreversible electron transfer

$$i_p = \left(2.99 \times 10^5\right) \alpha^{1/2} A C^* D^{1/2} \nu^{1/2}$$
(4.3)

with units of A for i_p , cm² for A, mol/cm³ for C^* , cm²/s for D, and V/s for v.¹ The CVs are shown in Figure 4.4. Due to the complex homogeneous reactions occurring in the electrochemical system, such a simple equation cannot accurately model the



Figure 4.4: CV scan rate series of 0.5 mM t BuI on (a) Ag and (b) Au. CVs of 50 mM t BuI on (c) Ag and (d) Au. Scan rates of 500, 400, 300, 200, 100, 70, 50, 30, and 10 mV/s are used.

kinetics. Instead, the trends of D as a function of ^tBuI concentration is used to form hypotheses. Only peak A is used to determine D, as Equation 4.3 more accurately models peak A which is uncoupled to any previous electron transfer. Moreover, peak B is not captured by the CV at 50 mM ^tBuI within the electrochemical stability window of the electrolyte.

Table 4.3: Estimated D of ^tBuI at concentrations of 0.5 mM, 10 mM, and 50 mM on Ag and Au electrodes from a CV concentration series

Electrode	D at 0.5 mM	<i>D</i> at 10 mM	D at 50 mM
	(cm^2/s)	(cm^2/s)	(cm^2/s)
Ag	5.6×10^{-4}	7.8×10^{-6}	4.3×10^{-6}
Au	1.8×10^{-4}	1.1×10^{-5}	3.0×10^{-6}

The estimated D of ^tBuI at different concentrations on Ag and Au are shown in Table 4.3. Andrieux *et al.* estimated the diffusion coefficient of ^tBuI in DMF to be 0.95×10^{-6} using the Stokes-Einstein relation. ^{117,118} The estimated D decreases with concentration in a non-linear fashion. In addition, D varies significantly between Ag and Au. D increases by an order of magnitude as the concentration decreases from 10 mM to 0.5 mM. While the trend of increasing D with a decrease in substrate concentration may suggest aggregation, the magnitude of the increase appears largely unphysical. ¹³⁴ Furthermore, D is measured using chronopotentiometry and Sand's equation
$$\frac{i\tau^{1/2}}{C^*} = \frac{nFAD^{1/2}\pi^{1/2}}{2} \tag{4.4}$$

where τ is the Sand's time, or the time required to deplete the substrate at the electrode surface, and *n* is the number of electrons.¹³⁵ *D* calculated by Sand's equation reveals the opposite trend, where *D* increases as a function of substrate concentration (Table S4.8). The opposing trends measured from two different electrochemical methods suggest that the shift in E_p as a function of ^tBuI concentration is due to the dimerization of the intermediate ^tBu radical, rather than a change in *D* with concentration.



Figure 4.5: Proposed mechanism of the electrochemical reduction of ^{*t*}BuI on Au and Ag, as both ^{*t*}BuI and the ^{*t*}Bu radical adsorbs onto the metal electrode surface



Figure 4.6: Proposed mechanism of the electrochemical reduction of t BuI on GC in the absence of any adsorption

Based on the data collected herein and in literature, we propose a possible mechanism for the reduction of t BuI. The proposed mechanism on catalyzing metals Ag and

Au are shown in Scheme 4.5. On Ag and Au, the halide on the substrate adsorbs onto the metal surface and the M···X interaction activates ^{*t*}BuI, thus shifting the E^0 positive and α by changing the transition state. Au activates the halide more than Ag due to the larger *d*-orbitals of Au resulting in a stronger M···X interaction.

Upon reduction, the ^{*t*}Bu radical can adsorb onto Ag and Au surfaces as well.^{121,122} However, the steric bulk of the ^{*t*}Bu radical as well as the stability of a tertiary carbon radical results in a relatively significant population of the free radical. The adsorbed radical cannot undergo deleterious homogeneous reactions, thus improving the yield of the carbanion product in bulk electrolysis. In the absence of the adsorbing effects on GC however, the increased stability of ^{*t*}Bu does not occur on GC, as shown in Scheme 4.6.

