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HIGH ENERGY AND HIGH POWER MAGNESIUM BATTERIES

A Dissertation

Presented to

The Faculty of the Materials Science and Engineering Program

University of Houston

In Partial Fulfillment

of the Requirement for the Degree

Doctor of Philosophy

in Materials Science and Engineering

by

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August 2019

HIGH ENERGY AND HIGH POWER MAGNESIUM BATTERIES

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Acknowledgments

There are many people who have earned my gratitude for their contribution to my time at University of Houston. More specifically, I would like to thank six groups of people, without whom this dissertation would not have been possible: my advisor, my committee members, my labmates, my industrial collaborators, my roommate, and my family.

My deep gratitude goes first to my advisor, Prof. Yan Yao. Since my first day at UH, Prof. Yao gave me endless support. It all started in Fall 2015 when he offered me such a great opportunity to join his lab. On the academic level, Prof. Yao taught me fundamentals of conducting scientific research. Under his supervision, I learned how to define a research problem, find a solution to it, and finally published the results. On a personal level, Prof. Yao inspired me by his hardworking and passionate attitude. I could not have imagined having a better advisor and mentor for my Ph.D. study.

Besides my advisor, I would like to extend my sincere thanks to the rest of my dissertation committee, Prof. Alamgir Karim, Prof. T. Randall Lee, Prof. Cunjiang Yu, and Prof. Xiaonan Shan for their great support, insightful comments and encouragement.

I would also like to extend my gratitude to my lab mates for their continued support. This dissertation would not have been possible without the intellectual contribution from Dr. Yanliang liang, an assistant research professor in our group. Moreover, I am thankful to Dr. Yifei Li, Dr. Yan Jing, Dr. Saman Gheytni, Fang Hao, Ye Zhang, Karun K Rao, Dr. Yi Shi, Yang Chen, Dr. Jibo Zhang, Dr. Xiaojun Wang, Dr. Xiaowei Chi for their collaboration and contribution in various projects related to this dissertation.

I am also grateful to my industrial collaborators. I had a summer internship at Toyota North America where I collaborated with wonderful scientists in the materials research department. More specifically, I would like to thank Dr. Rana Mohtadi and Dr. Oscar Tutusaus for their continuous support and for providing me the great opportunity to work on Mg batteries and solid-state batteries with them. Without their precious support it would not be possible to conduct this research.

Thanks should also go to my roommate, Yunbao Sun. He provided me with a lot of support and encouragement over the years.

Finally, to my family, who have always been there for me. I am grateful in more ways than I can express for your support and encouragement over the years. To my dear parents, Liping Dong and Kemei He, without whom none of this would have been possible, I owe you an immeasurable debt of gratitude for the long hard hours you worked throughout my youth to give me the opportunity to follow my dreams, and for all of the tremendous love you've shown me along the way.

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Abstract

Magnesium batteries are emerging as attractive candidates for energy storage in terms of safety, energy density, and scalability because Mg metal has ideal properties as a battery anode: high volumetric capacity, low redox potential, dendrite-free plating, and earth-abundant resources. One persistent challenge is the lack of high-performance cathodes, since Mg^{2+} ingress and diffusion within cathodes are kinetically sluggish. The main objective of this dissertation is to demonstrate new research approaches that could effectively overcome these barriers and eventually lead to high-performance Mg batteries.

In this dissertation, I proposed two strategies to achieve this goal, including Mg-Na hybrid batteries and Mg-organic batteries. First, I developed an Mg-Na hybrid battery, which can circumvent the intercalation of Mg^{2+} by using a Na-insertion cathode in a $\text{Na}^+/\text{Mg}^{2+}$ hybrid electrolyte. However, as a matter of fact that the cathode and anode employed different charge carriers, the cell energy was limited by the concentration of Na^+ in the electrolyte.

The second strategy was to utilize organic compounds as Mg battery cathodes. I first revealed that previously reported organic cathodes all operated on an MgCl -storage chemistry sustained by a large amount of electrolyte that significantly reduced cell energy. I then demonstrated Mg batteries featuring an Mg^{2+} -storage chemistry using chloride-free electrolytes. The observed specific energy (243 Wh kg^{-1}), and cycling stability ($87\% @ 2500 \text{ cycles}$) of Mg-storage cells consolidated polymers as promising cathodes for Mg batteries.

Finally, I reported a quinone molecule, pyrene-4,5,9,10-tetraone (PTO), that can circumvent sluggish Mg^{2+} diffusion through a dissolution-precipitation reaction, and its intrinsic ion-coordination charge storage mechanism does not involve bond-breaking and bond-formation, therefore demonstrating potential to achieve high power. By coupling PTO cathode with a high-performance electrolyte, $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DME/G2, I created an Mg battery with a specific energy of 566 Wh kg^{-1} and an ultra-high power of 30 kW kg^{-1} , which surpassed all previously reported Mg batteries.

I hope that the work described in this dissertation provides an in-depth understanding of the technical challenges of Mg batteries and effective solutions to address them.

