UC Riverside UC Riverside Electronic Theses and Dissertations

Title

Understanding the Electrode/Electrolyte Interphase in Magnesium-Ion Electrolytes with Simple Mg Salts

Permalink https://escholarship.org/uc/item/78r7d2d5

Author Jay, Rahul

Publication Date

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA RIVERSIDE

Understanding the Electrode/Electrolyte Interphase in Magnesium-Ion Electrolytes with Simple Mg Salts

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Rahul Jay

December 2018

Dissertation Committee: Dr. Juchen Guo, Chairperson Dr. Vincent Lavallo Dr. Ruoxue Yan

Copyright by Rahul Jay 2018 The Dissertation of Rahul Jay is approved:

Committee Chairperson

University of California, Riverside

ACKNOWLEDGMENTS

These past 4 years have been the greatest of learning experience of my life. I had so many highs and lows in both my professional and personal life. The people who I refer to in this section have been of the greatest help for me to achieve my dream of getting a PhD degree. Firstly, I am thankful to University of California Riverside, especially the Chemical and Environmental Engineering Department for accepting me as PhD student and letting spent the past 4 years at this facility. I would also like to thank my committee members who has taken time out of their busy schedule to help with my dissertation process, I would like to thank Dr. Vincent Lavallo and his group for your help with synthesizing the carborane electrolytes and helping me understand the chemistry behind synthesizing salts and also distilling solvents. I would like to give a big thank you to my advisor Dr. Juchen Guo. I was in a very bad place mentally when he took me into this lab. He showed great patience helped through the toughest times of my life. I have no doubt in my mind much greater success will be coming your way. His honesty and great work ethic has been a constant inspiration for me to strive to better myself. I only hope I gave you at least 10% of the joy that you have given me over the past 4 years. I would like to thank Dr Alexander Couzis who was my first mentor from CCNY in NY. You encouraged me to chase my dream and guide me out of some tough paths into the right one. I took your advice to go for my "goals" rather than stay for comfort. I've been through the least comfortable situations in the past four years and I have come out a better man for it. My lab mates have helped me when in need whether it is something small like check up on an experiment or driving 50 miles to Irvine to help with an experiment. I am very much grateful for all the help I have received

from all of you. I would like to thank my undergrad Audrey, who was immense help throughout my PhD. Without, her help most of the work in this thesis wouldn't have gone this swiftly or this smoothly. I hope you find a job very soon you are a great worker and a friend as well. The most important people who guided me through the past 4 years here in UCR are my friends and my family. I have made some great friends over the past 4 years who helped me learn a lot not just professionally but also personally. Whether it was the soccer, board games, tennis, or playing video games all of you made the graduate school life very enjoyable. Something that kept me going throughout this experience was the constant calls of support from my home. Mom I love you, I hope I made you proud. I didn't get to be the kind of doctor you wanted me to be. Hopefully this would suffice. Lastly, I would like to thank the latest additions to my personal life my niece Hima and my fiancé Dr. Vijayalakshmi. The last few months have been the hardest and the most stressful I have been through my entire PhD. But, the video calls we have makes start the day with the big smile and positive attitude and it is all down to you. There is a reason I like seeing you all the time because your smiles bring a great calmness in me and makes motivates me to drive forward and look forward to the time when we can be together. Thank you to everyone who have influenced my life one way or another. Every experience I had shaped me to the man I am today, and I am indebted to you all for helping me achieve it. Chapter 3 of this dissertation in full, is a reprint of the material as it appears in "Below the 12-vertex: 10vertex carborane anions as non-corrosive, halide free, electrolytes for rechargeable Mg batteries" published in Chem Comm in March 2017. the publication was co-first authored with Scott G. McArthur.

To my loving parents, Lathika Nair, Jayamohan Nair & rest of my very large family

To my dear fiancé, Dr. Vijayalakshmi Kavanal

To my first mentor Dr. Alexander Couzis

To the best Boss, Dr. Juchen Guo

ABSTRACT OF THE DISSERTATION

Understanding the Electrode/Electrolyte Interphase in Magnesium-Ion Electrolytes with Simple Mg Salts

by

Rahul Jay Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering University of California, Riverside, December 2018 Dr. Juchen Guo, Chairperson

A typical electrochemical cell contains an anode (negative electrode), a cathode (positive electrode) in an ion-conducting medium (electrolyte). With the increase in energy demands there is great interest in high energy density energy storage devices. Researchers are highly interested in Magnesium-ion (Mg-ion) electrochemistry owing to its high natural ambulance, high volumetric capacity/energy density and non-dendritic platting/stripping of Mg metal anodes. Commercialization of Mg-ion rechargeable batteries is hampered due to the lack of practical electrolytes and cathode materials. A comparative study on the SEI formed in Magnesium(II) Bis(trifluoromethanesulfonyl)imide (Mg(TFSI)₂) in tetraglyme (G4) and Magnesium Monocarborane (Mg(CB₁₁H₁₂)₂) in G4 was performed. Reversible deposition/stripping was observed in both electrolytes Mg(TFSI)₂ displayed high

overpotential of deposition and stripping and high potential hysteresis. Whereas; $Mg(CB_{11}H_{12})_2$ displayed considerably lower overpotential and hysteresis under the same conditions. X-ray Photoelectron Spectroscopy (XPS) measurements conducted on Mg deposited on Copper (Cu) surface indicated side products from the Mg(TFSI)₂ electrolyte but not for the $Mg(CB_{11}H_{12})_2$ electrolyte. SEM, and XPS analysis were also conducted on Mg metal surface after chronopotentiometry experiments to get a thorough understanding of Mg metal as an anode for the proposed electrolytes. The surface characterization results indicated $Mg(TFSI)_2$ has unstable anion prone to cathodic decomposition leading to the formation of SEI that severely impedes efficient deposition and stripping of Mg. Electrochemical activity of alternate carborane molecule $Mg(CB_9H_{10})_2$ with simpler/cheaper synthesis route was tested. Results showed promising electrochemical behavior similar to its predecessor. Sulfur electrode was proposed as a promising candidate for the $Mg(CB_{11}H_{12})_2$ electrolyte. Initial coin-cell although shows compatibility between the electrode and electrolyte, polysulfide shuttle mechanism witnessed during the charge process impedes reversible electrochemical activity of the cell. Nano-confined sulfur composites were used to restrict the shuttle mechanism providing mixed results. Methods for thorough understanding of the conversion reaction at the cathode side like XPS and UV-vis were used, and additional experiments are proposed to bring to light a new high energy density Mg-ion battery.

TABLE OF CONTENTS
ABSTRACTvii
LIST OF FIGURES xi
LIST OF TABLES xiv
Chapter 1: Introduction 1
1.1 Rechargeable Battery Overview
1.2 Electrochemical Cell Principles and Li-ion Batteries
1.3 Mg-ion Batteries7
1.3.1 Motivation for Mg – ion Batteries7
1.3.2 Mg-ion electrolyte Systems
1.3.3 Mg-ion Cathode materials14
1.4 Direction of our research
Reference
Chapter 2: A Comparative Study of $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ at the
Magnesium/Electrolyte Interface
2.1 Introduction
2.2 Experimental Methods
2.2.1 Preparation of electrolytes
2.2.2 Electrochemical analyses and materials characterizations
2.3 Results & Discussion
2.3.1 Electrochemical activity of 0.75M Mg(CB ₁₁ H ₁₂) ₂ & 0.5 M Mg(TFSI) ₂ in G433
2.3.2 Surface Characterization of Mg deposits on Cu
2.3.3 Surface Characterization of Mg metal after soaking

2.3.3 Surface Characterization of Mg metal after stripping/ redeposition	
2.4 Conclusion	
Reference	55
Chapter 3: Below the 12-vertex: 10-vertex carborane anions as non-corrosive, h	alide free,
electrolytes for rechargeable Mg batteries	59
3.1 Introduction	59
3.2 Experimental Methods	
3.2.1 Synthesis of Mg(CB ₉ H ₁₀) ₂	
3.2.2 X-ray Structure Determination	
3.2.3 Electrochemical Measurements	
3.3 Results & Discussion	
3.3.1 Solid state structure of Mg(CB ₉ H ₁₀) ₂	
3.3.2 Electrochemical Measurements of Mg(CB9H10)2	
3.4 Conclusion	73
Reference	74
Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono	ocarborane
Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane
Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane 77 77
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 4.2.2 Synthesis of 0.75M Mg(CB₁₁H₁₂)₂ & 0.5M Mg(TFSI)₂ in G4 4.2.3 Synthesis of Magnesium Sulfide 4.2.4 Electrochemical Measurements 	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 4.2.2 Synthesis of 0.75M Mg(CB₁₁H₁₂)₂ & 0.5M Mg(TFSI)₂ in G4 4.2.3 Synthesis of Magnesium Sulfide 4.2.4 Electrochemical Measurements 4.2.5 Material Characterization 	ocarborane
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane 77 77 82 82 83 83 84 84 85 86
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte	ocarborane 77 77 82 82 83 83 84 84 85 86 86
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 4.2.2 Synthesis of 0.75M Mg(CB₁₁H₁₂)₂ & 0.5M Mg(TFSI)₂ in G4 4.2.3 Synthesis of Magnesium Sulfide 4.2.4 Electrochemical Measurements 4.2.5 Material Characterization 4.3 Results and Discussion 4.3.1 Electrochemical Activity of IKB-S Cathode 4.3.2 Three electrode Discharge of IKB-S Cathode and Characterization 	ocarborane 77 77 82 82 83 83 84 84 84 84 85 86 86 91
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 4.2.2 Synthesis of 0.75M Mg(CB₁₁H₁₂)₂ & 0.5M Mg(TFSI)₂ in G4 4.2.3 Synthesis of Magnesium Sulfide 4.2.4 Electrochemical Measurements 4.2.5 Material Characterization 4.3 Results and Discussion 4.3.1 Electrochemical Activity of IKB-S Cathode 4.3.2 Three electrode Discharge of IKB-S Cathode and Characterization 4.3.3 Electrochemical Activity of CF10-S Cathode 	ocarborane 77 77 82 82 82 82 82 82 83 84 84 85 86
 Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Mono Electrolyte 4.1 Introduction 4.2 Experimental Methods 4.2.1 Synthesis of Sulfur-Carbon composite 4.2.2 Synthesis of 0.75M Mg(CB₁₁H₁₂)₂ & 0.5M Mg(TFSI)₂ in G4 4.2.3 Synthesis of Magnesium Sulfide 4.2.4 Electrochemical Measurements 4.2.5 Material Characterization 4.3 Results and Discussion 4.3.1 Electrochemical Activity of IKB-S Cathode 4.3.2 Three electrode Discharge of IKB-S Cathode and Characterization 4.3.3 Electrochemical Activity of CF10-S Cathode 4.4 Conclusion 	ocarborane

Chapter 5 Conclusion 10	06
-------------------------	----

LIST OF FIGURES

Figure 1.1 Schematic of the 1st generation Li-ion battery
Figure 2.1 CV scans and coulombic efficiency of both electrolytes
Figure 2.2 Chronopotentiometry curves for the Mg deposition
Figure 2.3 XRD pattern of the Mg deposited from both electrolytes
Figure 2.4 SEM images of Mg deposits on Cu for both electrolytes
Figure 2.5 SEM image with EDS mapping and XPS spectra of Mg deposits from
$Mg(CB_{11}H_{12})_2$ salt
Figure 2.6 B1s XPS Spectrum of the pristine Mg(CB ₁₁ H ₁₂) ₂ salt
Figure 2.7 SEM image with EDS mapping and XPS spectra of Mg deposits from
Mg(TFSI) ₂ salt
Figure 2.8 SEM image and XPS spectrums of the Mg surface soaked in both the
electrolyte
Figure 2.9 Digital images before and after soak in Mg $(CB_{11}H_{12})_2$ and Mg2p XPS
spectrum of the polished Mg surface
Figure 2.10 SEM image and EDS spectra of Mg metal was soaked in Mg(CB ₁₁ H ₁₂) ₂ 45

Figure 2.11 Digital images before and after soak in Mg(TFSI) ₂ and Mg2p XPS spectrum
of the polished Mg surface
Figure 2.12 SEM image and EDS spectra of Mg metal was soaked in in Mg(TFSI) ₂ 47
Figure 2.13 Chronopotentiometry curves of Mg foil in both electrolytes
Figure 2.14 SEM image; EDS mapping and XPS spectrum of Mg metal in $Mg(CB_{11}H_{12})_2$
electrolyte after stripping
Figure 2.15 SEM image; EDS mapping and XPS spectrum of Mg metal in Mg(TFSI) ₂
electrolyte after stripping
Figure 2.16 SEM image; EDS mapping and XPS spectrum of Mg metal in
Mg(CB11H12)2 electrolyte after redepostion
Figure 2.17 SEM image; EDS mapping and XPS spectrum of Mg metal in Mg(TFSI)2
electrolyte after redeposition

Figure 3. 1 Schematics of Mg(CB ₁₁ H ₁₂) ₂ (top) and Mg(CB ₉ H ₁₀) ₂ (bottom) synthesis	61
Figure 3. 2 Reaction schematics for the synthesis of $Mg(CB_9H_{10})_2$	63
Figure 3. 3 Solid state-structure of Mg(CB ₉ H ₁₀) ₂	67
Figure 3. 4 Selected CV Mg(CB ₉ H ₁₀) ₂ in G4 (inset-coulombic efficiency)	69
Figure 3. 5 CV on various WE's at 20 mV s ⁻¹ (inset – Enlargement oxidative onset	
potentials)	70
Figure 3. 6 Charge-discharge profiles $Mg(CB_9H_{10})_2$ in Mo6S8 cathode (inset – cycle	
stability).	72

LIST OF TABLES

Table 1.1 List of different Commercialized Battery Chemistries	2
Table 4. 1 List of commercial cathode materials	81

Chapter 1: Introduction

1.1 Rechargeable Battery Overview

With the rampant increase in energy demands and the dwindling energy resources like petroleum and coal and the adverse effects of these resources on the environment looming on our shoulders, demands for alternate energy sources has been increasing dramatically. High energy density energy storage devices are an essential factor in the storage and distribution of such energy sources. Batteries are electrochemical energy storage device that is made up of one or more electrochemical cells that provides a current at a voltage over a period of time. Rechargeable batteries are devices where the redox reaction can be reversed by applying an external current. Rechargeable batteries are used in a wide range of applications from hand held electronic devices, laptops, automobiles, even multitude of other stationary and grid scale applications. There is only a limited commercially viable rechargeable battery technology. Table 1.1 depicts an array of commercially available major battery systems with voltages, battery type, and specific energy and energy density values ¹. The table includes both primary and secondary (rechargeable) batteries. Leadacid batteries where the first battery technology to dominate the commercial rechargeable battery technology and is still the most commonly used secondary batteries, consuming more than 70% of world's lead production boasting a theoretical energy density of 252 Wh kg⁻¹ at 2.1 V. Although mature and well established the lead-acid technology may be, the knowledge of adverse effects of lead and the highly acidic nature of the electrolyte to the customer and the environment and the ever-increasing energy demands as driven the scientific community to look for multiple chemistries. Lithium-ion batteries (LIB's) is

currently at the forefront of high energy density electrochemical devices. LIB's can provide a theoretical specific energy of 410 Wh kg⁻¹ at 4.1 V which is significantly higher than lead-acid.

Battery Chemistry	Туре	Voltage (V)	Theoretical Specific Energy (W h kg ⁻¹)	Practical Specific Energy (W h kg ⁻¹)	Practical Energy Density (W h dm ⁻³)
Zn/MnO ₂ (alkaline)	Primary	1.5	358	145	400
Li/I ₂	Primary	2.8	560	245	900
Pb/acid	Secondary	2.1	252	35	70
Ni/Cd	Secondary	1.3	244	35	100
Ni/MH	Secondary	1.3	240	75	240
Na/S	Secondary	2.1	792	170	345
Na/NiCl ₂ (ZEBRA)	Secondary	2.6	787	115	190
Lithium-ion	Secondary	4.1	410	150	400

 Table 1.1 List of different Commercialized Battery Chemistries

1.2 Electrochemical Cell Principles and Li-ion Batteries

An electrochemical cell has three major components the anode, cathode and the electrolyte. Most commercially available electrochemical systems have solid electrodes (anodes and cathodes) and liquid electrolytes, which could vary from aqueous to organic. The electrolyte acts as an ion conducting medium between the chemical reaction in the anode and cathode. Electrons are forced to transfer from one electrode to another depending on the state of the battery (discharge or charge) through an external circuit, the ion transport across the electrolyte also ensures electroneutrality. During discharge anode undergoes oxidation and the electrons move from anode over the external circuit and is received at the cathode, undergoing the reduction process. The process is can be reversed by applying an external current in rechargeable cells. LIB's are used in this sub chapter to further explain the electrochemical principle. Development of LIB's was inspired from the work that was done by solid state chemists on intercalation chemistry in 1975 by Whittingham² and the development of the first commercial LIB by Goodenough³. Fig 1.1 shows a schematic of the first LIB⁴. The first-generation LIB's contained graphite as anode material and lithium cobalt oxide ($LiCoO_2$) as the cathode material, with Lithium hexafluorophosphate (LiPF₆) salt dissolved in a mixture of diethyl carbonate and propylene carbonate as electrolyte. Although, battery systems are also slightly more complex as showed in Fig 1.1 as both the anode and cathode materials are a mixture of the active material along with additives that increases electrical conductivity like carbon and polymeric binders (like polyvinylidene fluoride) pasted on copper (Cu) and aluminum (Al) current collector respectively. The electrodes are separated by porous polyethylene or

polypropylene separator film. The electrochemical process that drives these LIB's is known as intercalation/insertion chemistry. The half-reactions at the anode (1) and cathode (2) of the cell in Fig 1.1 is as follows

$$LiC_6 \rightleftharpoons C_6 + Li^+ + e^- \tag{1}$$

$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2 \tag{2}$$

During discharge as shown in equation (1) and (2) the anode goes through oxidation where Li^+ ions are extracted from the graphite and moves in between the layered cubic structure of CoO₂, the electrons that moves through the external circuit is accepted by the Al current collector and is transported to the redox centers as the cathode undergoes reduction and forms LiCoO₂. During charge both the reactions are reversed where the graphite anode undergoes reduction and the LiCoO₂ cathode undergoes oxidation. For this LIB the full reaction is as follows

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2 \tag{3}$$

These LIB's provides an energy density of around 250 Wh kg⁻¹ at a potential of 3.6 V. Although these LIB's came into existence in the early 90's and has been a constant subject for research for almost three decades significant increase in neither the energy density nor the cell voltage has not been achieved. The highly reactive nature of Li metal and the heavy safety concern it possesses when used as an anode material seriously hampers momentous change in the LIB landscape. The highly reactive nature of Li also hampers the efficiency of these Li-ion cells as the reaction between the solvent, electrolyte and the anode in the first charge cycle forming a Li⁺ permeable layer of chemical/electrochemical reaction byproducts on the anode surface which is referred to as the Solid Electrolyte Interphase (SEI) is responsible irreversible capacity as there is irretrievable loss of Li ions from the cathode during this process. Although these SEI layers contribute towards initial capacity loss in an LIB's they also prevent further electrolyte decomposition by forming a physical barrier between the pristine electrode and the electrolyte. Significant increase in capacity for LIB's can only be achieved by radical change in both the anode and cathode of the electrochemical cell. For example, implementation of Li metal as anode can radically increase the achievable capacity of Li-ion batteries. Sadly, such horizons are still long way away from being a reality. Hence, there is a lot of focus by the current electrochemical community to look beyond LIB's for fresh pastures in the development of secondary batteries. One of such pastures include use of metals with multivalent ions like Magnesium (Mg), Aluminum (Al) instead of the monovalent Li as a metal anode.



Figure 1.1 Schematic of the 1st generation Li-ion battery (LiCoO₂/ LiPF₆ /graphite)⁴.

