



MONASH University

In Silico Characterization of Electrolytes for Rechargeable Magnesium Batteries

Vallabh Vasudevan
M.Eng.

A thesis submitted for the degree of Doctor of Philosophy at
Monash University in 2021
Department of Materials Science and Engineering

COPYRIGHT NOTICE

© Vallabh Vasudevan (2021).

I certify that I have made all reasonable efforts to secure copyright permissions for third-party content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

ABSTRACT

Non-aqueous Rechargeable Magnesium batteries (RMBs) represent a safer, cheaper, and more powerful alternative to lithium-ion battery technology. However, at electrode/electrolyte interfaces (called Solid-Electrolyte Interfaces, SEIs), the high charge density of Mg^{2+} ions triggers the formation of ion impermeable deposits. To overcome the stability and reversibility issues caused by SEIs, the electrolytes used must be stable against reductive reactions at the anode/electrolyte interface during charge/discharge cycles in RMBs. Magnesium halide salts are an exciting prospect as durable and high-performance electrolytes for RMBs. By nature of their complex equilibria, these salts exist in solution as a variety of electroactive species (EAS) in equilibrium with counter ions such as AlCl_4^- . The dissertation investigates ion agglomeration and transport of several such EAS in MgCl_2 salts dissolved in ethereal solvents under both equilibrium and operating conditions using large-scale atomistic simulations. An observation was that the solution structures of EAS strongly govern the solute morphology and the presence of clusters strongly characterizes it. Specifically, the isotropic solvation of Mg^{2+} results in slow formation of the bulky cluster, compared with chain-like analogues observed in the Cl-containing EAS such as Mg_2Cl_3^+ , MgCl^+ , and $\text{Mg}_2\text{Cl}_2^{2+}$. The dissertation further illustrates that these clusters can reduce charge-carrying species' diffusivity in the MgCl_2 based electrolyte by at least an order of magnitude. We studied the transport mechanism of the ions in other solvents such as Glyme (DME), Diglyme (G2), Triglyme (G3), and Tetraglyme (G4) to highlight the role of the solvent. The solvent controls ion mobility by restricting the ion diffusion mechanism between the faster displacement diffusion in lighter solvents and the slower void diffusion in heavier solvents. The research, in addition, highlights the effect of ion coverage due to the number of ligand dentate sites on the solvent, which was significant in lighter solvents. The next step was to characterize the role of the anion and the solvent on the ion clustering by comparing weakly and

strongly interacting anions solvated in different solvents. Analysis shows that both the anions and solvents individually control the clustering rates and a combination of the two is always present. The work shows that the solvent control of the clustering mechanism is prominent in heavier solvents, with anions displacing lighter solvents and thus are in the anion control regime. My cluster formation, morphology, and kinetics findings can provide insight into the electrolyte's performance controls and identify the reactive species and electrochemical reaction mechanisms at the anode/electrolyte interface in RMBs.

DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signature:

Print Name: Vallabh Vasudevan

Date: 06-08-21

PUBLICATIONS DURING ENROLMENT

- M. Wang, V. Vasudevan, S. Lin, J. Jasieniak, S. Russo, N. Birbilis and N. V. Medhekar, Molecular mechanisms of thermal instability in hybrid perovskite light absorbers for photovoltaic solar cells. *Journal of Materials Chemistry A* 8, 17765 (2020). DOI: [10.1039/D0TA05356B](https://doi.org/10.1039/D0TA05356B)
- **Vasudevan V.**, Wang M., Yuwono J. A., Jasieniak J., Birbilis N., Medhekar N. V., Ion Agglomeration and Transport in MgCl₂-Based Electrolytes for Rechargeable Magnesium Batteries. *J. Phys. Chem. Lett.* 2019, 10, 24, 7856-786. DOI: [10.1021/acs.jpcllett.9b03023](https://doi.org/10.1021/acs.jpcllett.9b03023)
- Deivanayagam R., Cheng M., Wang M., **Vasudevan V.**, Foroozan T., Medhekar N. V., Shahbazian-Yassar R., Composite Polymer Electrolyte for Highly Cyclable Room-Temperature Solid-State Magnesium Batteries. *ACS Applied Energy Materials* 2019 2 (11), 7980-7990. DOI: [10.1021/acsaem.9b01455](https://doi.org/10.1021/acsaem.9b01455)
- Wang M., Yuwono J. A., **Vasudevan V.**, Birbilis N., Medhekar N. V., Atomistic Mechanisms of Mg Insertion Reactions in Group XIV Anodes for Mg-Ion Batteries. *ACS Appl. Mater. Interfaces*, Jan 2019, 11, 1, 774-783. DOI: [10.1021/acsami.8b17273](https://doi.org/10.1021/acsami.8b17273)

CONFERENCE PRESENTATIONS DURING ENROLMENT

- **Vasudevan V.**, Wang M., Birbilis N., Medhekar N. V., Ion Agglomeration and Transport in MgCl₂-Based Electrolytes for Rechargeable Magnesium Batteries. 2021 Virtual MRS Spring Meeting.

THESIS INCLUDING PUBLISHED WORKS DECLARATION

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original paper published in peer-reviewed journals. The core theme of the thesis is Electrolytes for Magnesium batteries. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the Department of Materials Science and Engineering under the supervision of Nikhil Medhekar.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research

In the case of **Chapter 4** my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status (published, in press, accepted or returned for revision, submitted)	Nature and % of student contribution	Co-author name(s) Nature and % of Co-author's contribution*	Co-author(s), Monash student Y/N*
Chapter 4	Ion Agglomeration and Transport in MgCl_2 -Based Electrolytes for Rechargeable Magnesium Batteries.	published	60%. Concept and collecting data and writing first draft	Mingchao Wang, input into manuscript and draft preparation 15% Jodie Yuwono, input into manuscript 5% Jacek Jasieniak, input into the manuscript, 2% Nick Birbilis, input into manuscript, 3% Nikhil Medhekar, concept, input into manuscript and supervision, 15%	No

I have not renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Student signature: Date: 06-08-21

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor signature: Date: 06-08-21

ACKNOWLEDGMENT

This research was supported by Monash Graduate Scholarship (MGS) and the Monash International Postgraduate Research Scholarship (MIPRS).

I would like to express my sincerest gratitude to my supervisor Nikhil Medhekar. You have been very helpful and accommodating to my various quirks. I must thank you for the freedom you provided me during this PhD and allowing me to explore a lot outside the scope of the original research topic. I am extremely grateful for the support that you provided me when I was at my lowest both physically and mentally. This endeavour has been very smooth and relaxed, and I cannot thank you more for this wonderful opportunity. I would like to also express my thanks for bringing me to Monash from Bombay, through all the administrative hurdles. Once again, Thank you.

To Nick Birbilis, my co-supervisor, thank you, despite your busy schedule, you were always ready to help whenever I had asked you. It was a pleasure to work with you.

One person I would like to highlight specially is Mingchao Wang. You are a good friend and an even better colleague. I have had some fascinating conversations with and have learned a lot from you. You helped me expand the scope of my research interests. You and I joined the group at around the same time, and it made settling into here so much easier. I would also like to thank you for all the help you provided whether it be drives to supermarket or with issues in simulations. I thank you.

Mahdi, Jodie, Abin and Madhav. You have made my time fly so fast. Through all these difficult times you have been great help distracting me just enough that I have able to keep myself grounded and focussed. It was a fun and interesting journey. Thank you for accompanying me on it.

Chutian, Yuefeng, Bernard, Victor, Zhezhong, Yong, Shenghan, Hong, Abhishek and Ayush. This group was so nice thanks to you all. It was fun having some great time with you and knowing I could always approach you with issues I ran into during my research here had me more reassured and not panicky. Thank you.

Kailash, Viswanath, Murali and Prasanth, strangers when I started in Bombay, great friends now. Long conversations with you have been fun. You were the board on which I was able to sketch my non-academic ideas. The long walks, that I miss so badly, I always look forward to and most importantly the philosophical conversations we had helped mould my viewpoint and temper it.

Muthu and Kaushik. You were great support for me here in Australia. I cannot thank you enough for all the help you have provided over the course of my stay here. Sandeep and Vivek, my housemates for the longest time, it was a wonderful and comfortable stay with you. You always made it easy for me to come home to a peaceful and quiet place even after a long and hard day.

To Seb, Jac and Laurence, my examiners during internal milestones, your questions helped me to focus my research and solidify my directions. Thank you. I would also like to thank Chris McNeill, Neil Cameron, and the office staff at MSE, Edna, Kris, and Michelle, who have provided me with wonderful support over the years.

I would also like to thank Samir Mushrif and Ajay Panwar. Two supervisors I started this journey with but was unable to complete it. Samir, you were a great teacher, you introduced me to the world of computational modelling and helped me fall in love with it. Ajay, I would like to apologize for the way I left. You were the kindest supervisor I had and had it not been for IIT-Bombay's administrative staff, this could have been a whole another story. Thank you both once again.

Finally, I would like to express my heartfelt gratitude to my parents and my brother. Amma and Appa, you have been my moral and psychological sponges, helping me keep my head straight and letting me vent all my frustrations on. Appa, I want to thank you especially as without you I may never have woken up on time. Viswa, thanks for all the help and direction you have given me during this PhD journey. I started before you but will be finishing it after.

To all the others I may have missed, Thank you.

TABLE OF CONTENTS

LIST OF FIGURES	XVI
CHAPTER 1: INTRODUCTION AND BACKGROUND	1
1.1 LITHIUM-ION BATTERIES	2
1.2 MAGNESIUM-ION BATTERIES/RECHARGEABLE MAGNESIUM BATTERIES	5
REFERENCES.....	9
CHAPTER 2: LITERATURE REVIEW	11
2.1. ANODE MATERIALS FOR MIBS/RMBs	12
2.1.1 Mg metal Anodes	12
2.1.2. Alloy-Based Anodes	13
2.1.3. Others.....	14
2.2. STABLE CATHODE MATERIALS FOR RMBs	14
2.3. INSIGHTS INTO ELECTROLYTE BEHAVIOR	16
2.3.1. Li-ion chemistry derived electrolyte selection	16
2.3.2. In situ generated and crystallized Magnesium Electrolytes	16
2.3.3. Corrosivity of Mg electrolytes and role of MgCl ₂	20
2.3.4. bis(trifluoromethane)sulfonimide (TFSI) based electrolytes.....	23
2.3.5. Speciation behavior and selectivity of the EAS.....	26
2.3.6. Electrolytic conditioning and factors affecting the EAS selectivity.....	30
2.3.7. Ionic clustering and EAS pairing	33

2.4. SUMMARY	34
REFERENCES.....	35
CHAPTER 3: OPPORTUNITIES AND AIMS.....	44
3.1 AIMS.....	47
CHAPTER 4: ION AGGLOMERATION AND TRANSPORT IN MgCl_2 BASED ELECTROLYTES FOR RECHARGEABLE MAGNESIUM BATTERIES.....	49
CHAPTER 5: CHARACTERIZATION OF SOLVENT CONTROLLED DIFFUSION OF Mg-Cl CATIONIC COMPLEXES IN HALIDE CONTAINING ELECTROLYTES FOR USE IN RECHARGEABLE MAGNESIUM BATTERIES.....	72
5.1. INTRODUCTION	73
5.2. METHODOLOGY	75
5.2.1. <i>Parameter Benchmarking and Initial System optimization</i>	75
5.3. RESULTS AND DISCUSSION	78
5.4. CONCLUSION	82
REFERENCES.....	82
CHAPTER 6: SOLVENT AND ANION CONTROLS ON ANION BRIDGED IONIC CLUSTERING OF Mg-Cl CATIONIC COMPLEXES IN HALIDE CONTAINING ELECTROLYTES FOR USE IN RECHARGEABLE MAGNESIUM BATTERIES	85
6.1. INTRODUCTION	86
6.2. METHODOLOGY	88

6.3. RESULTS AND DISCUSSION	89
6.3.1. Clustering in electrolytes containing ethereal solvents.....	89
6.3.2. Solvent effects on ionic clustering	95
6.3.3. Anion effects on clustering.....	96
6.4. CONCLUSION	97
REFERENCES.....	98
CHAPTER 7: CONCLUSIONS AND FUTURE WORK.....	102
7.1. CONCLUSIONS.....	103
7.1.1. Gap in literature	103
7.1.2. Cationic solvation and ionic clustering	104
7.1.3. Ionic mobility.....	104
7.1.4. Solvent influence on the mobility.....	105
7.1.5. Anion and solvent control on clustering.....	105
7.2. FUTURE WORK	106
7.2.1. Temperature effect on clustering.....	106
7.2.2. Mixed ionic systems	106
7.2.3. Anode-electrolyte interphase studies.....	107
7.3. SUMMARY	107
APPENDIX 1: SUPPORTING INFORMATION.....	108
S1. DETAILS OF MOLECULAR DYNAMICS (MD) SIMULATIONS	109
S2. VALIDATION OF MOLECULAR DYNAMICS SIMULATIONS.....	110
S3. CLUSTER ANALYSIS	111

S4. CALCULATION OF ION DIFFUSIVITY IN THE MgCl_2 -BASED ELECTROLYTE	112
REFERENCES.....	120

LIST OF FIGURES

Figure 1.1. Timeline of Li-ion battery development. Reproduced from Ref. 3 with permission from the Royal Society of Chemistry. ³	4
Figure 1.2. Abundance of different elements in the earth's crust. Reproduced from Ref. 6 with permission from the Royal Society of Chemistry. ⁶	5
Figure 1.3. Capacities and Reductive potentials of various metal anodes. Adapted with permission from Ref 7. Copyright {2021} American Chemical Society. ⁷	6
Figure 1.4. Architecture of a battery	7
Figure 2.1. Cyclic voltammograms of 0.4 M THF solution of the reaction product generated in situ from a 2:1 mixture of Bu ₂ Mg to EtAlCl ₂ (DCC) (blue) and of the crystal obtained from a 2:1 mixture of Bu ₂ Mg to EtAlCl ₂ (crystallized DCC) (red). Scan rate is 0.025 V s ⁻¹ . Adapted from Ref.28 Copyright (2021) Wiley. ²⁸	19
Figure 2.2. Representation of the key electroactive species (EAS) along with THF as the solvent. The EAS represented are Mg ₂ Cl ₃ .6THF (A), MgCl.5THF (B) and Mg.6THF (C). The Mg (grey), Cl (green), O (red), C (blue) are shown. The ratios in the parenthesis represent the stoichiometric composition of MgCl ₂ and AlCl ₃ in the raw materials.	20
Figure 2.3. (a) Optimized geometries of Mg(G3) ₂ ²⁺ complexes. Adapted with permission from Ref 37. Copyright {2021} American Chemical Society (b) First scan of acyclic voltammetry test of 0.75m MMC/G3 and 0.75m MMC/G4 on Pt electrode collected at 5mVs ⁻¹ . (Inset: enlargement of 3.0–5.0 V region). Adapted from Ref.38 Copyright (2021) Wiley (c) LSV of 0.12 M in 1:1 THF/CH ₃ CN, scanning at a rate of 25 mV·s ⁻¹ . Adapted with permission from Ref 39. Copyright {2021} American Chemical Society	22
Figure 2.4. (a) Mg-TFSI-diglyme solvation structure at 0.1 M and 0.4 M concentrations. Reproduced from Ref. 43 with permission from the Royal Society of Chemistry (b) Raman spectra of pure DME (brown line), U-phase (orange line), L-phase (yellow line), 1.25 M MgTFSI ₂ solution in DME, MgTFSI ₂ single crystal recrystallized from MgTFSI ₂ /DME solution, and pure MgTFSI ₂ . Adapted	

with permission from Ref 43. Copyright {2021} American Chemical Society (c) Proposed Mg metal anode degradation mechanism. Adapted with permission from Ref 45. Copyright {2021} American Chemical Society	24
Figure 2.5. Schematic of anions derived from TFSI. Adapted with permission from Ref 47. Copyright {2021} American Chemical Society	25
Figure 2.6. Formation free energy of Mg-EAS -THF at different THF coordination. Reproduced from Ref. 52 with permission from the Royal Society of Chemistry	28
Figure 2.7. Scheme showing the EAS selectivity controlled by stoichiometry. Reproduced from Ref. 55 with permission from the Royal Society of Chemistry	29
Figure 2.8. (a) Raman spectra of Mg_2Cl_3^+ and MgCl^+ complexes. Adapted with permission from Ref 64. Copyright {2021} American Chemical Society (b) Scheme representing the As-prepared and conditioned anode electrolyte interface. Adapted with permission from Ref 65. Copyright {2021} American Chemical Society	32
Figure 2.9. Cluster analysis. Parts (a) and (b) refer to the 4 M case, while (c) and (d) refer to the 1 M one. The plots on the left, (a)–(c), summarize the cluster compositions during the simulation. The plots on the right, (b)–(d), show the biggest cluster formations found during the dynamics. Adapted with permission from Ref 72. Copyright {2021} American Chemical Society	34
Figure 3.1. Cross-section of the anode-interface-electrolyte system. The Anion (red sphere), cation (yellow sphere) and the solvent (green sphere) are highlighted. Three key interactions of interest are also shown: Cation-anion (red arrow), cation-cation (yellow arrow) and cation-solvent (blue arrow).	48
Figure 5.1. Atomic structure and atom nomenclature of solvents used. (a) Dimethoxyethane (DME/glyme); (b) Tetrahydrofuran (THF); (c) diglyme (G2); (d) Triglyme (G3); (e) Tetraglyme (G4).	77
Figure 5.2. Mg-EAS diffusivity ($\times 10^{-7} \text{ m}^2/\text{s}$) in THF, DME, G2 and G3 at 0.4M concentration and 0.45 V/nm electric field	80

Figure 5.3. Spatial density Function of (a) THF and (b) DME around Mg_2Cl_3^+ at iso value of 0.02.
.....81

Figure 6.4. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{Mg}_2\text{Cl}_3^+ - \text{Mg}_2\text{Cl}_3^+$ coordination numbers with AlCl_4^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{Mg}_2\text{Cl}_3^+ - \text{Mg}_2\text{Cl}_3^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f)91

Figure 6.5. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{Mg}_2\text{Cl}_3^+ - \text{Mg}_2\text{Cl}_3^+$ coordination numbers with Cl^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{Mg}_2\text{Cl}_3^+ - \text{Mg}_2\text{Cl}_3^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f).92

Figure 6.6. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{MgCl}^+ - \text{MgCl}^+$ coordination numbers with AlCl_4^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{MgCl}^+ - \text{MgCl}^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f)93

Figure 6.7. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{MgCl}^+ - \text{MgCl}^+$ coordination numbers with Cl^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{MgCl}^+ - \text{MgCl}^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f).94

CHAPTER 1:

INTRODUCTION AND BACKGROUND

An electric battery is a device that uses chemical reactions to store energy and release it when required. They are so ubiquitous that they are an intrinsic, essential technology in much electronic equipment used today. Batteries come in an extended range of sizes, from Megawatt storage super batteries to the tiny button cells to power simple devices such as watches.

Benjamin Franklin coined the term battery in 1749 to describe a series of capacitors connected in parallel, which in time came to represent a collection of electrochemical cells connected in parallel. The earliest electrochemical cells were the Galvanic and Voltaic cells. Though archaeological evidence has shown the existence of a simple energy storage device from Mesopotamia called the ‘Baghdad Battery’, indicating that the development of human civilization goes hand in hand with development in energy storage technologies.¹

Over the years, the size and power of such batteries have increased, and their ability to power devices has led to a massive revolution in the world of technology that has given rise to modern-day laptops, mobile phones, and electric cars, among others. The development of Lithium-ion technology since the 1970s and early 1980s, pioneered by the likes of Prof. John B. Goodenough, awarded the Nobel Prize in Chemistry for 2019 alongside Akira Yoshino and M. Stanley Whittingham for their contribution towards the development of Li-ion battery has been the primary driving force behind the modern-day revolution in battery technology. Li-ion batteries paved the way for cheap, high performance, high stability commercial battery technologies that have facilitated shrinking energy-intensive processes such as computing.²

1.1 LITHIUM-ION BATTERIES

Lithium-Ion Batteries (LIBs) are used commonly as an energy storage device in modern-day electronics and are also being used to implement larger storage devices such as electric cars and offset

electric grid storage. The small size and relatively simple chemistry of Lithium-ion have made the most studied and implemented technology has led the way to rapid commercialization and economies of scale driven production of commercial LIBs. Still, there are some intrinsic drawbacks to using Li-ion both from the availability of Lithium and stability issues such as dendrite formation during Lithium deposition and the lower melting point of Li and lower storage capacity lead to a need to look at alternative Metal ion sources. Significant research attention towards state-of-the-art post-lithium-ion batteries has started taking place. These include Li-air, Li-sulphur batteries alongside development in electrode and electrolyte technologies such as organic electrodes and solid-state electrolytes.³ These have been proposed to improve Li-ion battery performances and may become commercially viable in the future, as predicted in **Figure 1.1**.

Another issue to contend with has been the less studied but growing relevance of the social and environmental impacts of lithium mining, extraction, and recycling.⁴ The inability of current technology to recycle LIBs has led to the dumping of these in landfills. The difficulty in recycling arises from the toxic components used, which enforces time-stacking and expensive recycling processes that need to address each component of the LIB separately. Though there are processes to recycle Li in these batteries, the cost and associated inherent difficulty have led to a very low commercial push towards these, which has caused the environmental viability of LIBs to plummet.

Another important aspect is the social impact of Li mining. Li is predominantly mined in lesser developed nations, significantly affecting these nations' social and economic conditions. The reduction in Li resources and the rapidly growing requirement for more LIBs to satisfy the growing consumer base targeting the clean and green energy trends has caused the rapid development of social and environmental issues related to the Li industry in these countries.⁵

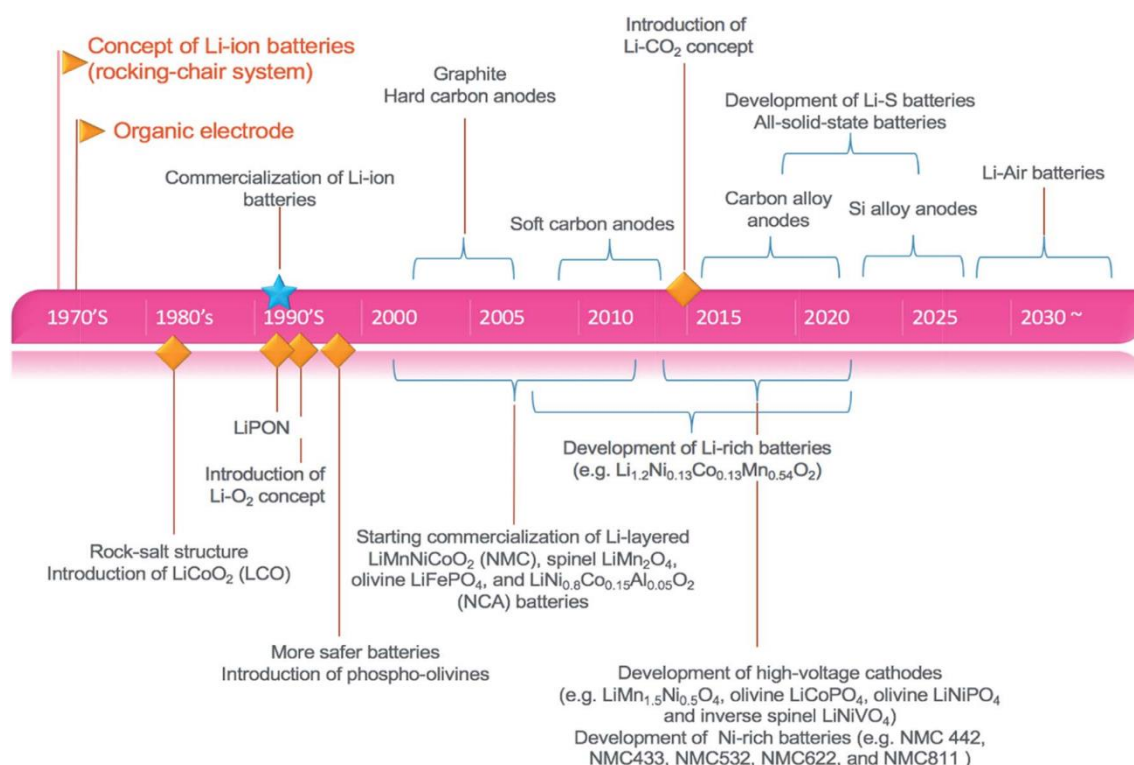


Figure 1.1. Timeline of Li-ion battery development. Reproduced from Ref. 3 with permission from the Royal Society of Chemistry.³

The research direction pointed towards replacing Li with other metal ions, primarily to circumvent issues with Li. Much more reactively stable and less corrosive alkali metals like Na and K were the initial starting phase of this research direction. Simultaneously research has also branched into multi-valent ions like Mg, Ca, Al, and Zn. The multi-valent ion batteries have a more significant charge, but the system's chemistry is very different from what is present in LIBs. The availability of the metal also dictates the choice of the metal ion in the earth's crust to be more economical, as can be seen in **Figure 1.2.**⁶

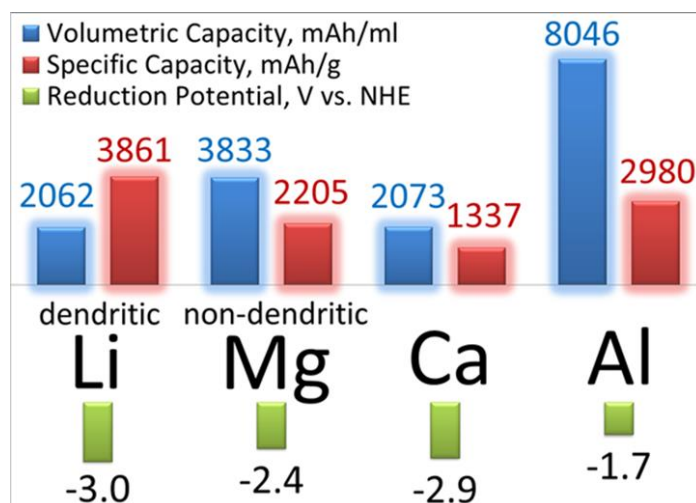


Figure 1.3. Capacities and Reductive potentials of various metal anodes. Adapted with permission from Ref 7. Copyright {2021} American Chemical Society.⁷

The anode, cathode, and electrolyte make up the three components of a battery. Upon completing the external circuit, the metal in the anode releases electrons and dissolves into the electrolyte. The electrons flow through the external circuit into the device, powering it, and then flow into the cathode. This change in the electron concentration causes an electric field inside the cell, causing an ionic drift in the electrolyte, which moves the metal ion from the anode side to the cathode side, where it takes the electrons and reacts with the cathode and moves out of the electrolyte. The process will continue until the circuit breaks, or the metal wholly migrates from the anode to the cathode, known in colloquial reference as ‘running out of charge.’ The charging supply of external energy drives the previous process in reverse, moving all the metals in the cathode into the anode. **Figure 1.4** is a depiction of this.

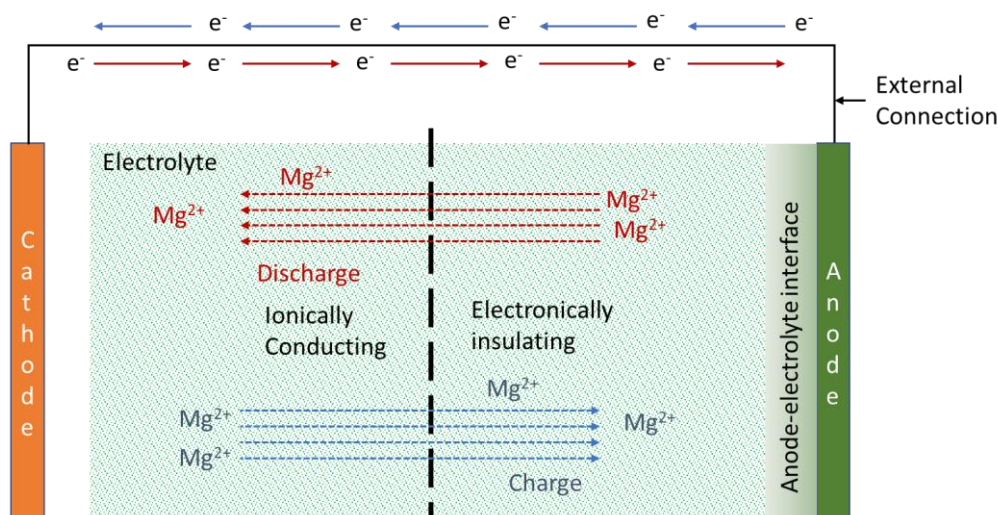


Figure 1.4. The architecture of a battery

The commonly accepted anode material for Magnesium batteries has been Magnesium metal.⁸ Use of Mg commonly leads to forming an impermeable interface on its surface, which decreases the amount of Mg ions in the electrolyte and blocks the transfer of ions from the anode, reducing the battery's discharge rate.⁷⁻¹¹ The reactions of the metal ion with the solvent and other additives in the electrolyte cause SEI formation. These reaction products are usually insoluble in the electrolyte and therefore deposit on the anode surface, reducing the metal content in the electrolyte to decrease. Studies about the formation and composition of the SEI for LIBs have taken place, but the same for MIBs have not. The SEI formation reactions in MIBs have increased complexity due to the extra charge on the Mg ion and the increased charge density on the Mg ion. The increased charge density also affects the overall charge delivered by the battery and thus needs a stable cathode that can withstand the charge difference.^{7-9, 11-12}

A thorough study of the three components, anodes, cathodes, and electrolytes is critical for developing a successful and commercial RMB and developing better materials. This research looks specifically into the role of the electrolyte with significant focus on the clustering of the cationic species. Ionic

clustering affects the mobility of the ions, possible interfacial interactions and overall battery performances. The need to focus on the solute morphology and solvation structures come from a requirement to understand the impact of the electrolyte on the battery performance.

This thesis investigated ion agglomeration and transport of several EAS in MgCl_2 salts dissolved in ethereal solvents under equilibrium and operating conditions using large-scale atomistic simulations. An identification that the presence of clusters characterizes the solute morphology strongly at the same time, the solvation structures of EAS govern it. Specifically, the isotropic solvation of Mg^{2+} results in the slow formation of bulky clusters, compared with chain-like analogues observed in the Cl-containing EAS such as Mg_2Cl_3^+ , MgCl^+ and $\text{Mg}_2\text{Cl}_2^{2+}$. Further, it is illustratable that these clusters can reduce the diffusivity of charge-carrying species in the MgCl_2 based electrolyte by at least an order of magnitude. To highlight the role of the solvent, as part of the thesis, the study of the transport mechanism of the ions in other solvents such as Glyme (DME), Diglyme (G2), Triglyme (G3) and Tetraglyme (G4) was taken up. The solvent controls ion mobility by restricting the ion diffusion mechanism between the faster displacement diffusion in lighter solvents and the slower void diffusion in heavier solvents. The findings highlight the effect of ion coverage due to the number of ligand dentate sites on the solvent, which was significant in lighter solvents. This finding helps to characterize the role of the anion and the solvent on the ion clustering by comparing weakly and strongly interacting anions solvated in different solvents. Analysis shows that both the anions and solvents individually control the clustering rates and a combination of the two is always present. Findings of the cluster formation, morphology, and kinetics can provide helpful insight into the electrolyte's performance controls and identify the reactive species and electrochemical reaction mechanisms at the anode/electrolyte interface in RMBs.

The thesis uses Molecular Dynamics (MD) to study the bulk properties of the halide containing Magnesium electrolytes and understand the role of cationic species in electrolyte behaviour. Chapter 2 will contain an extensive literature review on the current state of research in electrolytes for RMBs. Using the literature review, Chapter 3 will highlight the aims of this work. The presence of ion agglomerates and their role in the electrolyte behaviour will be shown in Chapter 4 followed by the effect of solvents on the transport and clustering of electrolytes will be discussed in Chapters 5 and 6. The thesis will then conclude with a conclusion and a proposed outline for carrying on this work.