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Publications

1. **Dong, H.;** Liang, Y. L.; Tutusaus, O.; Mohtadi, R.; Zhang, Y.; Hao, F.; Yao, Y. “Directing Mg-Storage Chemistry in Organic Polymers Towards High-Energy Mg Batteries.” *Joule* **2019**, 3 (3), 782–793. (Selected as Journal Cover)
2. **Dong, H.;** Li, Y. F.; Liang, Y. L.; Li, G. S.; Sun, C. J.; Ren, Y.; Lu, Y. H.; Yao, Y. “A Magnesium–sodium Hybrid Battery with High Operating Voltage.” *Chem. Commun.* **2016**, 52 (53), 8263–8266.
3. **Dong, H.;** Tutusaus, O.; Liang, Y. L.; Zhang, Y.; Zhang, J. B.; Yang, W. L.; Lebens-Higgins, Z.; Mohtadi, R.; Yao, Y. “High Power Mg-Organic Batteries.” In submission.
4. Liang, Y. L.; † **Dong, H.;** † Rao, K. K.; D. Aurbach; Yao, Y. “Promises and Reality of Multivalent-ion Batteries.” *Nature Nanotechnology*. In Revision. († **co-first authors**)
5. Cheng, Y. W.; † Chang, H. J.; † **Dong, H.;** † Choi, D. W.; Sprenkle, V. L.; Liu, J.; Yao, Y.; Li, G. S. “Rechargeable Mg–Li Hybrid Batteries: Status and Challenges.” *J. Mater. Res.* **2016**, 31 (20), 3125–3141. († **co-first authors**)
6. Liang, Y. L.; † Hao, F.; † **Dong, H.;** † Yao, Y. “Mechanistic insights into the lithium-doping conjugated redox polymers.” In submission. († **co-first authors**)
7. Yoo, H. D.; Liang, Y. L.; **Dong, H.;** Lin, J. H.; Wang, H.; Liu, Y. S.; Ma, L.; Wu, T. P.; Li, Y. F.; Ru, Q.; Jing, Y.; An, Q. Y.; Zhou, W.; Guo, J. H.; Lu, J.; Pantelides, S. T.; Qian, X. F.; Yao, Y. “Fast kinetics of magnesium monochloride cations in interlayer-expanded titanium disulfide for magnesium rechargeable batteries.” *Nat. Commun.* **2017**, 8, 339.

8. Hao, F.; Chi, X. W.; Liang, Y. L.; Zhang, Y.; Xu, R.; Guo, H.; **Dong, H.**; Zhao, K. J.; Lou, J.; Yao, Y. “Taming Active Material-Solid Electrolyte Interfaces with Organic Cathode for All-Solid-State Batteries.” *Joule* **2019**, 5, 1349. (Highlighted in Science)
9. Chi, X. W.; Liang, Y. L.; Hao, F.; Zhang, Y.; Whiteley, J.; **Dong, H.**; Hu, P.; Lee, S.; Yao, Y. “Tailored organic electrode material compatible with sulfide electrolyte for stable all-solid-state sodium batteries.” *Angew. Chem.* **2018**, 57, 2630.
10. Li, Y. F.; An, Q. Y.; Cheng, Y. W.; Liang, Y. L.; Ren, Y.; Sun, C. J.; **Dong, H.**; Tang, Z. J.; Li, G. S.; Yao, Y. “A high-voltage rechargeable magnesium-sodium hybrid battery.” *Nano Energy* **2017**, 34, 188.
11. Gheytni, S.; Liang, Y. L.; Wu, F. L.; Jing, Y.; **Dong, H.**; Rao, K. K.; Chi, X. W.; Fang, F.; Yao, Y. “An aqueous Ca-ion battery.” *Advanced Science* **2017**, 4, 1700465.
12. Hu, P.; Zhang, Y.; Chi, X. W.; Rao, K. K.; Hao, F.; **Dong, H.**; Guo, F. M.; Ren, Y.; Grabow, L.; Yao, Y. “Stabilizing the Interface between Sodium Metal Anode and Sulfide-based Solid-State Electrolyte with an Electron Blocking Interlayer.” *ACS Appl. Mater. Interfaces*. **2019**, 11 (10), 9672-9678.
13. Shi, Y.; Chen, Y.; Liang, Y. L.; Andrews, J.; **Dong, H.**; Yuan, M. Y.; Ding, W. Y.; Banerjee, S.; Ardebili, H.; Robertson, M.; Cui, X. L.; Yao, Y. “Chemically Inert Covalently Networked All-Solid Polymer Electrolytes for Lithium Metal Batteries.” *J. Mater. Chem. A*. In revision.
14. Chen, Y.; Shi, Y.; Liang, Y. L.; **Dong, H.**; Hao, F.; Wang, A.; Zhu, Y. X.; Cui, X.

- L.; Yao, Y. “Hyperbranched PEO-Based Hyperstar Solid Polymer Electrolytes with Simultaneous Improvement of Ion Transport and Mechanical Strength.” *ACS Appl. Energy Mater.* **2019**, 2 (3), 1608.
- 15.** Fu, M. S.; Yao, Z. P.; Ma, X.; **Dong, H.**; Sun, K.; Hwang, S. Y.; Hu, E. Y.; Gan, H.; Yao, Y.; Stach, E. A.; Wolverton, C.; Su, D. “Expanded Lithiation of Titanium Disulfide: Reaction Kinetics of Multi-step Conversion Reaction.” *Nano Energy*. **2019**, 63, 103882.
- 16.** Wang, X. Z.; Yao, Z. P.; Hwang, S. Y.; Pan, Y.; **Dong, H.**; Fu, M. S.; Na, L.; Sun, K.; Gan, H.; Yao, Y.; Xu, Q. Y.; Su, D. “In situ Investigation of Sodiation of Titanium Disulfide Nanoflakes.” *ACS Nano*. Under review.

Chapter 1 Introduction

1.1 Lithium-Ion Batteries

As one of the most prominent technologies in human history, Li-ion batteries (LIBs) have significantly reshaped our lives since their initial commercialization by Sony in 1991. Especially, this technology shows great promise as power sources that can lead us to the electric vehicle revolution.