1.3 Mg-ion Batteries

1.3.1 Motivation for Mg - ion Batteries

Mg metal possess immense potential to be a viable anode material as it boasts high volumetric capacity, 3832 mAh cm⁻³ as compared 837 mAh cm⁻³ by its commercial LIB counterpart graphite or 2061 mAh cm⁻³ by Li metal. The high abundance and the environmental benignity of the metal is also a huge boost towards looking into this material. Mg metal cannot compete with Li metal in terms gravimetric capacity, 2205 mAh g⁻¹ vs 3862 mAh g⁻¹ for Li. Li also possess a higher redox potential of - 3.0 V vs Standard Hydrogen Electrode (SHE) compared -2.3V vs SHE by Mg. However, commercialization of Li metal as anode for Li metal have been hindered due to the safety concerns attached to the Li metal during charge/discharge process of the battery. Li metal tends to form needle like dendritic structures during the charge process especially at higher rates which could lead to short circuit and thermal runaway. In direct contrast it has been well documented that Mg anode is not plagued by dendrite formation ⁵ and is free of such safety concerns. The interaction between Mg metal and the electrolyte is of great interest to Mg-ion researchers. Several challenges hamper the commercialization of Mg anode chemistry. The lack of practical electrolytes and cathode materials paired with sluggish kinetics not only makes Mg a weak candidate to replace LIB's but also far from practical usage. The absence of practical electrolytes in Mg-ion chemistry is attributed to the undesirable reactivity of Mg metal and the surface layer formation known as the Solid Electrolyte Interphase (SEI) layer formed during the stripping and deposition process. The decomposition of both salt and solvent occurs due to the highly reductive nature of metals like Mg and Li. SEI layer formed on Mg metal displays a stark contrast to that of Li, Although the passivating layer on both metal surfaces provides resistance from further decomposition of both salt and solvent, the SEI layer formed on the Mg surface unlike in case of Li prevents diffusion of Mg²⁺ ions into the metal surface due to the sluggish diffusion through the solid phase. This severely hampers the reversibility of the Mg systems. A systematic study on the morphology and nature of the Mg deposits is sorely lacking

1.3.2 Mg-ion electrolyte Systems

Although electrochemical properties of Mg were displayed as early as 1912 ⁶ from diethyl magnesium and magnesium iodide in diethyl ether. Although multiple other systems reported Mg deposition ⁷⁻¹², reversible deposition and stripping with an effort to build a Mg – ion battery was displayed by Gregory et.al ¹³ in 1990. His work on magnesium organoborates and organohaloaluminates was a major driving force for future high-profile Mg electrolyte systems ¹⁴⁻¹⁸. These works focused on the nature of the Lewis acid and the Grignard reagent to avoid the formation of the SEI layer which was deemed detrimental for the reversible electrochemical activity in Mg-ion chemistry. A detailed account of different Mg electrolyte systems will be discussed in the following sub chapters

1.3.2.1 Naked Magnesium Salts

Naked Mg salts are Mg salts where the Mg^{2+} cation coordinates to the solvent molecule. In Gregory's ¹³ report he states that the simple Mg salts does not have favorable electrochemical activity with Mg anode as SEI layer formed via the decomposition of the electrolyte acts a hindrance for Mg^{2+} diffusion into the metal and to most cathode material. Simple Mg salts with halide (Cl₂, Br₂, I₂) anions are deemed as an unworthy electrolyte material as they have extremely low solubility in ethereal solvents which are compatible with Mg metal. Although there have been reports of Mg deposition from MgI₂ there has been no concrete evidence to match the claims. Both Connor ⁹ and Sheha ¹⁹ reports reversible Mg deposition from high concentration MgBr₂ in 2-methyltetrahydrofuran and DMSO respectively. Mg-ion researchers has cast a bigger focus on salts whose complex anions are analogous to the LIB electrolytes. Early works on these electrolytes conducted by Genders ¹² and Gregory ¹³ shows most of these Li analog anions form very thick passivating layers on the Mg anode which resist magnesium transport. Although, recently Keyzer et al. ²⁰ reports reversible cycling deposition and stripping of $Mg(PF_6)_2$ in 1:1 THF: ACN solution. They also displayed a high oxidative stability for the electrolyte excess of 4V vs Mg. Tran et.al²¹ in 2012 reported that the reductive stability of ACN is -0.2V vs Mg which makes Kayzer's claim of Mg deposition suspicious. The most interesting analogs of Li salts is Mg(TFSI)₂ which was believed to form highly passivating SEI layers that inhibit further Mg interactions. Ha et.al ²² was among first report reversible deposition/stripping for Mg(TFSI)₂ in binary mixture of G1-G2 solvents with a high anodic stability of about 4V vs Mg. Ha also reported that higher glyme solvents (G3,G4) showed no deposition

under constant current deposition conditions due to the very high overpotentials. Ha's work also inspired Wattanabe²³ and Mc Farlane²⁴ who sucessfully deposited Mg(TFSI)₂ although by use of drying agents as additives in the electrochemical process like molecular sieves and Mg(BH₄)₂. More work on this electrolyte will be illustrated in Chapter 2 of this dissertation. Mohtadi ²⁵ displayed reversible deposition and stripping in Mg(BH₄)₂ in monoglyme/diglyme. The idea was to implement a strong reducing agent like BH_4^- ion that would be able to withstand the heavy reducing environment of Mg anode. Although, the electrolyte is non-corrosive low oxidation potentials of 1.7V on Pt, 2.2 V on SS were observed due to the catalytic effects of Pt on the decomposition of BH₄⁻. Gregory ¹³ reported on the first Mg salt with a naked cation. He proposed a reaction between Bu₃B a Lewis acid with Bu₂Mg to form Mg(Bu₄B)₂ in a solvent mixture of THF and DME. The solubility and the voltage stability of these salts heavily depends on the anion ligands. Reports have suggested that different anion ligands for Lewis acid and Grignard reagent causes aryl metathesis which causes scrambling of the aryl groups resulting in SEI layer formation, smaller reductive potentials which is detrimental to reversible Mg plating ²⁶. To avoid this aryl metathesis process ion exchange pathway of a Mg dimer to a silver intermediate were proposed, which can easily ion exchanged to the desired Mg salt. The borate cations that results from this process are water stable contrastingly, the aluminate analogs are not. Using these methods multiple electrolytes with superior solubilities and anodic stabilities were reported. Muldoon and coworkers ^{26,27} introduced Mg(BAr_F)₂ by reacting $MgBr_2$ and $Ag(BAr_F)$ in THF. The resulting electrolyte boasted high anodic stability more than 4V vs Mg on a stainless steel (SS) electrode. Magnesium

monocarborane (Mg(CB₁₁H₁₂)₂)was developed independently by Tutusaus et al. ²⁸ and McArthur et al. ²⁹ in 2015, displayed high anodic stability and low overpotential deposition and stripping with high coloumbic efficiency. Interphasial phenomenon of this electrolyte would be further discussed in Chapter 2 of this dissertation.

1.3.2.2 Dimer Magnesium Salts

A Dimer Mg salt refers to the dimer structure of its respective Mg cation where two magnesiums are coordinated to three halides and six solvent molecules. Since these cations carries two magnesiums per cation, they double the transference number of magnesium at the same concentration. These dimer cations also increase the solubility of these salts in organic solvents. Although, these salts are highly reactive and decomposes when exposed to air or water unlike the carborane salts. The presence of halides in most these salts also reduces their anodic stability regardless of the anions present. Most these dimer salts are products of two kinds of reactions. The reaction between Lewis acid and Grignard reagents in nonstoichiometric ratios results in the formation of the dimer cations. Inspired by the work done by Gregory, Aurbach investigated the electrochemical properties of different electrolytes formed by the reaction of multiple combinations of dialkylmagnesiums to Lewis acid (alkyl aluminum chlorides) and how it effects the oxidative stability and coulombic efficiency. Aurbach developed Mg(AlCl₂BuEt₂)₂ (DCC) electrolyte ³⁰ by reacting one-part dibutylmagnesium to two parts ethylaluminum dichloride (4) in THF.

$$Bu_2Mg + 2EtAlCl_2 \rightarrow Mg(AlCl_2BuEt_2)_2 \tag{4}$$

The electrolyte exhibits reversible deposition and stripping with very low over potential and high coulombic efficiency of 100%. The presence of chlorine and the presence of other

by products due to the in-situ preparation of the electrolyte and a lack of purification process leads low oxidative stability of 2.2 V vs Mg in Pt electrode. Although, other researchers have disputed the claims of high coulombic efficiency of 100% by claiming the coulombic efficiency of the DCC electrolyte is considerably less in the early cycles ³¹, the study also suggested that the electrolyte is not ideal for use in a robust Mg-ion system as the GC and NMR analysis of the electrolyte points towards decomposition of the electrolyte. The recrystallized salt from the in-situ synthesized electrolyte did not show any reversible electrochemical activity ^{5,32,33}. The small operating voltage window greatly reduces the energy density of the battery, to improve upon the anodic stability of the DCC electrolyte Aurbach engineered the APC ³⁴ electrolyte which effectively improved the oxidative stability from 2.2 to 3.2 V in Pt vs Mg with similar coulombic efficiency results. The APC electrolyte was synthesized by the reaction of one-part aluminum trichloride with two parts phenyl magnesium chloride (5).

$$2PhMgCl + AlCl_3 \rightarrow Ph_2AlCl_2^- + Mg_2Cl_3^+$$
(5)

The substitution of alkyl group in the Grignard component with an aromatic group resulted in eliminating the prospects β -H elimination as a possible route for electrolyte decomposition. Due to the in-situ synthesis process, these magnesium organohaloaluminate electrolytes produces unwanted corrosive and nucleophilic side products which makes the electrolytes unusable for conversion cathodes like sulfur ¹⁵ and aluminum current collectors ³⁵. Muldoon ¹⁵ synthesized an electrolyte with an oxidative stability of 2.5 V vs Mg via mixing of three parts of a Hauser base hexamethyldisilazide magnesium chloride (HMDSMgCl) and one-part Lewis acid aluminum trichloride (AlCl₃) (6).

$$3HMDSMgCl + AlCl_3 \rightarrow Mg_2Cl_3^+ + HMDSAlCl_3^- + (HMDS)_2Mg \tag{6}$$

Muldoon claims that they were able to achieve reversible electrochemical activity on the electrolyte even after recrystallization and dissolving of the salt in the THF solvent contrary to APC electrolyte which was not chemically active after recrystallization. According to the report by Muldoon the nucleophilic reaction byproduct (HMDS₂Mg) can be removed during the process of recrystallization thus improving the oxidative stability and compatibility with high capacity cathode materials like sulfur. Zhao-Karger and co-workers ^{17,36,37} reported on similar Hauser base electrolytes by reacting MgHMDS₂ with AlCl₃ and MgCl₂ in the following reaction procedure (7) and (8).

$$2[(HMDS)_2Mg] + 4AlCl_3 \rightarrow Mg_2Cl_3^+ + HMDSAlCl_3^- + 3[(HMDS)AlCl_2]$$
(7)
$$[(HMDS)AlCl_2] + 2MgCl_2 \rightarrow Mg_2Cl_3^+ + HMDSAlCl_3^-$$
(8)

Zhao-Krager was motivated by Muldoon's work on the sterically hindered amides with low nucleophilicity. He was able to improve the oxidative stability of the electrolyte to 3.2 V vs Mg in Pt electrode. Muldoon also later proposed boron-based electrolytes with similar dimer chemistry which are known as GEN2 and GEN3³⁸ with increased oxidative stability and decreased corrosivity. The reaction equation for GEN2 and GEN3 electrolytes are shown in (9) and (10) respectively

$$3PhMgCl + Ph_3B \rightarrow Mg_2Cl_3^+ + Ph_4B^- + Ph_2Mg \tag{9}$$

$$3PhMgCl + (C_6F_5)_3B \rightarrow Mg_2Cl_3^+ + Ph(C_6F_5)_3B^- + Ph_2Mg$$
 (10)

Doe and co-workers ³⁹ from Pellion Technologies designed a new dimer-based magnesium electrolyte, by a stoichiometric reaction of MgCl2 and AlCl3 resulting in the MACC electrolyte as noted on (11)

$$2MgCl_2 + AlCl_3 \rightarrow Mg_2Cl_3^+ + AlCl_4^- \tag{11}$$

MACC electrolyte lacks the R₂Mg nucleophile by-product present in the in-situ synthesis like with majority of the dimer type electrolyte. Although the electrolyte reports a high conductivity and voltage stability of 3V vs Mg. the electrolyte requires heavy conditioning of the electrolyte before high coulombic efficiencies are observed ⁴⁰ and is also highly corrosive to current collector materials like Al and SS. Although, these dimer type electrolytes show reversible electrochemical activities with high coulombic efficiencies, the nucleophilic nature and the presence of chlorine in the anion and the cation makes these electrolytes not viable with current collector material like aluminum and stainless steel. Although there has been a plethora of work being put into the electrolyte systems. Mg-ion chemistry also sorely lacks in cathode materials to go with these electrolytes.

1.3.3 Mg-ion Cathode materials

The two fundamental issues facing the prospect of commercialization for Mg-ion batteries are absence of practical electrolytes and cathode materials. Although there is a plethora of work on multiple Mg electrolyte systems. Studies on cathode materials for majority of those systems is sorely lacking. Due to the major hurdles with Mg anode in finding practical electrolytes studies on developing major cathode materials for Mg-ion systems were put on hold. A proper well-defined study on different cathode systems for the rechargeable Mg ion systems is overdue. The biggest challenges researchers face in the current environment is improving the mobility of Mg^{2+} ions thus improving the diffusion pathways. Besides the efforts of electrochemical researchers, slow diffusion of Mg^{2+} ions and the instability of the cathode structures are the biggest hurdle in current Mg-ion battery technology. This sub chapter gives a brief account on different type of cathode materials

1.3.3.1 Intercalation/Insertion Cathode materials

Intercalation/Insertion cathode materials acts as a host to the guest cations. For intercalation materials the guest ions can be inserted and removed during the discharge and the charge process while maintaining the host's framework. These materials often undergo very significant volume expansion and contraction during the discharge and charge process. Good cathode materials should have low Fermi energy like with high oxidation state transitional materials, be chemically stable to the electrolyte, anode and other battery components, electronically conductive, have stable structure that can withstand the range of ion intercalation/deintercalation. Intercalation in Mg-ion has its own potential difficulties. The solid-state diffusion of Mg²⁺ has very slow kinetics due to the likelihood of being trapped in the defects. All the Mg-ion intercalation have inherently lower voltage hence there is a need to look at transitional metal oxides and polyanion based materials. Mg prefers octahedral coordination than tetrahedral coordination affecting the diffusion of ions. Reactive nature of Mg electrolytes leading to the chemical instability of these cathode materials also severely hampers the choices for cathode materials. None of the reported insertion cathode materials for Mg-ion can compete with current Li-ion technologies in capacity or operational voltages. An account of intercalation cathode materials for Mg-ion are given below.

1.3.3.1.1 Chevrel Phase Mo₆S₈

Aurbach ³¹ first demonstrated the capability of Mo_6S_8 as a promising cathode material for Mg-ion systems for his DCC electrolyte system. Aurbach demonstrated reversible intercalation and de intercalation behavior with a capacity of around 70 mAh g⁻¹ with up to 1.3V over a period of 2000 cycles. Mo_6S_8 had a rhombohedral crystal structure with cubic cavities between the Mo_6S_8 blocks. These cubic cavities contain six tetrahedral coordination sites. Although, the electrostatic repulsion limits the insertion to a single Mg^{2+} ion per cavity which limits the specific capacity of the electrode reaching its theoretical specific capacity. The electrode was shown to have a very stable performance with less than 15% of capacity fade at a 100% depth of discharge (DOD). The discharge profile of Mo_6S_8 shows two distinct plateaus at 1.4V and 1.1V which corresponds to the insertion of the Mg^{2+} ion into the inner region between the two Mo_6S_8 blocks (12) and the plateau at 1.1V shows further insertion of Mg into the adjacent outer site with higher energy after (13) respectively.

$$Mo_6S_8 + Mg^{2+} + 2e^- \leftrightarrow MgMo_6S_8 \tag{12}$$

$$MgMo_6S_8 + Mg^{2+} + 2e^- \leftrightarrow Mg_2Mo_6S_8 \tag{13}$$

Mo6S8 is still the most successful and widely used cathode material for Mg-ion battery systems. The electrode has been set as the standard cathode material for all Mg-ion electrochemical systems. Studies has also revealed that the substitution of the sulfur with the more polarizable material like selenium (Se), and tellurium (Te) via structural modifications helps in reducing Mg^{2+} trapping and better mobility leading to higher

capacities close to theoretical capacity 41,42 . Cycling at elevated temperature and reducing the size of the Mo₆S₈ particles were also shown to increase diffusion kinetics of Mg²⁺.

1.3.3.1.2 Other Intercalation Cathodes

Researchers in search of cathodes and capacity investigated layered oxides, sulfides, and other polyanion materials that are well studied in LIB technologies. The layered vanadium pentoxide (V_2O_5) is one such material that has gathered lot of attention due to its high energy densities, facile synthesis and low costs. In LIB chemistries V₂O₅ can accommodate more than 3 mol of Li⁺ into its layered structure and boast a theoretical capacity of 400 mAh g^{-1} and is highly reversible due to its variable oxidation states. Although V₂O₅ was/is a strong perspective candidate. A large activation barrier for the solid diffusion limits results is high overpotentials and the charge rates. The V₂O₅ structure consists edge and corner sharing VO₅ square pyramids with a corner sharing tetrahedral site. Novak et.al ⁴³ investigated a single-crystal V_2O_5 that could host very small amounts of Mg^{2+} on the crystal's surface because the diffusion into the bulk single crystal was very slow at ambient conditions. It was also shown that presence of water molecules has a significant role to play in the easing of the Mg^{2+} insertion process as the H₂O molecules can preferentially solvate Mg^{2+ 43-45}. It was also reported that presence of high concentration of water molecules were detrimental to the Mg metal anode as the water molecules accelerates the passivation layer on the anode surface resulting in severe capacity fade and horrendous cycle stability and cycle life. Although it was expected that V_2O_5 can insert 2 mol of Mg^{2+} ions, it only turned out close to 0.6 mol of Mg²⁺ ions were able to be inserted due to the presence of chemically bounded water molecules in the channel of the V₂O₅ host. The

ability to expand the interlayer spacing of layered hosts by exfoliation or ion exchange has led to materials like MoS₂ and MoO₂ with improved Mg²⁺ diffusion ^{46,47}. MnO₂ is another promising cathode material because of its extremely low cost and non-toxicity. MnO₂ materials have three different polymorphs: tunnel, layer phase and spinel structures that is represented in 1D, 2D, and 3D respectively. The tunnel structure α-MnO₂ cathode material ^{48,49} reported close to 100 mAh g⁻¹ at close to 2.25 V vs Mg which was significantly lower than the 308 mAh g^{-1} expected from the formation of Mg_{0.5}MnO₂. This significant capacity drop is attributed to the Mn²⁺ dissociation and the conversion of the Mg to MgO. Although the δ -MnO₂ ^{50,51} improved on the capacity by 230 mAh g⁻¹ at close to 2.8 V. The high capacity achieved was solely dependent on the wet nature of the electrolyte due to the involvement of proton. Capacity in non-aqueous electrolyte was noted to be close to 35 mAh g⁻¹ for Mn₂O₄ spinel structure material ^{52,53} proving the vital nature of water molecule in the intercalation process of these MnO₂ cathode materials. Along with Mo₆S₈, V₂O₅, MnO₂ another Mg-ion cathode material of great interest is materials with polyanion framework. Works done on materials with polyanion framework like MnSiO₄ ⁵⁴ and FeSiO₄ ⁵⁵ showed promising initial capacities of 240 and 330 mAh g⁻¹ at voltages around 1.6 and 2.5 V respectively. But the capacity was very low around 80 mAh g⁻¹ for electrodes made from MnSiO₄ powders as the sol-gel synthesized electrodes showed the superior performance and extremely low current densities had to be used to get these capacities. Cells containing non-aqueous electrolytes had very low cycle life of less than 5 cycles. As mentioned earlier of all the insertion cathode materials Mo₆S₈ is the most successful insertion cathode material. Although other materials like V2O5, MnO2, and polyanions

were used the high capacity was only achieved with the presence of water which is detrimental for the cycle life and capacity retention of the cell.