REFERENCES

1. Downes, D.; Meyerhoff, A., Battery, Baghdad, 250 BCE. *Museum of Ancient Inventions* **2000**.
2. Kamat, P. V., Lithium-Ion Batteries and Beyond: Celebrating the 2019 Nobel Prize in Chemistry – A Virtual Issue. *ACS Energy Letters* **2019**,4 (11), 2757-2759.
3. Kim, T.; Song, W.; Son, D.-Y.; Ono, L. K.; Qi, Y., Lithium-ion batteries: outlook on present, future, and hybridized technologies. *Journal of Materials Chemistry A* **2019**,7 (7), 2942-2964.
4. Agusdinata, D. B.; Liu, W.; Eakin, H.; Romero, H., Socio-environmental impacts of lithium mineral extraction: towards a research agenda. *Environmental Research Letters* **2018**,13 (12), 123001.
5. Liu, W.; Agusdinata, D. B.; Myint, S. W., Spatiotemporal patterns of lithium mining and environmental degradation in the Atacama Salt Flat, Chile. *International Journal of Applied Earth Observation and Geoinformation* **2019**,80, 145-156.
6. Sawicki, M.; Shaw, L. L., Advances and challenges of sodium ion batteries as post lithium ion batteries. *RSC Advances* **2015**,5 (65), 53129-53154.
7. Muldoon, J.; Bucur, C. B.; Gregory, T., Quest for Nonaqueous Multivalent Secondary Batteries: Magnesium and Beyond. *Chemical Reviews* **2014**,114 (23), 11683-11720.
8. Bucur, C. B.; Gregory, T.; Oliver, A. G.; Muldoon, J., Confession of a Magnesium Battery. *The Journal of Physical Chemistry Letters* **2015**,6 (18), 3578-3591.

-
9. John, M.; B., B. C.; Thomas, G., Fervent Hype behind Magnesium Batteries: An Open Call to Synthetic Chemists—Electrolytes and Cathodes Needed. *Angewandte Chemie International Edition* **2017**, *56* (40), 12064-12084.
 10. Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S.-J., Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angewandte Chemie International Edition* **2012**, *51* (39), 9780-9783.
 11. 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 & Environmental Science* **2012**, *5* (3), 5941-5950.
 12. Aurbach, D.; Gofer, Y.; Schechter, A.; Chusid, O.; Gizbar, H.; Cohen, Y.; Moshkovich, M.; Turgeman, R., A comparison between the electrochemical behavior of reversible magnesium and lithium electrodes. *Journal of Power Sources* **2001**, *97-98*, 269-273.

CHAPTER 2: LITERATURE REVIEW

All batteries are made up of 3 important components: the cathode, anode and the electrolyte. There are significant interests in each of the individual components that have been explored individually. Though the battery as a whole is a single unit, there are behavior among the respective components that can be separated and studied. In this section we shall take a look at some of the studies that have been performed on the cathode, anode and electrolyte materials. We shall then look at the interface between the anode and electrolytes and some of the computational studies performed on the electrolytes and on the interfaces.

2.1. ANODE MATERIALS FOR MIBs/RMBs

The higher charge density, safer and dendrite free properties of Mg metal compared to Li metal are an attractive proposition for use as anode in batteries. But the formation of ion impermeable Solid-electrolyte interface (SEI) caused by the reactive breakdown solvent and additive species enabled by the high charge density of the Mg^{2+} cation negatively affects its applicability in the current landscape. To overcome this, it is crucial to develop anodes that can reduce the formation of passivation layers and improve the kinetics of Mg. At present modified Mg metal anodes, alloy-based materials, carbon-based materials and so on are mainly used as the materials for the anode of RMBs.

2.1.1 Mg metal Anodes

Mg metal with micro-nano structure can be used as an anode material that can effectively decrease the thickness of the passivating films. This can promote ion diffusion and improve the performance of Mg- storage. Chen et al reported the various Mg nano/mesoscale structures using a simple vapor-transport approach and tested their properties for application in Mg/air batteries.¹⁻² The results indicate polarization could be reduced due to the high specific surface area of Mg nanostructures. Removing the oxide layer on the surface of the Mg anode its electrochemical performance will be

significantly improved based on the method proposed by Yim et al.³ To overcome the formation of passive SEI layer formation many new approaches have been proposed. One such is the use of printed coating materials as proposed by Chen et al. who evaluated the electrochemical stability windows for non-redox active Mg binary, ternary, and selected quaternary compounds using the first-principles calculations.⁴ Coated Mg anodes displayed good stripping and deposition performances showing better reversibility over 1000 h of galvanostatic cycling in the PC-based electrolyte solution.

Another approach is to form stable magnesium ion-conducting surface films on the Mg anode surface by using appropriate solvents, salts, and/or additives that will develop, which may enable integration of Mg metal anode with conventional electrolyte solutions in rechargeable magnesium systems.⁵ Alternatively, a stable Li-species-containing SEI could be formed on Mg metal anode surface which blocks further parasitic reaction of Mg metal anode with electrolyte and leading to this electrolyte enduring long-term electrochemical cycles stably.⁶

2.1.2. Alloy-Based Anodes

Using insertion type anode materials that are synthesized by alloying process is another reasonable strategy to eliminate the existence of passivation film. BiSb alloy combines the advantages of Bi with low reduction/oxidation potential and Sb with high theoretical capacity, thereby improving the energy density of the anode.⁷ Nanostructure can effectively suppress the expansion of materials during charge/discharge and promote the transport of ions and electrons, Bi-NTs synthesized via hydrothermal reaction delivered high reversible specific capacity (3430 mAhcm⁻³ Bi), excellent stability (capacity retention rate remains at 92.3% after 200 cycles), and high Coulombic efficiency ($\approx 100\%$).⁸ It is desirable to develop more kinds of anode materials for RMBs that have lower Mg²⁺ insertion/extraction voltages and higher capacities since cell voltage is one of the factors that determine the energy density. Based on the DFT, both Sn and Bi with low diffusion barriers (0.43

and 0.67 eV, respectively) are good anode material candidates.⁹ When Sn was used as the anode, the Mg²⁺ insertion/extraction voltage (+0.15/0.20 V) was much lower than that of Bi previously reported (+0.23/0.32 V).¹⁰ Furthermore, the DFT results indicated that Sn anode has lower lattice expansions ($\approx 120\%$) and diffusion barriers (≈ 0.50 eV).¹¹ In addition, when using the SnSb alloy as anode materials for RMBs, it formed Mg₂Sn and Mg₃Sb₂, which analyzed by the structural reaction of SnSb with Mg ions and confirmed by DFT.¹²

2.1.3. Others

Carbon-based materials provide more choices for Mg anode materials. Shenoy and coworkers predicted that the defective graphene and graphene allotropes are suitable for Mg storage using DFT.¹³ They showed Mg storage capacities improved with increasing vacancies and topological defects concentration in the structure. DFT calculations suggest that graphite can serve as a substrate for Mg²⁺ intercalation, and can also achieve reversible co-intercalation with linear ether solvents such as DME and DEGDME.¹⁴ Guo et al used DFT calculations to demonstrate that the spinel Li₄Ti₅O₁₂ with low-strain characteristics could be employed as a Mg²⁺ insertion-type anode material with a high reversible capacity.¹⁵ DFT studies have shown that monolayer black P is a potential anode for RMBs.¹⁶ Borophene and phosphorene have also been predicted using DFT calculations to be good anode candidate material for RMBs.¹⁷⁻¹⁸

2.2. STABLE CATHODE MATERIALS FOR RMBs

One of the goals of developing a successful battery is to improve its energy density and higher energy storage potentials. One cost effective method used in Lithium ion Batteries (LIB) to increase energy density is by identifying cathode materials that can react with more Li ions and thereby increasing the amount of Li in the cathode.¹⁹ An example of one such material studied in VOPO₄. VOPO₄ has

been shown to have a theoretical capacity of 2 Li ions per VOPO_4 molecule, with a specific capacity $(305 \text{ mAh/g})^{20}$ nearly twice that of commercially available cathodes (170 mAh/g) .²¹ The Li intercalation is usually accompanied by the formation of multiple discharge potential plateaus.^{19, 22} These plateaus have been theorized to be caused due to the formation of new phases on the cathode.²³ Moreover the intercalation of more Li ions lead to an increase in the strain on the electrode structure and may cause stability.¹⁹

The selection of cathode materials must take into account the behavior of the Mg ion inside the cathode and its transport properties and product formations. Another important aspect to account for in RMB cathodes is that the cathode material must be able to accept two electrons.

The different cathodes can be classified into different types. Some of the major types of cathodes are:

- Intercalation cathodes: These cathodes work by allowing the Mg ion to intercalate to maintain the charge balance caused by the electrons flowing into the cathode. Layered cathode materials such as TiS_2 are good examples of this type of cathodes.
- Conversion cathodes: These materials react with Mg ion using the extra electrons drawn in by the circuit to form conversion products.
- Organic cathodes such as quinone based cathode materials
- Carbon based cathodes like graphene

There have been several cathode materials tried so far but Chevrel phase cathodes have shown the most stable behavior so far.

2.3. INSIGHTS INTO ELECTROLYTE BEHAVIOR

The development and selection of new electrolytes have a few daunting challenges to overcome. One such aspect to consider is the stability of the electrolyte against reductive reactions at the anode electrolyte interface during charge/discharge cycles. These reductive transformations have been shown to form an impermeable solid-electrolyte interface (SEI). The formation and characterization of the SEI has been well studied for LIBs. However, an important point to note is that the SEI structure in LIBs are ion permeable and in MIBs they are not. One reason for the impermeability can be attributed to the higher charge density on the Mg ion. Higher charge density leads to formation of more complex and interconnected SEI and a charge impeded transport. A key divergence in the direction of the selecting electrolytes for MIBs has been to remove the SEI in battery operations or at least reduce its impact.

2.3.1. *Li-ion chemistry derived electrolyte selection*

A key aspect of MIB electrolyte research has been the use of research frameworks developed for LIBs. There are great advantages for the use of such techniques which can help narrow down and accelerate new discovery by using a benchmark from a well-established and commercialized technology.^{19, 24-27} Given its significant advantage there are still some drawbacks to the method, this is especially prominent in electrolytes as some of the Magnesium analogues of commercial and well-studied electrolytes used in LIBs tend to form SEIs very easily. Thus, a focus towards developing electrolytes with a higher reductive stability and lesser reactivity with Magnesium has been.

2.3.2. *In situ generated and crystallized Magnesium Electrolytes*

The development of electrolytes for Rechargeable Magnesium Battery (RMB) started in the 1970s when Brenner and co-workers mixed Grignard's reagents with Boron based Lewis acids to improve

Magnesium electrodeposition baths for electroforming light weight engineering components to be used in satellites by NASA.²⁸ Grignard's reagents dissolved in ethereal solvents have been known to reversibly deposit Magnesium since the early 20th century. Though they allow reversible deposition of Mg, their oxidative stability is low (<1.5 V vs Mg)²⁹ and they tend to react with Sulphur and Oxygen and form poisonous components. To overcome these drawbacks, the initial approach for selecting electrolytes was to try to form more stable Grignard's reagent-based components and paired them with less toxic Lewis acids such as AlCl₃ as performed by Gregory et al. in the 1980s.²⁵ The mixing of Grignard's reagent such as Dialkyl Magnesium with a strong Lewis acid such as AlCl₃ has been shown to improve reversible deposition of Mg.²⁸⁻²⁹ This work led to the birth of Magnesium organohaloaluminates based electrolytes.

Gregory et al. combined dibutylmagnesium ((C₄H₉)₂Mg) and tri-n-butylborane (B(C₄H₉)₃) to synthesize an electrolyte (Mg[B(C₄H₉)₄]₂) which showed improved stability but lower coulombic efficiency.^{26, 30} In the early 2000s, based on the previous work done by Gregory et al, Aurbach et al. hypothesized that the stoichiometric ratio of organomagnesium salts to the Lewis acid additives will affect the coulombic efficiency and oxidative stability of the electrolytes. Surprisingly, after analyzing the combination of a wide variety of Lewis acids such as BPh₂Cl, BPhCl₂, B[(CH₃)₂N]₃, BEt₃, BBr₃, BF₃, etc. with dialkylmagnesium Lewis bases in Tetrahydrofuran (THF), it was found that there was no Magnesium deposition.³¹ Whereas when the same group reacted two equivalents of dibutylmagnesium with ethyl aluminum chloride they formed an electrolyte which had 100% coulombic efficiency with a stability of 2.4V vs Mg.³² In the 1990s di Noto et al replaced organomagnesium with MgCl₂ and formed an electrolyte. This process was later adopted by Aurbach and co-workers that led to the generation of Magnesium Aluminum Chloride Complexes (MACC).¹⁹

Comprehensive studies were later performed by replacing the Lewis base and Lewis acids with other organic groups and a series of in situ electrolytes were created such as DCC (Di), APC (All Phenyl Complex) which all showed good coulombic efficiency and moderate stability. Based on the behavior of these in situ solvents it has been theorized that the addition of a Lewis acid stabilizes the Grignard's reagent and literature so far has concurred with the same.

The DCC electrolyte has been studied to form a Magnesium complex in THF namely $[\text{Mg}_2(\mu\text{-Cl})_3.6\text{THF}]^+ [\text{EtAlCl}_3]^-$, where the μ implies a bridged Chlorine linking two Magnesium centers. These complexes have been crystallized and separated. The presence of the complex is an accepted result but the ability of the crystallized salt complex to perform as an electrolyte once redissolved has been contested by two opposing results from Gewirth et al. and Muldoon et al. with the latter group showing that the dissolved system is still electrochemically active. Muldoon et al. also showed that the dissolved crystal showed slightly better performances when compared to the in-situ electrolytes.³³ Later literature have attributed to the improvement in electrochemical behavior to the absence of byproducts usually found in in-situ electrolytes.²⁸(See **Figure 2.1**)

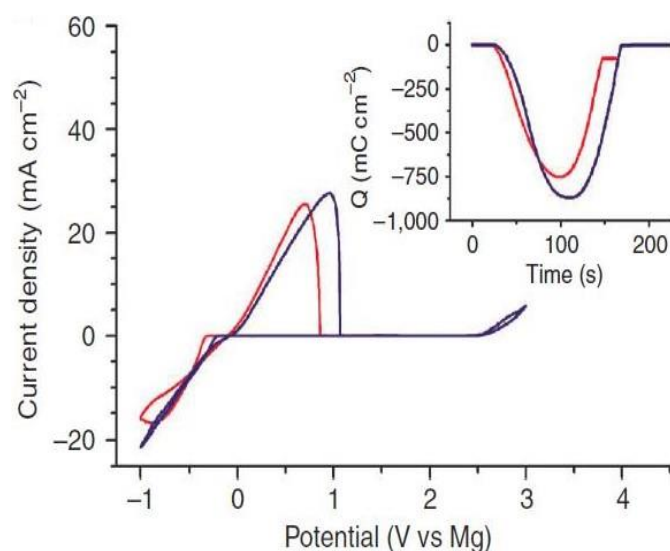


Figure 2.5. Cyclic voltammograms of 0.4 M THF solution of the reaction product generated in situ from a 2:1 mixture of Bu_2Mg to EtAlCl_2 (DCC) (blue) and of the crystal obtained from a 2:1 mixture of Bu_2Mg to EtAlCl_2 (crystallized DCC) (red). Scan rate is 0.025 V s^{-1} . Adapted from Ref.28 Copyright (2021) Wiley.²⁸

The presence of the Magnesium complexes as shown in **Figure 2.2a**, were later seen in other in situ electrolytes and have been understood to be the main driving molecule in the electrolyte and have been called as the Electro Active Species (EAS).²⁹ The electrolytes formed by the mixing of the EAS along with Lewis acids have shown significantly improved stability ($>3.0 \text{ V vs Mg}$). Further analysis has shown that the EAS formed has significantly advanced electrolyte stability. Moreover, based on the stoichiometric composition of the initial Lewis acid and Lewis base other EAS systems can also be isolated as can be seen in **Figure 2.2**.

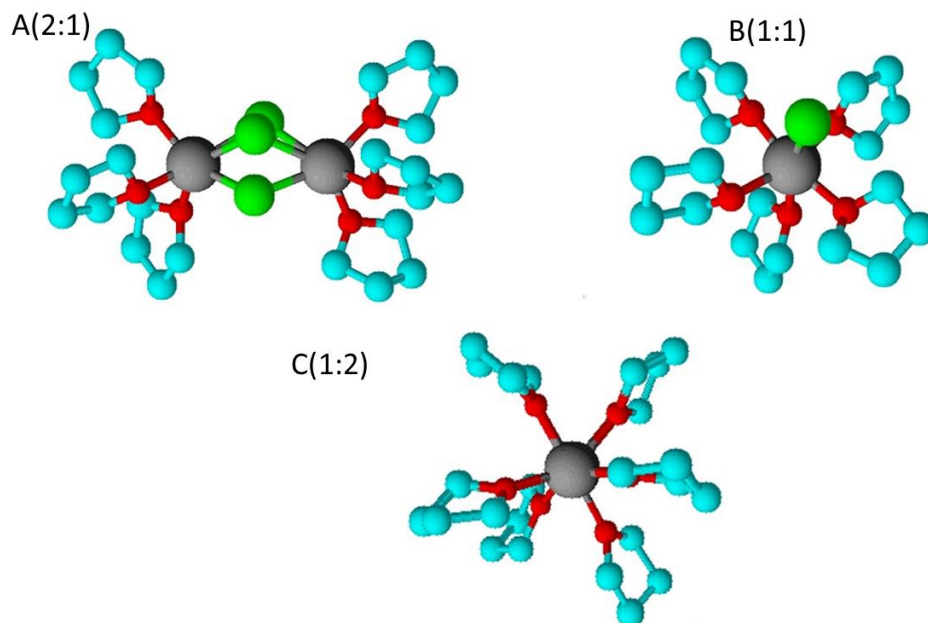


Figure 2.6. Representation of the key electroactive species (EAS) along with THF as the solvent. The EAS represented are $\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}$ (A), $\text{MgCl} \cdot 5\text{THF}$ (B) and $\text{Mg} \cdot 6\text{THF}$ (C). The Mg (grey), Cl (green), O (red), C (blue) are shown. The ratios in the parenthesis represent the stoichiometric composition of MgCl_2 and AlCl_3 in the raw materials.

2.3.3. Corrosivity of Mg electrolytes and role of MgCl_2

RMBs like other common batteries are made of other components such as current collectors, metallic substrates and metallic casing which are part of the circuit. Ideal electrolytes have to be inert towards these within the battery operation potential window. Corrosive electrolytes tend to lead to pitting corrosion on these metallic collectors and can cause an oxidative current to flow which can be caused by the dissolution of the collector metal into the electrolyte.

Mg containing organohaloaluminates are widely considered to be corrosive as it is having lower stability against Aluminum or Stainless steel as against Platinum electrodes. Other Mg containing electrolytes such as organoborates have shown better stability on Pt as well as on Stainless steel. The lower stability has been attributed to the presence of the $[\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+$ species formed by the

Chloride containing Magnesium species. Interestingly Nelson et al. studied in situ generated electrolyte made by phenylmagnesium chloride and aluminum triphenoxide which produces a halide free anion and reported high oxidative stability.³⁴ Lipson et al reported that the corrosive nature of the in situ generated electrolytes is due to the presence of free chloride ions.³⁵ Thus, electrolytes that do not produce these free chloride ions or halide free anions were studied.

To this extent a few electrolytes have been tested. As in the case with most MIB research attempts the baseline was used as established Li ion chemistry. Thus, the Mg analogues of LIB electrolytes such as LiTFSI, LiPF₆, etc. were tested. These electrolytes show good stability and good potential but there are still some drawbacks.^{19, 26-28, 36}

Kimura and co-workers studied the solvation of Mg(TFSI)₂ salts in triglyme (G3) to understand the solvation structure so that the system can be used by controlling the reactions that occur in the battery. They found that if Mg(TFSI)₂ completely disassociates, then energetically one common solvation structure is formed, the hexacomplexed Mg[(G3)₂]²⁺ as shown in see **Figure 2.3.a**. But when Raman spectroscopy was performed another type namely Mg [(tetra-G3) (bis G3)]²⁺ was also found.³⁷

Similarly, Tutusaus showed that Magnesium monocarborane can be used as a high-performance battery electrolyte. The solvent group has much promise but has not been studied in depth and thus not commonly seen in literature (see **Figure 2.3.b**).³⁸

Mg(PF₆)₂³⁹ has been studied as potential electrolyte for RMBs by Keyzer and co-workers. They found that these electrolytes have high conductivities and very good electrochemical stabilities of up to 4V vs Mg (see **Figure 2.3.c**). The electrolyte though proved to be too corrosive towards stainless steel in the collectors but did form a passive layer when Aluminum was used instead. Thus, with improved

corrosion resistance collectors $\text{Mg}(\text{PF}_6)_2$ electrolytes can be used as commercial electrolytes like those used in LIBs.

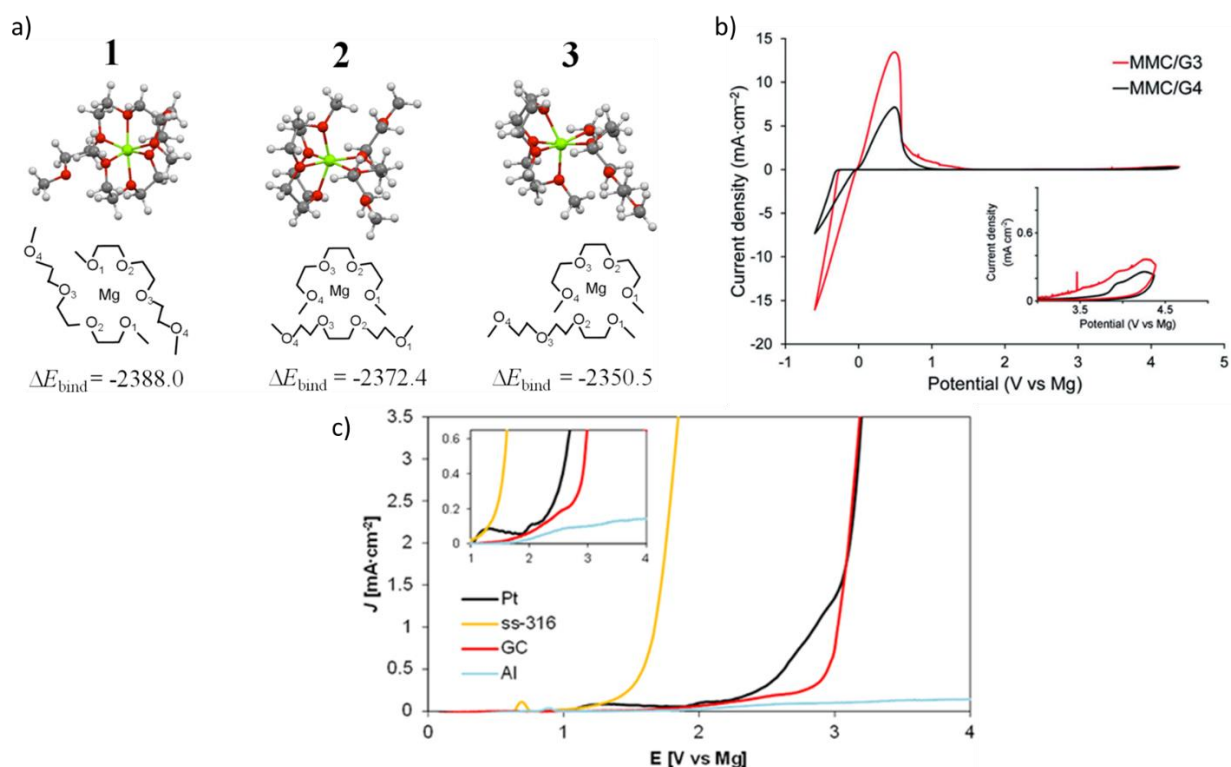


Figure 2.7. (a) Optimized geometries of $\text{Mg}(\text{G3})_2^{2+}$ complexes. Adapted with permission from Ref 37. Copyright {2021} American Chemical Society (b) First scan of acyclic voltammetry test of 0.75m MMC/G3 and 0.75m MMC/G4 on Pt electrode collected at 5mVs^{-1} . (Inset: enlargement of 3.0–5.0 V region). Adapted from Ref.38 Copyright (2021) Wiley (c) LSV of 0.12 M in 1:1 THF/ CH_3CN , scanning at a rate of $25\text{mV}\cdot\text{s}^{-1}$. Adapted with permission from Ref 39. Copyright {2021} American Chemical Society

Other salts of Magnesium containing ions such as BF_4^{-40} , BH_4^{-40} and HMDS^{-41} have also been studied. These electrolytes all have some stable species that keeps the system from decomposing. But the overpotential means that the use of the electrolytes is not very efficient. Magnesium Tetrafluoroborate and Magnesium Borane have both shown good electrolytic properties and have studied in great detail in recent years.⁴⁰ The ion pair formations as the Magnesium borohydride dissolves as well as the mobility behavior of the electrolyte species has been studied by Samuel et al.,

who reported the formation of ion pair clusters. These clusters could be useful in the transportation of charges and electronic mobility. Another interesting Mg salt-based electrolyte is $\text{Mg}(\text{HMDS})_2$ electrolytes. These have been shown to be exceptionally immune to the formation of passive layers on top of the anode, thereby shown good cyclability. These electrolytes need a Lewis acid such as AlCl_3 , which then releases some free Chlorides leading to the presence of Chloride driven corrosion on the anode side.⁴¹

2.3.4. *bis(trifluoromethane)sulfonimide (TFSI) based electrolytes*

The advantages of TFSI based solvents include the well-established TFSI based anion chemistry established in LIBs. Thus, TFSI based electrolytes have been in prime position for research by many people. The solution of $\text{Mg}(\text{TFSI})_2$ in glyme shows a unique behavior. As salt concentration in glyme increases the dissolved phase starts to form two immiscible and separate phases containing the same chemical composition. These are really interesting as the presence of such phases in a battery environment can cause different electronic properties of the electrolyte at different locations affecting cell behavior. Salama et al. used NMR, Raman spectroscopy (**Figure 2.4.b**) and X-ray diffraction coupled with DFT calculations to identify different conformers of TFSI around Mg and the two phases have different types of conformers, which leads to a thermodynamic difference which can be attributed to the phase separation.⁴² The presence of the conformers needs to be further analyzed and a further in depth study on the actual thermodynamics of the various conformers is needed to sufficiently identify the cause for the selective separation of the conformers.

Sa and co-workers studied the concentration effect of $\text{Mg}(\text{TFSI})_2$ dissolved in diglyme and identified that there was a non-linear relation in change in chemical properties to the change in concentration. They proposed that increased shielding in high electrolyte concentrations could affect the electrolyte behavior(see **Figure 2.4.a**).⁴³ The salt in diglyme also showed high stability and the reason for which

is still unknown. Baskin and Prendergast propose that the stability is highly dependent on the solvent structure and the ion pair interactions and that the thermodynamics of the dissolution is highly dependent on entropic contributions. A detailed analysis of this with a more focused identifications of physical and chemical effects could lead to a better understanding.⁴⁴

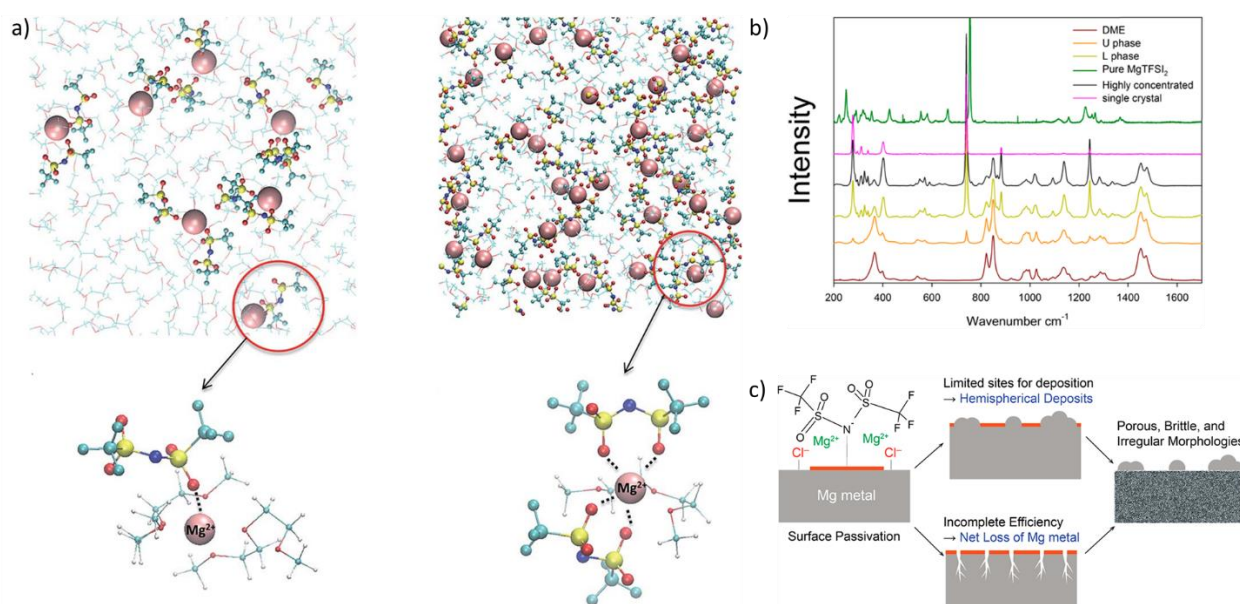


Figure 2.8. (a) Mg-TFSI-diglyme solvation structure at 0.1 M and 0.4 M concentrations. Reproduced from Ref. 43 with permission from the Royal Society of Chemistry (b) Raman spectra of pure DME (brown line), U-phase (orange line), L-phase (yellow line), 1.25 M MgTFSI₂ solution in DME, MgTFSI₂ single crystal recrystallized from MgTFSI₂/DME solution, and pure MgTFSI₂. Adapted with permission from Ref 43. Copyright {2021} American Chemical Society (c) Proposed Mg metal anode degradation mechanism. Adapted with permission from Ref 45. Copyright {2021} American Chemical Society

Yoo et al. studied the dissolution of Mg(TFSI)₂ in glyme based solvents and found that there is an incomplete reversible Mg deposition/dissolution occurring which leads to a corrosion of Mg anode. They propose that this occurs due to the formation of passivation layers on the anode surface as shown in **Figure 2.4.c** and these passivation layers might make TFSI based electrolytes extremely poor electrolytes especially if trace amounts of water is present.⁴⁵ Ma et al. tried to overcome this behavior

by adding $\text{Mg}(\text{BH}_4)_2$ along with $\text{Mg}(\text{TFSI})_2$ to remove the trace water molecules using the borohydride salt and improving stability.⁴⁶

With the advantages of a TFSI based structure and the drawbacks that are available and documented, Qu et al. tried to substitute different components in TFSI to improve stability and performance. They used a previously identified decomposition mechanism for TFSI and proposed targeted substitutions on positions that are more prone to decomposition reactions.⁴⁷ They proposed 15 new anions as shown in **Figure 2.5** and characterized them based on stability, tolerance towards hydrolysis and transport properties and narrowed down to two anionic species namely bis[(ditrifluoromethyl)phosphoryl]azanide (DTPA) and bis[methyl(ditrifluoromethyl)phosphoryl]azanide (MDPA) which showed better properties than TFSI. This is the first predictive screening study for electrolyte selection that I have seen.