Graphite- LiCoO_2 becomes the representative Li-ion battery system that powers most of the portable electronic devices, such as cell phone, laptops, etc. Figure 1.1 illustrates the working mechanism of a typical Li-ion battery based on graphite anode and LiCoO_2 cathode.¹ The main reactions are reversible Li-ion intercalation and de-intercalation between two layered compounds. During charge process, Li-ions are extracted from the cathode, and are inserted into the anode. Meanwhile, the electrons flow through the external circuit from the cathode to anode side. During discharge process, the whole process is reversed.

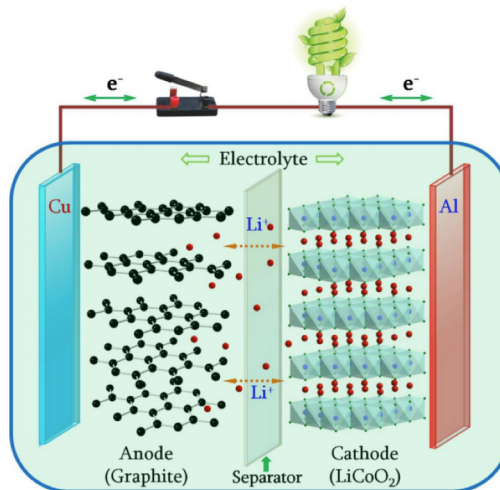


Figure 1.1 A schematic presentation of the most commonly used Li-ion batteries based on graphite anodes and LiCoO_2 cathodes. Reprinted with permission from Ref. 1. © 2016 Elsevier.

The cathode reaction is



The anode reaction is



To ensure the anodic stability of both the cathodes and electrolytes, the upper cut-off of the delithiation of LiCoO_2 is limited to 4.2 V vs. Li^+/Li , corresponding to half of its theoretical capacity of 140 mAh g^{-1} .² Graphite intercalates reversibly with Li-ion to form LiC_6 as the final product according (1-2), corresponding to a theoretical capacity of 372 mAh g^{-1} . Another key issue related to the operation of LIBs is the choice of electrolyte solutions. About 20 years ago, alkyl carbonates were found to be the best and most suitable solvents for LIBs. Figure 1.2 shows several structural formulae of relevant alkyl carbonates.³ A major discovery was the selection of binary solvent mixtures such as ethylene carbonate (EC) and either dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) or diethyl carbonate (DEC), and the Li salt, lithium hexa-fluorophosphate (LiPF_6), as the basic standard electrolyte solutions for LIBs.

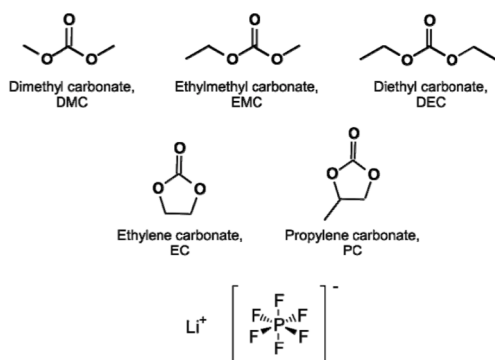


Figure 1.2 The family of alkyl carbonate solvents and Li salt for Li-ion batteries. Reprinted with permission from Ref. 3. © 2017 MDPI.

Lithium-ion batteries now surpass all previously competitive battery chemistries (for example, lead-acid and nickel metal hydride) but still require extensive further improvement in energy density to, in particular, extend the operation hours of portable electronic devices and the driving mileages of electric vehicles.⁴

1.2 Magnesium-Ion Batteries

Currently, lithium-ion batteries (LIBs) as a primary energy system have been widely used in our daily life and modern industry, however, it can no longer satisfy the application needs because of their low energy densities. For example, in pursuit of superior electric vehicles, the development of battery systems with enhanced energy and power densities, and improved device safety has gained substantial interest.

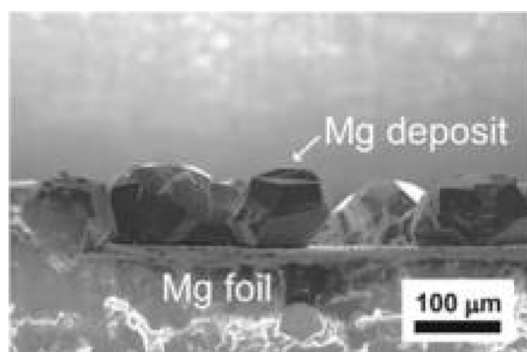


Figure 1.3 Cross-sectional SEM images of Mg-metal anode. Reprinted with permission from Ref. 8. © 2015 American Chemical Society.

Development of beyond lithium-ion batteries with higher energy density is considered to be a promising pathway to achieve above goals.⁵ Generally, PLIBs require the substitution of low-capacity lithiated graphite anode (372 mAh g^{-1}) with pure metal anode. Lithium metal is considered to be a good candidate as an anode to match a high capacity cathode in batteries such as Lithium-air and Li-sulfur due to its high specific capacity of 3862 mAh g^{-1} and very negative reduction potential of -3.04 V vs SHE .⁵⁻⁷

Unfortunately, at this time, metallic Li cannot be used as anode due to dendrite formation during the cycling.⁸ Dendritic growth is associated with the short circuiting, leading to thermal runaway due to exothermic chemical reactions involving battery components.