1.3.3.2 Conversion Cathode materials

Although intercalation cathode materials have characteristics that can result in long cycle life, the moderate capacity and operational voltage, and intrinsically slow Mg²⁺ diffusion into the cathode remains a challenge to create high capacity/ high energy density batteries. Conversion cathodes such as sulfur, oxygen and other metal halides are garnering great interest as a high capacity, high energy density cathode materials. Despite, these conversion cathodes having similar issues in both Mg and Li chemistry. The opportunity of the twoelectron reduction producing high capacity and high energy density batteries is enticing. Conversion reactions offer capacities five times as much as intercalation materials using cheap environmentally friendly materials like sulfur and oxygen. Unlike intercalation materials, conversion cathodes undergo significant structural change at both anode and cathode during charge/discharge process. This transformation involves complete oxidation and reduction of both anode and cathode and forming new compounds with entire different structure. The following sub-chapters identifies different conversion cathode materials for Mg-ion systems.

1.3.3.2.1 Magnesium-Sulfur (Mg-S)

Among all the conversion cathode materials sulfur is the most promising cathode material boasting a high theoretical capacity of 1671 mAh g^{-1} . Sulfur is also highly abundant, environmentally friendly and very cheap ticking all the boxes to be a perfect candidate for a high energy density Magnesium-ion battery. The two-electron conversion reaction (14) yields a theoretical cell voltage of 1.77V offering a theoretical energy density of 3200 Wh L-1 compared to 2800 Wh L-1 for Li-S systems with Li metal as anode.

$$Mg^{2+} + S + 2e^{-} \leftrightarrow MgS \tag{14}$$

The 24% volume expansion resulting from the reaction between Mg and S is significantly lower than the 72% expansion of Li-S systems when Li₂S is formed. Although, considerable advances have been made in the Li-S system, Mg-S battery systems is still at its infancy. Although there is a plethora of Mg-electrolytes with different compositions the electrophilic nature of sulfur excludes nucleophilic electrolytes such as DCC and APC. The first Mg-S cell was demonstrated by Muldoon's group from Toyota in 2011¹⁵ by reacting stochiometric ratio of Hauser-base HMDSMgCl and AlCl₃ as shown in equation (6). Eventhough, the cell exhibited a low open circuit potential (OCP) of 0.5V the cell exhibited a discharge plateau 0.85V boasting an initial discharge capacity of 1200 mAh g⁻¹. The first charge profile showed higher capacity than the discharge capacity and a capacity decline to 394 mAh g⁻¹ on the second cycle pointing towards the well-known polysulfide shuttle mechanism due to which Muldoon claims that the cell could only be cycled a few times. The use of THF as a solvent the presence of chlorine in both cation and anion we believe be detrimental for a high energy density cell that needs to cycle at high voltages. This electrolyte spurred on researchers like Zhao-Karger and co-workers ^{17,36,37} with a similar electrolyte following the reactions noted in equations (7) and (8) to Muldoon with higher anodic stability by using glyme solvents. Zhao-Karger and co-workers worked on diverse types of Mg-S cells changing the carbon matrix to graphene oxide for the Sulfur ³⁷. Using solvent mixtures of glyme and ionic liquid to increase the viscosity to reduce the polysulfide shuttling observed by Muldoon. Although they were able slightly raise the oxidative stability of the electrolyte, they were not able to significantly improve on the performance of the cell as it displayed large overpotential during charge, loss of active material from the cathode due to the polysulfide dissolution, and low coulombic efficiency. Although, other electrolyte systems have been reported to have compatibility with sulfur. All these systems fail to produce a high energy density cell due to the relatively low oxidative stability with respect to battery materials like aluminum and stainless steel due to the presence of chlorine and low coulombic efficiency. Chapter 4 of this thesis will focus on a possible new electrolyte candidate for Mg-S system.

1.3.3.2.2 Other Conversion Cathodes

One of the most popular and interesting conversion cathode material for both Li and Mg ion battery systems is oxygen. As these batteries theoretically can be incredibly economic and can produce high-energy densities that could rival any battery systems. Although this great concept is plagued by major drawbacks. The battery requires either an aqueous electrolyte and a metal ion conducting membrane to protect the metal anode from reacting with the electrolyte forming a thick passivating layer, or a non-aqueous electrolyte that would support reversible oxygen electrochemistry. Both requirements are hard to
materialize due to the highly reactive nature of the Mg metal anode and a lack of materials that is Mg2⁺ conducting and stable in aqueous systems. Shiga et.al ⁵⁶ reported on an I₂/DMSO complex capable of decomposing MgO with visible O₂ evolution. He reported the cycling data of the cell at 60 ⁰C, reporting initial discharge capacity of upwards of 2200 mAh g⁻¹. But, the cell showed massive capacity fade on the following cycles. The author also failed to discuss the reactivity of the complex to the Mg anode that could lead to self-discharge of the cell. Chilton ⁵⁷ reported on the only metal halide conversion cathode for a reversible Mg-ion battery system at ambient conditions. The solubility of the CuBr₂ cathode material in the diethyl magnesium-ether electrolyte resulted in low coulombic efficiencies of 40% with respect to discharge and 33% with respect to charge. We believe Mg-S system is the most promising contender for creating high capacity high energy density beyond Li-battery technology.

1.4 Direction of our research

Of all the electrolytes systems discussed above in this chapter we believe a simple naked Mg salt with a very stable but weakly coordinating anion like a monocarborane $(HCB_{11}H_{11})^{-}$ could be very interesting prospect for rechargeable Mg-ion battery systems. The chemical stability of the anion could be beneficial for the electrolytes compatibility with Mg metal in a real battery system. We believe the magnesium monocarborane $(Mg(CB_{11}H_{12})_2)$ electrolyte paired with sulfur conversion cathodes could yield the high capacity high energy density Mg-ion batteries as the oxidative stability of the electrolyte is close to 4.0V vs Mg. The following chapters in this thesis will focus on both anode and cathode interactions for Mg(CB₁₁H₁₂)₂ for Mg-ion battery systems.

Reference

- (1) Palacín, M. R. Recent Advances in Rechargeable Battery Materials: A Chemist's Perspective. *Chem. Soc. Rev.* 2009, *38* (9), 2565–2575.
- (2) Whittingham, M. S. Mechanism of Reduction of the Fluorographite Cathode. J. *Electrochem. Soc.* 1975, *122* (4), 526.
- (3) Mizushima, K.; Jones, P. C.; Goodenough LixCoO2 (0<x<-1): A new cathode material for batteries of high energy density. *Solid State Ionics* 1981, *4*, 171–174.
- (4) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem. Soc. 2013, 135 (4), 1167–1176.
- (5) Aurbach, D.; Cohen, Y.; Moshkovich, M. The Study of Reversible Magnesium Deposition by In Situ Scanning Tunneling Microscopy. *Electrochem. Solid-State Lett.* 2001, 4, A113–A116.
- (6) Jolibois, P.; Formula of the organomagnesium derivative and magnesium hydride. *Comptes Rendus* 1912, 155, 353–355.
- (7) Overcash, D.M.; Mathers, F.C. The electrodeposition of magnesium. *Trans Electrochem Soc*, 1933, 64, 305–311.
- (8) Evans, W.V.; Lee, F.H.; Lee C.H. The decomposition voltage of grignard reagents in ether solution. *J Am Chem Soc*, 1935, 57, 489–490.
- (9) Connor, J.H.; Reid W.E.; Wood, G.B. Electrodeposition of metals from organic solutions V. electrodeposition of magnesium and magnesium alloys. *J Electrochem Soc.* 1957,104, 38–41.
- (10) Findl, E.; Ahmadi, M.A.; Lui, K. Magnesium electrodeposition. U.S. Patent 3,520,780. July 1970.
- (11) Brenner A Note on the electrodeposition of magnesium from an organic solution of a magnesium-boron complex. *J Electrochem Soc.* 1971, 118, 99–100.
- (12) Genders, J.D.; Pletcher, D; Studies using microelectrodes of the Mg(II)/Mg couple in tetrahydrofuran and propylene carbonate. *J Electroanal Chem Interfacial Electrochem.* 1986, 199, 93-100.
- (13) Gregory, T. D.; Hoffman, R. J.; Winterton, R. C. Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. J. Electrochem. Soc. 1990, 137, 775– 780.

- (14) Aurbach, D.; Weissman, I.; Gofer, Y.; Levi, E. Nonaqueous Magnesium Electrochemistry and Its Application in Secondary Batteries. *Chem. Rec.* 2003, 3, 61–73.
- (15) Kim, H. S.; Arthur, T. S.; Allred, G. D.; Zajicek, J.; Newman, J. G.; Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J. Structure and Compatibility of a Magnesium Electrolyte with a Sulphur Cathode. *Nat. Commun. 2011*, 2, 427.
- (16) Wan, L. F.; Prendergast, D. The Solvation Structure of Mg Ions in Dichloro Complex Solutions from First-Principles Molecular Dynamics and Simulated X-Ray Absorption Spectra. J. Am. Chem. Soc. 2014, 136, 14456–14464.
- (17) Zhao-Karger, Z.; Zhao, X.; Fuhr, O.; Fichtner, M. Bisamide Based Non-Nucleophilic Electrolytes for Rechargeable Magnesium Batteries. *RSC Adv.* 2013, 3, 16330–16335.
- (18) Guo, Y.; Zhang, F.; Yang, J.; Wang, F.; NuLi, Y.; Hirano, S. Boron-Based Electrolyte Solutions with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. *Energy Environ. Sci.* 2012, 5, 9100–9106.
- (19) Sheha, E. Ion transport properties of magnesium bromide/dimethyl sulfoxide nonaqueous liquid electrolyte. J Adv Res. 2016,7, 29–36.
- (20) Keyzer, E.N.; Glass, H.F.J.; Liu, Z. Mg(PF₆)₂-based electrolyte systems: understandingelectrolyte–electrode interactions for the development of mg-ion batteries. J Am Chem Soc. 2016, 138, 8682–8685
- (21) Tran, T. T.; Lamanna, W. M.; Obrovac, M. N. Evaluation of Mg[N(SO₂CF₃)₂]₂/Acetonitrile Electrolyte for Use in Mg-Ion Cells. J. Electrochem. Soc. 2012, 159, A2005–A2009.
- (22) Ha, S.Y.; Lee, Y.W.; Woo, S.W.; Koo, B.; Kim, J.S.; Cho, J.; Lee, K.T.; Choi, N.S.; Magnesium(II) Bis(trifluoromethane sulfonyl) imide-based Electrolytes with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. ACS Appl. Mater. Interfaces 2014, 6, 4063–4073.
- (23) Terada, S.; Mandai, T.; Suzuki, S.; Tsuzuki, S.; Watanabe, K.; Kamei, Y.; Ueno, K.; Dokko, K.; Watanabe, M. Thermal and Electrochemical Sability of Tetraglyme-Magnesium Bis(trifluoromethanesulfonyl)amide Complex: Electric Field Effect of Divalent Cation on Solvate Stability. J. Phys. Chem. C, 2016, 120, 1353–1365.
- (24) Ma, Z.; Kar, M.; Xiao, C.; Forsyth, M.; MacFarlane, D.R. Electrochemical Cycling of Mg in Mg[TFSI]₂/Tetraglyme Rlectrolytes. *Electrochemistry Communications*. 2017,78, 29–32.

- (25) Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S. J. Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angew. Chemie - Int. Ed.* 2012, *51* (39), 9780–9783.
- (26) Muldoon, J.; Bucur, C.B.; Oliver, A.G. Corrosion of magnesium electrolytes: chlorides the culprit. *Energy Environ Sci*, 2013, 6, 482–487.
- (27) Bucur, C.B.; Gregory, T.; Muldoon, J. Why grignard's century old nobel prize should spark your curiosity. In: Zhang Z, Zhang SS (eds) Rechargeable batteries. *Springer International Publishing*, New York, 2015, 611–635
- (28) Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E.G.; Sevryugina, Y. V. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew. Chem. Int. Ed.* 2015, 54, 7900–7904.
- (29) McArthur, S.G.; Geng, L.X.; Guo, J.C.; Lavallo, V. Cation Reduction and Comproportionation as Novel Strategies to Produce High Voltage, Halide Free, Carborane Based Electrolytes for Rechargeable Mg Batteries. *Inorg. Chem. Front.* 2015, 12, 1101–1104.
- (30) Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E. Prototype Systems for Rechargeable Magnesium Batteries. *Nature 2000*, 407, 724–727.
- (31) Barile, C. J.; Spatney, R.; Zavadil, K. R.; Gewirth, A. A. Investigating the Reversibility of in Situ Generated Magnesium Organohaloaluminates for Magnesium Deposition and Dissolution. J.Phys. Chem. C, 2014, 118, 10694–10699
- (32) Gizbar, H.; Vestfrid, Y.; Chusid, O.; Gofer, Y.; Gottlieb, H. E.; Marks, V.; Aurbach, D. Alkyl Group Transmetalation Reactions in Electrolytic Solutions Studied by Multinuclear NMR. *Organometallics*. 2004, 23, 3826–3831.
- (33) Aurbach, D.; Gizbar, H.; Schechter, A.; Chusid, O.; Gottlieb, H. E.; Gofer, Y.; Goldberg, I. Electrolyte Solutions for Rechargeable Magnesium Batteries Based on Organomagnesium Chloroaluminate Complexes. J. Electrochem. Soc. 2002, 149, A115–A121
- (34) Pour, N.; Gofer, Y.; Major, D. T.; Aurbach, D. Structural Analysis of Electrolyte Solutions for Rechargeable Mg Batteries by Stereoscopic Means and DFT Calculations. J. Am. Chem. Soc. 2011, 133, 6270–6278.
- (35) Muldoon, J.; Bucur, C. B.; Oliver, A. G.; Sugimoto, T.; Matsui, M.; Kim, H. S.; Allred, G. D.; Zajicek, J.; Kotani, Y. Electrolyte Roadblocks to a Magnesium Rechargeable Battery. *Energy Environ. Sci.* 2012, 5, 5941–5950.

- (36) Zhao-Karger, Z.; Zhao, X.; Wang, D.; Diemant, T.; Behm, R. J.; Fichtner, M. Performance Improvement of Magnesium Sulfur Batteries with Modified Non-Nucleophilic Electrolytes. *Adv. Energy Mater.* 2015, 5 (3), 1–9.
- (37) Vinayan, B. P.; Zhao-Karger, Z.; Diemant, T.; Chakravadhanula, V. S. K.; Schwarzburger, N. I.; Cambaz, M. A.; Behm, R. J.; Kübel, C.; Fichtner, M. Performance Study of Magnesium-Sulfur Battery Using a Graphene Based Sulfur Composite Cathode Electrode and a Non-Nucleophilic Mg Electrolyte. *Nanoscale* 2016, 8 (6), 3296–3306.
- (38) Muldoon, J.; Bucur, C. B.; Oliver, A. G.; Sugimoto, T.; Matsui, M.; Kim, H. S.; Allred, G. D.; Zajicek, J.; Kotani, Y. Electrolyte Roadblocks to a Magnesium Rechargeable Battery. *Energy Environ. Sci.* 2012, 5, 5941–5950
- (39) Doe, R.E; Han, R.; Hwang, J. Novel, electrolyte solutions comprising fully inorganic salts with high anodic stability for rechargeable magnesium batteries. *Chem Commun.* 2013, 50, 243-245
- (40) Barile, C.J.; Barile, E.C.; Zavadil, K.R. Electrolytic conditioning of a magnesium aluminum chloride complex for reversible magnesium deposition. *J Phys Chem C*. 2014, 118, 27623-27630.
- (41) Levi, E.; Mitelman, a; Isnard, O.; Brunelli, M.; Aurbach, D. Phase Diagram of Mg Insertion into Chevrel Phases, MgxMo6T8 (T = S, Se). 3. The Crystal Structure of Triclinic Mg₂Mo₆Se₈. *Inorg. Chem.* 2008, 47 (6), 1975–1983.
- (42) Aurbach, D.; Suresh, G. S.; Levi, E.; Mitelman, A.; Mizrahi, O.; Chusid, O.; Brunelli, M. Progress in Rechargeable Magnesium Battery Technology. *Adv. Mater.* 2007, *19* (23), 4260–4267
- (43) Novák, P.; Desilvestro, J. Electrochemical Insertion of Magnesium in Metal Oxides and Sulfides from Aprotic Electrolytes. J. Electrochem. Soc. 1993, 140 (1), 140–144.
- (44) Sa, N.; Wang, H.; Proffit, D. L.; Lipson, A. L.; Key, B.; Liu, M.; Feng, Z.; Fister, T. T.; Ren, Y.; Sun, C. J.; Vaughey, J. T.; Fenter, P. A.; Persson, K. A.; Burrell, A. K. Is Alpha-V2O5 a Cathode Material for Mg Insertion Batteries? *J. Power Sources*. 2016, 323, 44–50.
- (45) Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* 2017

- (46) Nam, K. W.; Kim, S.; Lee, S.; Salama, M.; Shterenberg, I.; Gofer, Y.; Kim, J.-S.; Yang, E.; Park, C. S.; Kim, J.-S.; Seok-Soo, L.; Chang, W.-S.; Doo, S.-G.; Jo, Y. N.; Jung, Y.; Aurbach, D.; Choi, J. W. The High Performance of Crystal Water Containing Manganese Birnessite Cathodes for Magnesium Batteries. *Nano Lett.* 2015, *15* (6), 4071–4079.
- (47) Yin, J.; Takeuchi, E. S.; Takeuchi, K. J.; Marschilok, A. C. Synthetic Control of Manganese Birnessite: Impact of Crystallite Size on Li, Na, and Mg Based Electrochemistry. *Inorganica Chim. Acta*. 2016, *453*, 230–237.
- (48) Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* 2017.
- (49) Wang, H.; Senguttuvan, P.; Proffit, D. L.; Pan, B.; Liao, C.; Burrell, A. K.; Vaughey, J. T.; Key, B. Formation of MgO during Chemical Magnesiation of Mg-Ion Battery Materials. *ECS Electrochem. Lett.* 2015, *4* (8), A90–A93.
- (50) Arthur, T. S.; Kato, K.; Germain, J.; Guo, J.; Glans, P.-A.; Liu, Y.-S.; Holmes, D.; Fan, X.; Mizuno, F. Amorphous V₂O5–P₂O₅ as High-Voltage Cathodes for Magnesium Batteries. *Chem. Commun.* 2015, *51* (86), 15657–15660.
- (51) Nam, K. W.; Kim, S.; Lee, S.; Salama, M.; Shterenberg, I.; Gofer, Y.; Kim, J.-S.; Yang, E.; Park, C. S.; Kim, J.-S.; Seok-Soo, L.; Chang, W.-S.; Doo, S.-G.; Jo, Y. N.; Jung, Y.; Aurbach, D.; Choi, J. W. The High Performance of Crystal Water Containing Manganese Birnessite Cathodes for Magnesium Batteries. *Nano Lett.* 2015, *15* (6), 4071–4079.
- (52) Knight, J. C.; Therese, S.; Manthiram, A. On the Utility of Spinel Oxide Hosts for Magnesium-Ion Batteries. *ACS Appl. Mater. Interfaces* 2015, 7 (41), 22953–22961.
- (53) Kim, C.; Phillips, P. J.; Key, B.; Yi, T.; Nordlund, D.; Yu, Y. S.; Bayliss, R. D.; Han, S. D.; He, M.; Zhang, Z.; Burrell, A. K.; Klie, R. F.; Cabana, J. Direct Observation of Reversible Magnesium Ion Intercalation into a Spinel Oxide Host. *Adv. Mater.* 2015, 27 (22), 3377–3384.
- (54) Feng, Z.; Yang, J.; NuLi, Y.; Wang, J.; Wang, X.; Wang, Z. Preparation and Electrochemical Study of a New Magnesium Intercalation Material Mg1.03Mn0.97SiO4. *Electrochem. commun.* 2008, *10* (9), 1291–1294.
- (55) Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.; Okado, T.; Huang, Z.-D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.; Kageyama, H.; Uchimoto, Y. High Energy Density Rechargeable Magnesium Battery Using Earth-Abundant and Non-Toxic Elements. *Sci. Rep.* 2014, *4*, 5622.