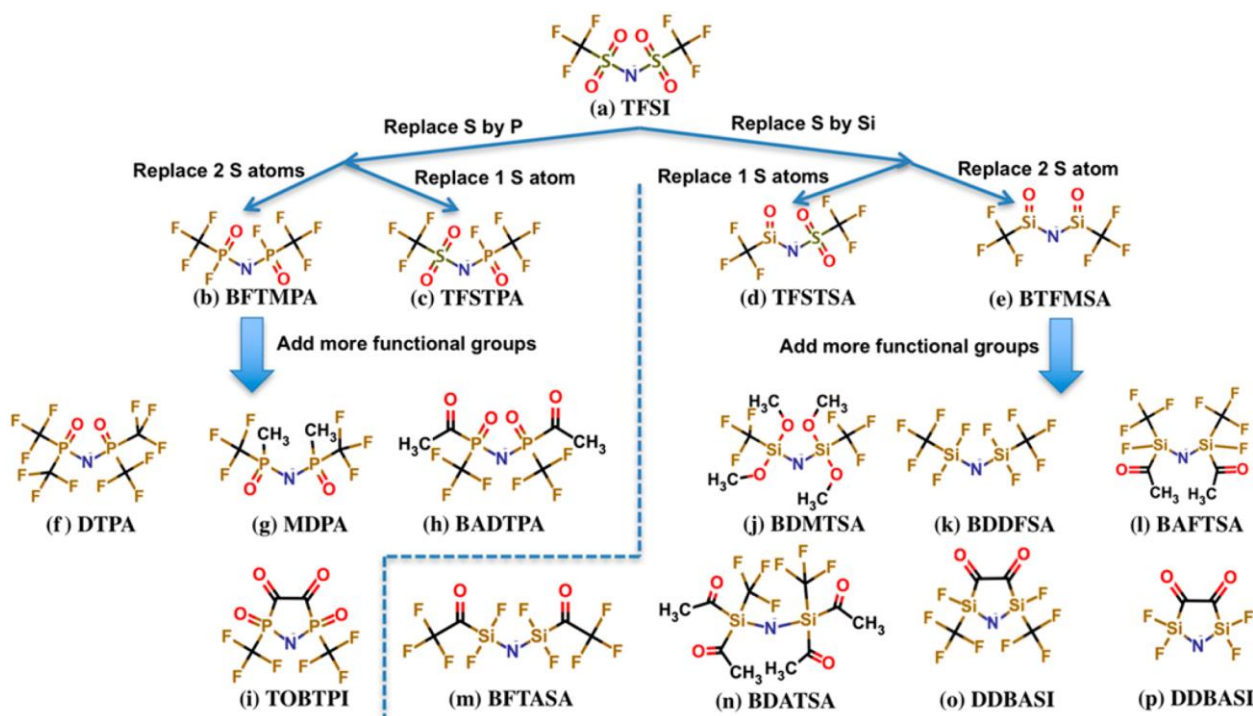


Figure 2.9. Schematic of anions derived from TFSI. Adapted with permission from Ref 47. Copyright {2021} American Chemical Society

Given the high stability, the main drawback of TFSI based solvents is the formation of surface passivation layers. To remove this surface passivation layer, Li and co-workers added MgI_2 , a Magnesium Halide to form an ion conducting layer at the anode interface. This method was successful and renders the electrolyte with its many advantages useful for application in Mg batteries.⁴⁸ This approach brings into play the Halides that were initially removed when salts such as $\text{Mg}(\text{TFSI})_2$ were proposed. Further, substitution of MgI_2 with MgCl_2 showed even better results and a significant improvement in TFSI based electrolyte behavior.⁴⁹ Similar effects have also been observed in HMDS based electrolytes as well.⁵⁰

The improvement in Magnesium salt-based electrolytes correlates with similar improvements in Organohaloaluminates of Magnesium. This improvement in electrolyte performance in both the cases has been shown to be the formation of the $[\text{Mg}_2\text{Cl}_3]^+$ based EAS.^{29, 51}

2.3.5. Speciation behavior and selectivity of the EAS

The Electroactive species have been shown to be the main driving force behind the performance of an electrolyte as seen earlier. But, the formation, selectivity and behavior of these species are yet to be fully understood. A lot of work has been done in identifying and understanding these EAS and they have shown to influence the performance of the whole cell. The results published though have a lot of contrast in them and thus end up proposing a lot of different EAS and also some contradictory results as well. This has led to the necessity of contrasting and comparing these different EAS intensively and understanding them to gain a better foothold in the process to develop novel electrolytes with substantially improved properties.

Mg ions in solutions are usually coordinated with anions and solvents. This is caused due to high charge density on the Mg^{2+} ions. The lone pairs on the ether oxygens tend to allow for significant

oxygen center coordination around Mg. There has been many different coordination for Mg-ion that have been observed. These include six-fold coordination, which is the most commonly reported, four-fold and five-fold coordination. The inability to identify the exact coordination may derive from the dynamic nature of Mg-solvent-anion equilibrium in solution. The coordination of the Mg species may significantly affect the EAS selectivity. Though experimental isolation of the six-fold coordinated EAS has been observed as discussed earlier, Canepa and coworkers have shown computationally that both Mg_2Cl_3^+ and MgCl^+ cations in solution exhibit lowered coordination.⁵² For Mg_2Cl_3^+ the most stable structure was five-fold coordination and for MgCl^+ it was the four-fold coordination (see **Figure 2.6**). This lowered coordination may significantly affect the lifetime of the EAS due to reduced coverage from the solvent. The lowered MgCl^+ coordination indicate a bias towards formation of the dimer $\text{Mg}_2\text{Cl}_2^{2+}$, though studies have shown that there is still significant presence of the monomer. The lack of literature discussing the effective role of the EAS selectivity driven by the cation coordination affects the understanding of the ionic behavior in the various regimes of the electrolyte.

Furthermore, there has been reported competition between monomeric and dimeric species that needs to be further investigated to understand the role of the EAS in the battery performance. Cheng et al. formulated and identified another new and unique cationic complex $[\text{Mg}_2(\mu\text{-Cl})_2.4\text{DME}]^{2+}$ by mixing MgCl_2 and AlCl_3 in the ratio of 1:1 in a DME solvent to form the mentioned EAS. The formation pathway follows the formation of the MgCl^+ monomer which dimerizes due to the strong stabilization of the solvent molecules. These electrolytes that produce such EAS show significant performance with near 100% cyclic efficiency and good stability (up to 3.5 V vs Mg).⁵³ A similar dimerized MgCl^+ cation has also been reported by Salama and co-workers who have shown the formation of the said EAS along with another species ($[\text{Mg}_3\text{Cl}_4]^{2+}$) which are both stabilized due to the bidentate nature of DME. They hypothesize that an increase in the number of Oxygen dentate positions can lead to a

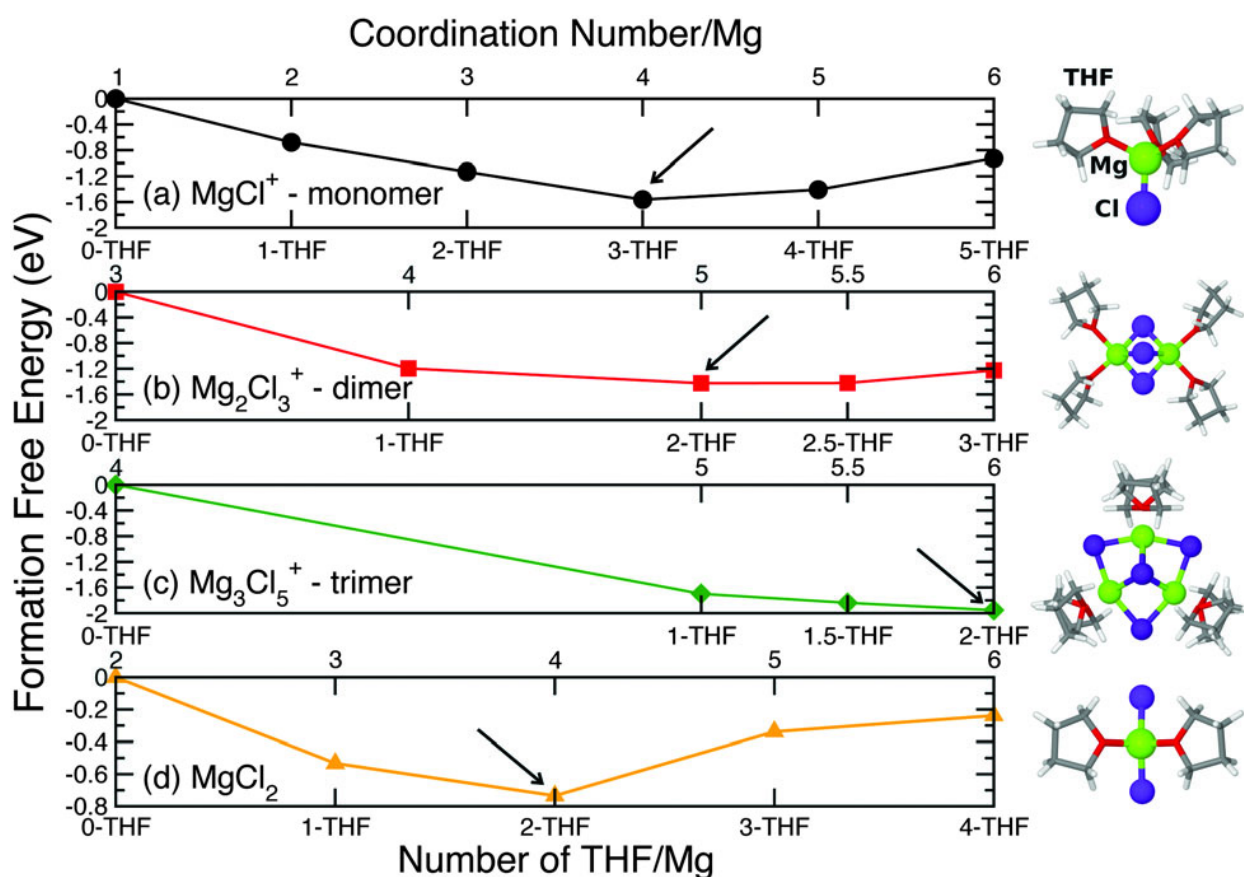


Figure 2.10. Formation free energy of Mg-EAS-THF at different THF coordination. Reproduced from Ref. 52 with permission from the Royal Society of Chemistry

better stabilization and form larger cations, but the effect and performance of a larger cationic species is still up for debate and may not necessarily be a positive contrary to the opinion of the authors. The authors also point out that the various species including the most common dimer the Mg_2Cl_3^+ system greatly improves the behavior of the electrolyte but postulate that the improvement may not be a completely solution-based phenomenon and may involve significant influence from surface or near surface phenomena.⁵⁴ In a similar chemistry and adding to the complexity and confusion, He and co-workers showed the formation of the monomeric MgCl^+ instead when the same 1:1 ratio of MgCl_2 and AlCl_3 are used (see **Figure 2.7.**). They propose that any water impurity, however small, in the system could drive the equilibrium towards a different less effective cationic species and must be

thoroughly accounted for.⁵⁵ Mandai and co-workers add that though the monomeric EAS show significant performance and is more stable, the more unstable bridged Chlorine complex of Mg_2Cl_3^+ would favorably affect the electrochemical activity of the system.⁵⁶ Thus, selective formation of EAS at different parts of the electrolyte could help in creating a more stable and extremely active electrolyte is an important question to be answered, though the existence of such a phenomenon is unverified and is one of the problems this project will look to answering.

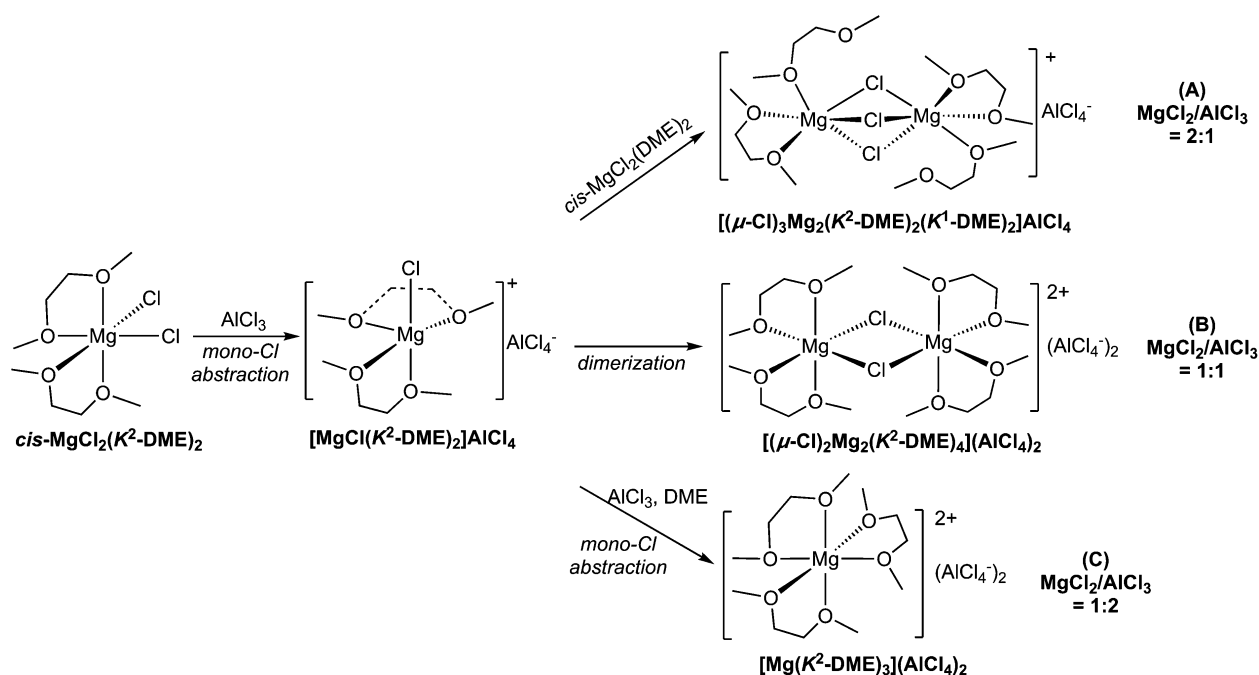


Figure 2.11. Scheme showing the EAS selectivity controlled by stoichiometry. Reproduced from Ref. 55 with permission from the Royal Society of Chemistry

Further work has shown contrasting approaches to the role of the EAS. The dimer species has been shown to have better solubility in THF⁵⁷ and DME⁵⁵ and has been reported to work conditioning free. It has been suggested that the thermodynamically unstable monomeric species may be the reason behind high overpotential observed in systems that are stoichiometrically driven towards monomeric species selection.⁵⁸ Further Barile et al., have shown that electrochemical deposition of the Mg-ion

can occur only when the dimeric species is present.⁵⁹ On the other hand, Wan et al studied the role of the Mg-cationic species using DFT and showed that the monomeric species is more conducive for deposition as the THF ligand in the dimeric species is thermodynamically harder to remove.⁶⁰ This is because the desolvation energy for Mg increases with the number of solvent molecules present around the cation. Experimental observations of the monomeric cation aided depositions in MACC electrolytes have not been reported but similar organohaloaluminates containing electrolytes have shown the presence of the monomeric Mg cation by Benmayza and co-workers who proposed that there was an equilibrium between monomeric and dimeric species though the monomeric species is selectively the one controlling the deposition mechanism.⁶¹ Liu et al showed that the both Mg_2Cl_3^+ and MgCl^+ may be present at the surface of the Mg anode and the rate determining step is the formation of the neutral $[\text{MgCl}]^0$ species.⁶² DFT studies conducted by Moss and co-workers support the experimental results from Liu.⁶³

2.3.6. *Electrolytic conditioning and factors affecting the EAS selectivity*

In MACC electrolytes the deposition of the Aluminum alongside Mg has been observed. This co-deposition occurs until the electrolyte conditioning is complete. Electrolyte conditioning is the process by which the electrolyte near the surface is selectively driven towards the presence of the cationic species. To overcome this, multiple factors have been studied.

The selection of the cation is also controlled by the Lewis acid donor as shown by Brouillet et al..⁵⁷ They solvated MgCl_2 in different Lewis acid donors and selectively generating mono-, di- and tri-nuclear cationic species of the general form Mg_xCl_y . The dimeric cation is shown to be the thermodynamically stable species but other species can be generated in significant concentrations. They also show that though one species is selectively present, it does not indicate the total absence of the others, rather they are present in smaller quantities. This introduces the question of whether the

concentration of the electrolyte is uniform or if the surface phenomena can create concentration profiles. Considering the size of the interfacial layer this may not be answerable using experiments alone and could be answered using a combination of computational and experimental techniques. The authors though have not attempted to answer the question and thus it remains a significant open problem with a lot of consequences.

The Mg deposition/dissolution kinetics are affected electrolyte concentration along with the associated current density. Though an increase in the Mg ion concentration is expected to increase the current density, but the enhancements in MACC electrolyte system cannot just be explained increase in concentration. See et al.⁶⁴ show that the increase in the salt concentrations directs the species selectivity towards on specific species and shifts the equilibria(see **Figure 2.8.a**). Increasing the concentration of MgCl_2 and AlCl_3 directs the equilibria towards the formation of $\text{Mg}_2\text{Cl}_3.6\text{THF}^+$ which results in faster electrolyte activation and increased deposition current. The authors suggest a conditioning process to increase the dimer cation concentrations to ensure best electrolyte performance. In an earlier work, the authors also point out that though conditioning drives species selection, the species is still present in the as prepared electrolyte though with competing cations (see **Figure 2.8.b**).⁶⁵ It should also be pointed out that the best conditioning technique is to introduce Cl^- into the solution⁶⁵, though free Chloride ions increase corrosion and their exact mechanism in driving the species selectivity is still unknown and is an interesting and important to be answered. Another important consideration is that equilibria for making an active MACC electrolyte is complex and is influenced by all components of the surrounding environment and thus must all be taken into consideration and even the slightest change in the system could affect the balance.

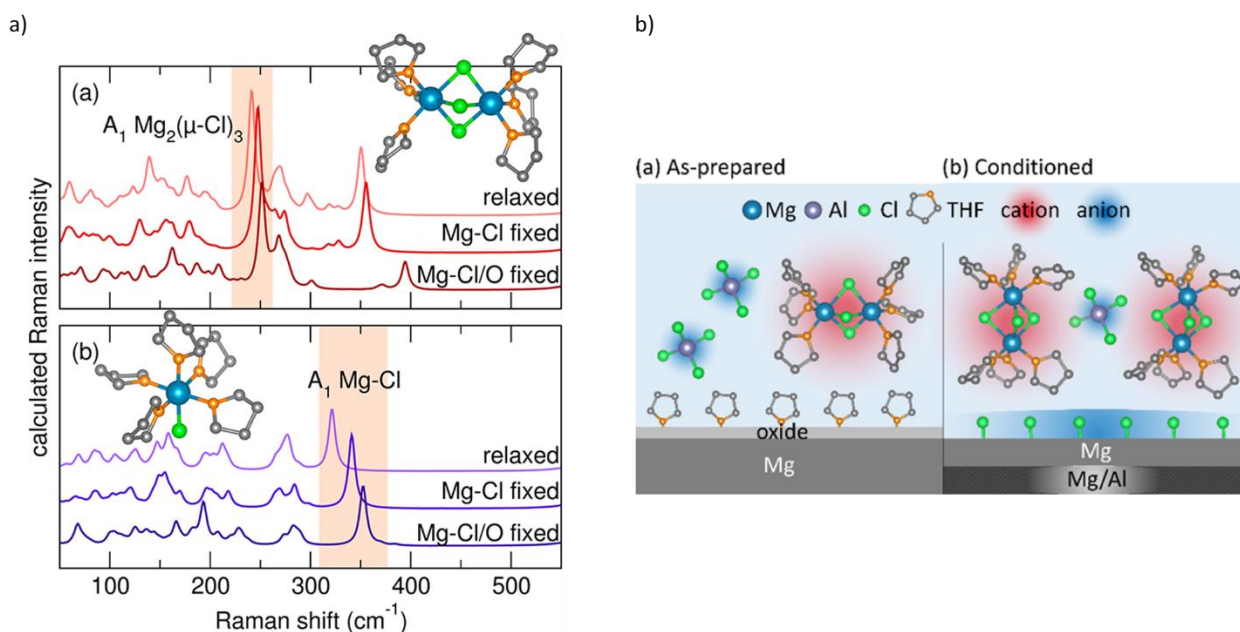


Figure 2.12. (a) Raman spectra of $Mg_2Cl_3^+$ and $MgCl^+$ complexes. Adapted with permission from Ref 64. Copyright {2021} American Chemical Society (b) Scheme representing the As-prepared and conditioned anode electrolyte interface. Adapted with permission from Ref 65. Copyright {2021} American Chemical Society

To direct selectivity and improve performance, there have been other attempts by adding other components to direct the equilibria as well as by adding moieties to the Lewis acid to reduce the competitive role of Al. Nist-Lund et al.⁶⁶ and Crowe et al.⁶⁷ took a similar path by adding moieties to the Grignard's reagent and exchanging the moieties to drive the equilibrium. Nist-Lund added tert-(triphenyl) butoxide ($[OCPh_3]^-$) while Crowe added alkyl substituted phenol-based Grignard's reagents. Another approach has been to introduce a metallic species like Mg metal and Cr^{3+} compounds.⁶⁸⁻⁶⁹ They have shown good performance leading to MACC-like species but with significant drawbacks especially with Cr containing systems as they are extremely toxic and may not be suitable for commercial purposes.

2.3.7. Ionic clustering and EAS pairing

The complexity of the cation-anion-solvent complexes are further compounded by the presence of ionic clusters formed within the system. Ionic cluster formation in other ionic electrolytes have been proposed due to discrepancies between experimental and theoretical results.⁷⁰ Experiments have been used directly or indirectly observe ion cluster formations in simpler electrolytes.⁷¹⁻⁷² Molinari et al. calculated the coordination of the cations as a function of anions and electrolyte concentration (see **Figure 2.9**).⁷⁰ The authors show that larger clusters tend to be richer in anions though the reason behind the asymmetry is still to be understood. Simulations have been performed on NaCl solutions at both ambient and supercritical conditions to observe ion cluster formation and further analyze the impact of the clusters formed.^{70, 73-74} Similar ion agglomerations have been shown to trigger side reactions at the anode-electrolyte interfaces in Mg batteries.^{52, 75} The agglomeration of Mg^{2+} - BH_4^- clusters in $\text{Mg}(\text{BH}_4)_2$ -based electrolytes for RMBs show lowered solubility as confirmed both experimentally and theoretically.^{40, 76-77} The presence of ion clusters have also shown to improve the Ca^{2+} surface deposition by enabling the presence of CaBH_4^+ cationic species in Calcium ion batteries.⁷⁸ Similar experimental work done on Magnesium amidohaloaluminates containing electrolytes show significant improvement in plating mechanism aided by the cluster forming cations.⁷⁹ Further modelling studies on Mg tetrakis(hexafluoroisopropoxy)borate in DME electrolytes show that the inclusion of clustering in models can further enhance accuracy of computed properties that can replicate experimental data.⁸⁰ Hence accounting for the ionic clustering in Mg-electrolytes is important gaining a thorough understanding of the underlying interactions in electrolyte performance.

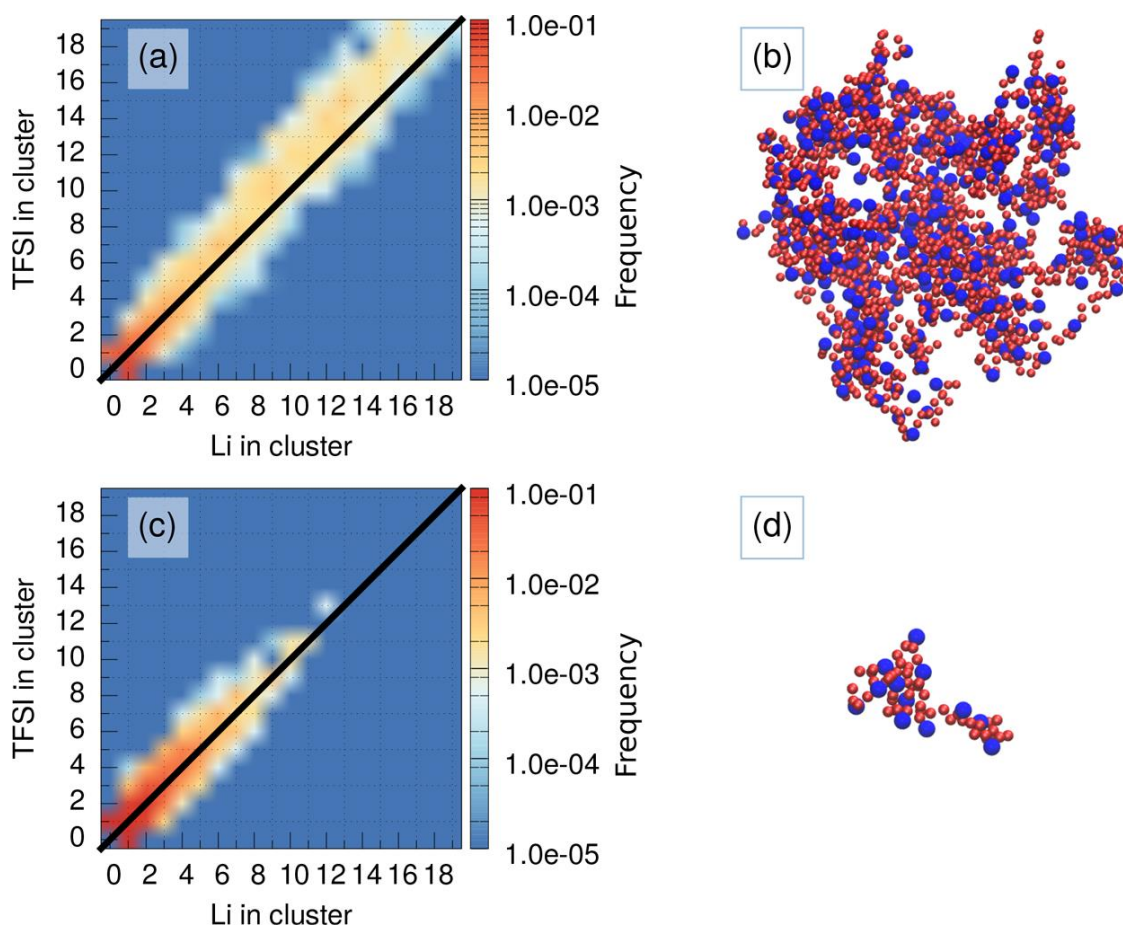


Figure 2.13. Cluster analysis. Parts (a) and (b) refer to the 4 M case, while (c) and (d) refer to the 1 M one. The plots on the left, (a)–(c), summarize the cluster compositions during the simulation. The plots on the right, (b)–(d), show the biggest cluster formations found during the dynamics. Adapted with permission from Ref 72. Copyright {2021} American Chemical Society

2.4. SUMMARY

In summary, it must be noted that there are different significant aspects of the MIB which need to be answered to produce a commercially viable battery. The electrolyte and the anode-electrolyte interface are an extremely complex and confusing part of this problem and the various electrolytes that are being tested lead to the one conclusion that MgCl_2 is important, but the plethora of cationic species produced and variety of factors and contradicting reaction products reported show that until

one gains a thorough understanding of the electrolyte system, one cannot really improve on existing battery performance. There are significant gaps in existing knowledge and plugging them will be an arduous task which this project will try and undertake. On a final note, the selection of solvents, electrodes and other materials for the MIB have used the tried and tested benchmark of LIBs but one must note a key point is that the only electroactive species in an LIB is Li^+ ion alone, which with all its quirks, is much easier to characterize compared to the bevy of cationic species formed due to Magnesium's high ionic charge density leading to a pageant of competing cationic species each with its own intricacies and advantages, hanging in the balance of equilibrium easily swayed by even minute external influences that selecting one would be ideal but may be impossible and multiple species must be accounted for and understood to gain a holistic perspective of the behavior of the electrolyte and of the battery as a whole.

REFERENCES

1. Li, W.; Li, C.; Zhou, C.; Ma, H.; Chen, J., Metallic Magnesium Nano/Mesoscale Structures: Their Shape-Controlled Preparation and Mg/Air Battery Applications. *Angewandte Chemie International Edition* **2006**, 45 (36), 6009-6012.
2. Liang, Y.; Feng, R.; Yang, S.; Ma, H.; Liang, J.; Chen, J., Rechargeable Mg Batteries with Graphene-like MoS_2 Cathode and Ultrasmall Mg Nanoparticle Anode. *Advanced Materials* **2011**, 23 (5), 640-643.
3. Yim, T.; Woo, S.-G.; Lim, S.-H.; Yoo, J.-Y.; Cho, W.; Park, M.-S.; Han, Y.-K.; Kim, Y.-J.; Yu, J., Magnesium Anode Pretreatment Using a Titanium Complex for Magnesium Battery. *ACS Sustainable Chemistry & Engineering* **2017**, 5 (7), 5733-5739.
4. Chen, T.; Ceder, G.; Sai Gautam, G.; Canepa, P., Evaluation of Mg Compounds as Coating Materials in Mg Batteries. *Frontiers in Chemistry* **2019**, 7 (24).

-
5. 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. *Nature Chemistry* **2018**, *10* (5), 532-539.
 6. Tang, K.; Du, A.; Dong, S.; Cui, Z.; Liu, X.; Lu, C.; Zhao, J.; Zhou, X.; Cui, G., A Stable Solid Electrolyte Interphase for Magnesium Metal Anode Evolved from a Bulky Anion Lithium Salt. *Advanced Materials* **2020**, *32* (6), 1904987.
 7. Arthur, T. S.; Singh, N.; Matsui, M., Electrodeposited Bi, Sb and Bi_{1-x}Sb_x alloys as anodes for Mg-ion batteries. *Electrochemistry Communications* **2012**, *16* (1), 103-106.
 8. Shao, Y.; Gu, M.; Li, X.; Nie, Z.; Zuo, P.; Li, G.; Liu, T.; Xiao, J.; Cheng, Y.; Wang, C.; Zhang, J.-G.; Liu, J., Highly Reversible Mg Insertion in Nanostructured Bi for Mg Ion Batteries. *Nano Letters* **2014**, *14* (1), 255-260.
 9. Jin, W.; Li, Z.; Wang, Z.; Fu, Y. Q., Mg ion dynamics in anode materials of Sn and Bi for Mg-ion batteries. *Materials Chemistry and Physics* **2016**, *182*, 167-172.
 10. Singh, N.; Arthur, T. S.; Ling, C.; Matsui, M.; Mizuno, F., A high energy-density tin anode for rechargeable magnesium-ion batteries. *Chemical Communications* **2013**, *49* (2), 149-151.
 11. Malyi, O. I.; Tan, T. L.; Manzhos, S., In search of high performance anode materials for Mg batteries: Computational studies of Mg in Ge, Si, and Sn. *Journal of Power Sources* **2013**, *233*, 341-345.
 12. Cheng, Y.; Shao, Y.; Parent, L. R.; Sushko, M. L.; Li, G.; Sushko, P. V.; Browning, N. D.; Wang, C.; Liu, J., Interface Promoted Reversible Mg Insertion in Nanostructured Tin–Antimony Alloys. *Advanced Materials* **2015**, *27* (42), 6598-6605.
 13. Er, D.; Detsi, E.; Kumar, H.; Shenoy, V. B., Defective Graphene and Graphene Allotropes as High-Capacity Anode Materials for Mg Ion Batteries. *ACS Energy Letters* **2016**, *1* (3), 638-645.
 14. Kim, D.-M.; Jung, S. C.; Ha, S.; Kim, Y.; Park, Y.; Ryu, J. H.; Han, Y.-K.; Lee, K. T., Cointercalation of Mg²⁺ Ions into Graphite for Magnesium-Ion Batteries. *Chemistry of Materials* **2018**, *30* (10), 3199-3203.
 15. Wu, N.; Lyu, Y.-C.; Xiao, R.-J.; Yu, X.; Yin, Y.-X.; Yang, X.-Q.; Li, H.; Gu, L.; Guo, Y.-G., A highly reversible, low-strain Mg-ion insertion anode material for rechargeable Mg-ion batteries. *NPG Asia Materials* **2014**, *6* (8), e120-e120.
-

-
16. Jin, W.; Wang, Z.; Fu, Y. Q., Monolayer black phosphorus as potential anode materials for Mg-ion batteries. *Journal of Materials Science* **2016**, *51* (15), 7355-7360.
 17. Mortazavi, B.; Dianat, A.; Rahaman, O.; Cuniberti, G.; Rabczuk, T., Borophene as an anode material for Ca, Mg, Na or Li ion storage: A first-principle study. *Journal of Power Sources* **2016**, *329*, 456-461.
 18. Sibari, A.; Marjaoui, A.; Lakhal, M.; Kerrami, Z.; Kara, A.; Benaissa, M.; Ennaoui, A.; Hamedoun, M.; Benyoussef, A.; Mounkachi, O., Phosphorene as a promising anode material for (Li/Na/Mg)-ion batteries: A first-principle study. *Solar Energy Materials and Solar Cells* **2018**, *180*, 253-257.
 19. Bucur, C. B.; Gregory, T.; Oliver, A. G.; Muldoon, J., Confession of a Magnesium Battery. *The Journal of Physical Chemistry Letters* **2015**, *6* (18), 3578-3591.
 20. Song, Y.; Zavalij, P. Y.; Whittingham, M. S., ϵ -VOPO₄: Electrochemical Synthesis and Enhanced Cathode Behavior. *Journal of The Electrochemical Society* **2005**, *152* (4), A721-A728.
 21. Lu, C.; Rooney, D. W.; Jiang, X.; Sun, W.; Wang, Z.; Wang, J.; Sun, K., Achieving high specific capacity of lithium-ion battery cathodes by modification with "N-O[radical dot]" radicals and oxygen-containing functional groups. *Journal of Materials Chemistry A* **2017**, *5* (47), 24636-24644.
 22. Li, W.; Song, B.; Manthiram, A., High-voltage positive electrode materials for lithium-ion batteries. *Chemical Society Reviews* **2017**, *46* (10), 3006-3059.
 23. Liu, C.; Neale, Z. G.; Cao, G., Understanding electrochemical potentials of cathode materials in rechargeable batteries. *Materials Today* **2016**, *19* (2), 109-123.
 24. 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. *Journal of The Electrochemical Society* **2002**, *149* (2), A115-A121.
 25. Gregory, T. D.; Hoffman, R. J.; Winterton, R. C., Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. *Journal of The Electrochemical Society* **1990**, *137* (3), 775-780.
 26. 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 & Environmental Science* **2012**, *5* (3), 5941-5950.
 27. Song, J.; Sahadeo, E.; Noked, M.; Lee, S. B., Mapping the Challenges of Magnesium Battery. *The Journal of Physical Chemistry Letters* **2016**, *7* (9), 1736-1749.
-