One alternative approach is to use Mg metal instead of lithium, since it is well known that Mg-metal anode is resistant to dendrite formation due to the unique plating behavior that Mg favors planar hexagonal growth (Figure 1.3).⁹⁻¹¹ Figure 1.4 shows the working mechanism of Mg batteries, which are similar with that of Li-ion batteries.¹² Mg^{2+} goes from the anode to the cathode during discharge and vice versa. The only difference from Li-ion batteries is that a plating/stripping reaction occurs at Mg metal anode side instead of an intercalation/de-intercalation process in a layered compound anode.

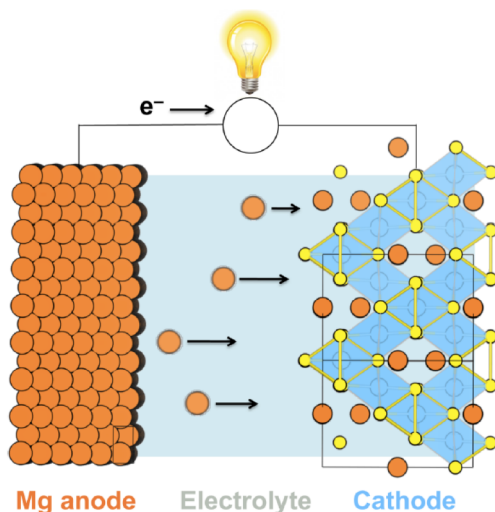


Figure 1.4 Representative schematic of a discharging Mg battery utilizing an Mg anode, electrolyte, and an intercalation cathode. Reprinted with permission from Ref. 12. © 2017 American Chemical Society.

Theoretically, Mg battery has an absolute advantage over current Li-ion battery in terms of cost, safety, and energy, however, its development has been severely hindered due to the lack of appropriate cathodes and practical electrolytes.¹¹⁻¹⁵ As shown in Figure

1.5, two major factors limit the development of Mg cathodes. First, as MgCl^+ -complex is the major electroactive species in typical chloride-containing electrolytes, the Mg-Cl bond needs to be broken to free up the intercalating Mg^{2+} species, which process requires a high activation energy of at least 3 eV.¹⁶⁻¹⁸ Second, most Mg-ion cathodes studied so far suffer from sluggish Mg^{2+} diffusion due to the extremely high-energy barrier for migration in host materials.¹⁹⁻²⁴ Although great progress has been made in cathodes (TiS_2 , S, polymers)^{20, 25-30} and electrolytes (non-nucleophilic and chloride-free electrolytes)³¹⁻³⁶, Mg battery based on Mo_6S_8 cathode still represents the benchmark Mg battery in terms of energy and cycling stability since it was demonstrated by Aurbach et al. 20 years ago.⁹ To realize high-energy and high-power Mg batteries, above two challenges have to be addressed.

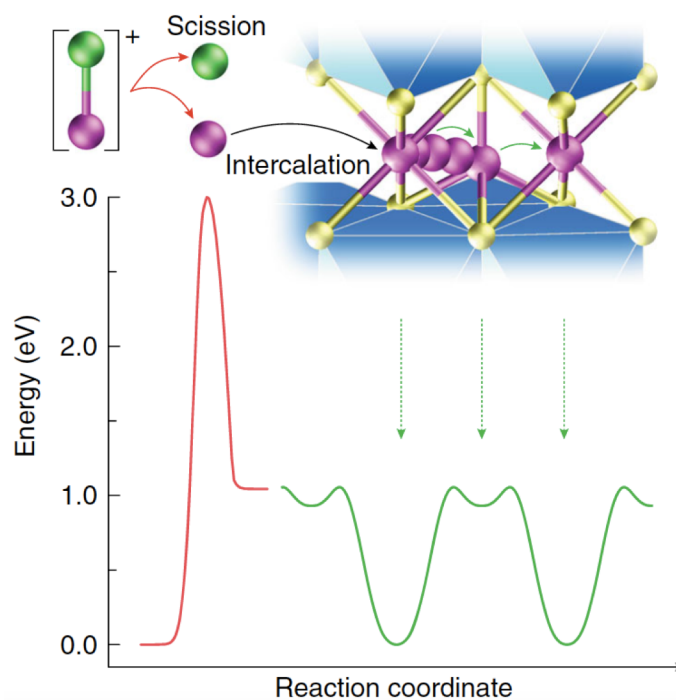


Figure 1.5 Energy diagrams for the intercalation and diffusion of Mg^{2+} , involving scission of MgCl^+ ions into Mg^{2+} and Cl^- . Reprinted with permission from Ref. 16. © 2017 Springer Nature.

1.3 Research Objective

The dissertation can be divided into two sections. First, I clarified the definition, key strengths, as well as common misconceptions of Mg batteries. Second, I identified and demonstrated two new research directions that can effectively overcome major barriers for development of Mg cathodes and eventually lead to high energy and high power Mg batteries.

1.4 Dissertation Organization

In Chapter Two, I reviewed the literature related to Mg batteries and other multivalent metal-ion batteries. I clarified the definition, key strengths, as well as common misconceptions of multivalent metal-based batteries. I then discussed methods for scrutinizing the morphology of metal anodes, electrolyte solutions efficiency, and possible chemistries of positive electrodes, with which unambiguous results may be obtained. Finally, I critically reviewed existing cathode materials and proposed strategies to enable genuine multivalent metal-ion storage materials with competitive performance.