- (56) Shiga, T.; Hase, Y.; Kato, Y.; Inoue, M.; Takechi, K. A Rechargeable Non-Aqueous Mg-O2battery. *Chem. Commun.* 2013, *49* (80), 9152–9154.
- (57) Chilton, J. E. J. New Cathode-anode Couples Using Nonaqueous Electrolytes; Flight Accessories Laboratory, Aeronautical SystemsDivision, Air Force Systems Command, United States Air Force: Dayton, OH, 1962.

Chapter 2: A Comparative Study of Mg(CB₁₁H₁₂)₂ and Mg(TFSI)₂ at the Magnesium/Electrolyte Interface

2.1 Introduction

Rechargeable Mg-ion batteries have received increasing attention as an energy storage technology beyond lithium-ion batteries. However, the development of Mg-ion batteries is hampered by the lack of high-capacity cathode materials and limited options of Mg-ion electrolytes. The conventional Mg-ion electrolytes are mainly based on organohaloaluminate complex originating from the seminal works by Gregory et al. in 1990¹ and Aurbach et al. in 2000.² These electrolytes typically contain a mixture of Grignard reagents (RMgCl or R₂Mg, R is alkyl, aryl, or carboranyl group) and Lewis acids (typically AlCl₃), ³⁻⁷ thus suffering from low anodic stability due to the nucleophilicity of the Grignard reagents. ^{2,5} Therefore, non-Grignard electrolytes have been developed including magnesium aluminum chloride complex (MgCl₂-AlCl₃), ⁸⁻¹² magnesium alkoxides 13,14 fluorinated alkoxides,¹⁵ and amides such as (ROMgCl or $Mg(OR)_2$). hexamethyldisilazide magnesium chloride (HMDSMgCl) 16 and magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂). ¹⁷⁻¹⁹ However, majority of the reported electrolytes still contain active chloride anions, which renders these electrolytes corrosive in nature, thus not compatible with battery components. ¹⁸ Therefore, the recent developments are more focused on non-Grignard and halide-free (or the halide sequestered in a polyatomic anion) electrolytes based on Mg salts with weakly coordinating anions including borohydride, ²⁰ hexafluorophosphate, ²¹ monocarborane (($CB_{11}H_{12}$)), ^{22,23} fluorinated alkoxyborate, ²⁴ and fluorinated alkoxyaluminate anions. ^{25,26}

Among all the "simple" Mg salts, magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)₂) is readily available and soluble in ethers, which are widely considered as the only type of solvents compatible with Mg metal anodes. ^{27,28} Therefore, its electrochemical properties have been the subject of several investigations. The early studies suggest Mg could not be deposited from acetonitrile solution of Mg(TFSI)₂ due to the reduction of acetonitrile at a potential of -0.2 V vs Mg, ²⁹ while the ethereal Mg(TFSI)₂ solutions seemed capable of reversible Mg plating-stripping, however, with an inferior overpotential. ³⁰⁻³² The theoretical investigations on Mg(TFSI)₂ indicated the ion pairing between partially reduced Mg^{2+} cation (to Mg^+) and TFSI⁻ facilitating the cathodic TFSI decomposition on the electrode surface. ³³ On the contrary, $Mg(CB_{11}H_{12})_2$, developed independently by Tutusaus et al.²² and McArthur et al.²³ in 2015, was demonstrated as one of the best Mg salts for Mg-ion electroyletes with excellent anodic stability and low Mg plating-stripping overpotential. The opposite electrochemical properties of the $Mg(TFSI)_2$ and $Mg(CB_{11}H_{12})_2$ electrolytes seem to originate from their different interfacial mechanisms. However, the Mg/electrolyte interphase in these electrolytes are not well understood, particularly for $Mg(CB_{11}H_{12})_2$. Therefore, in this study we aim to obtain the direct information on their interfacial behaviors and interphase compositions through a systematic investigation.

2.2 Experimental Methods

2.2.1 Preparation of electrolytes

All manipulations were carried out using standard Schlenk or glovebox techniques under a nitrogen or argon atmosphere unless otherwise stated. Mg(CB₁₁H₁₂)₂ was prepared by the method of McArthur et al. ²³ Tetraethylene glycol dimethyl ether (G4) (>99%, Sigma-Aldrich) was distilled over sodium metal under inert conditions on the Schlenk-line and stored with molecular sieves until electrolyte solution was mixed. Mg(TFSI)₂ salt (Solvionic, 99.5%) was dried inside a tube furnace at 180 °C under vacuum in an argon (Ar) filled glovebox for 48 hours. The preparation of both electrolytes was conducted inside the Ar-filled glovebox. Moisture content of G4 and the electrolytes were measured with Karl Fischer titrator.

2.2.2 Electrochemical analyses and materials characterizations

Cyclic voltammetry (CV) and chronopotentiometry of Mg plating-stripping are performed with the three-electrode setup inside the Ar-filled glovebox. Standard platinum working electrode (3mm disk) was used in the CV experiments. Copper (Cu) foil (Lyon Industries) was used in the Mg deposition experiments. Cu foils were polished by soaking in 2.0 M sulfuric acid (Fisher Chemicals) for 3 days. The soaked Cu foils were sonicated three times for five minutes each in anhydrous ethanol (Sigma Aldrich), the dried Cu foils were stored in the Ar-filled glovebox for use. Mg foil was used as electrode in the chemical compatibility study and the Mg stripping experiments. The Mg foil was polished with 1200 and 2500 grade sand papers inside the glovebox and then washed with anhydrous G4 before use. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was performed on NovaNanoSEM 450. Samples were carefully washed with G4 and THF inside the glovebox before being mounted on the sample stubs. To perform the X-ray photoelectron spectroscopy (XPS), samples were transferred from the glovevbox via sealed stainless steel transfer tubes to the XPS facility. XPS experiments were conducted with a Kratos Axis Supra with a dual anode Al/Ag monochromatic X-ray source. The samples were transferred into the analysis chamber via the integrated glovebox filled with inert gas.

2.3 Results & Discussion

2.3.1 Electrochemical activity of 0.75M Mg(CB11H12)2 & 0.5 M Mg(TFSI)2 in G4

Due to the insolubility of Mg(CB₁₁H₁₂)₂ in lower glymes, we selected G4 as the solvent for both Mg(CB₁₁H₁₂)₂ and Mg(TFSI)₂. Figure 2.1 shows the selected CV cycles of Mg plating-stripping in 0.5 M Mg(TFSI)₂ and 0.75 M Mg(CB₁₁H₁₂)₂ electrolytes at 50 mV s⁻¹ with Pt working electrode, Mg counter electrode, and Mg reference electrode in threeelectrode setup. The coulombic efficiency (CE) of the plating-stripping proceess over 50 cycles was calculated from the CV curves and shown as the inset. The water content in both electolytes was 8 ppm measured with Karl Fischer titration. The Mg(CB₁₁H₁₂)₂ electrolyte demonstrates low plating overpotential at -0.5 V vs Mg²⁺/Mg in the first cycle, which was further lowered to -0.35 V on subsquent cycles. The Mg stripping potential is at 0 V vs Mg²⁺/Mg thus resulting in a small plating-stripping potential hysterisis. On the other hand, although the Mg(TFSI)₂ electrolyte indeed displays a pair of reversible redox peaks, corresponding to Mg plating-stripping, the overpotentials are very high: -0.9 V for plating and 2.1 V for stripping vs. Mg^{2+}/Mg . Furthmore, the CE of Mg plating-stripping in the $Mg(CB_{11}H_{12})_2$ electrolyte is stabilized at approximately 97% over the course of 50 cycles. In comparison, the CE of Mg plating-stripping in the Mg(TFSI)₂ electrolyte is well below 40% during 50 cycles. We speculate the significantly different CE of the two electrolytes is due to their different solid electrolyte interphase (SEI) formation mechnisms during the Mg plating-stripping process.



Figure 2.1 Representative CV scans and coulombic efficiency of Mg plating-stripping in (a) 0.75 M Mg(CB₁₁H₁₂)₂ and (b) 0.5 M Mg(TFSI)₂ in G4 at 50 mV s⁻¹

2.3.2 Surface Characterization of Mg deposits on Cu

To study the SEI formation during the Mg plating, chronopotentiometry experiments Figure 2.2 were performed in both electrolytes at a current density of 1 mA cm⁻² for a period of 12 hours on a copper (Cu) electrode. The X-ray diffraction (XRD) measurements Figure 2.3 confirm the deposition of Mg metal from both electrolytes. The scanning electron microscopic (SEM) images in Figures 2.4a and 2.4b at different magnifications display uniform Mg deposition from the $Mg(CB_{11}H_{12})_2$ electrolyte. The digital image inset clearly shows the deposited Mg metal has a metallic grey color and smooth surface. On the contrary, the Mg deposited form the Mg(TFSI)₂ electrolyte has a distinctly different appearance and micromorphology. As depicted in the digital image inset in Figure 2.4c, the Mg deposited from Mg(TFSI)₂ electrolyte is aggregated black particles on the Cu substrate. The SEM images in Figure 2.4c and Figure 2.4d verify that the Mg deposition from Mg(TFSI)₂ electrolyte indeed is composed by particles instead of smooth layer deposition. The micromorphology of the Mg from the Mg(TFSI)₂ electrolyte is consistent with the previous Mg deposition, reported by Ha et.al, ²⁷ from Mg(TFSI)₂ in monoglyme and diglyme.



Figure 2.2 Chronopotentiometry curves for the Mg deposition from $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ electrolytes at 1 mA cm⁻² for 12 hours.



Figure 2.3 XRD pattern of the Mg deposited from $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ electrolytes.



Figure 2.4 SEM images at different magnification of Mg deposited from (a, b) $Mg(CB_{11}H_{12})_2$ and (c, d) $Mg(TFSI)_2$ electrolyte on Cu substrate with constant current at 1 mA cm⁻² for 12 hours. Insets are the digital images of Mg deposited on Cu.

To understand the stark contrast of Mg deposits from these two electrolytes, energydispersion X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were used to identify the surface composition of the deposited Mg. The EDS elemental mapping of the Mg surface deposited from $Mg(CB_{11}H_{12})_2$ electrolyte (Figure 2.5a) displays strong presence of Mg and oxygen. The corresponding Mg2p XPS spectrum (Figure 2.5b) consistently indicate that the Mg-containing composition on the surface includes metallic Mg and magnesium oxide (MgO). Considering the absence of oxygen atom in the $Mg(CB_{11}H_{12})_2$ salt and good resistance of G4 to electrochemical reduction, we believe the MgO layer is due to the oxidation from the environment. It is also worth noting that the XPS technique only probes a very thin surface layer of a few nanometers. Therefore, the composition ratio shown in the Mg2p XPS spectrum does not correlate to the actual content of MgO in the deposited Mg. Strong evidence for the stability of $Mg(CB_{11}H_{12})_2$ electrolyte also comes from the B1s and C1s XPS spectra on the Mg surface shown in Figures 2.5c and 2.5d. The B1s XPS spectrum shows the B-B and B-C bonds, which are consistent with the pristine $Mg(CB_{11}H_{12})_2$ salt (Figure 2.6 in Supporting Information), resulting from the salt residue on the Mg surface. The C1s XPS spectrum shows the signal from the

adventitious carbon contamination (C-C, C-O-C, and O-C=O bonds) and the C-B bond from salt residue without indication of G4 decomposition.



Figure 2.5 (a) SEM image with EDS elemental mapping and XPS spectra of (b) Mg2p, (c) B1s, and (d) C1s of Mg surface deposited from $Mg(CB_{11}H_{12})2$ electrolyte.



Figure 2.6 B1s XPS Spectrum of the pristine Mg(CB₁₁H₁₂)₂ salt.

In stark contrast to the excellent stability of the Mg(CB₁₁H₁₂)₂ electrolyte, analyses of the surface of Mg deposited from the Mg(TFSI)₂ electrolyte clearly indicates severe SEI formation. The EDS elemental mapping in Figure 2.7a displays surface composition including Mg, oxygen, fluorine, and sulfur. The Mg2p XPS spectrum in Figure 2.7b shows Mg bonds from magnesium sulfide (MgS) and MgO (Mg binding energy in these two compounds are very close), and magnesium fluoride (MgF₂) without indication of metallic Mg. The F1s XPS spectrum in Figure 2.7c confirms the existence of MgF₂ and compounds containing C-F bonds on the surface of Mg deposited from Mg(TFSI)₂. Similarly, the S2p XPS spectrum in Figure 2.7d indicates the existence of MgS and sulfur-oxygen bonds, which can be attributed to the sulfonyl group from the electrolyte residue, and/or sulfite

 (SO_3^{2-}) and dithionite $(S_2O_4^{2-})$ anions from the decomposition of TFSI⁻ anions. ^{31,34} The C1s XPS spectrum in Figure 2.7f only shows peaks from the adventitious carbon inconsistent with the C 1s spectrum from the Mg(CB₁₁H₁₂)₂ electrolyte, indicating G4 solvent is stable.



Figure 2.7 (a) SEM image with EDS elemental mapping and XPS spectra of (b) Mg 2p, (c) F 1s, (d) S 2p, and (e) C 1s of Mg deposited from Mg(TFSI)₂ electrolyte.

2.3.3 Surface Characterization of Mg metal after soaking

The EDS and XPS results in Figure 4 lead to the conclusion that SEI is formed during Mg deposition in Mg(TFSI)₂ electrolyte via TFSI⁻ anion reduction. Rajput et al. through their theoretical invetigation ³³ proposed the proneness of TFSI⁻ anion to reduction is due to a transient ion pair of Mg⁺–TFSI⁻ from partial reduction of Mg²⁺ cation. It is also known that metallic Mg is capable of reducing C-F, N-S, and S=O bonds,^{35,36} thus it is not surprising that the similar decomposition is observed electrochemically for TFSI⁻ anion. It is unlikely

that the monocarborane anion decomposes chemically in the presence of metallic Mg, since we prepare the electrolyte in high purity and yield *via* a Mg reduction. Therefore, to prove that TFSI anion specifically degrades in the presence of Mg metal anodes and the monocarborane anion does not, we investigated the chemical compatibility of Mg metal in both Mg(CB₁₁H₁₂)₂ and Mg(TFSI)₂ electrolytes. Figure 2.8a displays the SEM image of the soaked Mg surface with no indication of morphology change. The Mg2p XPS spectrum of the soaked Mg surface (Figure 2.8b) shows metllic Mg and MgO from the native oxide on the surface. (The native MgO layer cannot be completely removed by polishing as shown in the Mg2p XPS pesctrum of the polished Mg in Figure 2.9.). After being soaked in the $Mg(CB_{11}H_{12})_2$ electrolyte for 14 days, no visible change can be observed on the Mg surface Figure 2.9. The EDS spectrum in Figure 2.10 also evidence no composition change after soaking in $Mg(CB_{11}H_{12})_2$ electrolyte. On the other hand, the Mg electrode soaked in $Mg(TFSI)_2$ electrolyte demonstrates drastic visual change from metal grey to black as shown in Figure 2.11. Clear surface morphological change (pitting-like) can be observed in the SEM image in Figure 2.8c. EDS spectrum in Figure 2.12 clearly shows surface compounds containing significantly amount of O, F and S elements. The XPS spectra of Mg2p, F1s, and S2p (Figures 2.8d, 2.8e, and 2.8f) show very similar results to those on the

Mg surface electrochemically deposited from Mg(TFSI)₂ electrolyte. The XPS spectra are strong evidence that TFSI⁻ anion can also be chemically reduced by Mg metal.



Figure 2.8 (a) SEM image and (b) Mg2p XPS spectrum of the Mg surface soaked in $Mg(CB_{11}H_{12})_2$ electrolyte, (c) SEM image and (d) Mg2p, (e) F1s and (f) S2p XPS spectra of Mg surface soaked in Mg(TFSI)₂ electrolyte.



Figure 2.9 Digital image of (a) polished Mg foil and (b) the same Mg foil after soaking in $Mg(CB_{11}H_{12})_2$ for 14 days. (c) The Mg2p XPS spectrum of the polished Mg surface.



Figure 2.10 SEM image and EDS spectra at multiple locations of Mg metal was soaked in $Mg(CB_{11}H_{12})_2$. EDS spectra shows a high concentration of Mg



Figure 2.11 Digital image of (a) polished Mg foil and (b) the same Mg foil after soaking in $Mg(TFSI)_2$ for 14 days. (c) The Mg2p XPS spectrum of the polished Mg surface.



Figure 2.12 SEM image and EDS spectra at multiple locations on the Mg surface soaked in Mg(TFSI)₂ electrolyte. EDS spectra shows a significant concentration of O, F, and S on the Mg surface.

2.3.3 Surface Characterization of Mg metal after stripping/ redeposition

The distinctly different chemical stability of $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ with Mg metal (*i.e.*, different interfacial composition) results in very different behaviors of Mg stripping. As shown in Figures 2.13a and 2.13b, the Mg stripping at 1 mA cm⁻² in Mg(CB₁₁H₁₂)₂ electrolyte demonstrates an very low overpotential of 0.05 V vs Mg. On the controry, the Mg stripping with the same current density in Mg(TFSI)₂ electrolyte demonstrates a significantly higher overpotential at 1.4 V vs Mg. This high overpotential of Mg stripping could contribute to the previous observation that Mg-S two-electrode cells using Mg(TFSI)₂ electrolyte in monoglyme failed to demonstrate discharging capacity. ^{37,38} The interphase on Mg electrode also impacts the behavior of Mg plating following the stripping process as displayed in Figure 2.13c. Mg plating after stripping in $Mg(CB_{11}H_{12})_2$ electrolyte shows a modest overpotential of -0.25 V vs Mg; on the other hand, Mg plating after stripping in Mg(TFSI)₂ shows a high overpotnetial of -0.5 V vs Mg with a considerablely high potential overshoot. The EDS and XPS analysis of the Mg surfaces after stripping and re-plating (Figures 2.14 to 2.17) show consistent results with the analyses described above: Mg surface in Mg(CB₁₁H₁₂)₂ electrolyte is virtually interphasefree and the one in Mg(TFSI)₂ electrolyte contains oxide, sulfide, and fluoride compounds.



Figure 2.13 Chronopotentiometry Mg stripping curve in (a) $Mg(CB_{11}H_{12})_2$ electrolyte and (b) $Mg(TFSI)_2$ electrolyte, (c) chronopotentiometry curves of Mg stripping and plating. The current density is 1 mA cm⁻² and the duration is 5 hours for stripping and 5 hours for



Figure 2.14 SEM image; EDS elemental mapping and spectrum; Mg2p and B1s XPS spectra of Mg metal after stripping at 1 mA cm⁻² for 5 hours in Mg(CB₁₁H₁₂)₂ electrolyte.



Figure 2.15 SEM image; EDS elemental mapping and spectrum; Mg2p, F1s, and S2p XPS spectra of Mg metal after stripping at 1 mA cm⁻² for 5 hours in Mg(TFSI)₂ electrolyte.



Figure 2.16 SEM image; EDS elemental mapping; Mg2p and B1s XPS spectra of Mg metal after plating following stripping at 1 mA cm⁻² for 5 hours in Mg(CB₁₁H₁₂)₂ electrolyte.