-
28. John, M.; B., B. C.; Thomas, G., Fervent Hype behind Magnesium Batteries: An Open Call to Synthetic Chemists—Electrolytes and Cathodes Needed. *Angewandte Chemie International Edition* **2017**, *56* (40), 12064-12084.
29. Pan, B.; Huang, J.; Sa, N.; Brombosz, S. M.; Vaughey, J. T.; Zhang, L.; Burrell, A. K.; Zhang, Z.; Liao, C., MgCl₂: The Key Ingredient to Improve Chloride Containing Electrolytes for Rechargeable Magnesium-Ion Batteries. *Journal of The Electrochemical Society* **2016**, *163* (8), A1672-A1677.
30. Vestfried, Y.; Chusid, O.; Goffer, Y.; Aped, P.; Aurbach, D., Structural Analysis of Electrolyte Solutions Comprising Magnesium–Aluminate Chloro–Organic Complexes by Raman Spectroscopy. *Organometallics* **2007**, *26* (13), 3130-3137.
31. Doron, A.; Idit, W.; Yosef, G.; Elena, L., Nonaqueous magnesium electrochemistry and its application in secondary batteries. *The Chemical Record* **2003**, *3* (1), 61-73.
32. Pour, N.; Gofer, Y.; Major, D. T.; Aurbach, D., Structural Analysis of Electrolyte Solutions for Rechargeable Mg Batteries by Stereoscopic Means and DFT Calculations. *Journal of the American Chemical Society* **2011**, *133* (16), 6270-6278.
33. 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. *Nature Communications* **2011**, *2*, 427.
34. Matsui, M., Study on electrochemically deposited Mg metal. *Journal of Power Sources* **2011**, *196* (16), 7048-7055.
35. Nelson, E. G.; Brody, S. I.; Kampf, J. W.; Bartlett, B. M., A magnesium tetraphenylaluminate battery electrolyte exhibits a wide electrochemical potential window and reduces stainless steel corrosion. *Journal of Materials Chemistry A* **2014**, *2* (43), 18194-18198.
36. Muldoon, J.; Bucur, C. B.; Gregory, T., Quest for Nonaqueous Multivalent Secondary Batteries: Magnesium and Beyond. *Chemical Reviews* **2014**, *114* (23), 11683-11720.
37. Kimura, T.; Fujii, K.; Sato, Y.; Morita, M.; Yoshimoto, N., Solvation of Magnesium Ion in Triglyme-Based Electrolyte Solutions. *The Journal of Physical Chemistry C* **2015**, *119* (33), 18911-18917.
38. Oscar, T.; Rana, M.; S., A. T.; Fuminori, M.; G., N. E.; V., S. Y., An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angewandte Chemie International Edition* **2015**, *54* (27), 7900-7904.
-

-
39. 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. *Journal of the American Chemical Society* **2016**, *138* (28), 8682-8685.
40. Samuel, D.; Steinhäuser, C.; Smith, J. G.; Kaufman, A.; Radin, M. D.; Naruse, J.; Hiramatsu, H.; Siegel, D. J., Ion Pairing and Diffusion in Magnesium Electrolytes Based on Magnesium Borohydride. *ACS Applied Materials & Interfaces* **2017**, *9* (50), 43755-43766.
41. Merrill, L. C.; Schaefer, J. L., Electrochemical Properties and Speciation in Mg(HMDS)₂-Based Electrolytes for Magnesium Batteries as a Function of Ethereal Solvent Type and Temperature. *Langmuir* **2017**, *33* (37), 9426-9433.
42. Salama, M.; Shterenberg, I.; Gizbar, H.; Eliaz, N. N.; Kosa, M.; Keinan-Adamsky, K.; Afri, M.; Shimon, L. J. W.; Gottlieb, H. E.; Major, D. T.; Gofer, Y.; Aurbach, D., Unique Behavior of Dimethoxyethane (DME)/Mg(N(SO₂CF₃)₂)₂ Solutions. *The Journal of Physical Chemistry C* **2016**, *120* (35), 19586-19594.
43. Sa, N.; Rajput, N. N.; Wang, H.; Key, B.; Ferrandon, M.; Srinivasan, V.; Persson, K. A.; Burrell, A. K.; Vaughey, J. T., Concentration dependent electrochemical properties and structural analysis of a simple magnesium electrolyte: magnesium bis(trifluoromethane sulfonyl)imide in diglyme. *RSC Advances* **2016**, *6* (114), 113663-113670.
44. Baskin, A.; Prendergast, D., Exploration of the Detailed Conditions for Reductive Stability of Mg(TFSI)₂ in Diglyme: Implications for Multivalent Electrolytes. *The Journal of Physical Chemistry C* **2016**, *120* (7), 3583-3594.
45. Yoo, H. D.; Han, S.-D.; Bolotin, I. L.; Nolis, G. M.; Bayliss, R. D.; Burrell, A. K.; Vaughey, J. T.; Cabana, J., Degradation Mechanisms of Magnesium Metal Anodes in Electrolytes Based on (CF₃SO₂)₂N[−] at High Current Densities. *Langmuir* **2017**, *33* (37), 9398-9406.
46. Ma, Z.; Kar, M.; Xiao, C.; Forsyth, M.; MacFarlane, D. R., Electrochemical cycling of Mg in Mg[TFSI]₂/tetraglyme electrolytes. *Electrochemistry Communications* **2017**, *78*, 29-32.
47. Qu, X.; Zhang, Y.; Rajput, N. N.; Jain, A.; Maginn, E.; Persson, K. A., Computational Design of New Magnesium Electrolytes with Improved Properties. *The Journal of Physical Chemistry C* **2017**, *121* (30), 16126-16136.
-

-
48. Xiaogang, L.; Tao, G.; Fudong, H.; Zhaohui, M.; Xiulin, F.; Singyuk, H.; Nico, E.; Weishan, L.; Chunsheng, W., Reducing Mg Anode Overpotential via Ion Conductive Surface Layer Formation by Iodine Additive. *Advanced Energy Materials* **2018**, *8* (7), 1701728.
49. Sa, N.; Pan, B.; Saha-Shah, A.; Hubaud, A. A.; Vaughey, J. T.; Baker, L. A.; Liao, C.; Burrell, A. K., Role of Chloride for a Simple, Non-Grignard Mg Electrolyte in Ether-Based Solvents. *ACS Applied Materials & Interfaces* **2016**, *8* (25), 16002-16008.
50. Liao, C.; Sa, N.; Key, B.; Burrell, A. K.; Cheng, L.; Curtiss, L. A.; Vaughey, J. T.; Woo, J.-J.; Hu, L.; Pan, B.; Zhang, Z., The unexpected discovery of the Mg(HMDS)₂/MgCl₂ complex as a magnesium electrolyte for rechargeable magnesium batteries. *Journal of Materials Chemistry A* **2015**, *3* (11), 6082-6087.
51. Baofei, P.; Jinhua, H.; Meinan, H.; M., B. S.; T., V. J.; Lu, Z.; K., B. A.; Zhengcheng, Z.; Chen, L., The Role of MgCl₂ as a Lewis Base in ROMgCl–MgCl₂ Electrolytes for Magnesium-Ion Batteries. *ChemSusChem* **2016**, *9* (6), 595-599.
52. 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 & Environmental Science* **2015**, *8* (12), 3718-3730.
53. Cheng, Y.; Stolley, R. M.; Han, K. S.; Shao, Y.; Arey, B. W.; Washton, N. M.; Mueller, K. T.; Helm, M. L.; Sprenkle, V. L.; Liu, J.; Li, G., Highly active electrolytes for rechargeable Mg batteries based on a [Mg₂(μ-Cl)₂]²⁺ cation complex in dimethoxyethane. *Physical Chemistry Chemical Physics* **2015**, *17* (20), 13307-13314.
54. Salama, M.; Shterenberg, I.; J.W. Shimon, L.; Keinan-Adamsky, K.; Afri, M.; Gofer, Y.; Aurbach, D., Structural Analysis of Magnesium Chloride Complexes in Dimethoxyethane Solutions in the Context of Mg Batteries Research. *The Journal of Physical Chemistry C* **2017**, *121* (45), 24909-24918.
55. He, S.; Luo, J.; Liu, T. L., MgCl₂/AlCl₃ electrolytes for reversible Mg deposition/stripping: electrochemical conditioning or not? *Journal of Materials Chemistry A* **2017**, *5* (25), 12718-12722.
56. Mandai, T.; Akita, Y.; Yagi, S.; Egashira, M.; Munakata, H.; Kanamura, K., A key concept of utilization of both non-Grignard magnesium chloride and imide salts for rechargeable Mg battery electrolytes. *Journal of Materials Chemistry A* **2017**, *5* (7), 3152-3156.
-

-
57. Brouillet, E. V.; Kennedy, A. R.; Koszinowski, K.; McLellan, R.; Mulvey, R. E.; Robertson, S. D., Exposing elusive cationic magnesium–chloro aggregates in aluminate complexes through donor control. *Dalton Transactions* **2016**, 45 (13), 5590-5597.
58. Barile, C. J.; Nuzzo, R. G.; Gewirth, A. A., Exploring Salt and Solvent Effects in Chloride-Based Electrolytes for Magnesium Electrodeposition and Dissolution. *The Journal of Physical Chemistry C* **2015**, 119 (24), 13524-13534.
59. 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. *The Journal of Physical Chemistry C* **2014**, 118 (48), 27623-27630.
60. 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. *Journal of the American Chemical Society* **2014**, 136 (41), 14456-14464.
61. Benmayza, A.; Ramanathan, M.; Arthur, T. S.; Matsui, M.; Mizuno, F.; Guo, J.; Glans, P.-A.; Prakash, J., Effect of Electrolytic Properties of a Magnesium Organohaloaluminate Electrolyte on Magnesium Deposition. *The Journal of Physical Chemistry C* **2013**, 117 (51), 26881-26888.
62. 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 $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer electrolytes for rechargeable Mg batteries. *Chemical Communications* **2015**, 51 (12), 2312-2315.
63. Moss, J. B.; Zhang, L.; Nielson, K. V.; Bi, Y.; Wu, C.; Scheiner, S.; Liu, T. L., Computational Insights into Mg-Cl Complex Electrolytes for Rechargeable Magnesium Batteries. *Batteries & Supercaps* **2019**, 2 (9), 792-800.
64. See, K. A.; Liu, Y.-M.; Ha, Y.; Barile, C. J.; Gewirth, A. A., Effect of Concentration on the Electrochemistry and Speciation of the Magnesium Aluminum Chloride Complex Electrolyte Solution. *ACS Applied Materials & Interfaces* **2017**, 9 (41), 35729-35739.
65. See, K. A.; Chapman, K. W.; Zhu, L.; Wiaderek, K. M.; Borkiewicz, O. J.; Barile, C. J.; Chupas, P. J.; Gewirth, A. A., The Interplay of Al and Mg Speciation in Advanced Mg Battery Electrolyte Solutions. *Journal of the American Chemical Society* **2016**, 138 (1), 328-337.
66. Nist-Lund, C. A.; Herb, J. T.; Arnold, C. B., Improving halide-containing magnesium-ion electrolyte performance via sterically hindered alkoxide ligands. *Journal of Power Sources* **2017**, 362, 308-314.
-

-
67. Crowe, A. J.; Bartlett, B. M., Influence of steric bulk on the oxidative stability of phenolate-based magnesium-ion battery electrolytes. *Journal of Materials Chemistry A* **2016**, *4* (2), 368-371.
68. Ha, J. H.; Adams, B.; Cho, J.-H.; Duffort, V.; Kim, J. H.; Chung, K. Y.; Cho, B. W.; Nazar, L. F.; Oh, S. H., A conditioning-free magnesium chloride complex electrolyte for rechargeable magnesium batteries. *Journal of Materials Chemistry A* **2016**, *4* (19), 7160-7164.
69. Luo, J.; He, S.; Liu, T. L., Tertiary Mg/MgCl₂/AlCl₃ Inorganic Mg²⁺ Electrolytes with Unprecedented Electrochemical Performance for Reversible Mg Deposition. *ACS Energy Letters* **2017**, *2* (5), 1197-1202.
70. Ren, G.; Shi, R.; Wang, Y., Structural, Dynamic, and Transport Properties of Concentrated Aqueous Sodium Chloride Solutions under an External Static Electric Field. *The Journal of Physical Chemistry B* **2014**, *118* (16), 4404-4411.
71. Frege, C.; Ortega, I. K.; Rissanen, M. P.; Praplan, A. P.; Steiner, G.; Heinritzi, M.; Ahonen, L.; Amorim, A.; Bernhammer, A. K.; Bianchi, F.; Brilke, S.; Breitenlechner, M.; Dada, L.; Dias, A.; Duplissy, J.; Ehrhart, S.; El-Haddad, I.; Fischer, L.; Fuchs, C.; Garmash, O.; Gonin, M.; Hansel, A.; Hoyle, C. R.; Jokinen, T.; Junninen, H.; Kirkby, J.; Kürten, A.; Lehtipalo, K.; Leiminger, M.; Mauldin, R. L.; Molteni, U.; Nichman, L.; Petäjä, T.; Sarnela, N.; Schobesberger, S.; Simon, M.; Sipilä, M.; Stolzenburg, D.; Tomé, A.; Vogel, A. L.; Wagner, A. C.; Wagner, R.; Xiao, M.; Yan, C.; Ye, P.; Curtius, J.; Donahue, N. M.; Flagan, R. C.; Kulmala, M.; Worsnop, D. R.; Winkler, P. M.; Dommen, J.; Baltensperger, U., Influence of temperature on the molecular composition of ions and charged clusters during pure biogenic nucleation. *Atmos. Chem. Phys.* **2018**, *18* (1), 65-79.
72. Molinari, N.; Mailoa, J. P.; Kozinsky, B., Effect of Salt Concentration on Ion Clustering and Transport in Polymer Solid Electrolytes: A Molecular Dynamics Study of PEO–LiTFSI. *Chemistry of Materials* **2018**, *30* (18), 6298-6306.
73. He, Z.; Cui, H.; Hao, S.; Wang, L.; Zhou, J., Electric-Field Effects on Ionic Hydration: A Molecular Dynamics Study. *The Journal of Physical Chemistry B* **2018**, *122* (22), 5991-5998.
74. Murad, S., The role of external electric fields in enhancing ion mobility, drift velocity, and drift–diffusion rates in aqueous electrolyte solutions. *The Journal of Chemical Physics* **2011**, *134* (11), 114504.
-

-
75. 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. *Chemical Reviews* **2017**, *117* (5), 4287-4341.
76. Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S.-J., Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angewandte Chemie International Edition* **2012**, *51* (39), 9780-9783.
77. 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. *Angewandte Chemie International Edition* **2015**, *54* (27), 7900-7904.
78. Hahn, N. T.; Self, J.; Seguin, T. J.; Driscoll, D. M.; Rodriguez, M. A.; Balasubramanian, M.; Persson, K. A.; Zavadil, K. R., The critical role of configurational flexibility in facilitating reversible reactive metal deposition from borohydride solutions. *Journal of Materials Chemistry A* **2020**, *8* (15), 7235-7244.
79. J. Drews, T. Danner, P. Jankowski, T. Vegge, J. M. García Lastra, R. Liu, Z. Zhao-Karger, M. Fichtner and A. Latz, *ChemSusChem*, 2020, **13**, 3599-3604.
80. E. V. Brouillet, M. Amores, S. A. Corr and S. D. Robertson, *Inorganic Chemistry Frontiers*, 2020, **7**, 2305-2312

CHAPTER 3:

OPPORTUNITIES AND AIMS

The review of the literature shows a wide gap in the required knowledge to fully understand the key aspects of the Electrolyte-Electrode interface in a Magnesium battery. The role of the interactions at the interface cannot be neglected in the working of a Magnesium battery. The need for an in-depth analysis of the interface and the behavior of the various components and their influence on the battery performance is of the foremost importance.

The proposed project is focused on understanding the behavior of the electroactive species in the bulk and aims to provide a clearer understanding of the effect of the different components of the electrolyte on the performance of the battery thereby helping in the development of better battery materials for use in Rechargeable Magnesium Batteries (RMB). To satisfy the goal a few important questions must be studied as part of this project. They are:

Question 1: How are the electroactive species behaving in the presence of a solvent in the electrolyte and how does the behavior change when the battery is in operation?

The role of the electroactive species has been studied in the past and their presence in the electrolyte is still being studied. The present project will focus on understanding the solvation of the EAS in the solvent and characterizing the interactions between the EAS, anion and the solvent. To improve the spectrum of understanding, the effect of an external electric field will also be documented and analyzed to give a clearer understanding of the interaction landscape.

Question 2: How does the interaction of the EAS-anion-solvent affect the performance of the electrolyte?

A hypothesis as part of the present project is that the mobility of the EAS will change due to the influence of solvent and the anion as this will affect the solvation structure around the EAS. The

changes in the EAS solvation structure are important as this will help in determining the transport properties and may influence the reactive mechanism at the interfaces

Question 3: What changes are observed in the solvation structures and are larger extended solvation structures present in the Mg electrolytes?

The lack of insights into the formations of ionic clusters reported in other electrolytes is visible from a glance into the literature. These ionic clusters determine the ionic transport and possible reactive species. Furthermore, the presence of these ionic clusters in the interphase can fundamentally alter the study into reactive mechanism at the anode surface.

Question 4: How is the solvation and transport behavior of the EAS affected by changing the anions and solvents?

The role of the solvent and the anion will need to be investigated in further depth to determine factors that may influence the role of the EAS as well as affecting its selectivity and possible impact on the performance of the electrolyte.

These four questions will help in developing an interaction and behavior landscape of the electrolyte and help in further developing better and more stable electrolytes that can be used in commercial RMBs. To study these questions, large-scale molecular dynamics will be used. This study will try and identify key characteristics in the simulated systems that can be scaled and represented in a physical scale and can be measured experimentally.

Addressing these gaps in understanding of the electrolyte is being focused upon in this study. **Figure 3.1** highlights some of the key interactions that need to be mapped and understood to bridge the gap

in existing literature to pave the way towards the development of commercially viable rechargeable Mg batteries.

3.1 AIMS

Aim 1: Identify and understand the solvation behavior of the EAS in THF. THF will be used as it is having been commonly studied and has shown good electrolytic behavior. The solvation structure will be characterized under both operating and equilibrium conditions. Operating conditions will be modelled using a constant external electric field. This is to provide a key understanding into the larger ionic structures in the bulk electrolytes and highlight the impact of external factors like the electric field.

Aim 2: Characterize the influence of the EAS-solvation in structures on the performance of the battery and quantify the measurable impact on electrolytic performance. The main topic of interest here is the mobility of the cationic species and the role of the solvation structure in aiding or impeding the transport properties.

Aim 3: Study the role of the solvent by comparing the solvation and mobility in THF with other common electrolyte solvents such as Dimethoxy ethane (glyme), diglyme, triglyme and tetraglyme etc. This can provide insight into the EAS-solvent interactions which will enable in the understanding of the influence of the solvent in the larger ionic structure build-up.

Aim 4: Understand the role of the anion by comparing the strongly interacting and weakly interacting anions to generate insight into the interplay between EAS-EAS, EAS-solvent and EAS-anion interactions.

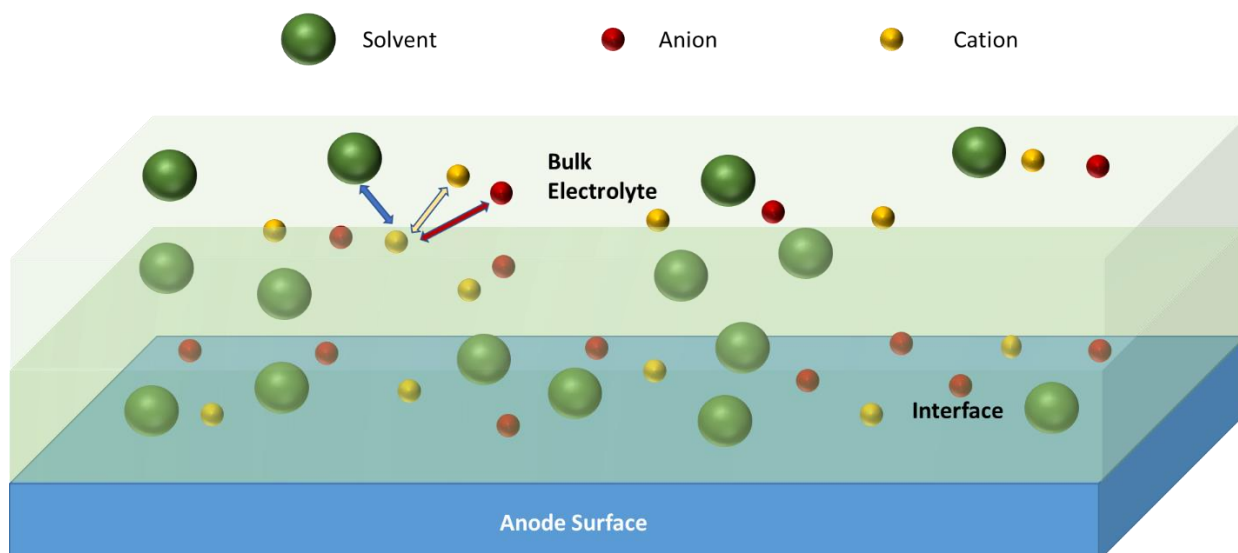


Figure 3.14. Cross-section of the anode-interface-electrolyte system. The Anion (red sphere), cation (yellow sphere) and the solvent (green sphere) are highlighted. Three key interactions of interest are also shown: Cation-anion (red arrow), cation-cation (yellow arrow) and cation-solvent (blue arrow).

CHAPTER 4:
ION AGGLOMERATION AND TRANSPORT IN MgCl_2
BASED ELECTROLYTES FOR RECHARGEABLE MAGNESIUM
BATTERIES

Ion Agglomeration and Transport in MgCl_2 -Based Electrolytes for Rechargeable Magnesium Batteries

Vallabh Vasudevan[†], Mingchao Wang^{†*}, Jodie A. Yuwono^{†‡}, Jacek Jasieniak[†], Nick Birbilis[§] and Nikhil V. Medhekar^{†*}

[†]Department of Materials Science and Engineering, Monash University, Faculty of Engineering, Clayton, Victoria 3800, Australia

[‡]School of Photovoltaics and Renewable Energy Engineering, University of New South Wales Sydney, Kensington, New South Wales 2052, Australia

[§]College of Engineering and Computer Science, Australian National University, Action, ACT 2601, Australia

Corresponding Authors: mingchao.wang@monash.edu (Dr. Mingchao Wang)

nikhil.medhekar@monash.edu (A/Prof. Nikhil Medhekar).

Abstract: Magnesium halide salts are an exciting prospect as stable and high-performance electrolytes for Rechargeable Mg batteries (RMBs). By nature of their complex equilibria, these salts exist in solution as a variety of electroactive species (EAS) in equilibrium with counter ions. Here we investigated ion agglomeration and transport of several such EAS in MgCl_2 salts dissolved in ethereal solvents under both equilibrium and operating conditions using large scale atomistic simulations. We find that the solute morphology is strongly characterized by the presence of clusters and is governed by the solvation structures of EAS. Specifically, the isotropic solvation of Mg^{2+} results in slow formation of bulky cluster, compared with chain-like analogues observed in the Cl-containing EAS such as Mg_2Cl_3^+ , MgCl^+ and $\text{Mg}_2\text{Cl}_2^{2+}$. We further illustrate these clusters can reduce the diffusivity of charge-carrying species in the MgCl_2 based electrolyte by at least an order of magnitude. Our findings of the cluster formation, morphology and kinetics can provide useful insight into the electrochemical reactions at the anode/electrolyte interface in RMBs.

Among the many “beyond-Li” battery technologies, rechargeable Mg batteries (RMBs) exhibit several advantages, such as greater abundance of Mg, high theoretical volumetric capacity with Mg metal as anode and dendrite-free deposition cycles.¹⁻³ To overcome the stability and reversibility issues caused by the formation of ion-impermeable solid electrolyte interfaces (SEIs) in RMBs, generally two design strategies are used, viz., design of novel electrodes or electrolytes.¹⁻⁴ In particular, electrolytes must be stable against reductive reactions at the electrolyte interface with Mg metal anode during charge/discharge cycles in RMBs. A promising endeavor is the usage of MgCl_2 salts which show a good recyclability towards deposition/dissolution cycles and improved stability.⁵⁻

⁹ These salts, or more generally, magnesium halides, were shown to form ion conducting layer at the anode/electrolyte interface, thereby preventing the formation of the passivation layer in $\text{Mg}(\text{TFSI})_2$, $\text{Mg}(\text{HMDS})_2$ and $\text{Mg}(\text{PF}_6)_2$ based electrolytes.¹⁰⁻¹² The Mg component in these electrolytes tends to rarely form Mg^{2+} ions, but instead is present as a multitude of solvent-stabilized complexes, in contrast to electrolytes in Li-ion batteries where the Li ion exists as monomeric species dissolved in solution.¹³ These Mg complexes, also called the electroactive species (EAS), are the primary charge-carriers and the electrochemically active entities in the electrolytes, and thus they govern the deposition/dissolution reactions at the anode/electrolyte interface. Therefore, a thorough understanding of the electrochemical behavior of various Mg EAS is a prerequisite for developing high performance electrolytes for RMBs.

A number of coexisting Mg complexes such as Mg_2Cl_3^+ , MgCl^+ , and its reversible dimer product $\text{Mg}_2\text{Cl}_2^{2+}$, have been identified as typical EAS in as-prepared MgCl_2 -based electrolytes. These EAS complexes exist in dynamic equilibrium with themselves as well as with other counter ions such as AlCl_4^- in MACC electrolytes. Their selectivity (relative concentrations in the electrolyte) is generally governed by factors such as the stoichiometric ratios of MgCl_2 , Lewis acids and solvents.^{6, 7, 14-16}

Recent experiments demonstrate an excellent cyclic efficiency and stability of MgCl^+ and Mg_2Cl_3^+ containing electrolytes.¹⁷ In particular, He and co-workers observed the formation of monomeric MgCl^+ when MgCl_2 and AlCl_3 are used in a ratio of 1:1.¹⁸ Mandai and co-workers also reported that the relatively unstable bridged chlorine complex Mg_2Cl_3^+ can further improve the electrochemical activity of electrolytes.¹⁶ However, the transport mechanisms of all Mg EAS under both equilibrium and non-equilibrium (operating conditions) remain yet to be understood. Understanding the underlying origins of the demonstrated electrolytic performance is necessary to develop better and more stable electrolytes.^{11, 19-21}

Given the complicated components of MgCl_2 containing electrolytes, it is often difficult to experimentally characterize the structural and kinetic behavior of various EAS in their co-existing states under working conditions. Recently, *ab initio* molecular dynamics (AIMD) simulations have been performed to successfully reveal bulk and interfacial properties of electrolyte systems.²²⁻²⁴ However, due to time- and length-scale limitations, these methods are unable to fully capture the slow dynamics of EAS-solvent interactions. In particular, the clustering of ionic species significantly governs the transport kinetics of charge carriers, and cluster formation may adversely affect surface deposition reactions which can lead to unexpected by-products. Here we conducted large-scale classical molecular dynamics (MD) simulations that enable us to investigate the solvation, clustering and transport behavior of various Mg EAS (i.e. MgCl^+ , $\text{Mg}_2\text{Cl}_2^{2+}$ and Mg_2Cl_3^+ in comparison with Mg^{2+}) individually solvated in tetrahydrofuran (THF) solvent. All simulations were performed using the refined parameters of GAFF force field by Canepa *et al*,²³ which accurately reproduces the solvation structures of single EAS-THF pairs as predicted from first-principles calculations (see details in the **Supporting Information (SI)**). To understand their respective equilibrium selectivity, each simulation considers only a single type of EAS. The effects of EAS concentrations, anions, and

external electric field on their structural and kinetic properties were explicitly taken into account. We also studied the role of the anion on the solvation structure and found that the anions tend to displace the solvent and have significant impact on the formation and transport of EAS. We observed that the simple MgCl_2 based electrolytes form ionic clusters irrespective of the complex species in the system. The formation of ionic clusters is significant for understanding the kinetics of charge transport in the electrolyte and the possible reactive deposition pathways on the anode surface.

We first analyzed the solvation structures of all Mg EAS under equilibrium as well as operating conditions. As illustrated by inset schematics in **Figure 1**, the arrangement of THF molecules around EAS can be identified by calculating the center of mass radial distribution functions (RDFs) of the EAS-THF and EAS-EAS pairs. **Figure 1(a)** shows that at an infinite dilution, Mg^{2+} possesses the highest intensity and the nearest location of the first peak in RDF, demonstrating the strongest electrostatic interaction with THF solvation shells. In contrast, when a Cl^- anion is present nearby (**Figure 1(b)**), the intensity of the first solvation peak reduces for all EAS. In particular, the overlapping RDF curves of MgCl^+ and $\text{Mg}_2\text{Cl}_2^{2+}$ show that the monomer and dimer have similar solvation structures and are largely interchangeable, thus facilitating a reversible monomer to dimer transition. Such a reversible mechanism has also been observed in recent *in-situ* experiments.²⁵ When

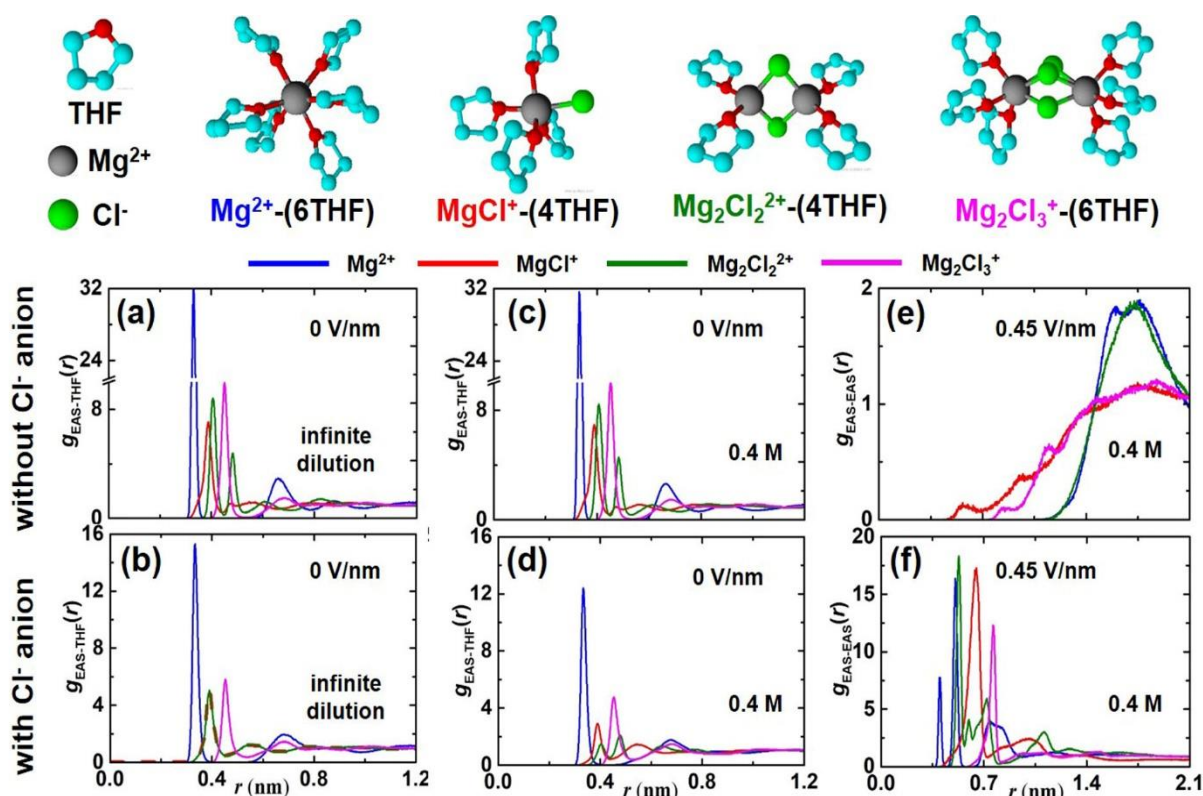


Figure 1. Solvation structures of various Mg electroactive species (EAS) including Mg^{2+} , MgCl^+ , $\text{Mg}_2\text{Cl}_2^{2+}$ and Mg_2Cl_3^+ in the MgCl_2 -based electrolyte. The first row presents the atomistic solvation structures of isolated Mg EAS-THF complexes in the absence of Cl^- anions, with coordination numbers obtained by integrating the radial distribution functions. (a-f) show the radial distribution functions of EAS-THF and EAS-EAS pairs with and without Cl^- anion at the infinite dilution and the concentration of 0.4 M.

an external electric field is applied in non-equilibrium conditions (see **Figure S2** in SI), there are no noticeable changes in the solvation structures of Mg^{2+} , MgCl^+ and Mg_2Cl_3^+ (see **Figure 1(b)** and **Figure S2(b)** in SI). There is a slight change in location of the first solvation peak for $\text{Mg}_2\text{Cl}_2^{2+}$ owing to the reorientation of THF molecules surrounding $\text{Mg}_2\text{Cl}_2^{2+}$ due to the external electric field. The unchanged coordination numbers of all EAS-THF pairs (**Table S3** in SI) indicate that cation-anion interactions are strong enough to overcome the effect of an applied electric field.