In addition to the processes outlined here, there are more homogeneous and surface reactions that are not accounted for in the proposed mechanism, as suggested by the anomalous reduction in the CV on Au. The anomalous redox feature on Au is clearly related to ^{*t*}BuI as j_p grows with concentration of ^{*t*}BuI, which also disproves any reductive fouling of the Au surface. However, the redox feature does not form unstable products (*i.e.* ^{*t*}Bu radical or carbanion) due to the chemical reversibility of the feature. Direct addition of I₂ or TBAI did not result in the anomalous feature either (Figure S4.4).

In an organic bulk electrolysis, the activation of the initial C–X bond leads to a more facile generation of the ^{*t*}Bu radical on Au than Ag or GC. The electrogenerated ^{*t*}Bu radical binds to the Au or Ag surface and stabilizes, resulting in more available ^{*t*}Bu radical to be reduced to the carbanion. However, the inconclusive electrolysis result convolutes the catalytic effect of Ag and Au, whether the catalysis only occurs for the initial reduction to the radical intermediate, or if the terminal reduction is catalyzed to improve the kinetic issues and ultimately lead to benefits in organic transformations.

4.4 Conclusion

In conclusion, the effect of Ag and Au on the electroreduction of ^{*t*}BuI is demonstrated. On Ag and Au, ^{*t*}BuI adsorbs onto the electrode surface, which catalyzes the reduction to the ^{*t*}Bu radical, which then undergoes several homogeneous and surface reactions that improves the kinetics of the second reduction to generate the carbanion compared to GC. In voltammetry, the catalytic enhancement is observed via an increase in the estimated α of both reductions A and B corresponding to the

^tBu radical and carbanion formation respectively. The catalytic strength increases in the trend of GC<Ag<Au, with Au being a superior catalyst to Ag likely as a result of the larger orbitals. The catalytic enhancement is further observed in a constant current bulk electrolysis of a tertiary alkyl iodide 2-iodo-2-methyl-4-phenyl butane, however it cannot be determined whether the catalytic enhancement is selective towards the desired terminal reduction for carbanion generation. Therefore, while the cyclic voltammetry suggests that the slow terminal reduction is catalyzed by Ag and Au, the convoluted electrolysis means a conclusion cannot be reached and further optimization of the electrolysis is necessary before implementation to the organic system.

4.5 Experimental

General considerations All manipulations were performed in a N₂-filled glovebox (MBraun, <1 ppm H₂O and O₂) unless otherwise stated. Tetrahydrofuran (THF, Fisher Scientific) was dried on a solvent purification system then stored over 4 Å sieves before use. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 99%, Sigma Aldrich), isoamylbenzene (95%, Combi-Blocks), methanesulfonic acid (98%, Combi-Blocks), 2-methyl-4-phenyl-2-butanol (99%, Ambeed), 2-iodo-2-methylpropane (^tBuI, 95% Oakwood Chemical), diethyl malonate-*d*₂ (Oakwood Chemical, 98% deuteration), *n*-pentane (Fisher Scientific, 98%), diethyl ether (Et₂O, Fisher Scientific, 99%), sodium iodide (NaI, Sigma-Aldrich, 99.5%), lithium bromide (LiBr, Sigma-Aldrich, 99%), ferrocene (Fc, Sigma-Aldrich, 98%), and ferrocenium hexafluorophosphate (FcPF₆, Combi-Blocks, 95%) were used as received.

Pt|Fc/Fc⁺ reference electrode The Pt|Fc/Fc⁺ reference electrode was prepared according to literature.^{103,136} A fritted glass tube (Pine Research Instrumentation) was filled with an electrolyte of 0.1 M TBAPF₆, 4 mM Fc, and 4 mM FcPF₆ in THF. The top of the glass tube was sealed with a rubber septum and pierced with a Pt wire.