Figure 2.17 SEM image; EDS elemental mapping; Mg2p, F1s, and S2p XPS spectra of Mg metal after plating following stripping at 1 mA cm⁻² for 5 hours in Mg(TFSI)₂ electrolyte.

2.4 Conclusion

Through systematic electrochemical analyses, microscopic and spectroscopic characterizations, we have demonstrated superior Mg plating-stripping performance of the Mg(CB₁₁H₁₂)₂ electrolyte in comparison with Mg(TFSI)₂. Such excellent electrochemical performance of Mg(CB₁₁H₁₂)₂ can be unambiguously attributed to the superb chemical and electrochemical stability at the Mg/electrolyte interface. Our results indicate virtually no interphase formation occurs during Mg plating due to the cathodic stability of the (HCB₁₁H₁₁)⁻ anion. On the contrary, we also demonstrate that Mg(TFSI)₂ is an inferior salt for Mg-ion electrolyte due to it severe interphase formation, which occurs both chemically and electrochemically due to the reduction of TFSI⁻ anion. Mg(TFSI)₂ may only be a feasible salt for Mg-ion electrolytes with proper Mg anode protection as demonstrated by Ban and coworker.³⁹ Undoubtedly, Mg(CB₁₁H₁₂)₂ is one of the most Mg-compatible salts for Mg-ion electrolytes to date.

Reference

- (1) Gregory, T. D.; Hoffman, R. J.; Winterton, R. C. Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. J. Electrochem. Soc. 1990, 137, 775–780.
- (2) Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E. Prototype Systems for Rechargeable Magnesium Batteries. *Nature 2000*, 407, 724–727.
- (3) Aurbach, D.; Schechter, A.; Moshkovich, M.; Cohen, Y. On the Mechanisms of Reversible Magnesium Deposition Processes. J. Electrochem. Soc. 2001, 148, A1004– A1014.
- (4) Aurbach, D.; Cohen, Y.; Moshkovich, M. The Study of Reversible Magnesium Deposition by In Situ Scanning Tunneling Microscopy. *Electrochem. Solid-State Lett.* 2001, 4, A113–A116.
- (5) Lv, D.; Xu, T.; Saha, P.; Datta, M. K.; Gordin, M. L.; Manivannan, A.; Kumta, P. N.; Wang, D. A Scientific Study of Current Collectors for Mg Batteries in Mg(AlCl₂EtBu)₂/THF Electrolyte. *J. Electrochem. Soc.* 2012, 160, A351–A355.
- (6) Aurbach, D.; Gofer, Y.; Lu, Z.; Schechter, A.; Chusid, O.; Gizbar, H.;Cohen, Y.; Ashkenazi, V.; Moshkovich, M.; Turgeman, R.; Levi, E. A Short Review on the Comparison between Li Battery Systems and Rechargeable Magnesium Battery Technology. J. Power Sources 2001, 97–98, 28–32.
- (7) Aurbach, D.; Gizbar, H.; Schechter, A.; Chusid, O.; Gottlieb, H. E.; Gofer, Y.; Goldberg, I., Electrolyte Solutions for Rechargeable Magnesium Batteries Based on Organomagnesium Chloroaluminate Complexes. J. Electrochem. Soc. 2002, 149, A115–A121.
- (8) Liu, T.; Cox, J. T.; Hu, D.; Deng, X.; Hu, J.; Hu, M. Y.; Xiao, J.; Shao, Y.; Tang, K.; Liu, J. A Fundamental Study on the [(μ-Cl)₃Mg₂(THF)₆]⁺ Dimer Electrolytes for Rechargeable Mg Batteries. *Chem. Commun.* 2015, 51, 2312–2315.
- (9) Liu, T.; Shao, Y.; Li, G.; Gu, M.; Hu, J.; Xu, S.; Nie, Z.; Chen, X.; Wang, C.; Liu, J. A Facile Approach Using MgCl₂ to Formulate High Performance Mg²⁺ Electrolytes for Rechargeable Mg Batteries. *J. Mater. Chem. A 2014*, 2, 3430–3438.
- (10) Barile, C. J.; Barile, E. C.; Zavadil, K. R.; Nuzzo, R. G.; Gewirth, A. A. Electrolytic Conditioning of a Magnesium Aluminum Chloride Complex for Reversible Magnesium Deposition. J. Phys. Chem. C 2014, 118, 27623–27630.

- (11) Canepa, P.; Jayaraman, S.; Cheng, L.; Rajput, N. N.; Richards, W. D.; Gautam, G. S.; Curtiss, L. A.; Persson, K. A.; Ceder, G. Elucidating the Structure of the Magnesium Aluminum Chloride Complex Electrolyte for Magnesium-Ion Batteries. *Energy Environ. Sci.* 2015, 8, 3718–3730.
- (12) Doe, R. E.; Han, R.; Hwang, J.; Gmitter, A. J.; Shterenberg, I.; Yoo, H. D.; Pour, N.; Aurbach, D. Novel Electrolyte Solutions Comprising Fully Inorganic Salts with High Anodic Stability for Rechargeable Magnesium Batteries. *Chem. Commun.* 2014, 50, 243–245.
- (13) Wang, F. F.; Guo, Y. S.; Yang, J.; Nuli, Y.; Hirano, S. I. A Novel Electrolyte System without a Grignard Reagent for Rechargeable Magnesium Batteries. *Chem. Commun.* 2012, 48, 10763–10765.
- (14) Nelson, E. G.; Kampf, J. W.; Bartlett, B. M. Enhanced Oxidative Stability of Non-Grignard Magnesium Electrolytes through Ligand Modification. *Chem. Commun.* 2014, 50, 5193–5195.
- (15) Crowe, A. J.; Stringham, K. K.; Bartlett, B. M. Fluorinated Alkoxide-Based Magnesium-Ion Battery Electrolytes That Demonstrate Li-Ion-Battery-like High Anodic Stability and Solution Conductivity. ACS Appl. Mater. Interfaces 2016, 8, 23060–23065.
- (16) Liao, C.; Sa, N.; Key, B.; Burrell, A. K.; Cheng, L.; Curtiss, L. A.; Vaughey, J. T.; Woo, J. J.; Hu, L.; Pan, B.; et al. The Unexpected Discovery of the Mg(HMDS)₂/MgCl₂ Complex as a Magnesium Electrolyte for Rechargeable Magnesium Batteries. *J. Mater. Chem. A 2015*, 3, 6082–6087.
- (17) Kim, H. S.; Arthur, T. S.; Allred, G. D.; Zajicek, J.; Newman, J. G.; Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J. Structure and Compatibility of a Magnesium Electrolyte with a Sulphur Cathode. *Nat. Commun. 2011*, 2, 427.
- (18) Zhao-Karger, Z.; Zhao, X.; Fuhr, O.; Fichtner, M. Bisamide Based Non-Nucleophilic Electrolytes for Rechargeable Magnesium Batteries, *RSC Adv. 2013*, 3, 16330–16335.
- (19) Merrill, L. C.; Schaefer, J. L. Conditioning-Free Electrolytes for Magnesium Batteries Using Sulfone-Ether Mixtures with Increased Thermal Stability. *Chem. Mater.* 2018, 30, 3971–3974.
- (20) Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S. J. Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angew. Chem. Int. Ed.* 2012, 51, 9780–9783.
- (21) Keyzer, E. N.; Glass, H. F. J.; Liu, Z.; Bayley, P. M.; Dutton, S. E.; Grey, C. P.; Wright, D. S. Mg(PF₆)₂-Based Electrolyte Systems: Understanding Electrolyte-

Electrode Interactions for the Development of Mg-Ion Batteries. J. Am. Chem. Soc. 2016, 138, 8682–8685.

- (22) Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E.G.; Sevryugina, Y. V. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew. Chem. Int. Ed.* 2015, 54, 7900–7904.
- (23) McArthur, S.G.; Geng, L.X.; Guo, J.C.; Lavallo, V. Cation Reduction and Comproportionation as Novel Strategies to Produce High Voltage, Halide Free, Carborane Based Electrolytes for Rechargeable Mg Batteries. *Inorg. Chem. Front.*, 2015, 12, 1101–1104.
- (24) Zhao-Karger, Z.; Gil Bardaji, M. E.; Fuhr, O.; Fichtner, M. A New Class of Non-Corrosive, Highly Efficient Electrolytes for Rechargeable Magnesium Batteries. J. Mater. Chem. A 2017, 5, 10815–10820.
- (25) Herb, J. T.; Nist-Lund, C. A.; Arnold, C. B. A Fluorinated Alkoxyaluminate Electrolyte for Magnesium-Ion Batteries. *ACS Energy Lett.* 2016, 1, 1227–1232.
- (26) Herb, J. T.; Nist-Lund, C. A.; Arnold, C. B. A Fluorinated Dialkoxide-Based Magnesium-Ion Electrolyte. *J. Mater. Chem. A 2017*, *5*, 7801–7805.
- (27) Ha, S.Y.; Lee, Y.W.; Woo, S.W.; Koo, B.; Kim, J.S.; Cho, J.; Lee, K.T.; Choi, N.S.; Magnesium(II) Bis(trifluoromethane sulfonyl) imide-based Electrolytes with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. ACS Appl. Mater. Interfaces 2014, 6, 4063–4073.
- (28) Ma, Z.; Kar, M.; Xiao, C.; Forsyth, M.; MacFarlane, D.R. Electrochemical Cycling of Mg in Mg[TFSI]₂/Tetraglyme Rlectrolytes. *Electrochemistry Communications*. 2017,78, 29–32.
- (29) Tran, T. T.; Lamanna, W. M.; Obrovac, M. N. Evaluation of Mg[N(SO₂CF₃)₂]₂/Acetonitrile Electrolyte for Use in Mg-Ion Cells. J. Electrochem. Soc. 2012, 159, A2005–A2009.
- (30) Fukutsuka, T.; Asaka, K.; Inoo, A.; Yasui, R.; Miyazaki, K.; Abe, T.; Nishio, K.; Uchimoto, Y. New Magnesium-Ion Conductive Electrolyte Solution Based on Triglyme for Reversible Magnesium Metal Deposition and Dissolution at Ambient Temperature. *Chem. Lett.* 2014, 43, 1788–1790.
- (31) Shterenberg, I.; Salama, M.; Yoo, H. D.; Gofer, Y.; Park, J.-B.; Sun, Y.-K.; Aurbach, D. Evaluation of (CF₃SO₂) ₂ N⁻ (TFSI) Based Electrolyte Solutions for Mg Batteries. *J. Electrochem. Soc.* 2015, 162, A7118–A7128.
- (32) Terada, S.; Mandai, T.; Suzuki, S.; Tsuzuki, S.; Watanabe, K.; Kamei, Y.; Ueno, K.; Dokko, K.; Watanabe, M. Thermal and Electrochemical Sability of Tetraglyme-Magnesium Bis(trifluoromethanesulfonyl)amide Complex: Electric Field Effect of Divalent Cation on Solvate Stability. J. Phys. Chem. C, 2016, 120, 1353–1365.
- (33) Rajput, N.N.; Qu, X.; Sa, N.; Burrell, A.K.; Persson, K.A. The Coupling Between Stability and Ion Pair Formation in Magnesium Electrolytes from First-Principles Quantum Mechanics and Classical Molecular Dynamics. *J. Am. Chem. Soc.* 2015, 137, 3411–3420.
- (34) Parimalam, B.S.; Lucht, B.L. Reduction Reactions of Electrolyte Salts for Lithium Ion Batteries: LiPF₆, LiBF₄, LiDFOB, LiBOB, and LiTFSI. *J. Electrochem. Soc. 2018*, 165, A251–A255.
- (35) Zhao, Y.; Zhu, J.; Ni, C.; Hu, J. Magnesium Metal-Mediated Reductive Trifluoromethylation of Aldehydes with Phenyl Trifluoromethyl Sulfone. *Synthesis* (*Stuttg*). 2010, No. 11, 1899–1904.
- (36) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. Activation of Carbon-Fluorine Bonds by Metal Complexes. *Chem. Rev.* 1994, *94* (2), 373–431.
- (37) Li, X.; Gao, T.; Han, F.; Ma, Z.; Fan, X.; Hou, S.; Eidson, N.; Li, W.; Wang, C. Reducing Mg Anode Overpotential via Ion Conductive Surface Layer Formation by Iodine Additive. *Adv. Energy Mater.* 2018, 8, 1701728.
- (38) Gao, T.; Ji, X.; Hou, S.; Fan, X.; Li, X.; Yang, C.; Han, F.; Wang, F.; Jiang, J.; Xu, K.; et al. Thermodynamics and Kinetics of Sulfur Cathode during Discharge in MgTFSI₂–DME Electrolyte. *Adv. Mater.* 2018, 30, 1704313.
- (39) Son, S. B.; Gao, T.; Harvey, S. P.; Steirer, K. X.; Stokes, A.; Norman, A.; Wang, C.; Cresce, A.; Xu, K.; Ban, C. An Artificial Interphase Enables Reversible Magnesium Chemistry in Carbonate Electrolytes. *Nat. Chem. 2018*, 10, 532–539.

Chapter 3: Below the 12-vertex: 10-vertex carborane anions as non-corrosive, halide free, electrolytes for rechargeable Mg batteries.

3.1 Introduction

Due to rapid technological advances in rechargeable portable devices and electric vehicles there is an urgent need to develop rechargeable batteries that are safer and have greater energy density compared to current state-of-the-art Li-ion cells.¹ Furthermore, given the low earth abundance of Li (Li⁺, 0.0017% of the earth's crust), and the fact that cells constructed with pure Li metal are inherently unsafe, due to dendrite formation, alternative anode materials based on other elements are of great interest. Mg-based batteries are a potentially game changing alternative to Li-ion systems because Mg is far less expensive, much more abundant (4% of the earth's crust), more tolerant of air, and does not form dendrites. The fact that Mg does not form dendrites allows the utilization of pure Mg anodes, which significantly increases both the volumetric and gravimetric energy densities of Mg-cells compared to Li-ion batteries. To realize high energy density Mg-cells appropriate cathode materials must be identified. However, the discovery of such cathode materials has been hampered by the lack of suitable electrolytes that facilitate the electrochemical oxidation and reduction reactions. In contrast to Li⁺ ions, Mg²⁺ ions from conventional Mg salts, such as $Mg(PF_6)_2$, $Mg(ClO_4)_2$ cannot reversibly penetrate the solid electrolyte interface (SEI) layer on Mg anodes.² Most of the current Mg electrolytes are composed of simple ethereal solvents and Mg-organic complex represented by Grignard reagents and similar compounds like organo borates ³⁻⁵, borohydrides⁶ and Grignard halo aluminates⁷⁻¹⁰. However, these compounds generally limited by low electrochemical oxidation potentials, i.e. narrow electrochemical stable window. Another caveat is that the

electrolyte cannot contain halide ions, since their oxidation leads to radicals or elemental halogens that corrode non-noble metal current collectors and battery casing materials.³ Recently, Mc.Arthur¹¹ and Mohtadi¹² and coworkers independently reported the synthesis and implementation of the non-corrosive and halide free electrolyte Mg(CB₁₁H₁₂)₂, featuring 12-vertex icosahedral carborane anions¹³ 1 (Scheme 1, A). The carborane anion (CB₁₁H₁₂⁻) is immune to any acids/bases¹⁴, is compatible with Mg metal, and does not undergo electrochemical oxidation until +5.36 V vs Mg^{0/42}.¹⁵ Prior to the discovery of Mg(CB₁₁H₁₂)₂ all other known electrolytes for Mg batteries had high halide content and or suffered from poor electrochemical stability. In contrast to Mohtadi's route to prepare Mg(CB₁₁H₁₂)₂, which uses a precious metal and results in material that is difficult to purify, we developed a superior method, namely cation reduction. As depicted in the reaction scheme from Fig 1, this cation reduction methodology utilizes magnesium metal to reduce trimethylammonium cations to produce Mg(CB₁₁H₁₂)₂ in high purity and without the consumption of precious metal.

While Mg(CB₁₁H₁₂)₂ meets the basic electrochemical requirements to enable the discovery of novel cathode materials that will result in the development of high capacity Mg batteries, the cluster 1 is rather expensive to produce. Furthermore, even if functional high capacity conversion cathodes such as sulfur¹⁶⁻²⁰ or moderate capacity high voltage cathodes such as transition metal oxides²⁰⁻²³ for Mg cells are discovered a library of electrolytes will be needed to optimize performance of the materials. Indeed, each cathode material will display distinct chemical behavior with different electrolytes. Here we report the discovery of a novel non-corrosive air stable electrolyte Mg(CB₉H₁₀)₂ that utilizes a

smaller 10-vertex carborane $(CB_9H_{10})^-$ (Fig 3.1)²⁴⁻²⁶. This electrolyte is less expensive to prepare compared to Mg $(CB_{11}H_{12})_2$ and displays similar electrochemical stability. $(CB_9H_{10})^-$ can be conveniently prepared without cyanide and Na metal, via a simple reaction of $B_{10}H_{14}$ with p-formaldehyde²⁵ followed by oxidation with I_2^{26} .



Figure 3. 1 Schematics of $Mg(CB_{11}H_{12})_2$ (top) and $Mg(CB_9H_{10})_2$ (bottom) synthesis via cat-ion reduction

3.2 Experimental Methods

3.2.1 Synthesis of Mg(CB9H10)2

The synthesis route of the 10-vertex route is provided in the reaction scheme in Fig 3.2. As mentioned above the anionic component of the electrolyte was synthesized by three easy steps. Decaborane ($B_{10}H_{14}$) was reacted with p-formaldehyde²⁵ in presence of base to install a carbon vertice in place of a boron to form an "arachno" species carborane (CB₉H₁₄) this reaction mechanism is known as the brellochs reaction. The resulting open cluster with all ten required vertices then underwent iodine oxidation with elemental iodine to form a fully closed carborane cluster $2-(CB_9H_{10})$ which is the 2-isomer of the required product. The 2-isomer was then refluxed in DME for 5 days to obtain the required anion of 1- (CB_9H_{10}) . The carborane cluster then underwent the familiar Mg reduction process from the Mg(CB₁₁H₁₂)₂ salt from Chapter 2, where (CB₉H₁₀)⁻ (HNMe₃⁺) (2.0 g, 10.3 mmol) was added to a suspension of Mg powder (4.0 g, 165 mmol) in a minimal amount of THF (5mL) and the resulting suspension was stirred for 1 hr. After 1 hr, additional THF (30mL) was added and the suspension was left to stir for 24 hours. The THF solution was then filtered through a medium porosity fritted funnel. The collected precipitate of white powder and excess magnesium was washed with DME, dissolving the white powder of the collected precipitate. Unreacted magnesium powder was collected and reused. The DME solvent was removed under high vacuum, resulting in compound $Mg(CB_9H_{10})_2$ as a white powder in 91% yield (4.1g 9.37 mmol). Once dried, compound Mg(CB₉H₁₀)₂ is only soluble in DME at cold temperatures -30°C (Note: Mg²⁺ counter cation is coordinated to three DME molecules).to obtain $Mg(CB_9H_{10})_2$.