In Chapter Three, I reported a high performance Mg-Na hybrid battery utilizing an Mg-Na dual-salt electrolyte, an Mg anode, and a Berlin green cathode. The cell delivered an average discharge voltage of 2.2 V and a reversible capacity of 143 mAh g⁻¹. I also demonstrated the cell with a specific energy of 135 Wh kg⁻¹ and a high specific power of up to 1.67 kW kg⁻¹.

In Chapter Four, I revealed that previous organic cathodes all operate on an MgCl₂-storage chemistry sustained by a large amount of electrolyte that significantly reduces cell energy. I then demonstrated Mg batteries featuring an Mg²⁺-storage chemistry using quinone polymer cathodes, chloride-free electrolytes, and Mg metal anode. Under lean

electrolyte conditions, the Mg^{2+} -storing organic cathodes deliver the same energy while using ~10% of the amount of electrolyte needed for the MgCl -based counterparts. The observed specific energy (up to 243 Wh kg^{-1}), power (up to 3.4 kW kg^{-1}), and cycling stability (up to 87% @ 2500 cycles) of Mg -storage cells consolidate organic polymers as promising cathodes for high-energy Mg batteries.

In Chapter Five, I reported a quinone molecule, pyrene-4,5,9,10-tetraone (PTO), which can circumvent sluggish solid-state Mg^{2+} diffusion through a liquid-solid two-phase reaction pathway, and its intrinsic ion-coordination charge-storage mechanism does not involve bond-breaking and bond-formation, giving it potential to achieve high power. Meanwhile, I reported a highly functioning Mg electrolyte, $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ (MMC) in DME/G2, which has unprecedented and extraordinary ability to cycle Mg at ultrahigh current densities in the order of 50 mA cm^{-2} with dendrite-free morphology. By coupling PTO cathode with MMC in DME/G2, I created an Mg battery with a specific energy of 566 Wh kg^{-1} and an ultra-high power of 30 kW kg^{-1} .

In Chapter Six, I described the principle and practice of useful methods and tools for research. At the end, in Chapter Seven, I summarized all my work and discussed future research directions for Mg batteries.

Chapter 2 Literature Review of State-of-the-Art Mg Batteries and Other Multivalent Metal-Ion Batteries

Even with lithium-ion batteries being under widespread evaluation as one of the energy storage solutions for grid applications and as major power sources for transportation, alternative battery technologies that use more abundant elements and may offer higher energy density and better safety features remain highly desirable. The top candidates for this purpose are multivalent metal-ion batteries: batteries where the charge carrier multivalent metal cations shuttle back and forth between the cathode and anode during the discharging and charging parts of a cycle without causing a net change in the electrolyte solution composition. Due to their close resemblance, much of the fundamental understandings and manufacturing experiences accumulated for lithium-ion batteries may be exploited for swift industry adaptation of multivalent metal-ion batteries technologies. Any advantage of a multivalent metal-ion battery would depend on whether the replacement of monovalent lithium with divalent magnesium, calcium, zinc, or trivalent aluminium brings about improvements in materials availability, system cost, energy density, and safety features.

While the reserve availability and potential price spike of lithium are under constant debate, magnesium, calcium, and aluminium are among the top ten most abundant elements in the Earth's crust. Zinc has a reserve that is similar to that of lithium (3.5 vs 2.3×10^{12} mol) but was produced 30 times more in 2017. Provided that other elements used in a multivalent metal-ion battery are no rarer than those used in lithium-ion batteries, the advantage of multivalent metals in availability, and in materials' cost, is obvious.

The energy density of multivalent metal-ion batteries needs some clarification. Even though multivalent metals transfer two or three electrons per atom as opposed to just one for lithium, they do not quite compete with lithium in terms of gravimetric capacity due to their higher atomic weights (Figure 2.1a). Still, a common assessment is that they would excel in volumetric capacity thanks to their higher densities than that of lithium. Concerning the anode side, multivalent metal-based batteries may have a great advantage over lithium-ion batteries because in the latter case the use of active metal (lithium) is too dangerous and problematic in terms of reversibility, what forces the use of lithium-carbon anodes, giving up more than 90% of anode specific capacity (372 mAh g^{-1} for lithiated graphite LiC_6 compared to $> 3700 \text{ mAh g}^{-1}$ for metallic lithium). Hence, for a cell that uses a multivalent metal anode (the typical configuration for multivalent metal-ion batteries), the volume of the anode is much smaller than the LiC_6 anodes used in lithium-ion batteries. Anyway, the energy density of rechargeable batteries as well as their volume, weight, and voltage are governed by both the anode and cathode sides. At this stage it is hard to provide a fully realistic comparison between multivalent metal-ion batteries and lithium-ion batteries that should be considered as benchmark systems, because optimal cathodes for multivalent metal-ion batteries are not available yet and require further extensive research and development work. We can however provide a virtual comparison, using important representative cathode materials available for practical lithium-ion batteries, assuming that they would react reversibly with multivalent metal ions in a similar manner as they react reversibly with lithium ions. Here we compare the theoretical energy content of metal-ion batteries considering two cathodes (Figure 2.1b): (1) the high-voltage, moderate-capacity Mn_2O_4 spinel which is an

established intercalation cathode material for lithium-ion batteries and has been also studied for intercalation of multivalent metal ions experimentally and/or theoretically,³⁷ and (2) the low-voltage, ultrahigh-capacity sulfur (conversion reaction) cathode material which has been experimentally paired with several multivalent metal anodes.³⁸