Electrochemical characterization Working electrodes were purchased from BASi as 3 mm diameter disks surrounded by PCTFE bodies, with the exception of Au electrodes for voltammetry, where a 1.6 mm diameter disk was used. All electrochemical measurements were made on the VMP3 potentiostat (Bio-Logic). The cell resistance was measured using electrochemical impedance spectroscopy, and 85% of the measured cell resistance was compensated via the EC-Lab software (Bio-Logic), and the remaining 15% was manually compensated for after the measurement. All

electrodes were polished using diamond paste of 9, 3, then 1 μ m particles, then electrochemically cleaned by performing a cyclic voltammetry between -3 and -1 V vs. Fc/Fc⁺ 5 times at 50 mV/s. Pt wires were cleaned using a H₂ flame before use. For experiments where successive measurements were collected (*i.e.* scan rate series, Sand's time chronopotentiometry measurements), a 5 min wait period took place in-between measurements to allow for sufficient time for the substrate to diffuse back to the surface.

Bulk electrolysis The bulk electrolysis was performed in a divided cell. In the working electrode compartment, an electrolyte solution containing 0.2 M TBAPF₆, 0.05 mmol alkyl halide substrate, and 0.075 mmol diethyl malonate- d_2 in THF was added, and the WE and the Pt|Fc/Fc⁺ reference electrode were inserted. In the counter electrode compartment of the divided cell, an electrolyte solution containing 0.2 M TBAPF₆ and 0.1 mmol Fc in THF was added, to which a Pt wire counter electrode was placed. The working electrode compartment was stirred vigorously. Upon completion of the electrolysis, the solution in the working electrode compartment and eluted through a silica plug. The eluent was reduced under reduced pressures to obtain the crude reaction mixture.

GC-MS analysis of the bulk electrolysis crude mixture The bulk electrolysis crude mixture was diluted with Et_2O to 10 mL before analysis. The products were quantified using a calibration made with an external standard of isoamylbenzene (0.168–0.744 mg/mL). GC-MS spectra were collected on a JEOL AccuTOF GC-Alpha (JMS-T2000GC) that was fitted with a LIFDI ionization source from Linden CMS. He was used as carrier gas for the electrolyses using diethyl malonate as deuterium source, and H_2 was used as carrier gas for every other spectra.

NMR characterization NMR spectra were collected on a Varian 400 MHz spectrometer at room temperature. Chemical shifts for ¹H NMR are reported in parts per million downfield from tetramethylsilane and are referenced to the solvent residual NMR solvent (CDCl₃ at 7.26 ppm, Cambridge Isotope Laboratories, 99.96%).

Synthesis of 2-iodo-2-methyl-4-phenyl butane The synthesis procedure was carried out according to literature. ^{137,138} In air, a round bottom flask was charged with acetonitrile (20 mL), NaI (1.5 g, 10 mmol, 2 eq.), 2-methyl-4-phenyl2-butanol (850 μ L, 5 mmol, 1 eq.), then cooled to 0 °C. To the solution methanesulfonic acid (650 μ L, 10 mmol, 2 eq.) was added dropwise then stirred and allowed to warm to room temperature over 3 hours. The reaction mixture was filtered with celite and concen-

trated under reduced pressures, then redissolved in *n*-pentane and passed through a silica plug with *n*-pentane. The eluent was concentrated under reduced pressures to yield a blood-red oil. Cu dust was added to the oil and kept in the dark before use to reduce decomposition of the iodide, after which the oil turned a pale yellow. The ¹H spectrum of the compound matched literature spectra.^{137,138}

¹H NMR (400 MHz, CDCl₃): *δ* 7.32-7.26 (m, 2H), 7.24-7.16 (m, 3H), 2.89-2.81 (m, 2H), 1.99 (s, 6H), 1.94-1.88 (m, 2H).