Figure 3. 2 Reaction schematics for the synthesis of $Mg(CB_9H_{10})_2$

3.2.2 X-ray Structure Determination

A colorless prism fragment (0.495 x 0.247 x 0.202 mm3) was used for the single crystal xray diffraction study of $[C_4H_{10}O_2]3Mg^{2+}2(CH_{10}B_9])^-$ (sample vL170SM_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 platform-CCD x-ray diffractometer system (fine focus Mo-radiation, $\lambda = 0.71073$ Å, 50KV/30mA power). The CCD detector was placed at a distance of 5.0600 cm from the crystal. A total of 3600 frames were collected for a sphere of reflections (with scan width of 0.30 in ω , starting ω and 2 θ angles of -300, and φ angles of 00, 900, 1200, 1800, 2400, and 2700 for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package and using a narrow-frame integration algorithm. Based on an orthorhombic crystal system, the integrated frames yielded a total of 75989 reflections at a maximum 2 θ angle of 61.996 (0.69 Å resolution), of which 10124 were independent reflections (Rint = 0.0484, Rsig = 0.0306, redundancy = 7.5, completeness = 100%) and 9094 (89.8%) reflections were greater than $2\sigma(I)$. The unit cell parameters were, a = 20.7310(10) Å, b = 10.6782(5)Å, c = 14.3738(7) Å, $\alpha = \beta = \gamma = 900$, V = 3181.9(3) Å3, Z = 4, calculated density Dc = 1.114 g/cm3. Absorption corrections were applied (absorption coefficient $\mu = 0.084$ mm-1; max/min transmission = 0.983/0.959) to the raw intensity data using the SADABS program. The Bruker SHELXTL software package was used for phase determination and structure refinement. The distribution of intensities (E2-1 = 0.762) and systematic absent reflections indicated two possible space groups, Pna2(1) and Pnma. The space group Pna2(1) (#33) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit of the unit cell. With subsequent isotropic refinement, all the non-hydrogen atoms were identified. There was one cation of $(C_4H_{10}O_2)3Mg^{2+}$ and two anions of $(CH_{10}B_9)^{-}$ present in the asymmetric unit of the unit cell. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached, except the H-atoms of the two CH-group of the carboranes were refined unrestrained. The refinement converged at R1 = 0.0353, wR2 = 0.0811, with intensity I>2 σ (I). Absolute structure parameter cannot be reliably determined because no heavy atom is present in the structure. The largest peak/hole in the final difference map was 0.223/-0.157 e/Å3.

3.2.3 Electrochemical Measurements

Experimental: Conductivity of the electrolyte was measured using an electrochemical cell with two symmetric Pt film-electrodes. Potentiostatic EIS program from Gamry reference 1000 potentiostat was used to measure the impedance across the cell for each concentration. Conductivity was calculated by using the following equation

$$\sigma = \frac{l}{RA} \tag{1}$$

where σ is the conductivity, 1 is the distance between the electrodes, A is the crosssectional area and R is the resistance. The cell was calibrated using standard aqueous KCl solution. Three electrode experiments were conducted in a bob-cell on a Gamry reference 1000 with polished standard electrodes like Pt, Au and glassy carbon (GC). And polished foils like Ni,SS, and Al as working electrodes with polished Mg foil as reference and counter. All three electrode experiments were conducted in an argon filled glovebox. Mgion battery performances were demonstrated with coin cells (CR2032) with Mg anode and Chevrel phase Mo_6S_8 cathode using 0.45 M Mg(CB₉H₁₀)₂ in G4. Chevrel phase Mo_6S_8 was prepared with a method previously established by Aurbach et.al⁷, Mo_6S_8 electrodes were prepared by mixing 70wt% active material, 20% carbon black and 10% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The mixed paste was then applied as a thin uniform coating on a Ni foil and then dried in a vacuum oven overnight at 50 °C. Cells were assembled in an argon filled glovebox. 6mm diameter disc of Mo₆S₈ coating on Ni foil were punched out as the cathode and placed on the bottom base of the CR2032 coin cells, 40μ l of the Mg(CB₉H₁₀)₂ in G4 was pippetted onto the cathode. A polypropelene seperator was carefully placed over the cathode and 60µl electrolyte was added (total of 100 μ l) to wet the seperator surface. A polished Mg disc of 6mm in diameter was placed on the wetted seperator the cell was then filled with two spacers and a washer to fill the base, the top cap was then placed on the top and the cell was hydraulically pressed to seal the cell. The cells where cycled in and arbin cyler at a C-rate of C/10.

3.3 Results & Discussion

3.3.1 Solid state structure of Mg(CB9H10)2

While the 10-vertex anion was discovered by Knoth²⁴ in 1967 very little is known about its electrochemical properties. While the reductive stability of 2 is unknown a single report from Hawthorne²⁷ claims that the anion is oxidatively stable to +1.95 V vs SCE (+4.56 V vs $Mg^{0/2+}$). Therefore, we became interested in exploring the reductive stability of the cluster and its potential use as an electrolyte for Mg batteries. We envisioned utilizing our cation reduction methodology to prepare Mg(CB9H10)2 from its corresponding trimethylammonium salt (HNMe₃⁺) (CB₉H₁₀)⁻. Cation reduction is not only the most efficient way to prepare halide free Mg electrolytes, but it is also a chemical test to prove the compatibility of an electrolyte with Mg metal anodes (reductive stability). $Mg(CB_9H_{10})_2$ is a solvent separated ion pair and the cluster is compatible with metallic Mg. Indeed, stirring a solution of Mg(CB₉H₁₀)₂ with activated Mg powder for one-month results in no decomposition of the electrolyte. Similar to $Mg(CB_{11}H_{12})_2$, the salt $Mg(CB_9H_{10})_2$ precipitates from the THF solution and can be collected by filtration or extraction with DME. The structure of $Mg(CB_9H_{10})_2$ was unambiguously confirmed by a single crystal xray diffraction study. In the solid state the Mg^{2+} ion is coordinated by three chelating DME molecules and the two carborane counteranions are not interacting with the metal center (Fig 3.3).



Figure 3. 3 Solid state-structure of $Mg(CB_9H_{10})_2$ with 3 coordinated DME molecules to the Mg cation. Hydrogen atoms omitted for clarity. (color code: brown = boron; red = oxygen; green = Mg; grey = carbon)

3.3.2 Electrochemical Measurements of Mg(CB9H10)2

At room temperature, the ionic conductivity of $Mg(CB_9H_{10})_2$ in tetraglyme (G4) was measured as a function of concentration (Fig 3.4) between 0.15 and 0.65 M. A maximum conductivity of 1.57 mS cm⁻¹ was achieved at 0.45 M, which is comparable to the optimal conductivity of Mg(CB₁₁H₁₂)₂ in G4 (1.8 mS cm⁻¹) at a much higher concentration of 0.75 M. the experiment also revealed that although the electrolyte's conductivity increases to increase in concentration after 0.6 M there is decline in ionic conductivity. Three electrodes cyclic voltammetry (CV) experiments of 0.45 M Mg(CB₉H₁₀)₂ in G4 shown in Fig 3.5 with Platinum as working electrode and Mg foil as counter and reference demonstrates reversible Mg deposition/stripping. Coulombic efficiency measurements conducted over a perion of 50 cycles (inset Fig 3.4a) shows respectable initial coulombic efficiency of around 89% at its peak and declined to 80% over the course of 50 cycles. This might indicate to a possible presence of slight impurities from the synthesis process and can be mitigated by a better crystallization/ cleanup process. Excellent anodic (electrochemical oxidation) stability on a variety of metal working electrodes including platinum (Pt), gold (Au), glassy carbon (GC), nickel (Ni), 316 stainless steel (SS) and aluminum (Al). Oxidative onset occurs at around 3.5 V vs Mg^{0/2+} on all current collectors as shown in Fig. 3.5, which is at the solvents oxidative stability limit. In other words, like $Mg(CB_{11}H_{12})_2$ the solvent in $Mg(CB_9H_{10})_2$ is oxidized before the carborane anion.



Figure 3. 4 Selected CV curves of Magnesium deposition-stripping for 0.45M $Mg(CB_9H_{10})_2$ in G4 (inset- The coulombic efficiency of 0.45M $Mg(CB_9H_{10})_2$ in G4 with respect to cycle number)



Figure 3. 5 First CV scan of 0.45M $Mg(CB_9H_{10})_2$ in G4 on various WE's at 20mV s⁻¹ (inset – Enlargement of 2.0 to 4.5V region of the anodic scan depicting the oxidative onset potentials).

We next sought to test the electrolyte with a working cathode material in Mg battery. Due to the limitation of suitable electrolytes, the only reliable cathode material yet discovered for such applications is the Chevrel Phase $Mo_6S_8^{7}$. Coin cell Mg-ion battery performance was demonstrated with Mg anode and Mo_6S_8 cathode using 0.45 M Mg(CB₉H₁₀)₂ in G4 as the electrolyte. The prepared cells were cycled at a current density of 12.9 mA g^{-1} (0.1C). Initial discharge capacity of 93 mAh g⁻¹ was achieved in the first discharge, but the capacity of the following cycles decreases to approximately 40 mAh g⁻¹ (Fig 3.6). While the observed performance of this Mg/Mo₆S₈ battery is slightly lower than the analogous cell utilizing $Mg(CB_{11}H_{12})_2$ as an electrolyte, these results serve as proof of principle that smaller carborane anions are viable alternatives. Furthermore, while the mechanism of the irreversible capacity and the capacity fade is currently under investigation, it is conceivable that chemical modifications to the tunable cluster's surface might lead to improved performance. Importantly, one must realize that cathode materials other than Mo_6S_8 materials may behave completely different, thus $Mg(CB_9H_{10})_2$ would be a good candidate to include in any screens of novel high capacity/voltage cathode materials being developed.



Figure 3. 6 Charge-discharge profiles of selected cycles of a Mg-ion cell with 0.45M $Mg(CB_9H_{10})_2$ in G4 electrolyte and chevrel phase Mo6S8 cathode (inset – cycle stability of Mg-ion cells for a span of 30 cycles).

3.4 Conclusion

This chapter introduces a new paradigm in the development of Mg batteries, by showing that *closo*-carborane anions having less than 12 vertices are enabling electrolytes. These 10-vertex anions are less expensive to produce than their larger cousins and thus should be more amenable to commercialization if high capacity secondary Mg batteries are realized. Reversible cycling behavior was obtained for this newly synthesized electrolyte. More work can be done by creating a library of clusters with different carborane anions to see the viability as a Mg-ion electrolyte. Better crystallization process may help in mitigating the dip in coulombic efficiency that has been observed. Deposition experiments and surface characterization as seen in Chapter 2 can also be done to further understand the reaction at the electrode/electrolyte interphase.

Reference

- (1)Noorden, R. Van. A Better Battery. Nature 2014, 507, 26–28.
- (2)Gregory, T. D.; Hoffman, R. J.; Winterton, R. C. Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. *J. Electrochem. Soc.* 1990.
- (3)Mohtadi, R.; Mizuno, F. Magnesium Batteries: Current State of the Art, Issues and Future Perspectives. *Beilstein J. Nanotechnol.* 2014, *5* (1), 1291–1311.
- (4)Muldoon, J.; Bucur, C. B.; Oliver, A. G.; Sugimoto, T.; Matsui, M.; Kim, H. S.; Allred, G. D.; Zajicek, J.; Kotani, Y. Electrolyte Roadblocks to a Magnesium Rechargeable Battery. *Energy Environ. Sci.* 2012, 5 (3), 5941–5950.
- (5)Guo, Y.; Zhang, F.; Yang, J.; Wang, F.; NuLi, Y.; Hirano, S. Boron-Based Electrolyte Solutions with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. *Energy Environ. Sci.* 2012, 5, 9100–9106.
- (6)Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S. J. Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angew. Chemie Int. Ed.* 2012, *51* (39), 9780–9783.
- (7)Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E. Prototype Systems for Rechargeable Magnesium Batteries. *Nature* 2000.
- (8) Aurbach, D.; Schechter, A.; Moshkovich, M.; Cohen, Y. On the Mechanisms of Reversible Magnesium Deposition Processes. *J. Electrochem. Soc.* 2001.
- (9) Aurbach, D.; Gofer, Y.; Lu, Z.; Schechter, A.; Chusid, O.; Gizbar, H.;Cohen, Y.; Ashkenazi, V.; Moshkovich, M.; Turgeman, R.; Levi, E., A short review on the comparison between Li battery systems and rechargeable magnesium battery technology, *J. Power Sources*. 2001, 97, 28.
- (10)Aurbach, D.; Gizbar, H.; Schechter, A.; Chusid, O.; Gottlieb, H. E.;Gofer, Y.; Goldberg, I., Electrolyte solutions for rechargeable magnesium batteries based on organomagnesium chloroaluminate complexes., *J. Electrochem. Soc.* 2002, 149, A115.
- (11)McArthur, S.G.; Geng, L.X.; Guo, J.C.; Lavallo, V. Cation Reduction and Comproportionation as Novel Strategies to Produce High Voltage, Halide Free,

Carborane Based Electrolytes for Rechargeable Mg Batteries. *Inorg. Chem. Front.* 2015, 12, 1101–1104.

- (12)Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E.G.; Sevryugina, Y. V. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew. Chem. Int. Ed.* 2015, 54, 7900–7904.
- (13)Messina, M. S.; Axtell, J. C.; Wang, Y.; Chong, P.; Wixtrom, A. I.; Kirlikovali, K. O.; Upton, B. M.; Hunter, B. M.; Shafaat, O. S.; Khan, S. I.; et al. Visible-Light-Induced Olefin Activation Using 3D Aromatic Boron-Rich Cluster Photooxidants. *J. Am. Chem. Soc.* 2016, *138* (22), 6952–6955.
- (14) Douvris, C.; Michl, J. Update 1 of: Chemistry of the Carba- *Closo* Dodecaborate(-) Anion, CB ₁₁ H ₁₂⁻. *Chem. Rev.* 2013, *113* (10), PR179-PR233.
- (15)Boeré, R. T.; Bolli, C.; Finze, M.; Himmelspach, A.; Knapp, C.; Roemmele, T. L. Quantum-Chemical and Electrochemical Investigation of the Electrochemical Windows of Halogenated Carborate Anions. *Chem. - A Eur. J.* 2013, *19* (5), 1784– 1795.
- (16)Kim, H. S.; Arthur, T. S.; Allred, G. D.; Zajicek, J.; Newman, J. G.;Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J., Structure and compatibility of a magnesium electrolyte with a sulphur cathode. *Nat. Commun.* 2011, 2, 427.
- (17) Zhao-Karger, Z.; Zhao, X.; Fuhr, O.; Fichtner, M., Bisamide based nonnucleophilic electrolytes for rechargeable magnesium batteries, *RSC Adv.* 2013, 3,16330.
- (18) Vinayan, B. P.; Zhao-Karger, Z.; Diemant, T.; Chakravadhanula, V. S. K.; Schwarzburger, N. I.; Cambaz, M. A.; Behm, R. J.; Kübel, C.; Fichtner, M. Performance Study of Magnesium-Sulfur Battery Using a Graphene Based Sulfur Composite Cathode Electrode and a Non-Nucleophilic Mg Electrolyte. *Nanoscale* 2016, 8 (6), 3296–3306.
- (19) Zhao-Karger, Z.; Zhao, X.; Wang, D.; Diemant, T.; Behm, R. J.; Fichtner, M. Performance Improvement of Magnesium Sulfur Batteries with Modified Non-Nucleophilic Electrolytes. *Adv. Energy Mater.* 2015, *5* (3), 1–9.
- (20) Li, W.; Cheng, S.; Wang, J.; Qiu, Y.; Zheng, Z.; Lin, H.; Nanda, S.; Ma, Q.; Xu, Y.; Ye, F.; et al. Synthesis, Crystal Structure, and Electrochemical Properties of a Simple Magnesium Electrolyte for Magnesium/Sulfur Batteries. *Angew. Chemie Int. Ed.* 2016, *55* (22), 6406–6410.

- (21)Novák, P.; Desilvestro, J. Electrochemical Insertion of Magnesium in Metal Oxides and Sulfides from Aprotic Electrolytes. *J. Electrochem. Soc.* 1993, *140* (1), 140–144.
- (22) Sa, N.; Wang, H.; Proffit, D. L.; Lipson, A. L.; Key, B.; Liu, M.; Feng, Z.; Fister, T. T.; Ren, Y.; Sun, C. J.; Vaughey, J. T.; Fenter, P. A.; Persson, K. A.; Burrell, A. K. Is Alpha-V2O5 a Cathode Material for Mg Insertion Batteries? *J. Power Sources*. 2016, *323*, 44–50.
- (23)Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* 2017.
- (24) Knoth, W. H. 1-B₉H₉CH⁻ and B₁₁H₁₁CH⁻. *J. Am. Chem. Soc.* 1967, 89 (5), 1274–1275.
- (25) B. Brellochs, J. Bac'kovsky', B. S'ti'br, T. Jeli'nek, J. Holub, M. Bakardjiev, D. Hnyk, M. Hofmann, I. Ci'sar'ova', B. Wrackmeyer, *Eur. J. Inorg. Chem.* 2004 3605.
- (26) B. Ringstrand, D. Bateman, R. K. Shoemaker and Z. Janous'ek, *Collect. Czech. Chem. Commun.*, 2009, 74, 419–431.
- (27)Wiersema, R. J.; Hawthorne, M. F. Electrochemistry and Boron-11 Nuclear Magnetic Resonance Spectra of Monocarbon Carboranes. *Inorg. Chem.* 1973, *12* (4), 785–788.

Chapter 4: Electrochemical Magnesium-Sulfur Reactions in Magnesium Monocarborane Electrolyte

4.1 Introduction

With rise in technological advances in the current society, there has been vast increase in energy demands and decreasing energy resources like coal and petroleum., knowledge of lasting effects of these resources on the environment and individual health has motivated researchers to investigate alternate energy resources that could battle this ever-rising energy demand tide. The idea is for renewable energy sources like solar or wind to compliment and eventually replace current commercial energy sources. Due to the irregular energy production nature of these sources i.e. non-windy times with wind and cloudy days with solar, there is a dire need of an efficient energy storage device capable of storing the energy produced to utilize at the time of need. Concerns over fuel emissions have also driven consumer interests into hybrid and electric vehicles. To tackle all these avenues in energy demand, there is a dire need of a low cost high energy density energy storage system. Batteries are electrochemical energy storage devices that provides a current over a period at a voltage as a response to the redox reaction that is taking place inside the electrochemical cell. Rechargeable batteries are batteries where the redox reaction can be reversed by applying an external current. Chapter 1 of this thesis document covers an array of rechargeable battery systems that has been commercialized. Although batteries are a simple concept their slow development can be directed towards the lack of suitable/pairable materials and the inability to understand and control the complexities of the redox reaction that drives them ¹. Lithium-ion batteries (LIB's) is currently at the pole position of high

energy density electrochemical devices. The first LIB was developed by Goodenough² and later by Sony in 1990³ geared towards commercialization. These LIB's possess high operating voltage around 3.6V vs Li and relatively high capacity for both anode (360 mAh g⁻¹) and cathode (140 mAh g⁻¹). The LiCoO₂ can only allow intercaltion/deintercalation upto 50% of Li⁺ ions while maintaining a stable structure ². Although LIB's brought forwards a technological revolution in the modern world by being the backbone of technologies involving hand held electronics, electric vehicles and multitudes of other technologies. After almost three decades after its inception the LIB technology seems to have hit a stagnation point in terms achievable capacity, the energy density of current LIB's is still 1/10th to that of gasoline. The safety concerns regarding the use of toxic solvents and dendritic formation which is amplified if Li metal is used and the use of high cost cathode materials like cobalt as cobalt is significantly higher priced than other transitional metals ⁴ and is also toxic. Hence, there is a lot of focus by the current electrochemical community to look beyond LIB's for fresh pastures in the development of secondary batteries. One of such pastures include use of metals with multivalent ions like Magnesium (Mg), Aluminum (Al) instead of the monovalent Lithium (Li) as a metal anode. Mg metal possess immense potential to be a viable anode material as it boasts high volumetric capacity, 3832 mAh cm⁻³ as compared 837 mAh cm⁻³ by its commercial LIB counterpart graphite or 2061 mAh cm⁻³ by Li metal. The high abundance (2000 times than Li) making the metal 1/25th the cost of Li and the environmental benignity of the metal is also a huge boost towards looking into this material. Mg metal cannot compete with Li metal in terms gravimetric capacity, 2205 mAh g⁻¹ vs 3862 mAh g⁻¹ for Li. Li also possess a higher redox