We next explored the solvation structures of various Mg EAS at the realistic concentrations of MgCl_2 salts representative of typical operating conditions. **Figure 1(c)** exhibits that the equilibrium solvation structures of various EAS at larger concentrations in the absence of anions in the vicinity are similar to those at infinite dilution. When the Cl^- anions are introduced (**Figure 1d**), a strong cation-solvent interaction still persists as indicated by an intense first solvation peak. This solvation shell forms a buffer layer between two EAS and helps to keep the highly concentrated system together. The solvent buffer traps not only EAS molecules but also anions, acting as a “glue” to hold cations/anions together and leading to the formation of large ionic clusters (as discussed later). Notably, the presence of an electric field does not affect the solvent structures of EAS either, as evident from **Figure S3** (see SI). This indicates that the field strength is not significant enough to induce the change in intermolecular interactions between strongly charged cations and the electronegative oxygen of THF molecules. Such field-insensitive solvation structure could also exist in other ethereal electrolytes such as diglyme and tetraglyme with their complex EAS.²⁶⁻²⁸ **Figure 1(e)** presents the electrostatic interaction between EAS-EAS pairs in the absence of Cl^- anions. EAS are expected to repel each other as reflected by the first peak locations (~ 1.7 nm) of EAS-EAS pairs. Some small RDF peaks of EAS-EAS pairs within 0.9 nm seen in **Figure 1(e)** highlight the statistical possibilities of Mg_2Cl_3^+ and MgCl^+ forced to occasionally move towards each other by the strong external electric field before electrostatic repulsion forces them apart. In contrast, for doubly charged Mg^{2+} and $\text{Mg}_2\text{Cl}_2^{2+}$ EAS, the electrostatic buffering from solvent is not strong enough to overcome the repulsive forces between the cations, and hence the corresponding RDF curves are marked by the absence of peaks around 0.9 nm distance. However, in case where Cl^- anions present (**Figure 1(f)**), the RDF are curves are characterized by many sharp peaks appearing at closer distances due to the anions acting as bridges between EAS. For instance, the first solvation shell for Mg^{2+} EAS is around 0.6 nm, while it is larger at 0.8 nm for the larger Mg_2Cl_3^+ EAS. The important qualitative features illustrated in **Figure 1(a-f)**,

persist with different concentrations of MgCl_2 as well as for different strengths of electric fields (see **Figure S2-S3** in **SI**). This suggests that these observations are intrinsic to the chemistry of ionic electrolytes.

Recent studies have reported that ionic clusters in several electrolytic systems strongly influence the transport behavior of charge-carrying species. For instance, ion agglomeration can trigger side reactions at the anode-electrolyte interfaces in Mg batteries.^{23, 24} A significant agglomeration of Mg^{2+} - BH_4^- clusters results in a low solubility of $\text{Mg}(\text{BH}_4)_2$ -based electrolytes for RMBs as confirmed both experimentally and theoretically.²⁶⁻²⁸ Therefore, we analyzed the formation of Mg EAS clusters in MgCl_2 based electrolytes under both as-prepared and operating conditions. To simulate the complete process of large-scale ion agglomerations within the electrolyte, a declustered system with well separated EAS and Cl^- anions was first obtained and then allowed to cluster again during simulation (see S3 in **SI** for the detailed description of the declustered and clustered systems). Generally, we find that all Mg EAS react with Cl^- to gradually form ion pairs, and subsequently, clusters. Magnesium EAS mediated by Cl^- anions form large ionic clusters under the as-prepared condition, but the electric field prevents significant agglomeration.

We next discuss the ion agglomeration of Mg EAS under operating conditions with the applied electric field, while the ion agglomeration under equilibrium conditions is presented in **Figure S4**. **Figure 2(a)** shows the formation of Mg EAS clusters at a concentration of 0.2 M, investigated by tracking the coordination number of the EAS-EAS, EAS- Cl^- and EAS-THF pairs. The data for 0.1 M and 0.4 M concentrations is available in **Figure S5**. The increasing coordination number of EAS-EAS ($N_{\text{EAS-EAS}}$) and EAS- Cl^- ($N_{\text{EAS-Cl}}$) pairs points to the formation of ion clusters, while the

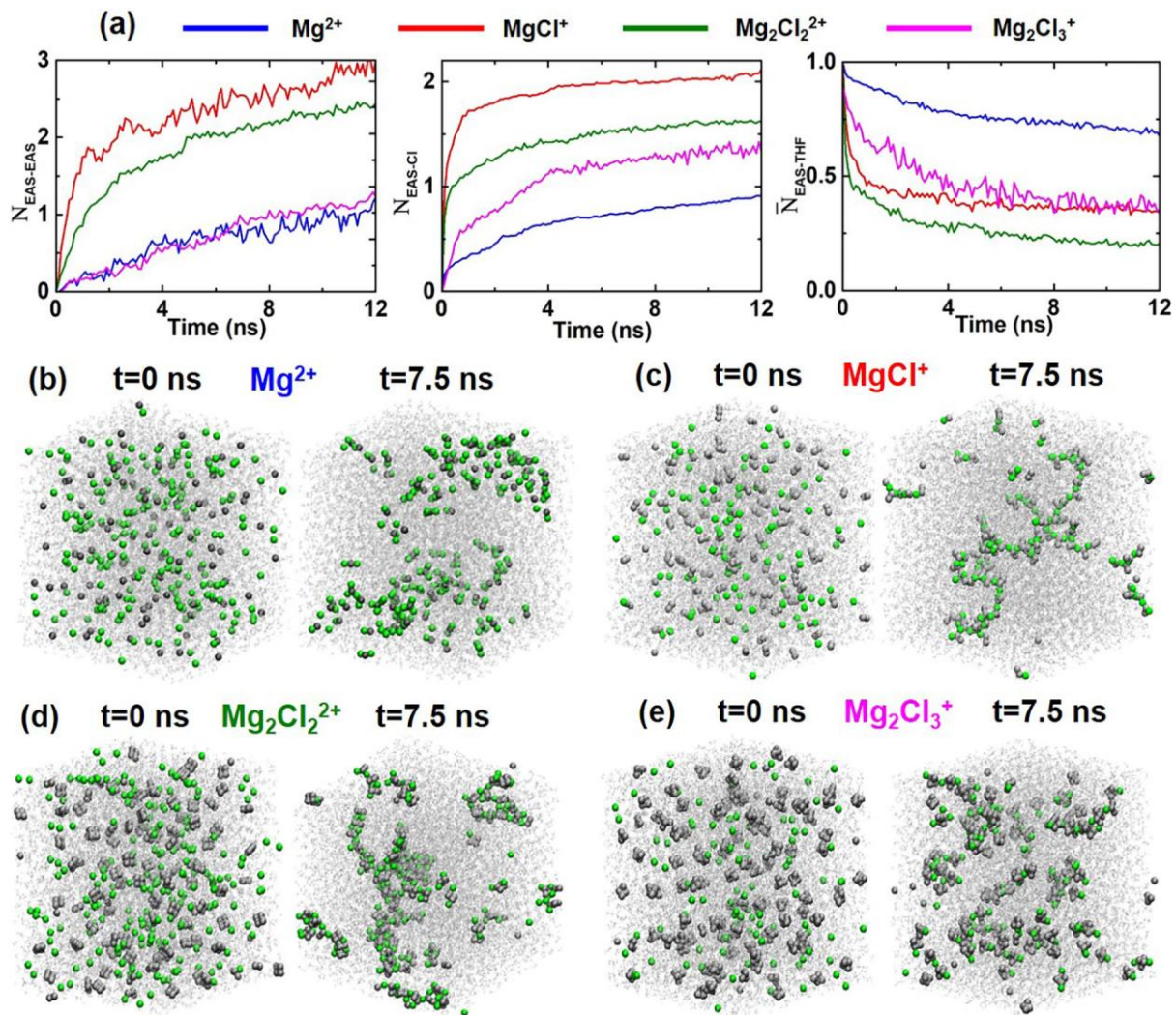


Figure 2. Cluster formation of various Mg electroactive species (EAS) in the MgCl_2 -based electrolyte under the applied electric field of 0.45 V/nm and at the concentration of 0.2 M. (a) The average coordination numbers of EAS-EAS, EAS- Cl^- and EAS-THF pairs during the formation of clusters. (b-e) exhibit completely isolated ions and newly formed clusters of EAS- Cl^- complexes at the simulation time of 0 and 7.5 ns.

decreasing normalized coordination number of EAS-THF pair ($\bar{N}_{\text{EAS-THF}}$) illustrates the breaking of solvation structures by Cl^- anions. Surprisingly, it was found that Mg^{2+} exhibited the smallest values of $N_{\text{EAS-EAS}}$ and $N_{\text{EAS-Cl}}$, followed by Mg_2Cl_3^+ , $\text{Mg}_2\text{Cl}_2^{2+}$ and MgCl^+ , despite having largest charge density. To understand such counter-intuitive trend to that of the charge densities of Mg EAS, we visualized the ion clusters of different Mg EAS. **Figure 2(b)** shows that Mg^{2+} prefer to form bulky

but small clusters. In contrast, the rest of Mg EAS prefers to form chain-like clusters as shown in **Figure 2(c-e)**. In MgCl^+ EAS in particular, the chain clusters are bound together to form branched structures, as a result leading to its larger coordination number of EAS-EAS and EAS- Cl^- pairs.

We further analyzed the relationship between solvation structures and clusters for different Mg EAS. **Figure 3(a)** depicts both iso-surfaces of solvation structures at the beginning and after a long run of simulation. During agglomeration of $\text{Mg}^{2+}\text{-Cl}^-$, the strong electrostatic interaction is compensated by breaking of the compact, isotropic solvation shells of Mg^{2+} (**Figure 3(a)**). This reduces the rate of $\text{Mg}^{2+}\text{-Cl}^-$ clustering, as confirmed by the discussion of the coordination numbers earlier. The isotropic structure of Mg^{2+} facilitates the formation of bulky clusters. As for the rest of Mg EAS, they possess

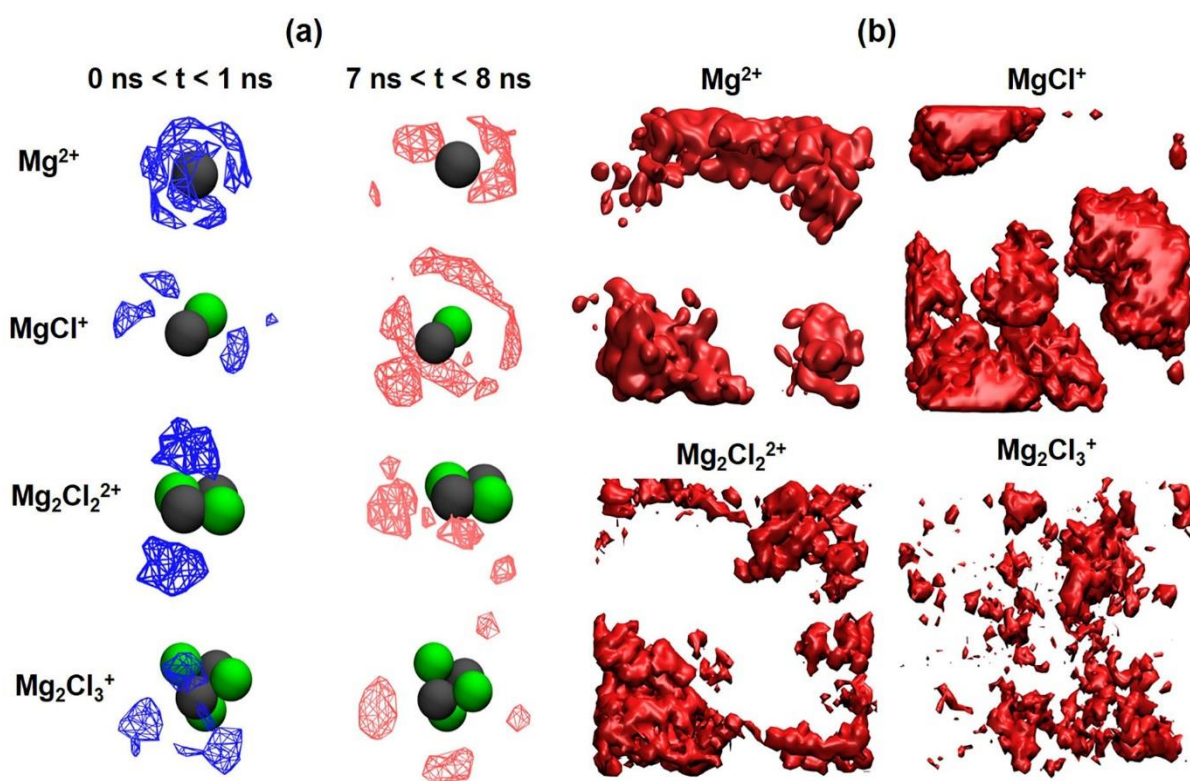


Figure 3. (a) Iso-surfaces of THF solvation structures around Mg electroactive species (EAS) before (0–1 ns) and after (7–8 ns) cluster formation of Mg EAS under the applied electric field of 0.45 V/nm and at 0.2 M concentration. (b) Time average spatial distribution of Mg EAS over 4 ns after the formation of clusters in the MgCl_2 -based electrolyte.

anisotropic solvation shells, and leave free spaces for Cl^- anions to interact with Mg EAS (see **Figure 3(a)**), thus enhancing the rates of EAS- Cl^- pairing. The relatively slow agglomeration rate of Mg_2Cl_3^+ compared to MgCl^+ and $\text{Mg}_2\text{Cl}_2^{2+}$ can be attributed to its much stronger electrostatic repulsion between bonded Cl and free Cl^- in the electrolyte. While for MgCl^+ and $\text{Mg}_2\text{Cl}_2^{2+}$, they show weaker electrostatic repulsion. The anisotropic atomic structures of all Cl-containing EAS only allow free Cl^- to interact with Mg center, which consequently enable them to form chain-like clusters.

The time averaged spatial distribution of Mg EAS after complete clustering are shown in **Figure 3(b)**. These reveal regions of high clustering of the cationic species, which are mobile with the applied electric field, as indicated by clustering near the edges of the box. Since the ions in the clusters are easy to transport across the bulk of the electrolyte, the clusters are likely to be present at the electrode/electrolyte interface. The reactive pathways for deposition of Mg at the anode that involve clustered ionic species can lead to localized deposits rather than a uniform plating, which hitherto has not been studied. Significantly, newly-formed clusters also trap the solvent molecules, thereby increasing the possibility of reactive by-products which can act as SEI precursors. The observation of these clusters in the bulk of the electrolyte posits that derivative structures may be present at the anode/electrolyte interface.

Finally, we investigated the transport behavior of all Mg EAS and the impact of their agglomeration on charge/discharge rates. In the absence of applied electric field, the diffusivities of Mg EAS are inversely correlated to their charge densities (see **Figure 4(a)**), irrespective to whether the EAS are

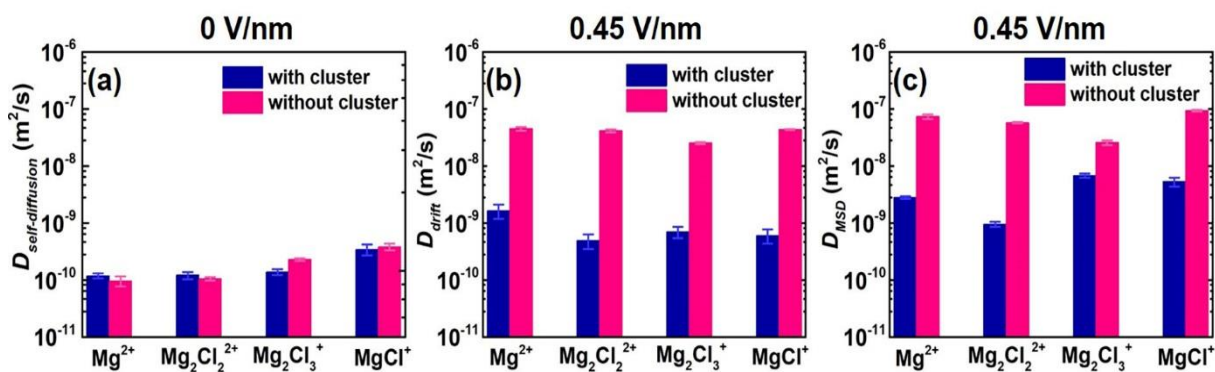


Figure 4. Ionic diffusivities of Mg electroactive species (EAS) with and without external electric field at the concentration of 0.4 M. (a) Self diffusivities of Mg EAS ($D_{self-diffusion}$) in the absence of the electric field. (b-c) Ionic diffusivities of Mg EAS evaluated from drift velocity (D_{drift}) (b) and mean square displacement (MSD) (D_{MSD}) (c) under the applied electric field.

clustered (with Cl^- anions) or not (without Cl^- anions). Monovalent $Mg_2Cl_3^+$ and $MgCl^+$ species have weaker electrostatic interactions with THF than the divalent Mg^{2+} and $Mg_2Cl_2^{2+}$, and consequently have larger ion diffusivities. The diffusivity values for all EAS are in the range of 1×10^{-10} to 5×10^{-10} m^2/s in the absence of applied electric field. These values are of similar order in magnitude compared to the reported values for Mg^{2+} diffusion in $Mg(BH_4)_2/THF$ (7×10^{-10} m^2/s), as well as Mg^{2+} diffusion in $Mg(BH_4)_2/THF$ (2.8×10^{-10} m^2/s).^{26, 29} These diffusivity values of Mg EAS are also within one order of magnitude compared to experimental results.³⁰ It should be mentioned that here we do not consider the dynamics and lifetime of EAS- Cl^- based ionic clusters, however, the plateauing coordination numbers in Figure 2(a) after the initial clustering stage and small fluctuations thereafter indicate these clusters are relatively stable with a greater tendency for local rearrangement.

In the presence of an electric field, however, it has been suggested that the applicability of Einstein's relation to calculate diffusivities using mean square displacements may not be accurate.³¹ To accurately represent the effect of the applied field, we also calculated the diffusivity of the cations by measuring the drift velocity as shown in **Figure 4(b)** (D_{drift} , See SI). For completeness, we compare

these diffusivities against those calculated using Einstein's relation (D_{MSD} , **Figure 4(c)**). In the absence of clusters (in the absence of Cl^- anions), it can be seen that both methods predict similar diffusivities. However, for all EAS species in the clustered form, the Einstein's method overpredicts their diffusivities by an order of magnitude, thus highlighting the importance of considering drift velocities to calculate diffusivities in the presence of external bias fields in nonequilibrium systems.

With the electric field, positively charged species repel each other and are driven by the field. This causes the diffusivities of all Mg EAS in the un-clustered form to be expectedly larger by nearly two orders of magnitude compared to the clustered morphologies. Meanwhile for all EAS, the diffusivities in the clustered form ($\sim 10^{-10} \text{ m}^2/\text{s}$) are similar to the diffusivities in the absence of electric field. This indicates the clusters locally screen the applied electric field effectively. Furthermore, here the effective kinetics can be characterized by cluster diffusion rather than the ionic diffusion and could lead to the formation of distinct diffusion zones (within and outside clusters). Such diffusion zones could ensure variations in the local composition at the electrode-electrolyte interface and lead to significant differences in deposition/dissolution reactions during charge/discharge cycles. For completeness, we also investigated diffusion of EAS as a function of concentration and the strength of the electric field. These studies show that as the concentration increases, the diffusion becomes slower due large cluster sizes and bulkier diffusing species (see **Figure S6**). Meanwhile, a drastic increase in the diffusivities is observed when the field is large enough (larger than 0.6 V/nm) to prevent the formation of large, bulky clusters (see **Figure S7**). In a practical sense, such large fields would only be seen at the interface of operating devices, suggesting that different clustering distributions may be observed at the interface, which could be favorable for electrochemical processes.

Although experimental or computational studies of ionic clusters in the MgCl_2 -based electrolytes are not available in the literature, we can still provide concise implications for the influence of ionic clusters on the electrochemical reactions at the electrolyte/anode interface. This study focuses on singly solvated EAS, however, in the practical battery operating conditions, these EAS co-exist in dynamic reactive equilibrium in the solution. The anion-induced clustering is controlled by short-range electrostatic interactions and hence is expected to be present in all MgCl_2 -disassociated electrolytic systems. The clustering of the cationic species maintains the proximity of various EAS to each other and can lead to a relatively easy transformation from one species to another and possibly also to the formation of larger transitional cationic complexes. This aspect of multiple co-existing EAS in MgCl_2 -based electrolytes is beyond the scope of this work and will be considered in the future. Few experimental and computational studies on MACC electrolytes in THF solvent have found that the monomer MgCl^+ is a prevalent species during the initiation of Mg deposition.^{9, 23, 30} As a result, the presence of MgCl^+ clusters may impact surface energetics and may lead to slow reaction kinetics. Moreover, clusters in ionic liquids have been shown to dominate the capacitive properties of the electrolyte especially at elevated temperatures, due to the cluster polarization induced higher capacitance.³² The higher capacitance in the electric double layers at the anode surface has also been shown to increase the impedance (and further overpotential) of Li ion batteries as well as affecting the intercalation reactions.^{33, 34} Such comprehensive understanding of interfacial reactions is not yet available for RMBs, however, is necessary to fully characterize issues affecting the SEI formation and its impact on the battery performance.

In summary, we have performed large-scale MD simulations to investigate the ion agglomeration of Mg^{2+} , $\text{Mg}_2\text{Cl}_2^{2+}$, MgCl^+ , and Mg_2Cl_3^+ EAS and their transport behavior in MgCl_2 -based electrolytes for RMBs. We found that the solvation structures of Mg EAS are not affected by the solute

concentration. Cl^- anions tend to displace the solvent and play an important role in maintaining the equilibrium in the monomer/dimer $\text{MgCl}^+/\text{Mg}_2\text{Cl}_2^{2+}$ system. The formation of EAS clusters is highly dependent on their solvation structures— Mg^{2+} prefers to form small bulky clusters owing to its isotropic solvation structures, while the other EAS tend to form chain-like clusters. These structural differences cause the anion-bridged clusters to have a lower ionic mobility compared to their unclustered form. This factor could play a role in introducing distinct diffusion zones inside the electrolyte, as well as enable control of charge and discharge rates through a judicious selection of cluster size and variability of the clustering zones. It was further found that the diffusivity of these clusters was weakly dependent on electric fields at low field strengths. However, very high electric fields ($> 0.6 \text{ V/nm}$) induced a reduction in cluster size, thus leading to faster diffusion kinetics. This may have profound implications on the electrolyte morphology near the interfaces, where electric field strengths tend to be high. To understand this behavior, a deeper look into the role of clusters in electrochemical reactions at the electrode/electrolyte interface is required. Such studied will also provide key insights into the formation mechanism of SEI layers in RMBs. Both of these areas will be considered in future work.

METHODS

We performed all classical molecular dynamics (MD) simulations using GROMACS package.³⁵⁻⁴⁰ Tetrahydrofuran (THF) was selected to solvate all EAS and anions as a representative for ethereal solvents.^{3, 9, 14, 15, 41} The influence of both anions and external electric field on the cationic solvation and kinetics of EAS was also considered. Simulations in the absence of anions were performed by substituting explicit anions with a background charge. The effect of an external electric field was studied by applying a uniform external potential along x axis. The Generalized AMBER Force Field (GAFF)⁴² was utilized to describe intra- and inter-molecular interactions of EAS²³ and THF^{43, 44}

molecules (See **Supporting Information** for details and validation of MD simulations, a description of explicit and implicit anions, cluster analysis, and calculations of ion diffusivities).

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI.

Simulation sections, tables and figures showing the computational details and validation of MD simulations, force field parameters for MD simulations, radial distribution functions of electroactive species at the infinite dilution and the concentration of 0.4 M under the electric field, cluster analysis, and calculation of ion diffusivities in the MgCl₂-based electrolyte (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: mingchao.wang@monash.edu

*E-mail: nikhil.medhekar@monash.edu

ACKNOWLEDGMENTS

All authors acknowledge support from the Monash University Cluster, the Australian National Computing Infrastructure (NCI), and the Pawsey Supercomputing Centre for high performance computing, as well as the financial support from Australian Research Council's Discovery Project scheme (DP160103661).

REFERENCES

- (1) Attias, R.; Salama, M.; Hirsch, B.; Goffer, Y.; Aurbach, D. Anode-Electrolyte Interfaces in Secondary Magnesium Batteries. *Joule* **2019**, *3*, 27-52.
- (2) 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.
- (3) Tutusaus, O.; Mohtadi, R.; Singh, N.; Arthur, T. S.; Mizuno, F. Study of Electrochemical Phenomena Observed at the Mg Metal/Electrolyte Interface. *ACS Energy Letters* **2017**, *2*, 224-229.
- (4) 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. *Chemical Reviews* **2017**, *117*, 4287-4341.
- (5) 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.
- (6) Pan, B.; Huang, J.; He, M.; Brombosz, S. M.; Vaughey, J. T.; Zhang, L.; Burrell, A. K.; Zhang, Z.; Liao, C. The Role of MgCl_2 as a Lewis Base in ROMgCl-MgCl_2 Electrolytes for Magnesium-Ion Batteries. *ChemSusChem* **2016**, *9*, 595-599.
- (7) Pan, B.; Huang, J.; Sa, N.; Brombosz, S. M.; Vaughey, J. T.; Zhang, L.; Burrell, A. K.; Zhang, Z.; Liao, C. MgCl_2 : The Key Ingredient to Improve Chloride Containing Electrolytes for Rechargeable Magnesium-Ion Batteries. *J. Electrochem. Soc.* **2016**, *163*, A1672-A1677.

-
- (8) 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.
- (9) See, K. A.; Chapman, K. W.; Zhu, L.; Wiaderek, K. M.; Borkiewicz, O. J.; Barile, C. J.; Chupas, P. J.; Gewirth, A. A. The Interplay of Al and Mg Speciation in Advanced Mg Battery Electrolyte Solutions. *Journal of the American Chemical Society* **2016**, *138*, 328-337.
- (10) Sa, N.; Pan, B.; Saha-Shah, A.; Hubaud, A. A.; Vaughey, J. T.; Baker, L. A.; Liao, C.; Burrell, A. K. Role of Chloride for a Simple, Non-Grignard Mg Electrolyte in Ether-Based Solvents. *ACS Appl. Mater. Interfaces* **2016**, *8*, 16002-16008.
- (11) 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 $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2$ Complex as A Magnesium Electrolyte for Rechargeable Magnesium Batteries. *J. Mater. Chem. A* **2015**, *3*, 6082-6087.
- (12) Shterenberg, I.; Salama, M.; Gofer, Y.; Aurbach, D. Hexafluorophosphate-Based Solutions for Mg Batteries and the Importance of Chlorides. *Langmuir* **2017**, *33*, 9472-9478.
- (13) Yoo, H. D.; Shterenberg, I.; Gofer, Y.; Gershinsky, G.; Pour, N.; Aurbach, D. Mg Rechargeable Batteries: An On-Going Challenge. *Energy Environ. Sci.* **2013**, *6*, 2265-2279.
- (14) Brouillet, E. V.; Kennedy, A. R.; Koszinowski, K.; McLellan, R.; Mulvey, R. E.; Robertson, S. D. Exposing Elusive Cationic Magnesium–Chloro Aggregates in Aluminate Complexes through Donor Control. *Dalton Trans.* **2016**, *45*, 5590-5597.
-

-
- (15) Salama, M.; Shterenberg, I.; Gizbar, H.; Eliaz, N. N.; Kosa, M.; Keinan-Adamsky, K.; Afri, M.; Shimon, L. J. W.; Gottlieb, H. E.; Major, D. T. *et al.* Unique Behavior of Dimethoxyethane (DME)/Mg(N(SO₂CF₃)₂)₂ Solutions. *J. Phys. Chem. C* **2016**, *120*, 19586-19594.
- (16) Mandai, T.; Akita, Y.; Yagi, S.; Egashira, M.; Munakata, H.; Kanamura, K. A Key Concept Of Utilization Of both Non-Grignard Magnesium Chloride and Imide Salts for Rechargeable Mg Battery Electrolytes. *J. Mater. Chem. A* **2017**, *5*, 3152-3156.
- (17) Salama, M.; Shterenberg, I.; J.W. Shimon, L.; Keinan-Adamsky, K.; Afri, M.; Gofer, Y.; Aurbach, D. Structural Analysis of Magnesium Chloride Complexes in Dimethoxyethane Solutions in the Context of Mg Batteries Research. *J. Phys. Chem. C* **2017**, *121*, 24909-24918.
- (18) He, S.; Luo, J.; Liu, T. L. MgCl₂/AlCl₃ Electrolytes for Reversible Mg Deposition/Stripping: Electrochemical Conditioning or Not? *J. Mater. Chem. A* **2017**, *5*, 12718-12722.
- (19) Ma, Z.; Kar, M.; Xiao, C.; Forsyth, M.; MacFarlane, D. R. Electrochemical Cycling of Mg in Mg[TFSI]₂/Tetraglyme Electrolytes. *Electrochem. Commun.* **2017**, *78*, 29-32.
- (20) Carter, T. J.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Zhang, R.; Shirai, S.; Kampf, J. W. Boron Clusters as Highly Stable Magnesium-Battery Electrolytes. *Angew Chem. Int. Ed.* **2014**, *53*, 3173-3177.
- (21) Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E. G.; Severyugina, Y. V. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew Chem. Int. Ed.* **2015**, *54*, 7900-7904.
-

-
- (22) 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.
- (23) 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.
- (24) Canepa, P.; Gautam, G. S.; Malik, R.; Jayaraman, S.; Rong, Z.; Zavadil, K. R.; Persson, K.; Ceder, G. Understanding the Initial Stages of Reversible Mg Deposition and Stripping in Inorganic Nonaqueous Electrolytes. *Chem. Mater.* **2015**, *27*, 3317-3325.
- (25) Cheng, Y.; Stolley, R. M.; Han, K. S.; Shao, Y.; Arey, B. W.; Washton, N. M.; Mueller, K. T.; Helm, M. L.; Sprenkle, V. L.; Liu, J. *et al.* Highly Active Electrolytes for Rechargeable Mg Batteries Based on a $[\text{Mg}_2(\text{m-Cl})_2]^{2+}$ Cation Complex in Dimethoxyethane. *Phys. Chem. Chem. Phys.* **2015**, *17*, 13307-13314.
- (26) Samuel, D.; Steinhäuser, C.; Smith, J. G.; Kaufman, A.; Radin, M. D.; Naruse, J.; Hiramatsu, H.; Siegel, D. J. Ion Pairing and Diffusion in Magnesium Electrolytes Based on Magnesium Borohydride. *ACS Appl. Mater. Interfaces* **2017**, *9*, 43755-43766.
- (27) 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.
- (28) Tutusaus, O.; Mohtadi, R. Paving the Way towards Highly Stable and Practical Electrolytes for Rechargeable Magnesium Batteries. *ChemElectroChem* **2015**, *2*, 51-57.
-

-
- (29) 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.
- (30) Benmayza, A.; Ramanathan, M.; Arthur, T. S.; Matsui, M.; Mizuno, F.; Guo, J.; Glans, P.-A.; Prakash, J. Effect of Electrolytic Properties of a Magnesium Organohaloaluminate Electrolyte on Magnesium Deposition. *J. Phys. Chem. C* **2013**, *117*, 26881-26888.
- (31) Murad, S. The Role of External Electric Fields in Enhancing Ion Mobility, Drift Velocity, and Drift-Diffusion Rates in Aqueous Electrolyte Solutions. *J. Chem. Phys.* **2011**, *134*, 114504.
- (32) Ma, K.; Forsman, J.; Woodward, C. E. A Classical Density Functional Study of Clustering in Ionic Liquids at Electrified Interfaces. *J. Phys. Chem. C* **2017**, *121*, 1742-1751.
- (33) Lück, J.; Latz, A. Theory of Reactions at Electrified Interfaces. *Phys. Chem. Chem. Phys.* **2016**, *18*, 17799-17804.
- (34) Lück, J.; Latz, A. The Electrochemical Double Layer and Its Impedance Behavior in Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2019**, *21*, 14753-14765.
- (35) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. Gromacs: High Performance Molecular Simulations through Multi-Level Parallelism from Laptops to Supercomputers. *SoftwareX* **2015**, *1-2*, 19-25.
- (36) Berendsen, H. J. C.; van der Spoel, D.; van Drunen, R. GROMACS: A Message-Passing Parallel Molecular Dynamics Implementation. *Comput. Phys. Commun.* **1995**, *91*, 43-56.
-

-
- (37) David, V. D. S.; Erik, L.; Berk, H.; Gerrit, G.; E., M. A.; C., B. H. J. GROMACS: Fast, Flexible, and Free. *J. Comput. Chem.* **2005**, *26*, 1701-1718.
- (38) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *J. Chem. Theory Comput.* **2008**, *4*, 435-447.
- (39) Lindahl, E.; Hess, B.; van der Spoel, D. GROMACS 3.0: A Package for Molecular Simulation and Trajectory Analysis. *Mol. Model. Annual* **2001**, *7*, 306-317.
- (40) Pronk, S.; Páll, S.; Schulz, R.; Larsson, P.; Bjelkmar, P.; Apostolov, R.; Shirts, M. R.; Smith, J. C.; Kasson, P. M.; van der Spoel, D. *et al.* GROMACS 4.5: A High-Throughput and Highly Parallel Open Source Molecular Simulation Toolkit. *Bioinform.* **2013**, *29*, 845-854.
- (41) Bucur, C. B.; Gregory, T.; Oliver, A. G.; Muldoon, J. Confession of a Magnesium Battery. *J. Phys. Chem. Lett.* **2015**, *6*, 3578-3591.
- (42) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of A General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157-1174.
- (43) Caleman, C.; van Maaren, P. J.; Hong, M.; Hub, J. S.; Costa, L. T.; van der Spoel, D. Force Field Benchmark of Organic Liquids: Density, Enthalpy of Vaporization, Heat Capacities, Surface Tension, Isothermal Compressibility, Volumetric Expansion Coefficient, and Dielectric Constant. *J. Chem. Theory Comput.* **2012**, *8*, 61-74.
- (44) van der Spoel, D.; van Maaren, P. J.; Caleman, C. GROMACS Molecule & Liquid Database. *Bioinform.* **2012**, *28*, 752-753.
-

CHAPTER 5:
CHARACTERIZATION OF SOLVENT CONTROLLED DIFFUSION OF
Mg-Cl CATIONIC COMPLEXES IN HALIDE CONTAINING
ELECTROLYTES FOR USE IN RECHARGEABLE MAGNESIUM
BATTERIES

5.1. INTRODUCTION

The desire for cheaper and higher capacity energy storage devices has led to an increase in interest towards the development of “beyond-Li” batteries such as magnesium (Mg) batteries. Rechargeable Mg batteries (RMBs) with Mg metal anodes exhibit several advantages over lithium batteries, such as high abundance of Mg in earth’s crust, high theoretical volumetric capacity (3866 mAh cm^{-3}) and dendrite-free deposition cycles. The adoption and development of RMBs are hampered by the high charge density of Mg^{2+} ions which triggers the formation of ion impermeable reactive deposits formed by solvent breakdown at anode/electrolyte interface. These solid-electrolyte interfaces (SEIs) result in the lowered Mg^{2+} ion kinetics and progressive loss of active Mg^{2+} ions in the electrolyte through the operational lifetime. To reduce growth of SEIs, the solvent stability and reversibility of interfacial reactions must be overcome. To this end, two general battery design strategies have been approached, namely, the design of novel anode materials and development of more stable electrolytes. The high theoretical volumetric capacity of using Mg metal anode over other anode candidates has led to great research effort towards developing electrolytes with a higher reductive stability and lower reactivity with Mg^{2+} ions.