Synthesis of 2-bromo-2-methyl-4-phenyl butane The synthesis procedure was carried out according to literature.¹³⁹ In air, a round bottom flask was charged with a solution of LiBr (1.74 g, 20 mmol, 2 eq.) in concentrated HBr (10 mL) at 0 °C. To the mixture 2-methyl-4-phenyl2-butanol (1.7 mL, 10 mmol, 1 eq.) was added slowly while stirring, then allowed to warm to room temperature overnight. To the reaction mixture Et_2O was added (30 mL), then the layers were separated. The organic layer was washed with H_2O (20 mL), saturated NaHCO₃ (20 mL), brine (20 mL), then dried with MgSO₄, filtered and concentrated under reduced pressure then redissolved in *n*-pentane and eluted through a silica plug with *n*-pentane. The eluent was concentrated under reduced pressure, yielding a colorless oil. The ¹H spectrum of the compound matched literature spectra.¹³⁹

¹H NMR (400 MHz, CDCl₃): *δ* 7.7.32-7.27 (m, 2H), 7.24-7.17 (m, 3H), 2.89-2.82 (m, 2H), 2.12-2.06 (m, 2H), 1.83 (s, 6H).

4.6 Funding acknowledgement

This work was supported by the NSF Center for Synthetic Organic Electrochemistry, CHE-2002158. The NMR spectra were collected at the California Institute of Technology liquid NMR facility, supported by the NIH RR027690 grant.

4.7 Supplemental information

Concentration	Retention	Area (arb.
$(\mu L/mg)$	time (min)	units)
0.168	4.857	1275446.64
0.312	4.857	2646349.46
0.456	4.858	3842807.67
0.6	4.861	4946728.31
0.744	4.866	7298360.87

Table S4.1: Calibration curve of isoamyl benzene in Et₂O for GC-MS

Electrode	Compound	Retention	Area (arb.	Mass-to-
		time (min)	units)	charge ratio
				(m/z)
	Alkane	4.877	35790.85	148.2
glassy car-	Olefin 1	4.957	402393.68	146.1
bon				
	Olefin 2	5.104	346547.79	146.1
	Ferrocene	5.917	1670756.22	186.00
	Alkane	4.857	1405984.28	148.2
	Olefin 1	4.95	734082.33	146.1
Ag	Olefin 2	5.101	1975456.51	146.1
	Unknown	5.167	1188866.11	142.14
	Ferrocene	5.921	2322675.96	186.00
	Alkane	4.858	1922454.08	148.2
Au	Olefin 1	4.949	991909.27	146.1
	Olefin 2	5.099	1495415.12	146.1
	Ferrocene	5.917	1428950.65	186.00

Table S4.2: GC-MS results for the electrolysis of 2-iodo-2-methyl-4-phenyl butane

Table S4.3: The linear fit of $v^{1/2}$ vs. j_p from the CVs of 10 mM ^tBuI

Reduction	<i>m</i> (mA $s^{1/2}$	b	(mA	r^2
peak	$mV^{-1/2} cm^{-2}$)	cm^2)		
GC_A	-0.11 ± 0.002	-0.30	±	0.999
		0.02		
GC_B	-0.074 ± 0.001	-0.24	±	0.998
		0.02		
Ag _A	-0.098 ± 0.002	-0.64	±	0.998
		0.03		
Ag _B	-0.080 ± 0.002	-0.11	±	0.995
		0.03		
Au _A	-0.12 ± 0.001	-0.34	±	0.999
		0.01		
Au _B	-0.077 ± 0.003	-0.56	±	0.991
		0.04		
Au _{anomaly}	-0.074 ± 0.003	-0.36	±	0.989
2		0.04		

Reduction	<i>m</i> (V)	<i>b</i> (V)	r ²
peak			
GC_A	-0.29 ± 0.01	-2.1 ± 0.02	0.991
GC_B	-0.25 ± 0.01	-2.8 ± 0.01	0.990
Ag _A	-0.24 ± 0.02	-1.5 ± 0.04	0.959
Ag_B	-0.21 ± 0.01	-2.7 ± 0.01	0.984
Au _A	-0.20 ± 0.008	-1.4 ± 0.02	0.991
Au _B	-0.14 ± 0.007	-3.1 ± 0.02	0.983
Au _{anomaly}	-0.12 ± 0.01	-2.4 ± 0.02	0.959