potential of - 3.0 V vs Standard Hydrogen Electrode (SHE) compared -2.3V vs SHE by Mg. However, commercialization of Li metal as anode for Li metal have been hindered due to the safety concerns attached to the Li metal during charge/discharge process of the battery. Li metal tends to form needle like dendritic structures during the charge process especially at higher rates which could lead to short circuit and thermal runaway. In direct contrast it has been well documented that Mg anode is not plagued by dendrite formation and is free of such safety concerns ⁵. However, several challenges hamper the commercialization of Mg anode chemistry. The lack of practical electrolytes and cathode materials paired with sluggish kinetics not only makes Mg a weak candidate to replace LIB's but also far from practical usage. The concerns regarding the different electrolyte systems were discussed in Chapter 1 and 2 of this document. This chapter will focus on in identifying the right cathode material of Mg-ion chemistry. Gregory ⁶ investigated several transition metal oxides and sulfides, and borides as a contender for reversible Mg²⁺ intercalation. The slow kinetics of the diffusion of Mg²⁺ through solid state and the reactive nature of the Mg metal makes for an arduous task to find ideal candidates that can be strong contender to provide a high energy density secondary Mg-ion battery. Intercalation of Mg²⁺ ions into Chevrel phase Mo₆S₈ demonstrated by Aurbach ⁷⁻¹⁰ in 2000 ⁷ was the first breakthrough on reversible Mg-ion batteries from the cathode front. A multitude of cathode materials involving intercalation chemistry have been studied. Materials like V₂O₅ ^{11,12}, TiS₂^{13,14}, MoO₃¹⁵, MnO₂¹⁶⁻¹⁸ and poly anions like MnSiO₄¹⁹ and FeSiO₄²⁰. Prospects of these materials are thoroughly discussed in Chapter 1 and is also shown on Table 4.1. but as described in Chapter 1, we believe the ideal cathode material of future Mg-ion chemistry is Sulfur. The conversion of Sulfur to MgS provides a theoretical capacity of 1671 mAh g⁻ ¹ and energy density of 3200 Wh L⁻¹ compared Li-S batteries that can provide 2800 Wh L⁻ ¹ (Li metal anode) or 1100 Wh L⁻¹ for graphite anode. The first Mg-S batteries were proposed by Muldoon²¹, followed by Fichtner and coworkers²²⁻²⁴ using the Hauser base electrolytes described in Chapter 1. Mg-S cells were also reported for other electrolyte systems like MACC ²⁵, Mg(TFSI)₂-MgCl₂ ^{26,27}. Although all these cells showed Mg-S conversion reaction and compatibility with Sulfur. The capacity fade from cycle to cycle due to the polysulfide shuttle process, low coulombic efficiency, and low operational voltage limits these Mg-S systems from being the next high energy density Mg-ion batteries. We believe that magnesium monocarborane $(Mg(CB_{11}H_{12})_2)$ electrolyte independently developed by Tutusaus et.al²⁸ and Mc Arthur et.al²⁹ could be the best electrolyte candidate for Mg-S batteries. The $(HCB_{11}H_{11})^{-1}$ ion is one of the most stable anions known to the chemistry world ²⁹. Derivatives of this anion cluster have been used either spectator anions for reactive molecular species ³⁰ or as ligand substituents ³¹. The high oxidative stability close to 4V vs Mg with respect to most metals (Al, SS,Ni,C) and non-reactive nature of the anion should make this electrolyte system a perfect candidate for high energy density Mg-S battery system.

	Capacity achieved		
Cathode	(Theoretical	Voltage	
Material	capacity) (mAh g ⁻¹)	(V vs Mg)	Notes
			>2000 cycles. Full capacity
			achieved when cycling at 60
Mo_6S_8	70 (128)	1.1	°C).
			Cycled at 60 °C. Significant
Layered - TiS ₂	20 (260)	< 0.75	capacity fade.
			Using the All-Phenyl Complex
			electrolyte. 90 mAh g ⁻¹ when
			using Mg(AlCl ₂ BuEt) ₂
Spinel – TiS_2	200 (260)	1.2	electrolyte.
			Poor diffusion kinetics, aided by
	130 as a powder, 250		formation of gels (aero- or xero-
Ortho-V ₂ O ₅	as a gel (295)	~3.0) or high temperatures.
			Tunnel structure. Significant
			capacity loss due to conversion
α -MnO ₂	~100 (308)	<2.25	to MgO and Mn ²⁺ dissolutions.
			Capacity achieved dependent on
			electrolyte. "Wet" electrolytes
δ -MnO ₂			give greater capacities, proton
(Birnessite)	Up to 230 (308)	~2.8	involvement demonstrated.
			Significant capacities only
	150 in aqueous	5	achieved in aqueous
	electrolytes, 35 in	L	electrolytes. Mg intercalation
Mn2O ₄	non-aqueous (308)	2.5 - 3.0	proven even in aqueous system
			Cell life of 5 cycle in non-
FeSiO ₄	330 (362)	~2.5	aqueous electrolytes.
			Low current densities used. 80
MnSiO ₄	240 for sol-gel (364)	1.6 and 1.1	mAh g ⁻¹ as powder.

Table 4.1 List of commercial cathode materials

4.2 Experimental Methods

4.2.1 Synthesis of Sulfur-Carbon composite

80 wt% of Sulfur was mixed with 20 wt% of the Integrated Ketjen Black (IKB) carbon and thoroughly mixed in mortar and pestle until the yellow of the sulfur was visually integrated with the IKB. The powder was then transferred to a small vial under a hood where carbon disulfide (CS_2) was slowly added into the powder enough to completely wet and drown the powdered mixture. The CS₂ dissolves the sulfur and thoroughly mixes with the carbon. The vial was left overnight on hot plate at 60 °C for drying. The resulting mixture was then sealed under vacuum in a glass tube. And heated at 155 °C at a heating rate of 5 °C min⁻¹ for 10 hours. The resulting sulfur- carbon composite was used to make the IKB-S electrodes in this chapter. Synthesis of CF10-S composite material was in accordance to the publication by Fu et.al ³² where the 1:1 mixture of Sulfur and the carbon fiber (CF10) purchased from Kuraray Chemical Co., Japan was mixed, sealed, heated as the procedure established for IKB-S composite. The only difference being after the initial heating were the sulfur melts and enters the pores of CF10 carbon, the composite is then transferred into a ceramic boat and heated at 200 °C in flowing argon for 8 hours to remove the sulfur that has been deposited on the surface of CF10. Unlike IKB-S composite, CF10-S composite does not have any sulfur content on the surface and is only limited to inside the pores.

4.2.2 Synthesis of 0.75M Mg(CB11H12)2 & 0.5M Mg(TFSI)2 in G4

The electrolyte synthesis is exactly same as mentioned in Chapter 2. Tetraethylene glycol dimethyl ether (G4) (>99%, Sigma-Aldrich) was distilled over sodium metal under inert conditions on the Schlenk-line and stored with molecular sieves until electrolyte solution was mixed. The preparation of the electrolyte was conducted inside the Ar-filled glovebox. Moisture content of G4 and the electrolytes were measured with Karl Fischer titrator. All manipulations were carried out using standard Schlenk or glovebox techniques under a nitrogen or argon atmosphere unless otherwise stated. Tetrahydrofuran (THF) was distilled from a solvent still over potassium metal and refluxed for several days. Cs(CB₁₁H₁₂), was prepared following a procedure from Reed et al. ³⁰ Following recrystallizations, the trimethylammonium salt (HNMe₃⁺) (HCB₁₁H₁₁)⁻ was obtained from dissolution of $C_{S}(CB_{11}H_{12})$ in hot water followed by addition of 1.0 equiv. trimethylamine hydrochloride to yield a white powder. (HNMe₃⁺) (HCB₁₁H₁₁)⁻ (2.0 g, 10.3 mmol) was added to a suspension of Mg powder (4.0 g, 165 mmol) in a minimal amount of THF (5mL) and the resulting suspension was stirred for 1 hour. After 1-hour, additional THF (30mL) was added and the suspension was left to stir for 24 hours. The THF solution was then filtered through a medium porosity fritted funnel. The collected precipitate of white powder and excess magnesium was washed with 1,2-dimethoxyethane (DME), dissolving the white powder of the collected precipitate. Unreacted magnesium powder was collected and reused. The DME solvent was removed under high vacuum, resulting in compound $Mg(CB_{11}H_{12})_2$ as a white powder in 91% yield (5.44 g, 9.37 mmol) (Note: Mg^{2+} counter cations contain 3 coordinated DME molecules).

4.2.3 Synthesis of Magnesium Sulfide

Magnesium Sulfide (MgS) was synthesized via solid state heating of stoichiometric mixture of Mg and S. Mg powder (Alfa Aesar) was activated after the process of ballmilling two times for 30 minutes with 10 minutes break in between. The Mg powder was then transferred into a vial where vacuum was pulled while stirring the powder overnight. The activated Mg powder was then mixed with Sulfur at a 1:1 ratio in a mortar and pestle. Then was vacuum sealed in a quartz tube. The sealed quartz tube was then moved into a muffle furnace and was heated to 700 °C at a rate of 5 °C min⁻¹ for 80 hours. MgS is very sensitive to air, most steps were conducted in a Ar filled glovebox.

4.2.4 Electrochemical Measurements

Electrodes for both IKB-S and CF10-S was comprised of 80 wt % of the sulfur-carbon composite, 20 wt% carbon black (Super P) and 10 wt% of polyvinylpyrrolidone (PVP) (Sigma-Aldrich) binder in N-methyl-2pyrrolidone (NMP) solvent. This ingredient mixture was mixed in a ball mill for 20 minutes 3 times with ten-minute breaks after each run. The resulting slurry was then pasted on aluminum foil (99.45%, Alfa Aesar). The electrodes were dried overnight under a hood then transferred to a vacuum oven operating at 50 °C and dried for 24 hours to remove all the NMP solvent from the electrode. CR 2032 cells were made for charge/discharge experiments with the prepared cathodes. A 6mm diameter cathode (IKB-S, CF10-S) was punched out and placed in the base of the coin cell casing. 30 μ l of the synthesized electrolyte was pipetted onto the cathode. A polypropelene separator was over the cathode and an additional 20 μ l of electrolyte was added (total of 50 μ l) to sufficiently wet the separator. The Mg foil (100 μ m thick, MTI) was polished

with 1200 and 2500 grade sand papers inside the glovebox and then washed with anhydrous G4 before use. 6mm diameter of polished Mg metal discs where punched out and placed over the wet separator. The cell was then filled with a spacer and a washer and capped with the top cap. The cell was hydraulically pressed to seal the cell. Charge/Discharge experiments were conducted with 2032 cells on an Arbin cycler. The three-electrode discharge was conducted in a bob cell with rectangular pieces of the IKB-S of width of 5mm as working electrode and polished Mg foil as counter and reference.

4.2.5 Material Characterization

To perform the X-ray photoelectron spectroscopy (XPS), samples were transferred from the glovevbox via sealed stainless steel transfer tubes to the XPS facility. XPS experiments were conducted with a Kratos Axis Supra with a dual anode Al/Ag monochromatic X-ray source (280 W). The samples were transferred into the analysis chamber via the integrated glovebox filled with inert gas. The crystal structure of the synthesized MgS was confirmed by X-ray powder diffraction (XRD, PANalytical Empyrean) analysis. UV-vis spectroscopy (Horiba Aqualog) was conducted on the discharged electrolytes after the three electrode discharge. Electrolye samples where diluted with G4 solvent and pipetted into quartz cells which were sealed with a cap and secured by wrapping with parafilm to avoid introduction of air, moisture into the system with the added insentive to avoid spillage.

4.3 Results and Discussion

4.3.1 Electrochemical Activity of IKB-S Cathode

2032 Coin cells with IKB-S composite material as cathode and Mg as anode were used to conduct charge/discharge experiments. Coin cells for both electrolytes $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ were cycled at a constant current at a rate of C/100. Where is C having to deal with the rate of charge/discharge need to achieve the theoretical capacity of the sulfur. Theoretical capacity can be calculated by the following equation (1)

$$Q = \frac{nF*1000}{Mw*3600}$$
(1)

Where Q is the theoretical capacity of the material in terms amount of charge per unit mass/volume (gravimetric/volumetric), n is the number of electrons transferred, F is the Faraday Constant and Mw is the molecular weight of the material. The numerical fraction are just constants to convert the calculations to mAh g⁻¹. So, at C/100 the cell is expected to take 100 hours during discharge and charge to achieve the theoretical capacity Q. Current I can be calculated by the following equation (2), where m is the mass of active material and in a given time t

$$I = \frac{Q \ast m}{t} \tag{2}$$

Fig 4.1 shows the discharge/charge profile of IKB-S for $Mg(CB_{11}H_{12})_2$ (top) and $Mg(TFSI)_2$ (bottom) at C/100. Cell containing $Mg(CB_{11}H_{12})_2$ clearly shows distinct discharge profile with two distinct plateaus at 1.4 V and 0.6 V. the cell shows a discharge capacity of around 680 mAh g⁻¹. Studies done by Zhao-Karger also shows a similar two distinct discharge plateaus; Although, at different voltages describes the reaction as a twostep process where 1) there is fast solid-liquid reduction process from solid phase S₈ to

high-order polysulfides like MgS₈, MgS₆ and MgS₄. That has high solubility in the ether solvent and exists solely in the liquid phase. 2) slow liquid-solid reduction from higher order poly sulfides to lower order polysulfides like MgS₂ and MgS. Which have little to no solubility. The charge profile shows the overcharging behavior attributed to the polysulfide shuttle mechanism which was also seen by Muldoon in his report ²¹. Polysulfide shuttle reaction can be attributed to similar reaction that is prevalent in Li-S cells. The poly sulfide shuttle happens when the higher-order poly sulfides formed during the charge process diffuses to the Mg electrode and reacts to form lower-order polysulfides and they in-turn diffuses back to the cathode to form higher-order polysulfides, creating this shuttle mechanism of going back and forth³³. This mechanism shows up in the charge profile as overcharging behavior although this mechanism does not contribute to the actual charge capacity of the cell. Mg(TFSI)₂ on the other hand did not show any discharge profile due to the extremely high overpotential associated with the electrolyte which was discussed in Chapter 2 of this thesis. Moreover, the cell showed corrosion behavior during the charge behavior of the cell indicating the decomposition of the electrolyte due to the presence of sulfur at higher voltages. We also investigated charge/discharge profiles with a charge protocol first to confirm the presence of the shuttle process. The idea behind the experiments was to see if we see similar shuttle behavior if there is no higher order polysulfides available during first charge. Fig 4.2 shows charge/discharge profiles of IKB-S for $Mg(CB_{11}H_{12})_2$ (top) and $Mg(TFSI)_2$ (bottom) at C/100 with a charge first protocol. The Mg(CB₁₁H₁₂)₂ cell as expected did not show the shuttle behavior during the 1st charge profile but showed the same overcharging behavior noted earlier during the second charge profile confirming our suspicions. Cells with Mg(TFSI)₂ electrolyte on the other hand showed similar corrosion like behavior even in the initial charging stage showing the probable instability of the electrolyte with respect to the sulfur electrode. To further understand the reaction during the discharge process three electrode chronopotentiometry discharge was used with IKB-S as working electrode (W.E) and Mg foil as counter (CE) and reference (RE) for both the electrolytes.



Figure 4. 1 Charge/Discharge profile for the IKB-S cathode material at a rate of C/100 with discharge to 0.3V as the first step for $Mg(CB_{11}H_{12})_2$ (top) & $Mg(TFSI)_2$ (bottom)



Figure 4. 2 Charge/Discharge profile for the IKB-S cathode material at a rate of C/100 with charge to 2.8V as the first step for $Mg(CB_{11}H_{12})_2$ (top) & $Mg(TFSI)_2$ (bottom)

4.3.2 Three electrode Discharge of IKB-S Cathode and Characterization

Having a dedicated reference electrode that does not contribute to the electrochemical reaction would provide accurate voltage measurements for the discharge profile. The three electrode chronopotentiometry experiments were done at C rate of C/200. Thick WE with about 7-8 mg cm⁻² of the electrode material was immersed in both the electrolytes in a bob cell with polished Mg foil either side as CE and RE. Slow C-rate for the experiment was to ensure good conversion of the IKB-S at the working electrode and not get skipped due to the overpotential of the system (mainly with Mg(TFSI)₂). Fig 4.3 shows the chronopotentiometry curves of IKB-S for both $Mg(CB_{11}H_{12})_2$ (red) and $Mg(TFSI)_2$ (black) at C/200. The Mg(CB₁₁H₁₂)₂ shows two plateaus unlike the profile from Fig 4.1 the first plateau at 1.4V vs Mg seems to be much longer than the second plateau around 0.8 V vs Mg indicating the dissolution of higher polysulfides in excess electrolyte which can be corroborated by the UV-vis measurement of the electrolyte after the discharge shown in Fig 4.4 (top) that shows significant high intensity peaks at 240-250nm which corresponds to S_8 , 300nm which corresponds to S_6^{2-} and 400 nm that corresponds to S_4^{2-} , the numbers are consistent with polysulfide dissolution studied by Bieker³⁴. Zhao-Karger²⁴ also noted similar data where he noted that the dissolution of elemental sulfur is more dominant than that of other polysulfides which could be attributed to the low capacity due to the loss of active material. Interestingly, $Mg(TFSI)_2$ shows a discharge profile unlike the data from Fig 4.1 where no discharge profile was seen due to the high overpotential. Although, the discharge profile of $Mg(TFSI)_2$ is quite different as it only showed one plateau at around 0.8 V. the OCP was considerably lower for the Mg(TFSI)₂, little over 1.0V vs Mg which

is significantly lower than the first discharge plateau for the $Mg(CB_{11}H_{12})_2$ electrolyte. The UV-vis data in Fig 4.4 (b) shows similar data to that of $Mg(CB_{11}H_{12})_2$ showing increased S_8 and higher order polysulfide dissolution which probably results in the low capacity. To understand the cathode surface before and after discharge XPS was conducted on the IKB-S electrode for both the electrolytes. Fig 4.5 shows the deconvoluted S2p spectra of the IKB-S electrode a) pristine electrode, b) after C/200 discharge for $Mg(CB_{11}H_{12})_2$ electrolyte, c) after C/200 discharge for Mg(TFSI)₂ electrolyte. S2p peaks comes as twin peaks where S2p $\frac{1}{2}$ is 1.16eV apart from S2p $\frac{3}{2}$ at around half the size. We can see form the XPS spectra of the pristine electrode there is a presence of sulfate as an impurity on the electrode along with the S_8 peaks at around 164 eV for S2p 3/2. The deconvoluted S2p spectra of the W.E after discharge at C/200 for $Mg(CB_{11}H_{12})_2$ shows heavy presence of the converted product after reduction of the sulfur electrode MgS at around 161.5 eV for the S_{2p} 3/2. along with unreacted sulfur and sulfate impurity. All this data unequivocally confirms the compatibility of sulfur with $Mg(CB_{11}H_{12})_2$ and can undergo the conversion reaction at the sulfur electrode. Although, XPS data for the Mg(TFSI)₂ electrolyte showed same peaks as the $Mg(CB_{11}H_{12})_2$ sample, the MgS peaks were overshadowed by the sulfate peak which is not only available in the pristine electrode as an impurity it also heavily present in the excess electrolyte that was in contact with the electrode. Efforts taken to eliminate/diminish this sulfate impurity peak by etching via using depth profile function in the XPS turned unfruitful as the sulfate peak got reduced so did the MgS peak indicating that the IKB-S material deeper into the electrode surface did not react during the discharge process. MgS particle was synthesized via the solid-state heating at extremely high temperature. XRD data shown in Fig 4.6 shows evidence of successful synthesis of MgS. The idea is to make electrodes with MgS as active material and re-do the surface/electrolyte study for the charge protocol to see if the polysulfide shuttle is as prevalent if there is no higher polysulfides dissolved in the electrolyte at the beginning of charge process.