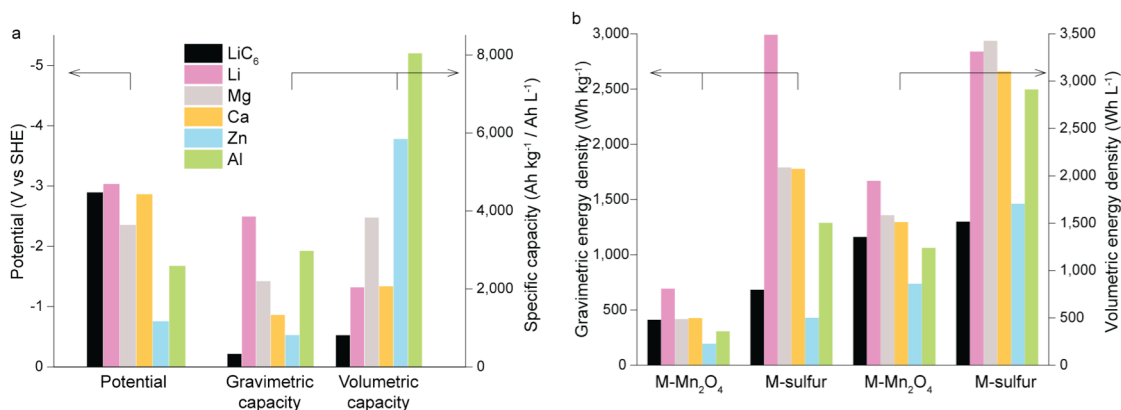


Figure 2.1 Electrochemical characteristics comparison. (Data available in Table 2.1).

Graphite, the standard anode material for lithium-ion batteries, is included herein as a benchmark. With a Mn₂O₄ cathode (if would interact reversibly with the metals ions), battery systems with multivalent metal anodes may deliver to the best similar gravimetric and up to 10% higher volumetric energy densities compared to that of LiC₆-Mn₂O₄ battery systems. Lithium metal-Mn₂O₄ is the clear winner by both energy density metrics. With a sulfur cathode, most multivalent metals easily beat LiC₆ as anodes and, in terms of volumetric energy density, M-S (M = metal or LiC₆) batteries with multivalent metal anodes may approach that of lithium-sulfur systems. Batteries with aluminium and zinc metal anodes, which exhibit the highest volumetric specific capacities, should be inferior in terms of energy density compared to lithium-ion battery systems, due to their lower operating voltage (their red-ox potentials are 1.2 and 2.2 V higher compared to that of lithium metal, respectively).

The analysis above shows that multivalent metal-ion batteries may provide competitive, but not outright higher, energy densities compared with those of lithium-based batteries. Two questions have to be addressed:

Are there other motivations to move from lithium to multivalent metals in designing and producing advanced rechargeable batteries?

What is the feasibility to develop practical rechargeable battery systems based on multivalent metal anodes? Do we have suitable electrolyte systems and cathodes for them?

Table 2.1 Electrochemical parameters for Figure 2.1. ^aFormula weight. ^bVolume considered as the sum of cathode and anode materials at the charged state.

Anode (M)	Fw ^a	Density	Potential (V vs SHE)	Gravi-/volumetric capacity		Gravimetric energy (Wh kg ⁻¹)		Volumetric energy (Wh L ⁻¹) ^b	
				Ah kg ⁻¹	Ah L ⁻¹	M–Mn ₂ O ₄	M–S	M–Mn ₂ O ₄	M–S
LiC ₆	79.0	2.25	~–2.9	339	764	413	684	1355	1517
Li	6.94	0.53	–3.04	3861	2062	693	2991	1948	3313
Mg	24.3	1.74	–2.36	2205	3833	418	1791	1585	3426
Ca	40.1	1.55	–2.87	1337	2073	428	1779	1511	3103
Zn	65.4	7.14	–0.76	820	5853	195	431	862	1705
Al	27.0	2.70	–1.68	2980	8046	308	1289	1240	2913

For the calculation of energy densities, the following parameters are assumed. The specific capacities of Mn₂O₄ and sulfur are 154 (1-electron per formula) and 1672 mAh g⁻¹ (2-electron per S), respectively. Theoretically predicted voltage values are used for multivalent M–Mn₂O₄: 2.9 (Mg), 3.1 (Ca), 1.5 (Zn), 2.1 (Al). Typical experimental voltage values are used for Li systems: 4.0 (Li), 3.9 (LiC₆). The voltage values of M–sulfur is derived as the difference in standard reduction potentials between M and sulfur (–0.476 V vs SHE). The only exception is Zn–sulfur, for which an alkaline cell is considered and the potential of the Zn anode is –1.26 V vs SHE. The densities of Mn₂O₄

and sulfur are 4.14 and 2.07 g cm⁻³, respectively. The gravimetric energy density E_{grav} is calculated as

$$E_{\text{grav}} = (C_{\text{c}}^{-1} + C_{\text{a}}^{-1})^{-1} \times (E_{\text{c}} - E_{\text{a}}), \quad (2-1)$$

where C_{c} and C_{a} are the specific capacity of the cathode and anode materials, respectively, and E_{c} and E_{a} are the standard reduction potential of the cathode and anode, respectively. The volumetric energy density E_{vol} is calculated as

$$E_{\text{vol}} = [(C_{\text{c}} \times \rho_{\text{c}})^{-1} + (C_{\text{a}} \times \rho_{\text{a}})^{-1}]^{-1} \times (E_{\text{c}} - E_{\text{a}}), \quad (2-2)$$

where ρ_{c} and ρ_{a} are the density of the cathode and anode materials, respectively.