Table S4.4: The linear fit of log(v) vs. E_p from the CVs of 10 mM ^tBuI

Table S4.5: The linear fit of $v^{1/2}$ vs. i_p for peak A from the CVs of 0.5 and 10 mM ^tBuI on Ag and Au

Electrode	[^t BuI]	$m (\mathrm{mA}\mathrm{s}^{1/2}\mathrm{mV}^{-1/2})$	<i>b</i> (mA)	r ²
	(mM)			
Ag	0.5	$-2.5 \times 10^{-5} \pm 5 \times 10^{-7}$	$-1.7 \times 10^{-4} \pm 8 \times 10^{-6}$	0.997
Ag	50	-0.0028 ± 0.0002	0.009 ± 0.002	0.981
Au	0.5	$-0.00050 \pm 2 \times 10^{-6}$	$-7 \times 10^{-5} \pm 3 \times 10^{-5}$	0.999
Au	50	-0.063 ± 0.0001	-0.032 ± 0.002	0.997

Table S4.6: Measured Sand's time τ of ^tBuI on Ag from chronopotentiometry

[^t BuI]	j	τ (s)
(mM)	(mA/cm^2)	
0.5	0.035	29
	0.04	22.5
	0.045	17.5
	0.05	16.5
	0.055	12.5
	0.06	9.5
10	0.5	57
	0.6	31
	0.7	21
50	2.5	67.5
	2.7	49
	2.8	44.5
	2.9	37

[^t BuI]	j	τ (s)
(mM)	(mA/cm^2)	
0.5	0.035	34.5
	0.04	24
	0.045	19
	0.05	16
	0.055	12.5
	0.06	10
10	0.7	47.6
	0.8	24
	0.9	16.6
	1.0	12.5
	1.1	9.8
	1.2	8
50	3.0	62.6
	3.25	39
	3.5	22.2

Table S4.7: Measured Sand's time τ of ^tBuI on Au from chronopotentiometry

Table S4.8: Estimated D of ^tBuI at concentrations of 0.5 mM, 10 mM, and 50 mM on Ag and Au electrodes from chronopotentiometry

Electrode	D at 0.5 mM	D at 10 mM	D at 50 mM
	(cm^2/s)	(cm^2/s)	(cm^2/s)
Ag	5.0×10^{-8}	1.6×10^{-5}	4.9×10^{-4}
Au	5.2×10^{-8}	1.7×10^{-5}	5.7×10^{-4}



Figure S4.1: ¹H spectrum of 2-iodo-2-methyl-4-phenyl butane.



Figure S4.2: ¹H spectrum of 2-bromo-2-methyl-4-phenyl butane.



Figure S4.3: Blank CVs of (a) GC, (b) Ag, and (c) Au electrodes in 0.2 M $TBAPF_6/THF$ electrolyte at 50 mV/s.

Table S4.9: GC-MS results for the electrolysis of 2-iodo-2-methyl-4-phenyl butane with excess diethyl malonate- d_2 on Au

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Alkane	4.844	385663.48	148.12
Olefin 1	4.935	844453.06	146.09
Olefin 2	5.083	1790177.69	146.09
Ferrocene	5.897	1094765.08	186.00



Figure S4.4: CVs of (a) 10 mM tetrabutylammonium iodide and (b) 5 mM I_2 on Au electrodes in 0.2 M TBAPF₆/THF electrolyte at 50 mV/s.



Figure S4.5: CV of 50 mM diethyl malonate-d2 on Ag electrodes in 0.2 M TBAPF₆/THF electrolyte at 50 mV/s.