A promising endeavor is the usage of MgCl_2 salts added to Magnesium salt based electrolytes and its derivatives.¹⁻³ Although the presence of free Cl^- in the electrolyte have shown to increase the corrosion of current collectors, MgCl_2 containing electrolytes present strong recyclability towards deposition/dissolution cycles and improved stability.⁴⁻⁶ Some common MgCl_2 containing electrolytes include Magnesium Aluminum Chloro Complex (MACC) electrolytes and mixed salt systems such as $\text{Mg}(\text{TFSI})_2\text{-MgCl}_2$. Magnesium Halide added to $\text{Mg}(\text{TFSI})_2$ containing electrolytes have shown better performance with the improvement in performance also dependent on the halide anion used.⁶ Studying the speciation of the Mg-species in the electrolyte shows that the Mg^{2+} ion is rarely formed

when the MgCl_2 salt is added and instead a partially dissociated solvent stabilized Mg-Cl containing complexes are favored. These Mg-Cl complexes called as electroactive species (EAS), are the primary charge-carrying/reactive species during the battery operation and deposition/dissolution reactions at the anode/electrolyte interface. Hence, a thorough understanding of the electrochemical behavior of these Mg-EAS is a prerequisite for developing high performance electrolytes for RMBs.

A bevy of Mg-EAS complex structures have been shown to occur in solution, the selectivity of which are generally governed by the external factors such as stoichiometry, Lewis acid present and solvent.^{4, 5, 7-9} Of the different Mg-EAS reported, two, MgCl^+ and Mg_2Cl_3^+ , are of particular interest as they have been the most commonly reported. Cheng et al. found that the formation of MgCl^+ monomer show significant performance improvement with near 100% cyclic efficiency and good stability (up to 3.5 V vs Mg).¹⁰ Salama and co-workers have shown the formation of MgCl^+ is stabilized by the bidentate nature of DME. They hypothesize that an increase in the number of Oxygen dentate positions can lead to a better stabilization and form larger cations, but the effect and performance of a larger cationic species is still up for debate and may not necessarily be a positive. The authors also point out that the improvement in electrolyte performance may not be a completely solution-based phenomenon and may involve significant influence from surface or near surface phenomena.¹¹ Mandai and co-workers add that though the monomeric EAS show significant performance and is more stable, the more unstable bridged Chlorine complex of Mg_2Cl_3^+ would favorably affect the electrochemical activity of the system.⁸ Recent study has argued that MgCl^+ is a better cationic species for electrolyte conditioning at the anode interface but the dinuclear Mg_2Cl_3^+ cationic species has more commonly been observed.^{12, 13} Understanding the underlying interactions of these cationic species and their interactions with the anionic components and solvents is a key requirement for developing novel electrolytes for RMBs.¹⁴⁻¹⁷

In this work we perform a comprehensive profile of the transport properties of Mg-EAS solvated in different ethereal solvents. We compare and contrast the diffusion mechanism of the cationic species, which is controlled by the molecular weight of the solvent. The diffusion mechanism is significant in controlling the kinetic properties of the battery.

5.2. METHODOLOGY

To study the effect of anions and electric field on cationic solvation and dynamics Molecular Dynamics (MD) simulations were performed using GROMACS¹⁸⁻²³ for pure Electroactive Species (EAS). The chosen EAS were MgCl^+ and Mg_2Cl_3^+ . Five solvents, Tetrahydrofuran (THF), Glyme (DME), Diglyme (G2), Triglyme (G3) and tetraglyme (G4) were used, as these ethereal solvents which have shown good stability and cycling performance.^{3, 7, 9, 24, 25} All systems were studied at 0.4M concentrations. The effect of an external electric potential was studied by applying a range of external potential of 0.45 V/nm in the positive X-direction and compared with simulations run on the same initial systems with the electric potential turned off. The simulations were performed using the Optimized potential for liquid solvents (OPLS-AA) force field.²⁶

5.2.1. Parameter Benchmarking and Initial System optimization

In this work diffusion of Magnesium Electroactive Species (Mg-EAS) containing chloride was studied in five different ethereal solvents namely tetrahydrofuran (THF), glyme (DME), diglyme(G2) , triglyme (G3) and tetraglyme (G4).

Initially, the system is parameterized to ensure accuracy of physical representation of the various molecules by comparing with known physical quantities. Here density was used as a comparative property. The parameters chosen for this work were able to calculate density within a tolerance of 5% (See **Table 4**).

An ion concentration of 0.4M was chosen and the simulation protocol established in Chapter 4 was followed. The system was initially relaxed using an energy minimization performed at 0K. It was then run in an NVT ensemble at 8 different temperatures to create a sample space of 8 independent statistical samples. These samples were then equilibrated at 298K with a short run NVT ensemble simulation. This was then followed by a density optimization run at 298K using an NPT ensemble. This prepares a well optimized sample which can then be simulated and studied. The final production run is then performed using a NVT ensemble for a longer simulation time.

After the production run was performed on the Mg-EAS-G4 and Mg-EAS-G3 systems, it was found that the minor voids that were formed coalesced to form a single large void, which was large enough that the current state of the software considers it a vacuum. This means that these voids will be unusable as the ions are not energetic enough to enter the void, thereby reducing the volume over which the ions can diffuse.

To overcome this, we performed additional steps to eliminate any extra voids present in the system before the production run. Once the density optimization was performed during the initial NPT ensemble an NVT ensemble at a very high temperature (500K) was performed. Following this an NPT ensemble step was run at 500K and then at 298K to eliminate all additional vacancies in the system. Finally, some additional solvent molecules were introduced into the system to fill up all the leftover spaces.

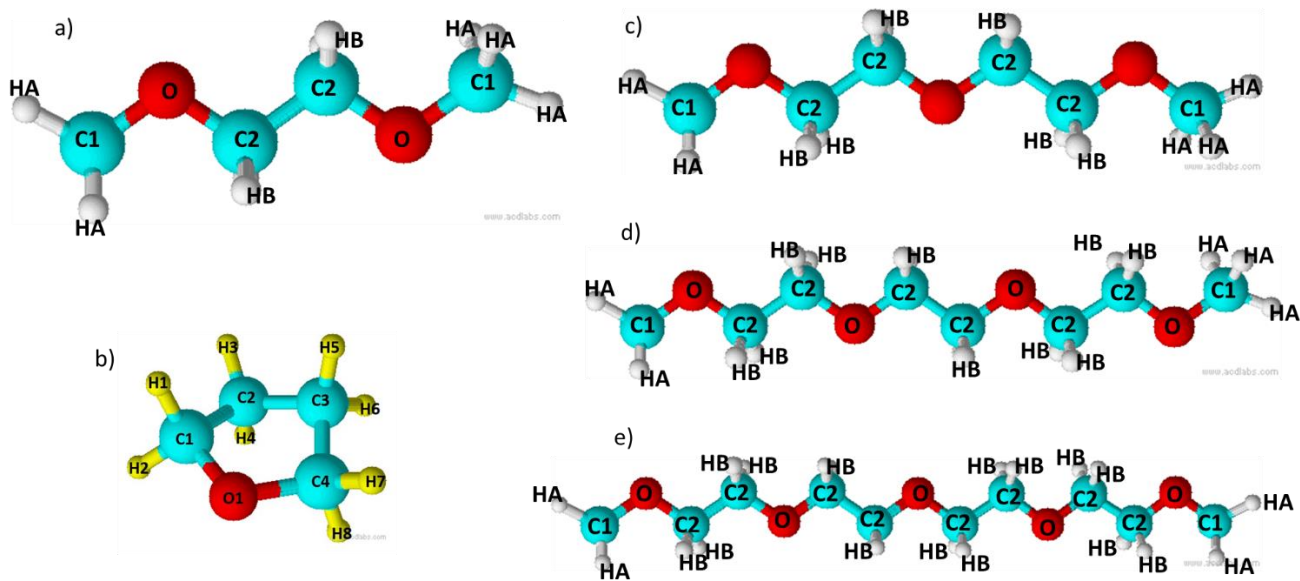


Figure 5.15. Atomic structure and atom nomenclature of solvents used. (a) Dimethoxyethane (DME/glyme); (b) Tetrahydrofuran (THF); (c) diglyme (G2); (d) Triglyme (G3); (e) Tetraglyme (G4).

Table 1. Force field parameters for Mg electroactive species (EAS).

EAS	Atom	q	σ (nm)	ε (kJ/mol)
MgCl^+	Mg	+ 1.4021	0.164	3.68
	Cl	- 0.4021	0.402	2.97
Mg_2Cl_3^+	Mg	+ 1.2621	0.164	3.68
	Cl	- 0.5081	0.402	2.97

Table 2. Force field parameters for Tetrahydrofuran (THF).

Atom	q	σ (nm)	ε (kJ/mol)
C1/C4	0.23	0.34	0.45
H1/H2/H7/H8	0.06	0.247	0.0657
C2/C3	-0.18	0.34	0.45
H3/H4/H5/H6	0.06	0.247	0.0657
O1	-0.58	0.3	0.71128

Table 3. Force field parameters for Glyme family (DME, G2, G3 and G4).

Atom	q	σ (nm)	ϵ (kJ/mol)
C1	-0.016	0.34	0.45
HA	0.06	0.247	0.0657
C2	0.158	0.34	0.45
HB	0.03	0.247	0.0657
O	-0.4	0.3	0.71128

Table 3. Comparison of predicted densities of solvents and the experimental densities

Solvent	Predicted density (kg/m ³)	Experimental density (kg/m ³)
THF	878	887
DME	859	868
G2	951	937
G3	1001	986
G4	1067	1009

5.3. RESULTS AND DISCUSSION

The potential induced diffusion of Mg EAS at operating conditions for all solvents and anions was first analyzed. The diffusivity calculation was done next using drift velocity measurements which has been previously shown to better represent diffusion under an external bias.

Based on the density of solvents and molecular sizes, it was initially predicted that the ionic diffusivity will reduce with increasing molecular weight and density. Solvents with larger molecular weight and densities have steric hinderances towards mobility of solute particles. Studies have shown that in glyme-based solvents the lower order glyme tend to prefer a diffusion process by which the solute

moves from domains of solute-solvent aggregates and in higher order glyme it prefers diffusing through voids and gaps in the solvents.²⁷ Studies on supercritical water have shown that denser solvents have more compact networks and higher tighter binds leading to smaller voids which facilitate diffusion.²⁸ This similar tendency can be approximated here with higher order glyme though the relatively larger sizes of the glyme molecules and the possibility of solvent configurational changes in larger molecules could lead to formation of larger voids aiding in the transfer of ions in the system. Another key factor affecting the solute kinetics is the solute shape. A study of different solute configurations in same solvents have shown that planar solutes (MgCl^+) tend to be more mobile than spherical solutes (Mg_2Cl_3^+).²⁹

Figure 5.2 shows the diffusivities of Mg EAS in THF, monoglyme, diglyme, triglyme and tetraglyme. The predicted decrease in diffusivity from THF to triglyme, tetraglyme is observed for both cations. The diffusivity of THF is higher than the higher order glyme systems due to the diffusion process. The diffusion mechanism of THF is like the diffusion in lower order glymes mentioned previously. This process of cation moving from one solute-solvent agglomeration to another in THF has been previously reported by us and the effect of this mechanism on the rate of ionic clustering has been discussed.

DME shows a different behavior and this study shows that the diffusivity in DME is higher than THF, contrary to our previous hypothesis. All diffusivities are in the same order of magnitude (10^{-10} m²/s) and compare well with previous results.²⁹⁻³²

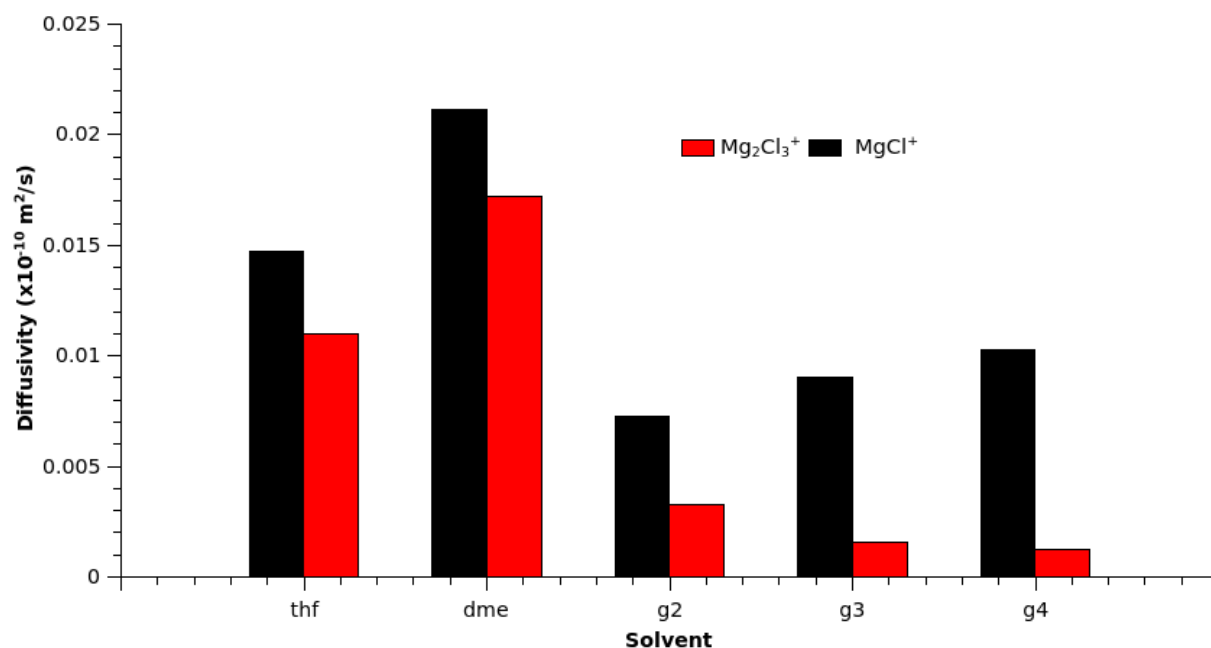


Figure 5.16. Mg-EAS diffusivity ($\times 10^{-7} \text{ m}^2/\text{s}$) in THF, DME, G2 and G3 at 0.4M concentration and 0.45 V/nm electric field

The increase in ionic diffusivity in DME based systems is related to the number of ligand-dentate sites on the solvent molecules. Here the dentate sites are the ethereal oxygen present in the solvent. THF has one dentate site and DME has two sites. Every Mg in the cations studied have an odd number of ligand vacancies (3 for Mg_2Cl_3^+ and 5 for MgCl^+). This implies that there will be between 3 to 5 oxygen sites around each Mg thereby increasing the probability of incomplete coverage from DME due to the inability of complete DME molecules to cover all ligand sites unlike THF. It raises the hypothesis that this incomplete DME coverage will allow for easier displacement of solvent molecules even though DME is denser and heavier. As previously stated, the diffusion in THF and DME are through the solute moving through by displacing the solvent the ease of solvent displacement can lead to better diffusivity as can be seen from our results.

Volumetric density functions to calculate the coverage of THF and DME around the cations was performed. The figure below shows the calculated VDF for Mg_2Cl_3^+ systems. At the same iso values the coverage for DME (blue) is much lesser than the coverage for THF (red). This adds credence to the hypothesis. A similarly higher diffusivity is not observed in diglyme though it has been shown to favor diffusion through solvent displacement which highlights that there may be limit at which the solvent density may play a bigger role than the solvent coverage.

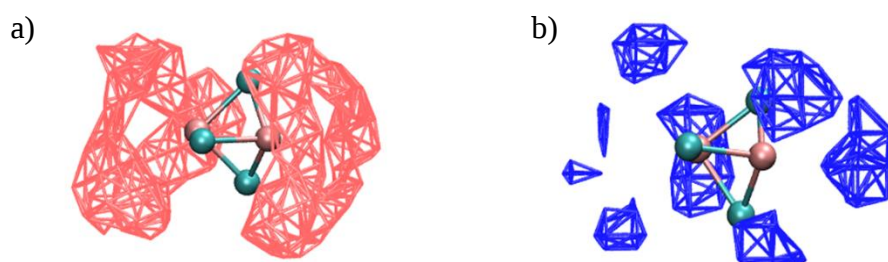


Figure 5.17. Spatial density Function of (a) THF and (b) DME around Mg_2Cl_3^+ at iso value of 0.02.

The shape of the cation also has significant implications on the ionic mobility. The diffusivities of MgCl^+ is higher than Mg_2Cl_3^+ . This increase in diffusivity can be attributed to the smaller size of the cation as well as the changes in configuration mentioned earlier. The planar structure of MgCl^+ helps the cation to better occupy voids without rearranging the surrounding solvents relative to Mg_2Cl_3^+ . The impact of this can be further seen in higher order glyme systems for both cations where the diffusivity of Mg_2Cl_3^+ decreases from diglyme whereas in MgCl^+ there is a slight increase. The higher density and longer chains of tri- and tetraglyme mean that solvent networking structures are extensive with possibility of voids of different sizes. The spherical configuration of Mg_2Cl_3^+ makes it bulkier and reduces the number of voids occupiable. The lesser energy requirements for MgCl^+ mobility can also be an additional cause for its increased selective presence in higher order glymes.³³

5.4. CONCLUSION

In summary, large scale molecular dynamics simulations were performed to investigate the role of solvents and anions on the ion agglomerations in halide containing Mg electrolytes. Two distinct diffusion mechanisms were exhibited based on the weight of the solvent. The lighter solvents THF and DME enable displacement diffusion which is faster. The heavier solvents G2, G3 and G4 all exhibit void diffusion. The diffusivity of Mg-EAS in DME is higher than in THF due to the multidentate nature of DME which leads to lesser number of DME molecules around the cation enabling easier displacement compared to monodentate THF. Characterizing the diffusion process is important to understand the transport and kinetic performance of RMBs. Further studies must be performed at elevated temperatures to characterize the effects on the diffusivity and further work involving a combination of anions need to be carried out to better understand realistic working conditions of RMBs.

REFERENCES

1. D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer and I. Goldberg, *Journal of The Electrochemical Society*, 2002, **149**, A115-A121.
2. D. Aurbach, Y. Gofer, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, M. Moshkovich and R. Turgeman, *Journal of Power Sources*, 2001, **97-98**, 269-273.
3. C. B. Bucur, T. Gregory, A. G. Oliver and J. Muldoon, *The Journal of Physical Chemistry Letters*, 2015, **6**, 3578-3591.
4. P. Baofei, H. Jinhua, H. Meinan, B. S. M., V. J. T., Z. Lu, B. A. K., Z. Zhengcheng and L. Chen, *ChemSusChem*, 2016, **9**, 595-599.
5. B. Pan, J. Huang, N. Sa, S. M. Brombosz, J. T. Vaughey, L. Zhang, A. K. Burrell, Z. Zhang and C. Liao, *Journal of The Electrochemical Society*, 2016, **163**, A1672-A1677.
6. N. Sa, B. Pan, A. Saha-Shah, A. A. Hubaud, J. T. Vaughey, L. A. Baker, C. Liao and A. K. Burrell, *ACS Applied Materials & Interfaces*, 2016, **8**, 16002-16008.

-
7. E. V. Brouillet, A. R. Kennedy, K. Koszinowski, R. McLellan, R. E. Mulvey and S. D. Robertson, *Dalton Transactions*, 2016, **45**, 5590-5597.
 8. T. Mandai, Y. Akita, S. Yagi, M. Egashira, H. Munakata and K. Kanamura, *Journal of Materials Chemistry A*, 2017, **5**, 3152-3156.
 9. M. Salama, I. Shterenberg, H. Gizbar, N. N. Eliaz, M. Kosa, K. Keinan-Adamsky, M. Afri, L. J. W. Shimon, H. E. Gottlieb, D. T. Major, Y. Gofer and D. Aurbach, *The Journal of Physical Chemistry C*, 2016, **120**, 19586-19594.
 10. Y. Cheng, R. M. Stolley, K. S. Han, Y. Shao, B. W. Arey, N. M. Washton, K. T. Mueller, M. L. Helm, V. L. Sprenkle, J. Liu and G. Li, *Physical Chemistry Chemical Physics*, 2015, **17**, 13307-13314.
 11. M. Salama, I. Shterenberg, L. J.W. Shimon, K. Keinan-Adamsky, M. Afri, Y. Gofer and D. Aurbach, *The Journal of Physical Chemistry C*, 2017, **121**, 24909-24918.
 12. E. V. Brouillet, M. Amores, S. A. Corr and S. D. Robertson, *Inorganic Chemistry Frontiers*, 2020, DOI: 10.1039/C9QI01606F.
 13. Z. He, H. Cui, S. Hao, L. Wang and J. Zhou, *The Journal of Physical Chemistry B*, 2018, **122**, 5991-5998.
 14. T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizuno, R. Zhang, S. Shirai and J. W. Kampf, *Angewandte Chemie International Edition*, 2014, **53**, 3173-3177.
 15. C. Liao, N. Sa, B. Key, A. K. Burrell, L. Cheng, L. A. Curtiss, J. T. Vaughey, J.-J. Woo, L. Hu, B. Pan and Z. Zhang, *Journal of Materials Chemistry A*, 2015, **3**, 6082-6087.
 16. Z. Ma, M. Kar, C. Xiao, M. Forsyth and D. R. MacFarlane, *Electrochemistry Communications*, 2017, **78**, 29-32.
 17. O. Tutusaus, R. Mohtadi, T. S. Arthur, F. Mizuno, E. G. Nelson and Y. V. Sevryugina, *Angewandte Chemie International Edition*, 2015, **54**, 7900-7904.
 18. M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, *SoftwareX*, 2015, **1-2**, 19-25.
 19. H. J. C. Berendsen, D. van der Spoel and R. van Drunen, *Computer Physics Communications*, 1995, **91**, 43-56.
 20. V. D. S. David, L. Erik, H. Berk, G. Gerrit, M. A. E. and B. H. J. C., *Journal of Computational Chemistry*, 2005, **26**, 1701-1718.
 21. B. Hess, C. Kutzner, D. van der Spoel and E. Lindahl, *Journal of Chemical Theory and Computation*, 2008, **4**, 435-447.
-

-
22. E. Lindahl, B. Hess and D. van der Spoel, *Molecular modeling annual*, 2001, **7**, 306-317.
 23. S. Pronk, S. Páll, R. Schulz, P. Larsson, P. Bjelkmar, R. Apostolov, M. R. Shirts, J. C. Smith, P. M. Kasson, D. van der Spoel, B. Hess and E. Lindahl, *Bioinformatics*, 2013, **29**, 845-854.
 24. K. A. See, K. W. Chapman, L. Zhu, K. M. Wiaderek, O. J. Borkiewicz, C. J. Barile, P. J. Chupas and A. A. Gewirth, *Journal of the American Chemical Society*, 2016, **138**, 328-337.
 25. O. Tutusaus, R. Mohtadi, N. Singh, T. S. Arthur and F. Mizuno, *ACS Energy Letters*, 2017, **2**, 224-229.
 26. W. Junmei, W. R. M., C. J. W., K. P. A. and C. D. A., *Journal of Computational Chemistry*, 2004, **25**, 1157-1174.
 27. S. R. Galle Kankanamge, K. Li, K. D. Fulfer, P. Du, R. Jorn, R. Kumar and D. G. Kuroda, *The Journal of Physical Chemistry C*, 2018, **122**, 25237-25246.
 28. D. Chakraborty and A. Chandra, *Journal of Molecular Liquids*, 2011, **162**, 12-19.
 29. T. C. Chan, H. T. Li and K. Y. Li, *The Journal of Physical Chemistry B*, 2015, **119**, 15718-15728.
 30. A. Benmayza, M. Ramanathan, T. S. Arthur, M. Matsui, F. Mizuno, J. Guo, P.-A. Glans and J. Prakash, *The Journal of Physical Chemistry C*, 2013, **117**, 26881-26888.
 31. N. N. Rajput, X. Qu, N. Sa, A. K. Burrell and K. A. Persson, *Journal of the American Chemical Society*, 2015, **137**, 3411-3420.
 32. D. Samuel, C. Steinhäuser, J. G. Smith, A. Kaufman, M. D. Radin, J. Naruse, H. Hiramatsu and D. J. Siegel, *ACS Applied Materials & Interfaces*, 2017, **9**, 43755-43766.
 33. G. Bieker, M. Salama, M. Kolek, Y. Gofer, P. Bieker, D. Aurbach and M. Winter, *ACS Applied Materials & Interfaces*, 2019, **11**, 24057-24066.

CHAPTER 6:
SOLVENT AND ANION CONTROLS ON ANION BRIDGED IONIC
CLUSTERING OF Mg-Cl CATIONIC COMPLEXES IN HALIDE
CONTAINING ELECTROLYTES FOR USE IN RECHARGEABLE
MAGNESIUM BATTERIES

6.1. INTRODUCTION

Rechargeable magnesium batteries are a promising alternative to the existing Li-ion battery technologies due to the high energy density and low production cost.¹ To ensure commercial viability of RMB technologies several challenges must be solved regarding the electrochemical behavior of the various components of the battery. One such important problem involves development of stable and efficient electrolytes. To aid in this development a thorough understanding of the underlying electrolytic structures is important. The higher charge density of Mg^{2+} compared to Li^+ leads to complex electrochemical behavior in the electrolytes.^{1, 2} This causes a significant tendency to form local clusters and larger agglomerates. These clusters and agglomerates affect the performance of the electrolyte and may govern the various electrochemical pathways in the battery. Hence to develop better electrolytes an understanding of the ionic cluster and agglomerates is necessary.

One promising electrolyte candidate for RMBs is chloride containing electrolyte. It has been shown that due to the high charge density on Mg^{2+} , Mg tends to form complex species which are the main charge carrying component of the electrolyte. These are called electroactive species. These EAS are the main charge carrying components. Work has been done to show the existence of Mg-Cl complexes such as MgCl^+ , Mg_2Cl_3^+ which have been shown to be the most common EAS in Mg battery electrolytes.³⁻⁷ Studies have shown the Mg-Cl cationic complexes are stabilized by the surrounding solvent. Hence, an in-depth analysis of the cation – anion – solvent interaction is necessary.

Its stability against metallic magnesium limits the choice of solvent. Ethers are the most employed.⁸ Despite their low dielectric constant, Ethers work well in dissolving and creating charge carriers,

despite their low dielectric constant, which is explained by the redissociation phenomena.⁹ Commonly used tetrahydrofuran (THF) is found to work well with many salts; however, the bulkier structure of the ring limits its coordination abilities. Hence, multidentate glymes ($\text{CH}_3\text{O}-(\text{C}_2\text{H}_4\text{O})_n-\text{CH}_3$) are widely applied to increase the solubility of Mg-salts. The flexibility of glymes allows them to wrap tightly around the cations and adopt to different conformations, resulting in strong solvating abilities.¹⁰ Glyme length determines the properties of the electrolyte which change with an increase of glyme length, thus higher denticity of the solvent. The shortest, monoglyme (DME), was commonly used many times instead of THF, and did not show problems with desolvation of Mg^{2+} at the electrode. Also, longer glymes, up to tetraglyme (G4), have been used successfully, although some increase in over potential is observed.¹⁰⁻¹² In general, an increase in glyme length gives a (desired) lower volatility of the electrolyte, but at the cost of higher viscosity and slower transport kinetics.^{10, 13-15}

The complexity of the cation-anion-solvent complexes are further compounded by the presence of ionic clusters formed within the system. Ionic cluster formation in other ionic electrolytes have been proposed due to discrepancies between experimental and theoretical results.¹⁶ Experiments have been used directly or indirectly observe ion cluster formations in simpler electrolytes.^{17, 18} Simulations have been performed on NaCl solutions at both ambient and supercritical conditions to observe ion cluster formation and further analyze the impact of the clusters formed.^{16, 19, 20} In the previous it has been shown using Molecular Dynamics (MD) that ionic clustering occurs in Mg-Cl systems which significantly affect ionic mobility and ionic solvation and this study is used to further.²¹ Similar ion agglomerations have been shown to trigger side reactions at the anode-electrolyte interfaces in Mg batteries.^{5, 22} The agglomeration of $\text{Mg}^{2+}-\text{BH}_4^-$ clusters in $\text{Mg}(\text{BH}_4)_2$ -based electrolytes for RMBs show lowered solubility as confirmed both experimentally and theoretically.²³⁻²⁵ The presence of ion

clusters have also shown to improve the Ca^{2+} surface deposition by enabling the presence of CaBH_4^+ cationic species in Calcium ion batteries.²⁶ Hence accounting for the ionic clustering in Mg-electrolytes is important gaining a thorough understanding of the underlying interactions in electrolyte performance

Here my work shows the existence of ionic clusters in all the solvents used, and, that the clustering mechanism has two components, the solvent effect and anion effect. The solvent effect is more dominant in the heavier solvents while the anion effect plays a more significant role in the lighter solvents. The monodentate THF shows lower clustering compared to the multidentate glyme family due to the need for anions to displace more solvent molecules in THF. A comprehensive understanding of the cluster controls is useful in understanding and characterizing the role of the ionic clusters during battery operation.