2.1 Multivalent Metal Anodes: Where Both Promises and Uncertainties Lie

One of the most quoted advantages of multivalent metal-ion batteries is the possibility to use the highly capacity-dense metals as the anode material. The reputation was mainly earned by magnesium which has been widely reported to show dendrite-free plating, compared to the almost always dendritic/mossy morphologies of lithium that have caused safety concerns and short cycle life. For more than a decade following the first report on a highly reversible prototype, magnesium-ion battery had been the only multivalent metal-ion batteries that attracted research interests.⁹ The recent urge for alternatives to lithium-ion chemistries has sparked rapid growth of activities on calcium, zinc, and aluminium, but the suitability of these metals as anodes for rechargeable batteries has not been equally scrutinized as magnesium. Plating morphology is a particularly important metric that deserves a critical review.

In most of the electrolyte solutions in which magnesium anodes behave reversibly, magnesium deposition was found to form densely packed crystals (Figure 2.2a).³⁹⁻⁴⁰ Compact crystalline plating morphology is very favorable for rechargeable battery

applications as it is least likely to puncture separators or cause particles detachment upon cycling. Also, such a morphology leads to a relatively low anodes' specific surface area, what means minimum side reactions if any. This behavior holds true for both main categories of magnesium electrolyte solutions: chloride-free ones where magnesium ions are solvated by the ethereal molecules of the solvent and only partially associated to anion, and chloride-containing ones where the solvation shell of the magnesium ions includes both the ethereal solvent molecules and Cl^- ions. The active cation species in the latter case are MgCl^+ or Mg_2Cl_3^+ complex ions which undergo a two-step chemical–electrochemical deposition mechanism.⁴¹ Magnesium dendrites are only reported in electrolyte solutions that show poor or unknown reversibility, and the dendritic deposits are characterized by complicated surface composition instead of being pure magnesium.⁴²⁻⁴³ It thus seems that the dendrite-free plating behavior is intrinsic to the formation of magnesium deposits (probably via nucleation, clusters formation, and their growth to magnesium crystallites) rather than to the exact composition and structure of the electrolyte solution (provided that the magnesium metal substrate and the magnesium deposits are fully bare and free of surface films). The possible mechanisms of magnesium deposition were explored over the years. These mechanisms are affected by the dependence of the magnesium deposition over-potential on the electrolyte solution concentration,³⁹ the large energy differences between crystals with different phase/shape, what give an advantage to certain morphologies of compact crystalline form,⁴⁴⁻⁴⁵ and fast ad-atoms self-diffusion on the deposited nuclei/crystals surfaces, which promote a fast rearrangement of the deposits in crystalline forms.⁴⁶

Calcium has been found to be reversibly plated/stripped in only two electrolyte solutions,⁴⁷⁻⁴⁸ in both calcium can be deposited in dense and thick morphologies. If such favorable morphology stays the same in more stable electrolyte solutions that have to be developed in the future, calcium metal will be another attractive anode material for rechargeable batteries.

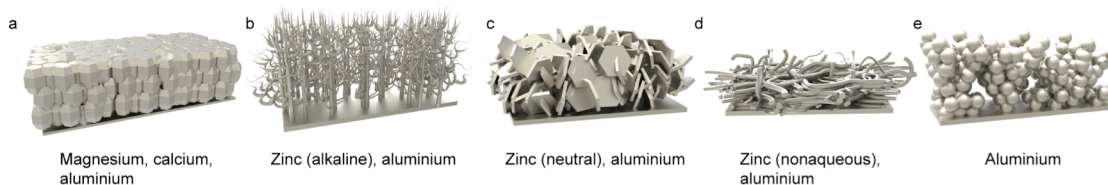


Figure 2.2 Typical plating morphologies of multivalent metal-ion metals. (a) Compact crystals. (b) Tree-like dendrite. (c) Connected platelets. (d) Random fibers. (e) Connected spheres.

Zinc notoriously plates into tree-like dendrites (Figure 2.2b) in alkaline aqueous electrolyte solutions, which are partially responsible for the short cycle life of alkaline rechargeable zinc batteries. Neutral electrolyte solutions give rise to interconnected platelets (Figure 2.2c),⁴⁹⁻⁵⁰ a less detrimental morphology, but coulombic efficiency remains a major concern.⁵¹ In nonaqueous electrolyte solutions, random fiber-like structures (Figure 2.2d) are formed.⁵² Similar structures are also observed for lithium and referred to as “mossy lithium” or simply dendrites.⁵³ Lithium anodes with these deposits suffer from aggressive side reactions (due to the high surface area) and electrolyte solution decomposition and consumption, leading to a very low coulombic efficiency and severe safety problems. Interestingly, zinc shows high coulombic efficiencies of >99% despite such structures, probably due to its much higher red-ox potential and hence low tendency to react with the electrolyte solutions.

Aluminium metal anodes can be cycled in Al_2Cl_7 -based ionic liquids with high coulombic efficiency, but its morphology seems to be highly dependent on the electrolyte solution composition and plating condition. Morphologies of tree-like dendrites, interconnected platelets/spheres (Figure 2.2e), random fibers, and even dense crystals have all been reported with largely similar electrolyte solutions.⁵⁴ The coulombic efficiency reported was generally high (>98%) regardless of morphology, probably due to the absence of side reactions of aluminium metal in any relevant ionic liquid-based electrolyte solutions in which aluminium plating/stripping is reversible.