Table S4.10: GC-MS results for the chemical reduction of 2-iodo-2-methyl-4-phenyl butane with NaOMe

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Olefin 1	3.852	5399270.41	146.12
Olefin 2	3.947	5283713.09	146.11



Figure S4.6: CVs of (a) 0.5 mM and (b) 50 mM ^tBuI on glassy carbon electrodes in 0.2 M TBAPF₆/THF electrolyte at 50 mV/s.



Figure S4.7: Chronopotentiograms on Ag electrodes of (a) 0.5 mM ^tBuI at j = 0.035-0.06 mA/cm², (b) 10 mM ^tBuI at j = 0.5-0.7 mA/cm², (c) 50 mM ^tBuI at j = 2.5-2.9 mA/cm². Chronopotentiograms on Au electrodes of (d) 0.5 mM ^tBuI at j = 0.035-0.06 mA/cm², (e) 10 mM ^tBuI at j = 0.7-1.2 mA/cm², (f) 50 mM ^tBuI at j = 3-3.5 mA/cm². In all the potentiograms, a sharp decrease in *E* is observed once ^tBuI depletes at the electrode surface. The onset of the depletion is taken as Sand's time τ .

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Alkane	3.817	201699.2	148.13
Olefin 1	3.877	964779.13	146.12
Olefin 2	3.978	2792652.51	146.13
Ferrocene	4.554	2377950.22	186.07
Unknown	5.056	111923.32	205.20

Table S4.11: GC-MS results for the chemical reduction of 2-iodo-2-methyl-4-phenyl butane with $\rm D_2O$ on Au

Table S4.12: GC-MS results for the chemical reduction of 2-iodo-2-methyl-4-phenyl butane with MeOD on Au

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Alkane	3.791	226907	148.12
Olefin 1	3.847	549217.07	146.11
Olefin 2	3.942	1251747.57	146.10
Ferrocene	4.458	1353133.51	186.03
Unknown	4.948	130215.88	205.17

Table S4.13: GC-MS results for the chemical reduction of 2-bromo-2-methyl-4-phenyl butane with MeOD on Au

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Alkane	3.787	1609661.76	148.16
Olefin 1	3.845	4488559.8	146.14
Olefin 2	3.938	4080757.71	146.14
Unknown	4.022	10673265.45	185.24
Ferrocene?	4.453	5040855.38	184.06

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Phenoxy olefin	3.652	5845439.69	134.12
Alkane	3.776	1068509.28	148.17
Olefin 1	3.831	1749303.2	146.15
Olefin 2	3.922	2813149.22	146.16
Ferrocene	4.416	3314895.73	186.06
3-phenoxypropyl bromide	4.658	1553036.06	214.08

Table S4.14: GC-MS results for the chemical reduction of 2-iodo-2-methyl-4-phenyl butane with 3-phenoxypropyl bromide on Au

Table S4.15: GC-MS results for the chemical reduction of 2-bromo-2-methyl-4-phenyl butane with 3-phenoxypropyl bromide on Au

Compound	Retention	Area (arb.	Mass-to-
	time (min)	units)	charge ratio
			(m/z)
Phenoxy olefin	3.651	3866919.14	134.12
Alkane	3.777	1783831.78	148.19
Olefin 1	3.832	1987537.53	146.18
Olefin 2	3.923	2031637.97	146.17
Ferrocene	4.423	4200756.02	186.07
3-phenoxypropyl bromide	4.670	2262320.29	214.08
Unknown	5.908	1026869.15	228.20

Chapter 5

FUTURE OUTLOOK

In Chapters 2 and 3, the electrodes and their surfaces were engineered to prevent undesirable side reactions such as dendrite growth, passivation, and chemical reactions. In Chapter 4, the electrode was chosen primarily to promote the desirable electrochemical reaction of ^{*t*}BuI reduction to the carbanion. However, there still lacks a fundamental understanding of a clear structure-property relationship in engineering the electrolyte/electrode interface. The interface is studied primarily on a system-by-system basis, and only in few systems a clear structure-property relationship is established.