6.2. METHODOLOGY

All MD simulations were performed using GROMACS Molecular Dynamics Package.²⁷⁻³² Two cationic EAS were chosen. Five solvents Tetrahydrofuran (THF), Glyme (DME), Diglyme (G2), Triglyme (G3) and Tetraglyme (G4) were used. One strongly interacting (Cl^-) and one weakly interacting (AlCl_4^-) anion were chosen. The system was simulated at three concentrations, 0.2 M, 0.4 M and 0.6 M. All atomic parameters were derived from the all-atom optimized potentials for liquid solvents (OPLS-AA) force field.³³ All force field parameters have been provided in the previous chapter. A simulation box size of 8 nm x 8 nm x 8 nm was used. A cut off distance of 1 nm was used for the Lennard – Jones Potential. The electrostatic interactions were mapped using Particle Mesh

Ewald (PME) with a cut off of 1 nm and a Fourier grid spacing of 0.12 was used. Periodic Boundary conditions were applied in all directions.

Energy minimization was initially performed for all simulations. This was followed by 100 ps of NVT simulations followed by 100 ps of NVT at an elevated temperature of 500 K was performed to remove all voids. This was followed by 500 ps of NPT simulations to optimize density calculations. A forced declustering step was run for 500 ps to capture initial clustering kinetics. A final production run was done for 16 ns and analysis was performed on 12 ns. The coordinates, forces, velocities and energies were recorded for every 0.1 ps along the MD trajectory. The output was visualized using VMD.

6.3. RESULTS AND DISCUSSION

6.3.1. *Clustering in electrolytes containing ethereal solvents*

Analysis of ion agglomerations of Mg-EAS under operating and equilibrium conditions was performed. The cation-cation coordination numbers were measured and tracked for concentrations of 0.2 M, 0.4 M and 0.6 M. **Figure 6.1-6.4** shows the formation of Mg EAS clusters investigated by tracking the coordination number of the EAS-EAS pairs. The coordination number of EAS-EAS ($N_{\text{EAS-EAS}}$) pairs points is either increasing or is stable above 1 for all electrolyte systems studied. This indicates that there are significant cation-cation interactions that lead to the formation of ion clusters. The formed clusters show a tendency to persist in size and stabilize around 7 ns of production run. Minor fluctuations were observed in the coordination numbers which are caused due to ion migration from one cluster to another. The mapping of these individual clusters is hard as there are no sharp

cluster boundaries to define. This has increased the complexity of understanding the behavior and effect of the ion clustering in the electrolytic performance.

The presence of the ionic clusters at all concentrations indicates the tendency of the ions to agglomerate and this implies that understanding the clustering process is a requirement to develop electrolytes for RMB. The effect of the concentration is not as pronounced as would be expected because of the distance cut-offs selected in this work which only looks at the immediate neighborhood of the cation.

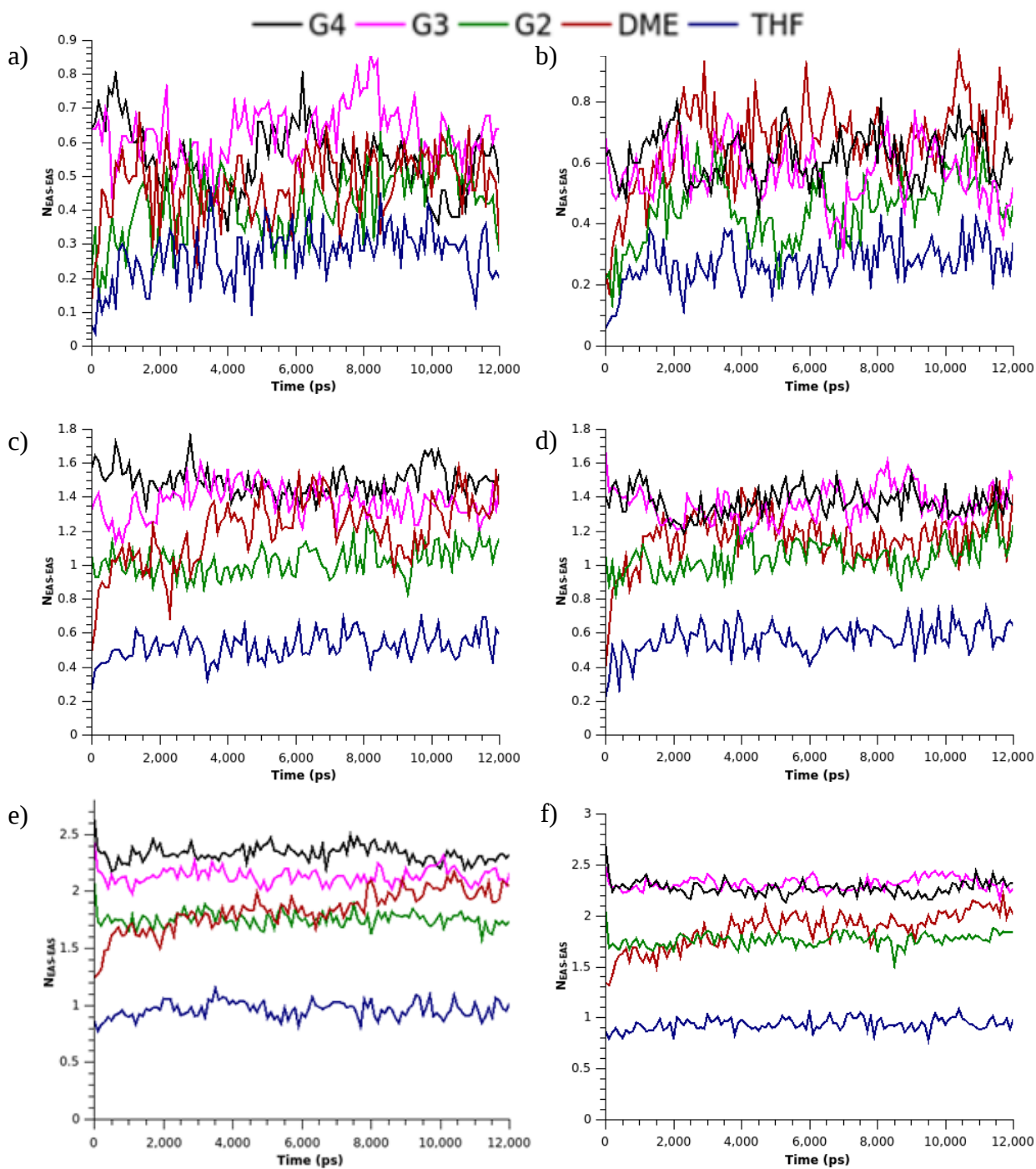


Figure 6.18. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $Mg_2Cl_3^+-Mg_2Cl_3^+$ coordination numbers with $AlCl_4^-$ anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $Mg_2Cl_3^+-Mg_2Cl_3^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f)

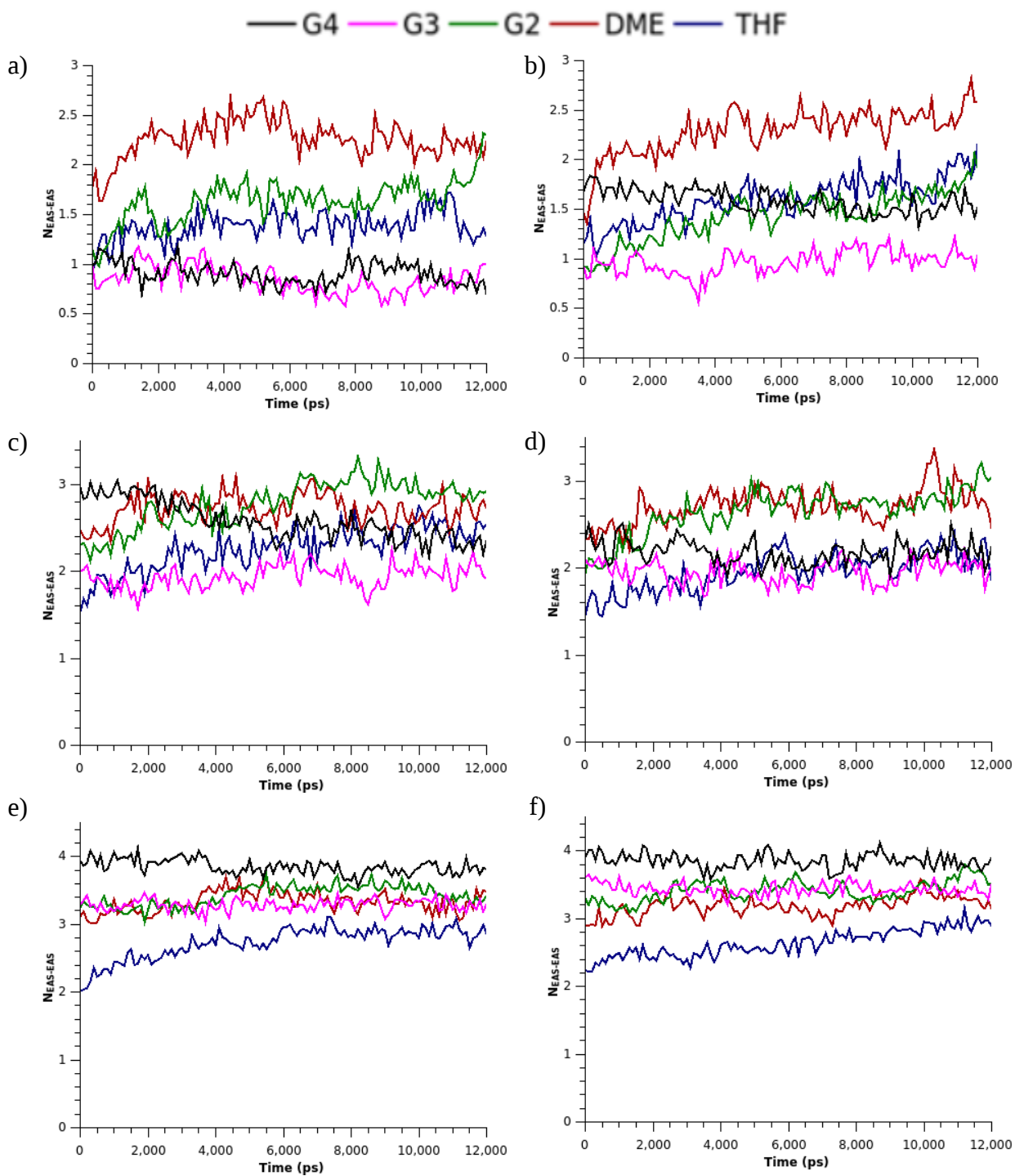


Figure 6.19. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $Mg_2Cl_3^+-Mg_2Cl_3^+$ coordination numbers with Cl^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $Mg_2Cl_3^+-Mg_2Cl_3^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f).

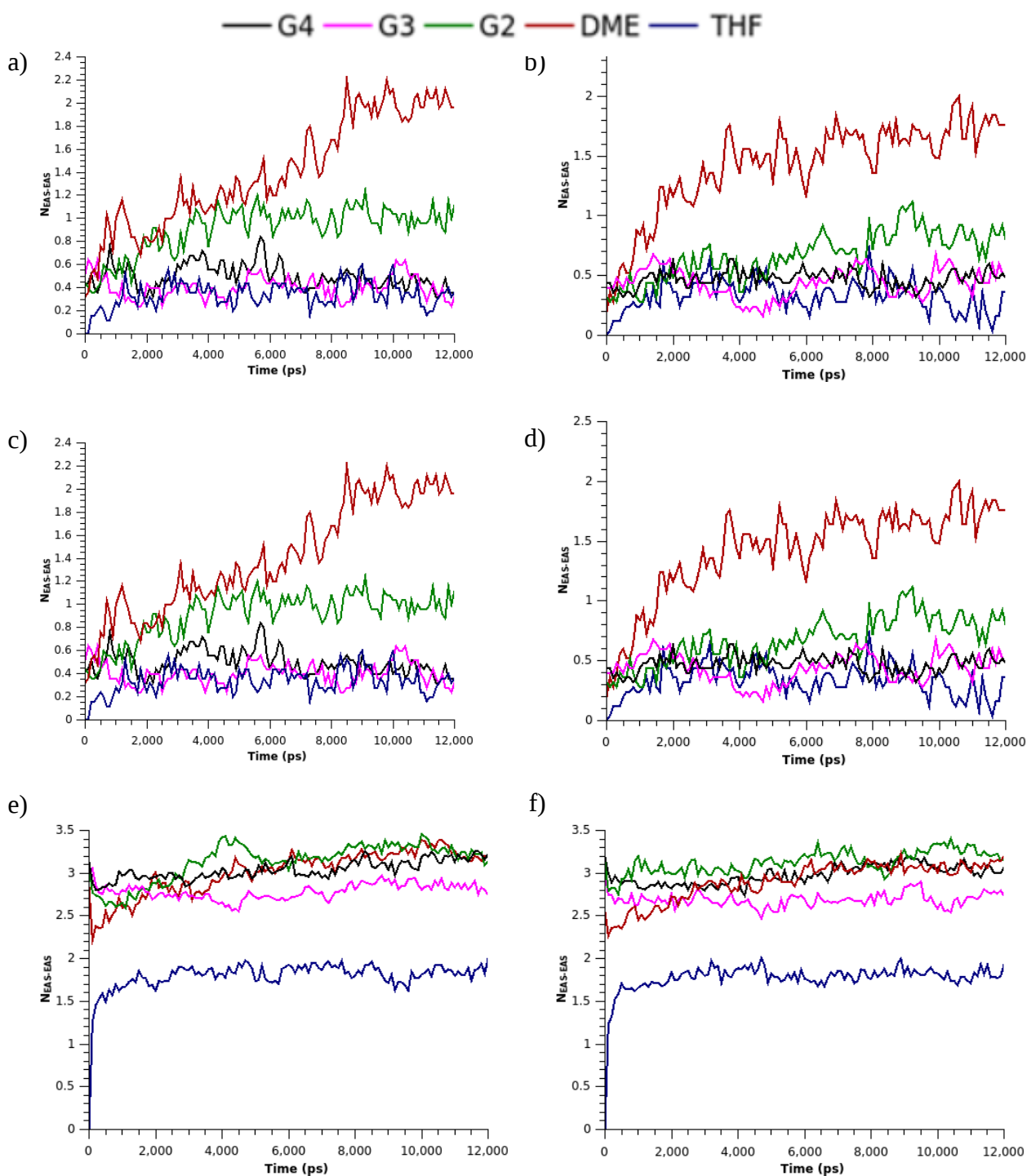


Figure 6.20. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{MgCl}^+-\text{MgCl}^+$ coordination numbers with AlCl_4^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{MgCl}^+-\text{MgCl}^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M(d) and 0.6M (f)

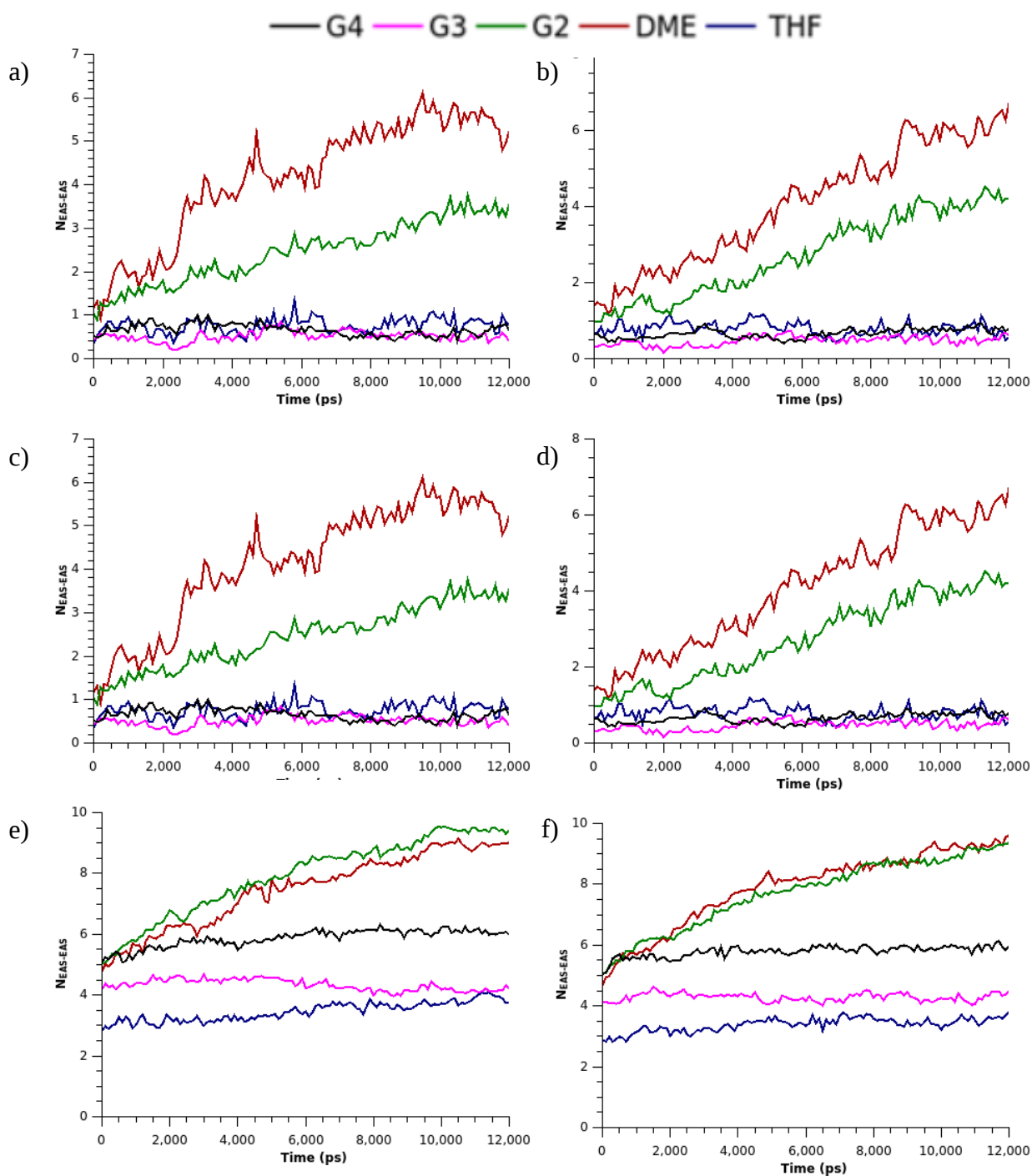


Figure 6.21. Ion pairing in halide containing Mg electrolytes. (a,c,e) Average $\text{MgCl}^+-\text{MgCl}^+$ coordination numbers with Cl^- anion under constant electric field of 0.45 V/nm at 0.2M (a), 0.4M (c) and 0.6M (e). (b,d,f) Average $\text{MgCl}^+-\text{MgCl}^+$ coordination numbers at equilibrium conditions at 0.2M (b), 0.4 M (d) and 0.6M (f).

6.3.2. Solvent effects on ionic clustering

The role of solvents in the clustering of the ions has been previously reported for Li-ion systems. Morales et al. have previously studied the role of the solvent, primarily the ethereal solvents of the glyme family on their role in the clustering of LiPF_6 containing electrolytes.¹⁴ They have reported that as the chain length reduces the ion association increases. The increase in association is related to the reduced solvation of the ions in DME as compared to heavier solvents such as G4. The reduced solvation is shown to form small nano phases of the ions that can increase agglomeration. Ion clustering has shown to improve battery performance in Sodium ion batteries by reducing the possibility of anion degradation reactions which facilitate faster electrolyte breakdown.³⁴

Next a comparative study of the clustering rates among different solvents was taken up and lead to the finding that the clustering rates for THF was the lowest. This shows that THF tends to shield the cations better. The increased shielding of THF compared to the glyme-family of solvents can be associated with the large ring structure of the THF which along with the single oxygen present in the molecule causes the formation of three large structures that cover the octahedral sites of the cation. This means that for the formation of larger clusters more THF molecules must be displaced compared to the other glymes. The high EAS-EAS coordination observed in DME is due to the relative ease of the anion displacing DME which can be caused due to the lower coverage of the EAS observed in the previous chapter. This lower coverage can aid in the increased association observed in Li-ion batteries.

The process of declustering that was performed prior to the start of the production run was not effective towards the heavier glyme systems. This can be observed from the near stationary coordination rates over the course of the simulation. The inability of the declustering step to separate the cationic species is due to the tight networking of the solvents. The heavier glymes tend to make

the cationic species undergo void diffusion. Void diffusion tends to be slower than displacement diffusion and thus the amount of time for the declustering was insufficient to complete the separation of the ionic species. The lowered mobility of the ions and the increased trapping by the solvent matrix leads to forced ion-clustering. This compares well with work done by Morales et al. where, as temperature increases the ion pairing reduces. This may be due to the increased ease of the diffusion mechanism caused by the formation of larger voids.

6.3.3. Anion effects on clustering

Next, I looked at the role of the anion on the clustering process. From **Figures 6.1-6.4** we can see that ion pairing is much higher for the Cl^- anion compared to the AlCl_4^- anion. It can still be seen that ion pairing occurs in both the anionic systems. The two anions selected in this work were done so to represent weakly coordinating anions (AlCl_4^-) and strongly coordinating anions (Cl^-). In the weakly coordinating anionic system, the ionic coordination increases as the size of the glyme increases. This is because, beyond the impact of the anions, the solvent plays a more significant role in trapping the ionic system ensuring higher coordination. Though coordination is lesser for THF and DME we can see that the clustering increases over time. This shows that though AlCl_4^- is weakly coordinating, the electrostatic interactions between the cation and the anion are sufficient to overcome the cationic repulsions.

For the strongly coordinating anionic system all solvents studied showed significant clustering. Though the higher clustering in the heavier glymes could be associated with the solvent effect the higher coordination numbers compared to AlCl_4^- systems indicate that the Cl^- anion aids in the increased clustering. To better separate the two effects for the studies, must be performed at higher temperatures to reduce the impact of the solvent. For the THF and DME the clustering rate is higher than the clustering rate with AlCl_4^- showing that the Cl^- aided clustering process can affect the

solvation of the solute and reduce mobility of the ion. It is also seen for MgCl^+ cationic systems the clustering in DME is much higher than in the other solvents. The increased clustering for MgCl^+ can be associated to the morphology of the clustering as observed in **Chapter 4**. The formation of branched chains leads to more cations close to each other, hence skewing the coordination numbers to much higher levels. The lowered coordination of cations in THF is due to the solvent effect caused by the increased cost in displacing three monodentate THF molecules compared to one or two multidentate glymes.

The role of clusters in the deposition / dissolution mechanism at the anode-electrolyte interface is an increasingly studied question. Previous work has shown that the presence of more than one type of anion can aid in driving the two-way process.³⁵ These systems contain one strongly coordinating and weakly coordinating anion, and these two anions show a cooperative behaviour with the weakly coordinating anion aiding deposition cycle and the strongly coordinating anion aiding the dissolution cycle. The observance of both types of anions at the anode electrolyte interface shows that though the strongly coordinating anion is much better at clustering, the weakly coordinating anion is still present at the interface. This implies that the role of the solvent in the clustering process is more significant than what has been discussed in this work and needs to be further investigated.

6.4. CONCLUSION

In summary, performed large scale molecular dynamics simulations to investigate the role of solvents and anions on the ion agglomerations in halide containing Mg electrolytes. The simulations helped to conclude that the heavier glymes aided in ion clustering by trapping ions together, whereas THF and DME allow for clustering by displacement of the solvent molecules. The role of the anion was also shown to be significant and the nature of the anion affected clustering rates. It was also seen that

it was hard to separate the effect of the anion and the solvent in the clustering process and a combination of the two is what contributes to clustering. Understanding the underlying nature of cluster formations and cluster controls is important to develop better electrolytes for RMBs. Further studies have to be performed to better separate the various interactions that control clustering and this may provide key insights into the deposition/dissolution mechanism at the anode-electrolyte interfaces.

REFERENCES

1. D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer and I. Goldberg, *Journal of The Electrochemical Society*, 2002, **149**, A115-A121.
2. C. B. Bucur, T. Gregory, A. G. Oliver and J. Muldoon, *The Journal of Physical Chemistry Letters*, 2015, **6**, 3578-3591.
3. E. V. Brouillet, M. Amores, S. A. Corr and S. D. Robertson, *Inorganic Chemistry Frontiers*, 2020, DOI: 10.1039/C9QI01606F.
4. E. V. Brouillet, A. R. Kennedy, K. Koszinowski, R. McLellan, R. E. Mulvey and S. D. Robertson, *Dalton Transactions*, 2016, **45**, 5590-5597.
5. P. Canepa, S. Jayaraman, L. Cheng, N. N. Rajput, W. D. Richards, G. S. Gautam, L. A. Curtiss, K. A. Persson and G. Ceder, *Energy & Environmental Science*, 2015, **8**, 3718-3730.
6. M. Salama, I. Shterenberg, H. Gizbar, N. N. Eliaz, M. Kosa, K. Keinan-Adamsky, M. Afri, L. J. W. Shimon, H. E. Gottlieb, D. T. Major, Y. Gofer and D. Aurbach, *The Journal of Physical Chemistry C*, 2016, **120**, 19586-19594.
7. P. Jankowski, J. M. G. Lastra and T. Vegge, *Batteries & Supercaps*, 2020, **3**, 1350-1359.
8. Z. Lu, A. Schechter, M. Moshkovich and D. Aurbach, *Journal of Electroanalytical Chemistry*, 1999, **466**, 203-217.

-
9. J. Self, N. T. Hahn, K. D. Fong, S. A. McClary, K. R. Zavadil and K. A. Persson, *The Journal of Physical Chemistry Letters*, 2020, **11**, 2046-2052.
 10. Y. Cheng, R. M. Stolley, K. S. Han, Y. Shao, B. W. Arey, N. M. Washton, K. T. Mueller, M. L. Helm, V. L. Sprenkle, J. Liu and G. Li, *Physical Chemistry Chemical Physics*, 2015, **17**, 13307-13314.
 11. R. Jay, A. W. Tomich, J. Zhang, Y. Zhao, A. De Gorostiza, V. Lavallo and J. Guo, *ACS Applied Materials & Interfaces*, 2019, **11**, 11414-11420.
 12. F. Tuerxun, Y. Abulizi, Y. NuLi, S. Su, J. Yang and J. Wang, *Journal of Power Sources*, 2015, **276**, 255-261.
 13. G. Horwitz, M. Factorovich, J. Rodriguez, D. Laria and H. R. Corti, *ACS Omega*, 2018, **3**, 11205-11215.
 14. D. Morales, R. E. Ruther, J. Nanda and S. Greenbaum, *Electrochimica Acta*, 2019, **304**, 239-245.
 15. C. Zhang, A. Yamazaki, J. Murai, J.-W. Park, T. Mandai, K. Ueno, K. Dokko and M. Watanabe, *The Journal of Physical Chemistry C*, 2014, **118**, 17362-17373.
 16. G. Ren, R. Shi and Y. Wang, *The Journal of Physical Chemistry B*, 2014, **118**, 4404-4411.
 17. C. Frege, I. K. Ortega, M. P. Rissanen, A. P. Praplan, G. Steiner, M. Heinritzi, L. Ahonen, A. Amorim, A. K. Bernhammer, F. Bianchi, S. Brilke, M. Breitenlechner, L. Dada, A. Dias, J. Duplissy, S. Ehrhart, I. El-Haddad, L. Fischer, C. Fuchs, O. Garmash, M. Gonin, A. Hansel, C. R. Hoyle, T. Jokinen, H. Junninen, J. Kirkby, A. Kürten, K. Lehtipalo, M. Leiminger, R. L. Mauldin, U. Molteni, L. Nichman, T. Petäjä, N. Sarnela, S. Schobesberger, M. Simon, M. Sipilä, D. Stolzenburg, A. Tomé, A. L. Vogel, A. C. Wagner, R. Wagner, M. Xiao, C. Yan, P. Ye, J. Curtius, N. M. Donahue, R. C. Flagan, M. Kulmala, D. R. Worsnop, P. M. Winkler, J. Dommen and U. Baltensperger, *Atmos. Chem. Phys.*, 2018, **18**, 65-79.
 18. N. Molinari, J. P. Mailoa and B. Kozinsky, *Chemistry of Materials*, 2018, **30**, 6298-6306.
 19. Z. He, H. Cui, S. Hao, L. Wang and J. Zhou, *The Journal of Physical Chemistry B*, 2018, **122**, 5991-5998.
 20. S. Murad, *The Journal of Chemical Physics*, 2011, **134**, 114504.
-

-
21. V. Vasudevan, M. Wang, J. A. Yuwono, J. Jasieniak, N. Birbilis and N. V. Medhekar, *The Journal of Physical Chemistry Letters*, 2019, **10**, 7856-7862.
22. P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson and G. Ceder, *Chemical Reviews*, 2017, **117**, 4287-4341.
23. R. Mohtadi, M. Matsui, T. S. Arthur and S.-J. Hwang, *Angewandte Chemie International Edition*, 2012, **51**, 9780-9783.
24. D. Samuel, C. Steinhauser, J. G. Smith, A. Kaufman, M. D. Radin, J. Naruse, H. Hiramatsu and D. J. Siegel, *ACS Applied Materials & Interfaces*, 2017, **9**, 43755-43766.
25. O. Tutusaus, R. Mohtadi, T. S. Arthur, F. Mizuno, E. G. Nelson and Y. V. Severyugina, *Angewandte Chemie International Edition*, 2015, **54**, 7900-7904.
26. N. T. Hahn, J. Self, T. J. Seguin, D. M. Driscoll, M. A. Rodriguez, M. Balasubramanian, K. A. Persson and K. R. Zavadil, *Journal of Materials Chemistry A*, 2020, **8**, 7235-7244.
27. M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, *SoftwareX*, 2015, **1-2**, 19-25.
28. H. J. C. Berendsen, D. van der Spoel and R. van Drunen, *Computer Physics Communications*, 1995, **91**, 43-56.
29. V. D. S. David, L. Erik, H. Berk, G. Gerrit, M. A. E. and B. H. J. C., *Journal of Computational Chemistry*, 2005, **26**, 1701-1718.
30. B. Hess, C. Kutzner, D. van der Spoel and E. Lindahl, *Journal of Chemical Theory and Computation*, 2008, **4**, 435-447.
31. E. Lindahl, B. Hess and D. van der Spoel, *Molecular modeling annual*, 2001, **7**, 306-317.
32. S. Pronk, S. Páll, R. Schulz, P. Larsson, P. Bjelkmar, R. Apostolov, M. R. Shirts, J. C. Smith, P. M. Kasson, D. van der Spoel, B. Hess and E. Lindahl, *Bioinformatics*, 2013, **29**, 845-854.
33. W. Junmei, W. R. M., C. J. W., K. P. A. and C. D. A., *Journal of Computational Chemistry*, 2004, **25**, 1157-1174.
-

-
34. H. Kumar, E. Detsi, D. P. Abraham and V. B. Shenoy, *Chemistry of Materials*, 2016, **28**, 8930-8941
35. J. G. Connell, M. Zorko, G. Agarwal, M. Yang, C. Liao, R. S. Assary, D. Strmcnik and N. M. Markovic, *ACS Applied Materials & Interfaces*, 2020, **12**, 36137-36147

CHAPTER 7:

CONCLUSIONS AND FUTURE WORK

7.1. CONCLUSIONS

In this thesis I have presented a new insight into understanding the fundamental electrolytic structures that influence and control the performance of halide containing electrolytes for use in Rechargeable Magnesium Batteries. My work highlighted key interplay between cations, anions and solvents in the bulk electrolytic systems under the influence of external electric fields to mimic realistic operating conditions.

7.1.1. Gap in literature

Halide-containing electrolytes have shown to be an extremely promising candidate for use in RMBs, due to their relatively higher stability and lower overpotential. Though it has been shown to have a high-performance characteristic, it has been highlighted that the use of these electrolytes has some fundamental drawbacks to it. These include the use of the corrosive Chloride anion and the complex chemistry caused by the high charge density on the Mg^{2+} cation. Furthermore, the characterization of these electrolytes shows that contrary to expectations, the large charge density on Mg causes the formation of larger multi-atomic cationic complexes rather than the simpler and smaller Mg^{2+} cation. Added to this, the exact cationic species present was hard to identify and it was found to be in a dynamic equilibrium between multiple species with the direction of the equilibrium controlled by various factors including stoichiometry, nature of solvent used, the anion present and external factors including operating and ambient conditions. To address this issue, work has been done to characterize the role of the cationic species and understand the solvation structure in the electrolyte. To this extent work has been done on determining the solvation properties of the various cationic species in different solvents. But the question of the solvation structure and its impact on the performance of the

electrolyte, not only about the electrochemical reactions at the anode-electrolyte interfaces, is yet to be studied.