Figure 4. 3 Three electrode chronopotentiometry discharge profile of the IKB-S cathode material at a C-rate of C/200 for $Mg(CB_{11}H_{12})_2 \& Mg(TFSI)_2$


Figure 4. 4 UV-vis data profile of $Mg(CB_{11}H_{12})_2$ (top) & $Mg(TFSI)_2$ (bottom) after discharge at a C-rate of C/200 with IKB-S as working electrode



Figure 4. 5 Deconvoluted S2p XPS profiles for IKB-S electrode, Pristine (top), after discharge in $Mg(CB_{11}H_{12})_2$ (middle), after discharge in $Mg(TFSI)_2$ (bottom)



Figure 4. 6 XRD profile of synthesized MgS (balck) and MgS reference (red)

4.3.3 Electrochemical Activity of CF10-S Cathode

From, Fig 4.1 charge/discharge profile we can see that the main issue plaguing a viable Mg-S cell for $Mg(CB_{11}H_{12})_2$ electrolyte is the overcharging feature that is attributed towards the polysulfide shuttle mechanism. This process is inhibiting the conversion of MgS back to sulfur during the charge process, making the cell irreversible. As described earlier in the chapter the conversion of sulfur reaction happens two steps as the solid sulfur reduces to form higher order polysulfides that is dissolved in the G4 solvent which is further reduced from liquid state to solid state MgS. Researchers believed porous structures could be employed to act as sulfur hosts which in-turn will act as a reservoir as a host for the polysulfides ³⁵. Work done by Fu ³² from our group for Li-S cells envisioned a sulfur host that could restrict the electroactive species inside the pores in solid state. A porous carbon fiber (CF10) with pore sizes between 0.4 - 1.0 nm was chosen, and sulfur was infused, and sulfur deposited was removed by the procedure mentioned in section 4.2.1. After a successful report on controlling the shuttle process via confining the conversion reaction to happen in solid state ³², the idea was to use the same material to see if it can be implemented into Mg-S chemistry. Fig 4.7 shows discharge/charge profiles of the first three cycles of CF10-S composite as cathode material. The first thing to note is unlike IKB-S composite, the CF10-S was able to cycle for more than one discharge and charge. Although, we do see a significant dip in initial capacity with little over 215 mAh g⁻¹. Rather than 2 distinct discharge plateaus we saw in Fig 4.1 we can only see one distinct plateau at 1.25 V. Regrettably, we also see the overcharging feature at the first charge cycle that is indicative of the polysulfide shuttle although, unlike the IKB-S material the CF10-S

composite seems to be reversible. That, explains the capacity fade in subsequent cycles. The reason for the presence of this overcharging feature is currently unknown. One possible avenue is due to presence of sulfur outside the pores (not witnessed in control Li-S cells, we did not see two distinct plateaus indicative of sulfur present on the surface of the electrode). Three electrode experiments described in section 4.3.2 would be able answer the question whether the CF10-S material was able to constrict the reaction in solid state as the color of the electrolyte will change from clear to yellow if polysulfide dissolution takes place and can be detected via UV-vis. Theoretical capacity of sulfur is 1671 mAh g⁻¹, for CF10-S the fact that we see a significantly less capacity is also a point of concern. The low initial capacity could be due to multitude of reason including low accessibility of the cations in large solvents like G4 into the sub nano pores of the carbon matrix due to the large solvation shell. Slow diffusion of the cations into the sub nano pores of the cF10-S pores could also result in low capacity due to the bulky nature of the electrolyte.



Figure 4. 7 Charge/Discharge profile for the CF10-S cathode material at a rate of C/100 with discharge to 0.3V as the first step for $Mg(CB_{11}H_{12})_2$

4.4 Conclusion

In this chapter, we gave a brief overview on different cathode materials that has been employed for Mg-ion systems. Although, a plethora of intercalation materials has been studied, we summarized that only Chevrel phase Mo6S8 came out as the front runner and only realistically viable candidate as an insertion cathode material. The low voltage and relative low capacity disqualifies Mo6S8 as a candidate for high energy density Mg-ion battery that could compete with Li-ion. We realized conversion cathode like sulfur with high theoretical capacity was the ideal candidate for the $Mg(CB_{11}H_{12})_2$ electrolyte. Initial charge/discharge profiles showed sulfur compatibility with the Mg(CB₁₁H₁₂)₂ electrolyte and promising discharge profile with a capacity close to 680 mAh g⁻¹. Although, the overcharging behavior indicative of polysulfide shuttle mechanism continues to be a road block. To understand the conversion reaction mechanism three electrode experiments were conducted where the cell was discharged at extremely slow rates and resulting electrolyte and electrode surface was characterized using UV-vis and XPS respectively which showed dissolution of higher order polysulfides including S₈ which is indicative of the initial capacity loss. XPS showed tangible proof of the conversion reaction on the cathodes by the presence of MgS. Strategies to study the charging mechanism for the cell was also proposed via the synthesis of MgS. Inspired by the work by Fu³², nano confined sulfur composite (CF10-S) was also used. Although, reversible cycling was achieved presence of the overcharging feature in the charge plateau suggests presence of polysulfide shuttle and initial low capacity of the cell is also matter that needs to be investigated further via three electrode experiments. once fundamental understanding of the reaction mechanism is

understood, we could work with different solvent and solvent mixtures to further relate Mg-S studies to Li-S so that we can understand the mechanism better. We believe, Mg-S cells for the $Mg(CB_{11}H_{12})_2$ electrolyte is a very promising candidate to move Mg-ion battery system forward.

Reference

- Armand, M.; Tarascon, J.-M. Building Better Batteries. *Nature* 2008, 451 (7179), 652–657.
- (2) Mizushima, K.; Jones, P. C.; Goodenough LixCoO2 (0<x<-1): A new cathode material for batteries of high energy density. *Solid State Ionics* 1981, *4*, 171–174.
- (3) Nagaura, T.; Tozawa, K. Lithium Ion Rechargeable Battery. *Prog. Batter. Sol. Cells* 1990, *9*, 209–217.
- (4) The Committee on Climate Change. *Cost and Performance of EV Batteries*; Element Energy Limited, 2012.
- (5) Rong, Z.; Malik, R.; Canepa, P.; Sai Gautam, G.; Liu, M.; Jain, A.; Persson, K.; Ceder, G. Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures. *Chem. Mater.* 2015, 27 (17), 6016–6021.
- (6) Gregory, T. D.; Hoffman, R. J.; Winterton, R. C. Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. *J. Electrochem. Soc.* 1990.
- (7) Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E. Prototype Systems for Rechargeable Magnesium Batteries. *Nature* 2000.
- (8) Aurbach, D.; Schechter, A.; Moshkovich, M.; Cohen, Y. On the Mechanisms of Reversible Magnesium Deposition Processes. *J. Electrochem. Soc.* 2001.
- (9) Aurbach, D.; Gofer, Y.; Lu, Z.; Schechter, A.; Chusid, O.; Gizbar, H.;Cohen, Y.; Ashkenazi, V.; Moshkovich, M.; Turgeman, R.; Levi, E., A short review on the comparison between Li battery systems and rechargeable magnesium battery technology, *J. Power Sources.* 2001, 97, 28.
- (10) Aurbach, D.; Gizbar, H.; Schechter, A.; Chusid, O.; Gottlieb, H. E.;Gofer, Y.; Goldberg, I., Electrolyte solutions for rechargeable magnesium batteries based on organomagnesium chloroaluminate complexes., *J. Electrochem. Soc.* 2002, 149, A115.
- (11) Novák, P.; Desilvestro, J. Electrochemical Insertion of Magnesium in Metal Oxides and Sulfides from Aprotic Electrolytes. J. Electrochem. Soc. 1993, 140 (1), 140–144

- (12) Legagneur, V.; An, Y.; Mosbah, A. LiMBO3(M= Mn, Fe, Co): Synthesis, Crystal Structure and Lithium Deinsertion/insertion Properties. *Solid State Ionics* 2001, *139*, 37–46.
- (13) Amir, N.; Vestfrid, Y.; Chusid, O.; Gofer, Y.; Aurbach, D. Progress in Nonaqueous Magnesium Electrochemistry. *J. Power Sources* 2007, *174* (2), 1234–1240.
- (14) Sa, N.; Wang, H.; Proffit, D. L.; Lipson, A. L.; Key, B.; Liu, M.; Feng, Z.; Fister, T. T.; Ren, Y.; Sun, C. J.; Vaughey, J. T.; Fenter, P. A.; Persson, K. A.; Burrell, A. K. Is Alpha-V2O5 a Cathode Material for Mg Insertion Batteries? *J. Power Sources*. 2016, *323*, 44–50.
- (15) Gershinsky, G.; Yoo, H. D.; Gofer, Y.; Aurbach, D. Electrochemical and Spectroscopic Analysis of Mg(2+) Intercalation into Thin Film Electrodes of Layered Oxides: V2O5 and MoO3. *Langmuir* 2013, 29 (34), 10964–10972.
- (16) Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* 2017.
- (17) Nam, K. W.; Kim, S.; Lee, S.; Salama, M.; Shterenberg, I.; Gofer, Y.; Kim, J.-S.; Yang, E.; Park, C. S.; Kim, J.-S.; Seok-Soo, L.; Chang, W.-S.; Doo, S.-G.; Jo, Y. N.; Jung, Y.; Aurbach, D.; Choi, J. W. The High Performance of Crystal Water Containing Manganese Birnessite Cathodes for Magnesium Batteries. *Nano Lett.* 2015, *15* (6), 4071–4079.
- (18) Knight, J. C.; Therese, S.; Manthiram, A. On the Utility of Spinel Oxide Hosts for Magnesium-Ion Batteries. *ACS Appl. Mater. Interfaces* 2015, 7 (41), 22953–22961.
- (19) Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.; Okado, T.; Huang, Z.-D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.; Kageyama, H.; Uchimoto, Y. High Energy Density Rechargeable Magnesium Battery Using Earth-Abundant and Non-Toxic Elements. *Sci. Rep.* 2014, *4*, 5622.
- (20) Feng, Z.; Yang, J.; NuLi, Y.; Wang, J.; Wang, X.; Wang, Z. Preparation and Electrochemical Study of a New Magnesium Intercalation Material Mg1.03Mn0.97SiO4. *Electrochem. commun.* 2008, *10* (9), 1291–1294.
- (21) Kim, H. S.; Arthur, T. S.; Allred, G. D.; Zajicek, J.; Newman, J. G.; Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J., Structure and compatibility of a magnesium electrolyte with a sulphur cathode. *Nat. Commun.* 2011, 2, 427.

- (22) Zhao-Karger, Z.; Zhao, X.; Fuhr, O.; Fichtner, M., Bisamide based non-nucleophilic electrolytes for rechargeable magnesium batteries, *RSC Adv.* 2013, 3,16330.
- (23) Vinayan, B. P.; Zhao-Karger, Z.; Diemant, T.; Chakravadhanula, V. S. K.; Schwarzburger, N. I.; Cambaz, M. A.; Behm, R. J.; Kübel, C.; Fichtner, M. Performance Study of Magnesium-Sulfur Battery Using a Graphene Based Sulfur Composite Cathode Electrode and a Non-Nucleophilic Mg Electrolyte. *Nanoscale* 2016, 8 (6), 3296–3306.
- (24) Zhao-Karger, Z.; Zhao, X.; Wang, D.; Diemant, T.; Behm, R. J.; Fichtner, M. Performance Improvement of Magnesium Sulfur Batteries with Modified Non-Nucleophilic Electrolytes. *Adv. Energy Mater.* 2015, 5 (3), 1–9.
- (25) Li, W.; Cheng, S.; Wang, J.; Qiu, Y.; Zheng, Z.; Lin, H.; Nanda, S.; Ma, Q.; Xu, Y.; Ye, F.; et al. Synthesis, Crystal Structure, and Electrochemical Properties of a Simple Magnesium Electrolyte for Magnesium/Sulfur Batteries. *Angew. Chemie Int. Ed.* 2016, *55* (22), 6406–6410.
- (26) Gao, T.; Hou, S.; Wang, F.; Ma, Z.; Li, X.; Xu, K.; Wang, C. Reversible S0/MgSxRedox Chemistry in a MgTFSI2/MgCl2/DME Electrolyte for Rechargeable Mg/S Batteries. *Angew. Chemie - Int. Ed.* 2017, *56* (43), 13526–13530.
- (27) Li, X.; Gao, T.; Han, F.; Ma, Z.; Fan, X.; Hou, S.; Eidson, N.; Li, W.; Wang, C. Reducing Mg Anode Overpotential via Ion Conductive Surface Layer Formation by Iodine Additive. *Adv. Energy Mater.* 2018, 8 (7).
- (28) Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E.G.; Sevryugina, Y. V., An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew. Chem., Int. Ed.* 2015, 54, 7900.
- (29)McArthur, S.G.; Geng, L.X.; Guo, J.C.; Lavallo, V., Cation reduction and comproportionation as novel strategies to produce high voltage, halide free, carborane based electrolytes for rechargeable Mg batteries. *Inorg. Chem. Front.*, 2015, 12, 1101.
- (30) Fail, T.; Reed, C. A. H⁺, CH₃⁺, and R₃ Si⁺ Carborane Reagents: When Triflates Fail. 2010, 43 (1), 121–128.
- (31) Estrada, J.; Woen, D. H.; Tham, F. S.; Miyake, G. M.; Lavallo, V. Synthesis and Reactivity of a Zwitterionic Palladium Allyl Complex Supported by a Perchlorinated Carboranyl Phosphine. *Inorg. Chem.* 2015, *54* (11), 5142–5144.

- (32) C. Fu, B.M. Wong, K.N. Bozhilov, J. Guo, Solid State Lithiation-Delithiation of Sulfur in Sub-Nano Confinement: A New Concept for Designing Lithium-Sulfur Batteries *Chemical Science* 2016, *7*, 1224-1232.
- (33) Mikhaylik, Y. V.; Akridge, J. R. Polysulfide Shuttle Study in the Li/S Battery System. *J. Electrochem. Soc.* 2004, *151* (11), A1969.
- (34) Bieker, G.; Wellmann, J.; Kolek, M.; Jalkanen, K.; Winter, M.; Bieker, P. Influence of Cations in Lithium and Magnesium Polysulphide Solutions: Dependence of the Solvent Chemistry. *Phys. Chem. Chem. Phys.* 2017, *19* (18), 11152–11162.
- (35) Ji, X.; Lee, K. T.; Nazar, L. F. A Highly Ordered Nanostructured Carbon-Sulphur Cathode for Lithium-Sulphur Batteries. *Nat. Mater.* 2009, *8* (6), 500–506.

Chapter 5: Conclusion

In the first chapter the concept of Rechargeable batteries was introduced. We moved on from basic concepts to the need of high energy density batteries by using Li-ion batteries as an example. We also concluded that major reform in the field of battery research is necessary to significantly improve the current state of the art LIB's due to its limitations. Mg-ion systems was introduced as a potential candidate for beyond Li high capacity/ high energy density batteries due to its high abundance lack of dendrite formation during deposition and stripping, making it a potential candidate for high energy density cells. A lack of practical electrolytes and cathode materials hamper the commercialization of Mgion cells. Chapter 1 further discussed multiple electrolyte systems that has been reported. Two main cation types comprise most of the Mg-ion electrolyte systems. Namely, "Naked" Mg salts & "Dimer" Mg salts. "Naked" Mg salts makes Mg²⁺ ions surrounded by the solvent molecules as its solvation structure like most simple salts including $Mg(TFSI)_2$ and $Mg(CB_{11}H_{12})_2$. "Dimer" Mg salts solvates as a Dimer cation complex like organhaloaluminates, MACC electrolytes, Hauser base electrolytes etc... forms $Mg_2Cl_3^+$. Although these electrolytes show reversible electrochemical behavior with high coulombic efficiency, presence of Cl₂ in both the cation and anion adversely effects prospects of high energy density cells as the oxidation stability of this electrolyte when it comes to metals like Al, and SS is very low. Also, the nucleophilic nature of most of these electrolytes also makes the electrolyte a bad choice for high capacity conversion cathode material like sulfur. "Naked" Magnesium salts like Mg monocarborane salts was deemed to be the most promising salt for Mg-ion cells due to the high stability of the eakly coordinating anion

under highly reductive conditions. A brief introduction to intercalation and conversion cathodes was also reported in Chapter 1. All the reports show that conversion cathodes like sulfur is the best way to achieve high energy density batteries.

Chapter 2 looked into the interphase between electrode and electrolyte during deposition and stripping of simple "Naked" Mg salts like Mg(TFSI)₂ and Mg(CB₁₁H₁₂)₂. Mg(CB₁₁H₁₂)₂ showed much superior electrochemical activity compared to Mg(TFSI)₂. Surface studies conducted on Mg deposited surfaces for both electrolytes showed a significant difference in the electrode surface layer (SEI) composition. While Mg deposited surface in Mg(CB₁₁H₁₂)₂ did not show any kind of surface layer. Mg deposited on Mg(TFSI)₂ on the other hand showed heavy oxide, sulfide and fluoride layer formations. Polished Mg metal soaked in Mg(TFSI)₂ for 2 weeks showed signs of decomposition reiterating the claims of (TFSI)⁻ being a weak anion prone to self-decomposition. While, Mg(CB₁₁H₁₂)₂ showed no signs of decomposition. The work reported in Chapter 2 shows the promising nature of the monocarborane molecule as a viable electrolyte for Mg-ion battery systems. Multiple studies on different simple non-halogenated Mg salts is the right path to take to understand Mg anode. Electrochemical and interfacial study of Li analogs like PF₆ would be an interesting research topic.

Chapter 3 introduced an alternate carborane cluster as a potential Mg-ion electrolyte with 10 vertices instead of 12. The new cluster was synthesized much faster and was significantly more economic. Electrochemical behavior of the electrolyte showed the new $Mg(CB_9H_{10})_2$ electrolyte as immense potential to be Mg-ion electrolyte. Reversible electrodeposition and stripping was observed along with high oxidative stability close to

4V vs Mg at much lower concentration compared to $Mg(CB_{11}H_{12})_2$. Slightly depleting coulombic efficiency may be due to the impurities present in either the solvent or prepared salt, that can be mitigated by much more rigorous recrystallization process. The electrolyte also showed reversible cycling behavior when paired with Chevrel phase Mo_6S_8 showing an initial capacity of around 90 mAh g⁻¹. Chapter 3 showed we were able to synthesize smaller carborane molecules with less vertices from the traditional 12 vertex cluster and have boast good electrochemical properties.

Chapter 4 we re-introduced different cathode materials for Mg-ion systems we re-iterated our conclusions from chapter 1 stating that sulfur is the most ideal candidate for high energy density Mg-ion battery systems. Charge/discharge profile of the synthesized sulfurcarbon composite showed 2 distinct discharge plateaus providing a capacity of around 700 mAh g⁻¹. An overcharging behavior indicative of the polysulfide shuttle mechanism was observed for the cells during the first charge. Characterization of the electrode and electrolyte via XPS and UV-vis showed massive amounts of higher order polysulfide dissolution leading to the low initial capacity and probable shuttle mechanism. Sub-nano confined sulfur-carbon composites were synthesized to act as polysulfide reservoir and force the conversion reaction to occur inside the sub-nano pores in solid state. Although, charge/ discharge profile shows reversibility the low capacity and the overcharging behavior is still present in the sub-nano confined material. The small pores on the cathode material can act as a barrier for bulky solvent molecules to diffuse through leading to lower capacity. Three electrode experiments with XPS and UV-vis was proposed for the sub nano-confined material to further understand what might have happened with the particle.

MgS was synthesized so as to study the electrochemical conversion reaction from MgS to S in a three-electrode cell without initial polysulfide dissolution in the system, Although, there is long way to go for a commercial Mg-ion battery. Materials like $Mg(CB_{11}H_{12})_2$ along with sulfur as a cathode material shows great promise for the next high capacity/ high energy density battery system.