In Li metal batteries, the SEI has been extensively been studied for years, which revealed that the SEI is made up of an inorganic and organic component.²⁰ It was discovered that the presence of LiF in the inorganic component of the SEI is critical to the performance of the SEI, with the LiF grain boundaries promoting uniform diffusion of Li⁺.^{140–143} The SEI on Li metal was characterized by *in-situ* neutron scattering, ¹⁴⁴, *in-situ* NMR, ¹⁴⁵, XPS, ¹⁴⁶, *in-situ* ellipsometry, ¹⁴⁷, microscopy, ¹⁴⁸ and addition of chemical additives such as fluoroethylene carbonate. ¹⁴⁹

One of the main difficulties of characterizing the electrode/electrolyte interface is the relatively tiny scale of the surface compared to the bulk electrolyte and electrode. As a result, many techniques with any amount of penetration (*i.e.* XRD) are not suitable. In addition, the interface often changes from when the cell is *in-operando*, *in-situ*, and *ex-situ*. As a result, many techniques that require a ultra-high vacuum *i.e.* XPS are not ideal for interfacial characterizations either. Thus, for an accurate characterization of the electrode/electrolyte interface to establish design principles, more *operando* characterization techniques need developing. One of the techniques that has been used *in-operando* effectively in Li batteries is NMR spectroscopy, where the technique has been deployed effectively to study the growth of Li dendrites during cell cycling.¹⁵⁰ However, one of the disadvantages of *operando*-NMR is the restrictive scope of materials due to the selection rules of NMR-active nuclei. Many nuclei are quadrupolar in nature which broadens the NMR bands observed, which makes resolving different peaks and drawing conclusions very difficult, requiring a high magnetic field. In addition, many nuclei are entirely NMR-inactive. Several

other techniques such as *in-situ* neutron scattering and *operando* Raman and infrared spectroscopies suffer from similar issues, from lack of widespread access to instrumentation to limited scope. As such, development of instrumentation and new analytical techniques is a key barrier that must be addressed for advancement of the field.

Another potential method to describe the electrode/electrolyte interface is by using computational modelling.^{151,152} In Li batteries, computational models have been used to describe the thermodynamics and kinetics of SEI formation, as well as the properties of the SEI.¹⁵³ In electrocatalysis, models can be used to calculate the free energy landscape of various intermediates and adsorption energies.^{154,155} However, computational models often require some experimental results to form the basis of a model due to the prohibitive computational cost of a brute force method.

One potential area in which more interfacial understanding is needed is in all-solidstate batteries (ASSBs). In ASSBs, especially Li metal ASSBs, the SEI is less well understood and characterized, especially because the solid-state electrolyte itself is also a focus of research. As such, during the material discovery cycle of a solidstate electrolyte, the SEI must also be characterized to determine the suitability of the electrolyte.^{156–158} Unfortunately, the characterization and prediction of the SEI is difficult and impractical as an additional step in electrolyte discovery. To promote electrolyte screening, computational methods may be useful to predict the SEI composition, with time-consuming experimental techniques such as XPS, SEM, atomic force microscopy (AFM), neutron-scattering, and NMR to follow later.¹⁵⁹

Interfacial engineering is also vitally important in electrocatalysis. Reactions such as CO₂ reduction, HER, and oxygen evolution (OER) are important electrochemical reactions for green energy. In electrocatalytic applications, the focus is on engineering optimal active sites on the interface rather than the construction of an optimal SEI.^{160,161} In many cases, synthetic techniques are used to modify the structure of the catalyst rather than engineering new compounds on the surface, such as controlling epitaxial growth^{162,163} and nanoclusters.^{164,165} Surface characterization techniques such as tunneling electron microscopy, XPS, and AFM are commonly used. Further studies in interfacial engineering of catalysts, especially in applications where the engineering is not as well-understood in popular reactions such as HER and OER, (*i.e.* organic electrosynthesis), may be a rich avenue to explore towards improving the selectivity and economic viability of electrosynthetic reactions.

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