7.1.2. Cationic solvation and ionic clustering

Addressing the issue of the cationic solvation structure, I used large scale MD studies to perform a comprehensive solvation structure study on four Mg-Cl complex cationic species, namely Mg^{2+} , MgCl^+ and its reversible dimer $\text{Mg}_2\text{Cl}_2^{2+}$ and Mg_2Cl_3^+ in the ethereal solvent THF. I was able to observe that if a larger solvation structure was studied, there was agglomeration of the cationic species in the electrolyte bridged by the anions. These larger agglomerations had not been reported before and may play an important role in the electrochemistry of the battery. The morphology of the ionic agglomerations was controlled by the structure of the cationic species. The isotropic Mg^{2+} formed bulky globular clusters while the anisotropic MgCl^+ , $\text{Mg}_2\text{Cl}_2^{2+}$ and Mg_2Cl_3^+ formed linear chains with the MgCl^+ cation forming branched chain structures due to the availability of more octahedral ligand sites.

7.1.3. Ionic mobility

The existence of the clustering species indicated a possibility that these agglomerations influence not only the solvation and electrochemistry, but also the working performance of the electrolyte by affecting the mobility of the ions. To this extent, compared the diffusivity of the cationic species in the clustered and unclustered electrolytic systems. The unclustered system was formed by removing the bridging anions which helped form the clusters. To calculate the diffusivity in a non-equilibrium condition caused by the external electric field, the work implements a drift velocity-based method instead of the traditional Einstein's method. It was found that when the ions were clustered, even under a very high electric field the mobility of the ions was lower by an order of magnitude and were

like mobilities calculated in equilibrium conditions. This indicated that cluster diffusion dominated over ionic diffusion and hence the clusters play a more significant role in the performance of the battery than had been previously studied.

7.1.4. Solvent influence on the mobility

After establishing the influence of the cationic clustering on the transport properties of the electrolyte, it was desired to qualify and quantify the role of the solvents used. To this effect, other commonly used ethereal solvents of the glyme family namely monoglyme (DME), diglyme (G2), triglyme (G3) and tetraglyme (G4) were taken up for study. These studies led to the conclusion that there exists two distinct diffusion regimes each controlled by a different diffusion mechanism. The lower molecular weight solvents whose molecular weights are lesser than or close to the molecular weight of the cations enabled the faster displacement diffusion, in which the solvent molecules were pushed away from their position and the cation moved into the vacancy formed. Furthermore, the ease of displacing the solvent molecules was affected by the coverage of the solvent around the cations which was determined by the denticity of the solvent molecule. The denticity of the solvent molecule is determined by the number of the Oxygen ligand sites that can attach to the cationic species. For the heavier solvents, the cations underwent the process of void diffusion, where the cations jumped from one void formed by the interlinking of the solvent molecules to another void in the solvent matrix.

7.1.5. Anion and solvent control on clustering

Necessity to further the understanding of the cluster formation and possible underlying controls for the clustering mechanism became important. A comparison of various solvents introduced in the previous studies was done and it was found that the heavier solvents forcibly held the clusters together by trapping the ionic species closer to each other. To further elucidate the influence of the solvents,

a weakly interacting anion, AlCl_4^- , was introduced and compared to the clustering rates formed when the strongly interacting Cl^- anion was used. It was shown that the Cl^- enabled faster clustering compared to AlCl_4^- and this anion-controlled clustering was more influential in the lighter solvents.

7.2. FUTURE WORK

7.2.1. *Temperature effect on clustering*

The role of the solvent, anion and cation in the cluster formation and its impact on the transport properties of the electrolyte have been established. To further improve the understanding of the clustering process, one would need to include other external conditions such as temperature. Since battery operations occur at a higher temperature than ambient and the batteries are used in a wide range of scenarios with vastly varying temperatures, it is important to rigorously study the role of external influence on the electrolytic behavior.

7.2.2. *Mixed ionic systems*

It has been established that the different cationic complexes are present in a dynamic equilibrium indicating that multiple cationic species are present at the same time. Furthermore, MgCl_2 is not used individually to reduce the possibility of atomic Cl which is highly corrosive, and it is used as an additive to another Mg salt electrolyte usually containing a weakly interacting anionic species such as AlCl_4^- , TFSI^- or PF_6^- . Thus, a thorough analysis of the various cation-anion mixtures containing different cationic and anionic species is necessary to thoroughly map the cation-anion-solvent interaction landscapes which can help in better designing commercially viable electrolytes for use in RMBs.

7.2.3. Anode-electrolyte interphase studies

Finally, once the bulk interactions are mapped, the studies must be shifted towards the interphase where the bulk of the electrochemical processes take place. This will provide valuable insights into not only the working mechanism of the RMB but will also generate new understanding of the causes of the Solid-electrolyte interface (SEI) and techniques that may be used to counter the formation of the SEI or at best control the nature of the SEI formed.

7.3. SUMMARY

In summary, this thesis has elaborated on the different influencing species present in the halide containing electrolytes for use in RMBs and the underlying structures and mechanisms that influence the performance of the electrolyte and the battery using large scale Molecular dynamics simulations which has provided key insights that will be useful in developing stable electrolytes for commercially viable Rechargeable Magnesium Batteries.

APPENDIX 1: SUPPORTING INFORMATION

Ion Agglomeration and Transport in MgCl_2 -Based Electrolytes for Rechargeable Magnesium Batteries

Vallabh Vasudevan[†], Mingchao Wang^{†*}, Jodie A. Yuwono^{†‡}, Jacek Jasieniak[†], Nick Birbilis[§] and
Nikhil V. Medhekar^{†*}

[†]Department of Materials Science and Engineering, Monash University, Faculty of Engineering,
Clayton, Victoria 3800, Australia

[‡]School of Photovoltaics and Renewable Energy Engineering, University of New South Wales
Sydney, Kensington, New South Wales 2052, Australia

[§]College of Engineering and Computer Science, Australian National University, Action, ACT 2601,
Australia

Corresponding Authors: mingchao.wang@monash.edu (Dr. Mingchao Wang)

nikhil.medhekar@monash.edu (A/Prof. Nikhil Medhekar).

S1. DETAILS OF MOLECULAR DYNAMICS (MD) SIMULATIONS

All MD simulations were performed using the Generalized AMBER Force Field (GAFF).¹ The GAFF parameters developed for Mg electroactive species (EAS) by Canepa *et al.*² were used in the present work. The tetrahydrofuran (THF) parameters from van der Spoel *et al.*^{3,4} were used and benchmarked by measuring the density of THF at 300K. All the force field parameters are given in **Table S1-S2**. The Lorentz-Berthelot combining rule was utilized to describe the non-bonded cross-term interaction between EAS and THF. Bond length constraints were applied for the electroactive species using the LINCS algorithm.⁵ The simulation box size of 4 nm × 4 nm × 4 nm were used in all simulation models. Each simulation system consists of 1 Mg salt molecule and 510 THF molecules for infinite dilution studies and 23 Mg salt and 490 THF molecules for simulations at 0.4 M concentration. The cut-off distance of 1.0 nm was used for Lennard-Jones potential. The Columbic potential was measured using Particle Mesh Ewald (PME)⁶ with a cut-off distance of 1.0 nm and Fourier grid spacing of 0.12. The neighbor list was updated every 0.01 ps within 1.0 nm. Periodic boundary conditions were applied in all directions.

We started MD simulations by initial energy minimization, followed by 100 ps of NVT simulation and 500 ps of NPT simulation with an integration time step of 0.001 ps. All the simulation systems were finally maintained at 298 K using the Nose–Hoover thermostat for 4 ns to collect simulation data.⁷ A time constant of 0.2 ps was applied for the temperature coupling. To study the impact of an external electric field, two scenarios were chosen, (1) a constant external electric field ranging 0.45 V/nm was applied along *x* axis for simulating the operating conditions and (2) no external electric field was applied (0 V/nm). We also considered other field strengths 0.2, 0.6, 0.8 and 1.0 V/nm to further understand the impact of the field strength on the kinetics of the ionic species. The coordinates, forces, velocities and energies were recorded for every 0.1 ps along the MD trajectory. The output

was visualized using VMD⁸ and the analysis of MD trajectories was performed using standard tools within VMD. The ionic spatial distribution was calculated using the GROMaps tool.⁹

To study the influence of anion, we also used two methods to study the anion effect on the solvation structures of distinct EAS, including (1) the explicit presence of Cl⁻ in the system and (2) replacement of the Cl⁻ by a background charge which influences the system by applying a force on each individual molecule. The second method approximates a system in which the cation and anion are separated by a large distance, or by a physical impervious wall across which the short-range ordering owing to van der Waals interactions are absent.

S2. VALIDATION OF MOLECULAR DYNAMICS SIMULATIONS

To ensure the accuracy of our simulation models of the electrolyte system, the force field parameters for THF were benchmarked by comparing the predicted density after equilibration to the experimental value. We set the density of THF as the benchmark since that the physical properties of solvents determine the solvation structures and mobility of Mg EAS in the electrolyte. The density of THF was calculated by running an equilibration run in a box of 4 nm side with periodic boundary conditions for 500 ps. As shown in **Figure S1**, the calculated density of THF (0.878 g/cm³) is very close to the experimental value (0.889 g/cm³).

To benchmark the EAS parameters, we identify the number of THF molecules in the vicinity of the EAS, namely THF coordination numbers of various Mg EAS (see **Table S3**) at infinite dilution. It was found that in the absence of an anion the expected 6 THF molecules were found around Mg₂Cl₃⁺. For MgCl⁺, we obtain THF coordination number of 4 rather than the full Mg octahedral 5 THF ligands, possibly because of the solvated, mobile nature of Mg EAS. There is a possibility of lower

THF coordination due to the intrinsic stabilization by the second solvation shell. Our evaluated THF coordination numbers of various Mg EAS are the same as those obtained by Canepa *et al*².

S3. CLUSTER ANALYSIS

The cluster analysis was performed in the simulation box of 8 nm × 8 nm × 8 nm. Such larger system size was used to ensure a sufficient number of clustering species. All simulation models were first optimized by using energy minimization, followed by 500 ps of NVT equilibration and 1 ns of NPT equilibration. The production NVT was run for 16 ns and the data selected was from the first 12 ns as sufficient clustering had been observed. These simulations were performed at different concentrations of 0.1 M, 0.2 M and 0.4 M, with 4500 THF molecules and 50, 100 and 200 Mg salts respectively, as well as with and without the applied electric field. The clustering was measured by counting the number of Cl⁻, THF and EAS within 0.4 nm, 0.5 nm and 0.8 nm of each EAS respectively. The coordination numbers of EAS-Cl⁻, EAS-EAS and EAS-THF pairs were collected for every 0.1 ns and the coordination number was averaged over all EAS residues with respect to the stoichiometric ratios. The averaged coordination number of EAS-THF pair during cluster formation was normalized by the evaluated coordination number without anion (see **Table S3**).

Prior to cluster analysis it was found that the process of ion pairing starts occurring during the equilibration of the system. This leads to significantly pre-clustered systems even before final production runs, which makes it difficult to isolate the competing electrostatic interactions among EAS, Cl⁻ and THF and to study the kinetics of cluster formation. To overcome such limitation, we performed an additional 100 ps of NVT run between the initial equilibration and the final NVT run, during which we turned off all electrostatic interactions between Cl⁻ and the EAS allowing for a nearly complete separation of anions and cations. This segregated phase has been labelled as ‘*de-clustered*’

in this work. The *de-clustered* phase is the prevalent phase for 0.5 ns, which was then followed by rapid ion pairing and agglomeration. The cation-anion pairs increase with the presence of other EAS near the cations (Fig 2a, S4a, S5a, S5b) leading to cluster formation and their plateau values around 7 ns, and this phase is labelled '*clustered*'. Due to the strong electrostatic interactions between the cation and anion, the *clustered* phase is the dominant phase for majority of the simulation time (>3 ns).

S4. CALCULATION OF ION DIFFUSIVITY IN THE MgCl_2 -BASED ELECTROLYTE

To account for the randomization of the initial system sampling for diffusivity calculations, we performed seven statistically independent simulations to sample the phase spaces. This was achieved by adding an extra NVT run at different elevated temperatures. The self-diffusion coefficients of EAS in their equilibrium states (without electric field) D were calculated by measuring the mean square displacement (MSD) and applying the Einstein's relation:

$$\langle \text{MSD} \rangle = \langle X^2(t) - X^2(0) \rangle = 6Dt \quad (1)$$

where $X(t)$ and $X(0)$ are the ion displacement at time t and 0 . The diffusive displacement of ions under an external electric field can be separated into the self-diffusive displacement used in the previous relation and the drift velocity induced displacement,

$$X(t) = X_r(t) + v_d t \quad (2)$$

where $X_r(t)$ and v are the diffusive displacement and the drift velocity. When the system is allowed to evolve for a long time period, the ensemble average of the diffusive component of the displacement will tend to zero, if the initial system is sufficiently random without any bias.

$$\langle X(t) \rangle = \langle X_t(t) \rangle + v_d dt, \quad \lim_{t \rightarrow \infty} \langle X_r(t) \rangle = 0 \quad (3)$$

Thus, one can calculate the drift velocity of the system

$$v_d = \lim_{t \rightarrow \infty} \frac{\langle X(t) \rangle}{t} \quad (4)$$

The mobility μ can be calculated from the drift velocity v_d from which the diffusivity D can be derived as,

$$\mu = \frac{v_d}{qE} \quad \text{and} \quad D = k_B T \mu \quad (5)$$

where q is the charge of the species, E the electric field and T the temperature of the system. All values of diffusivity presented are averaged over the different ensembles and the standard errors have been shown in each figure.

Table S1. Force field parameters for Mg electroactive species (EAS).

EAS	Atom	q	σ (nm)	ε (kJ/mol)
Mg ²⁺	Mg	+ 2.0000	0.164	3.68
MgCl ⁺	Mg	+ 1.4021	0.164	3.68
	Cl	- 0.4021	0.402	2.97
Mg ₂ Cl ₂ ²⁺	Mg	+ 1.4021	0.164	3.68
	Cl	- 0.4021	0.402	2.97
Mg ₂ Cl ₃ ⁺	Mg	+ 1.2621	0.164	3.68
	Cl	- 0.5081	0.402	2.97

Table S2. Force field parameters for tetrahydrofuran (THF). The denotation of atom types is given in the inset of Figure S1.

Atom	q	σ (nm)	ϵ (kJ/mol)
C1/C4	0.2549	0.34	0.45
H1/H2/H7/H8	-0.0024	0.247	0.0657
C2/C3	-0.0092	0.34	0.45
H3/H4/H5/H6	0.0032	0.247	0.0657
O1	-0.49460	0.3	0.71128

Table S3. The coordination numbers for electroactive species (EAS)–tetrahydrofuran (THF) pairs under different conditions.

EAS	NEAS-THF			
	without electric field		with electric Field	
	without anion	with anion	without anion	with anion
Mg ²⁺	6.0	3.6	6.0	3.4
MgCl ⁺	4.0	2.0	4.0	1.7
Mg ₂ Cl ₂ ²⁺	4.0	3.0	4.0	2.9
Mg ₂ Cl ₃ ⁺	6.0	3.9	6.0	3.8

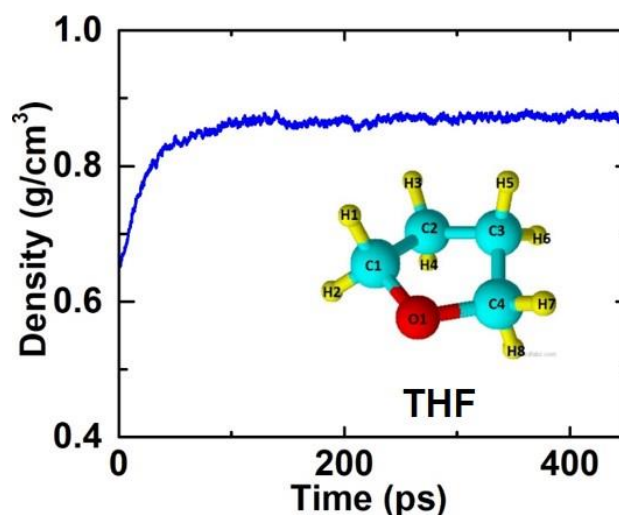


Figure S1. The predicted density of pure tetrahydrofuran (THF) solvent as a function of simulation time. The inset denotes the type of each atom in the THF molecule as mentioned in Table S2.

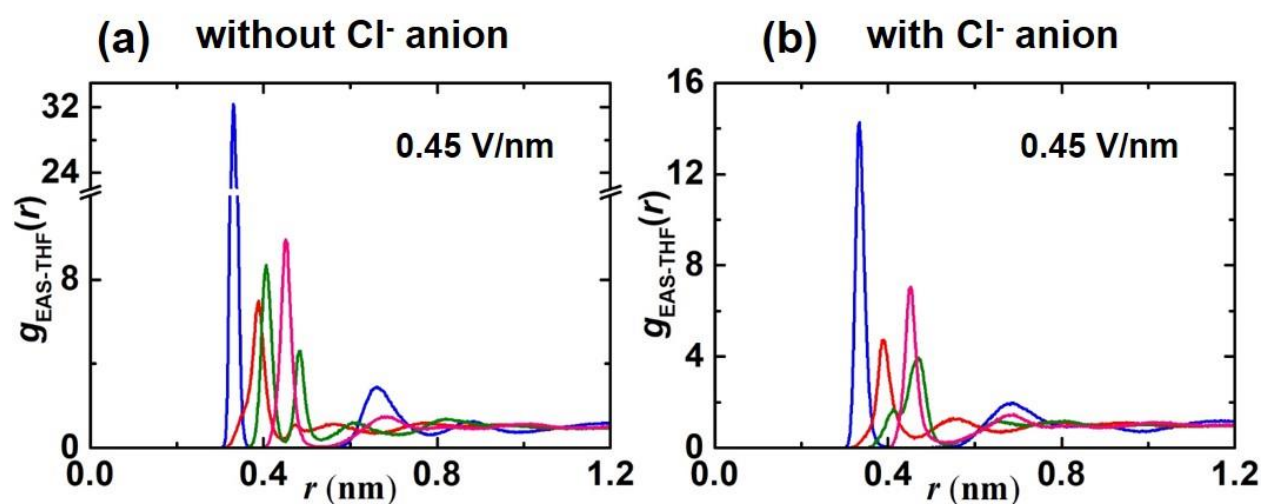


Figure S2. The radial distribution functions of electroactive species (EAS)-THF pairs with and without Cl^- anion at the infinite dilution under the electric field of 0.45 V/nm.

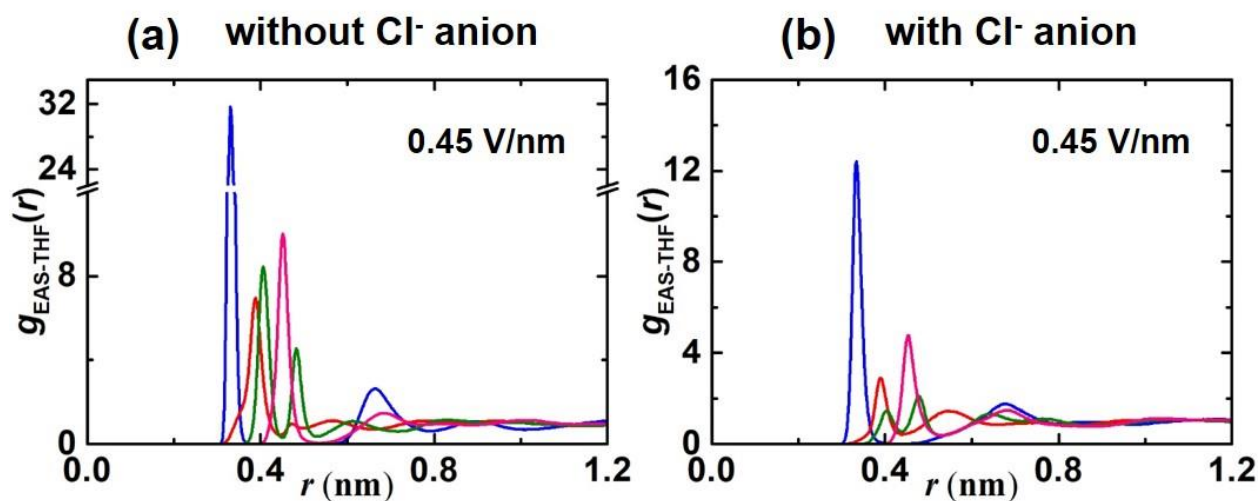


Figure S3. The radial distribution functions of electroactive species (EAS)-THF pairs with and without Cl^- anion at the concentration of 0.4 M under the electric field of 0.45 V/nm at the concentration of 0.4 M.

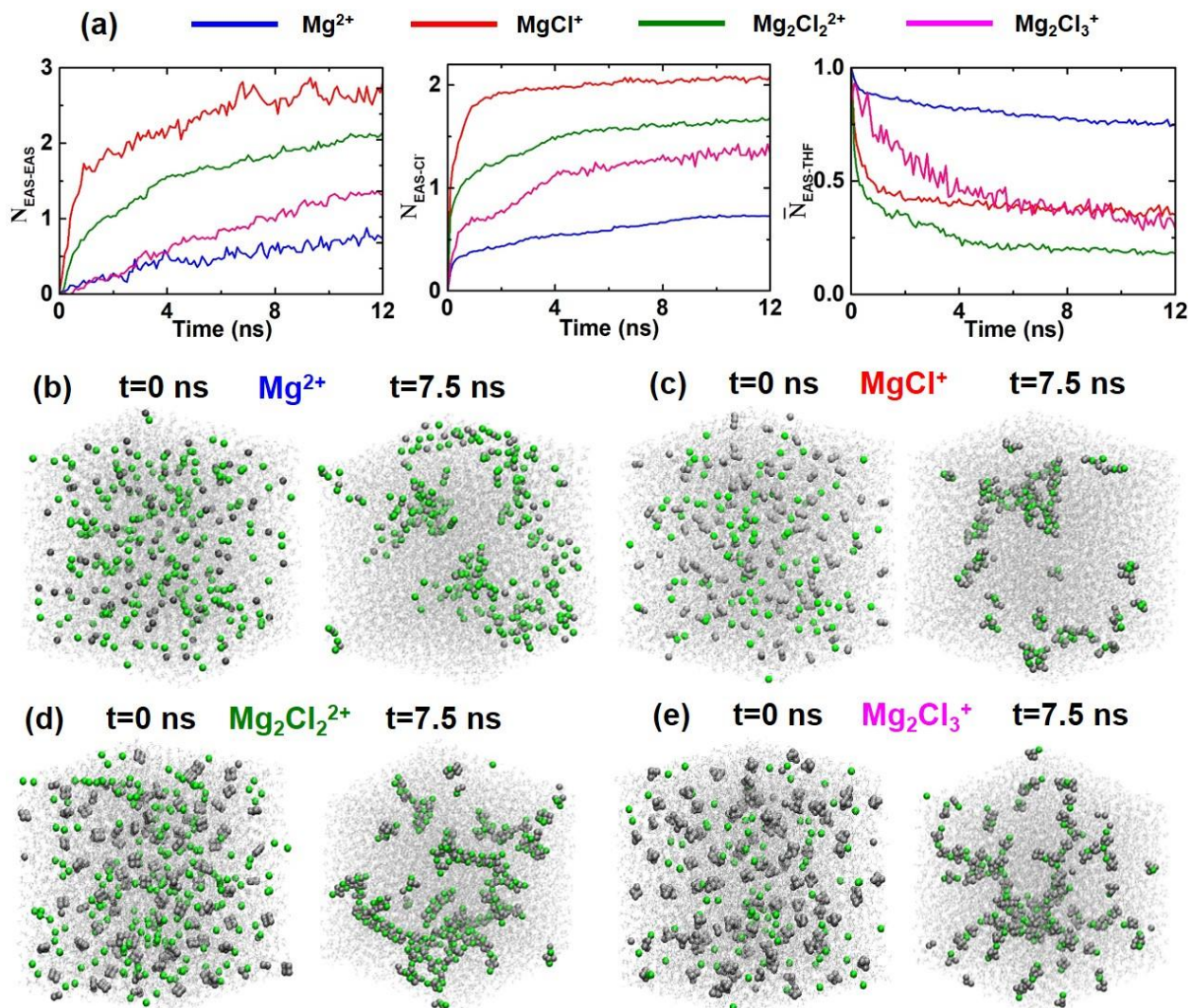


Figure S4. Cluster formation of various Mg electroactive species (EAS) in the MgCl₂-based electrolyte, at the concentration of 0.2 M and without the applied electric field. (a) The average coordination numbers of EAS-EAS, EAS-Cl⁻ and EAS-THF pairs during the formation of clusters. (b-e) exhibit completely isolated ions and newly formed clusters of EAS-Cl⁻ complexes at the simulation time of 0 and 7.5 ns.

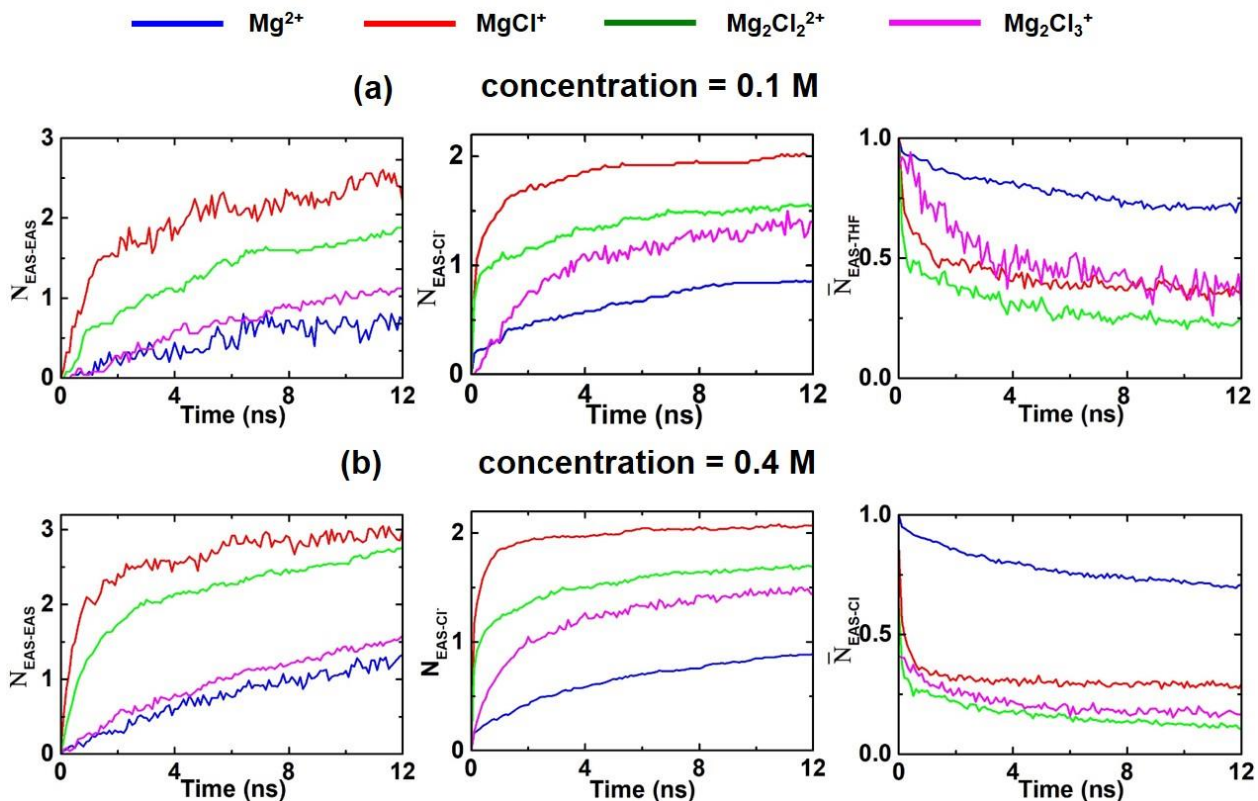


Figure S5. The average coordination numbers of EAS-EAS, EAS-Cl- and EAS-THF pairs during the formation of clusters at the concentrations of (a) 0.1 M, and (b) 0.4 M under the applied electric field of 0.45 V/nm.

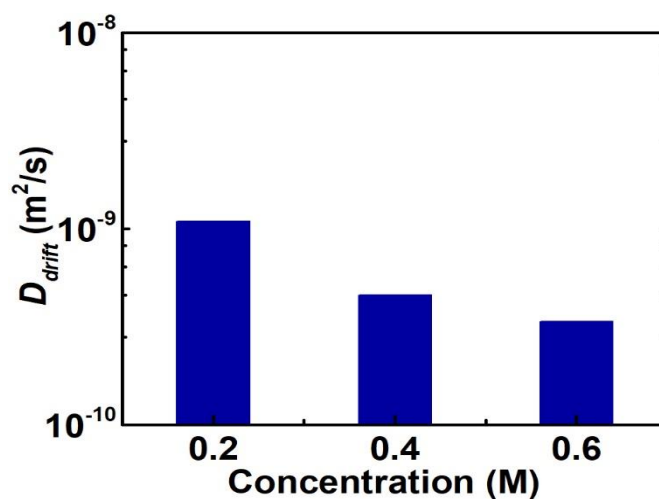


Figure S6. The ion diffusivities of Mg EAS evaluated from drift velocity (D_{drift}) as a function of EAS concentration under the applied electric field of 0.45 V/nm.

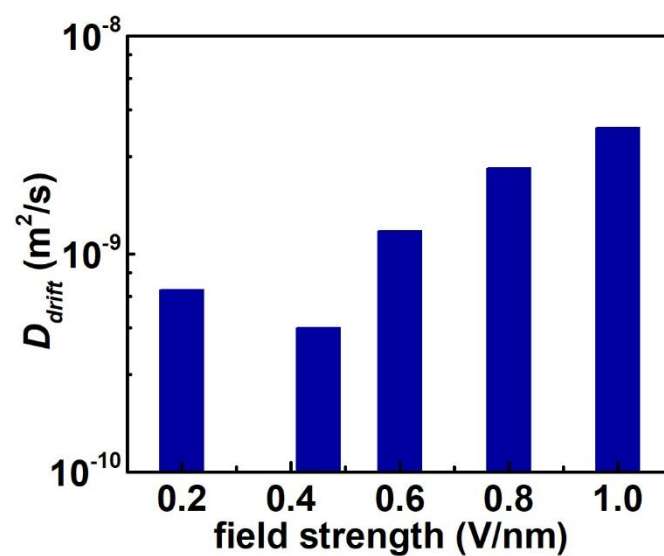


Figure S7. The ion diffusivities of Mg EAS evaluated from drift velocity (D_{drift}) as a function of electric field strength at the concentration of 0.4 M.

REFERENCES

- (1) Junmei, W.; M., W. R.; W., C. J.; A., K. P.; A., C. D. Development and testing of a general amber force field. *Journal of Computational Chemistry* **2004**, *25*, 1157-1174.
- (2) 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.
- (3) Caleman, C.; van Maaren, P. J.; Hong, M.; Hub, J. S.; Costa, L. T.; van der Spoel, D. Force Field Benchmark of Organic Liquids: Density, Enthalpy of Vaporization, Heat Capacities, Surface Tension, Isothermal Compressibility, Volumetric Expansion Coefficient, and Dielectric Constant. *J. Chem. Theory Comput.* **2012**, *8*, 61-74.
- (4) van der Spoel, D.; van Maaren, P. J.; Caleman, C. GROMACS Molecule & Liquid Database. *Bioinform.* **2012**, *28*, 752-753.
- (5) Hess, B. P-LINCS: A parallel linear constraint solver for molecular simulation. *Journal of Chemical Theory and Computation* **2008**, *4*, 116-122.
- (6) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: An $N \cdot \log(N)$ method for Ewald sums in large systems. *The Journal of chemical physics* **1993**, *98*, 10089-10092.
- (7) Evans, D. J.; Holian, B. L. The Nose–Hoover thermostat. *The Journal of Chemical Physics* **1985**, *83*, 4069-4074.
- (8) Humphrey, W.; Dalke, A.; Schulten, K. VMD: visual molecular dynamics. *Journal of molecular graphics* **1996**, *14*, 33-38.
- (9) Briones, R.; Blau, C.; Kutzner, C.; de Groot, B. L.; Aponte-Santamaría, C. GROmaps: A GROMACS-Based Toolset to Analyze Density Maps Derived from Molecular Dynamics Simulations. *Biophysical Journal* **2019**, *116*, 4-11.