The large variety of plating morphologies of multivalent metals calls for cautions when considering them as anode materials. The Young's moduli of these metals range from 20 (Ca) to 108 GPa (Zn), all significantly higher than lithium's 4.9 GPa. If the electrolyte solutions allow dendrites to form, most approaches proven effective for physical suppression of lithium dendrites may not work well for multivalent metallic deposits. Detailed characterization of the plating morphology under relevant test conditions is therefore indispensable for verifying the viability of suitable metal–electrolyte solution systems. High resolution, very reliable surface morphology imaging is possible today thanks to new microscopic techniques that enable operando measurements,⁵⁵⁻⁵⁷ but cross-sectional observation is equally important because the real deposits could be hidden underneath surface films, as was observed for aluminium dendrites covered by a smooth oxide top layer.⁵⁸ The possible operation of multivalent metal anodes for rechargeable batteries depends mostly on the availability of unique electrolyte solutions that enable their reversible behavior.

2.2 Non-Passivating Electrolyte Solutions: The Necessary Evil

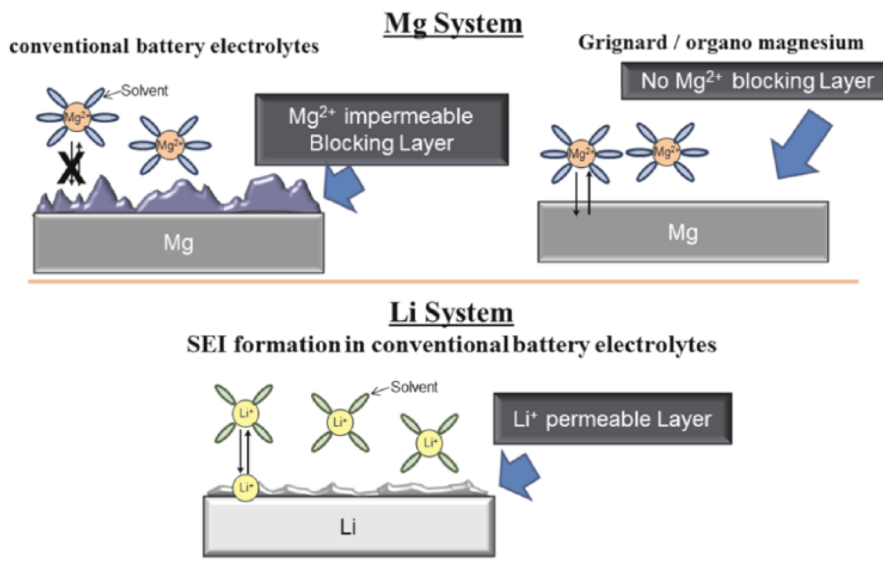


Figure 2.3 Schematic depicting a simplified image of metal-electrolyte interfaces for Mg and Li metals. Reprinted with permission from Ref. 63. © 2014 Mohtadi and Mizuno; licensee Beilstein-Institut.

Magnesium, calcium, and aluminium are all active metals which, very similarly to lithium, react easily with atmospheric components like oxygen, trace water, CO₂, and also with many polar solvents (*e.g.*, esters, alkyl carbonates, nitriles) and salt anions (*e.g.*, PF₆⁻, ClO₄⁻, BF₄⁻) to form surface species that passivate the active metal and form ionically blocking surface films.⁵⁹⁻⁶¹ In the case of lithium metal, Li-C, and Li-Si anodes, the surface films thus formed comprise ionic lithium compounds which behave like solid electrolyte interphase (the famous SEI model),⁶² which avoid continuous side reactions but allow an easy migration of lithium ions through them. Hence, all lithium-based anodes can reach full and effective passivation, while allowing fully reversible lithium plating or lithium-ion intercalation to occur beneath the surface films (Figure 2.3).⁶²⁻⁶³ In contrast, surface films formed on multivalent metal anodes, which always comprise ionic multivalent metal compounds, fully block any possible transport of multivalent metal

ions through them (Figure 2.3). Thereby, it is essential for multivalent metal-ion batteries to use only electrolyte solutions in which the metal anodes are bare and passivation-free with no tolerance to any side reactions that may form surface films.

A variety of complex electrolyte solutions in which multivalent metal anodes behave fully reversibly have been developed and explored during the last two decades. They are composed of solvents and electrolytes that have relatively low electrophilic tendency, like ethers. Some of them further contain chloride ions which help to dissolve passivating species by forming complex ions with multivalent metal ions. All reversible magnesium electrolyte solutions are based on ethers like tetrahydrofuran and glymes (polyethers) since they are the only polar aprotic solvents in which magnesium metal is fully stable (no surface reactions, no passive films formation).^{36, 64-69} Viable counter ions include weakly coordinating anions such as carborane anions and bulky borates and aluminates.^{26, 33} Simple anions, notably bis(trifluoromethane)sulfonimide (TFSI⁻), may also be used provided that the electrolyte solutions contain also chloride ions.⁷⁰⁻⁷¹ All of them have complex structures that are now reasonably well understood and the coulombic efficiency for magnesium plating/stripping in them could approach 100%.^{33, 36, 64-65} Calcium is also deposited/stripped in ethereal solutions with high efficiency, although the anion is so far limited to borohydride which is oxidized at moderate potentials.⁴⁸ Aluminium is highly reversible in Al₂Cl₇⁻-containing ionic liquids with apparently little dependence on electrolyte solution composition. Zinc has the highest tolerance to electrolyte solution components, with common polar organic solvents like acetonitrile and carbonate and common anions like TFSI⁻, triflate, and PF₆⁻ all being

viable,⁵² probably a result of its high redox potential and low tendency of passivation film formation.

While ethereal solvents and chloride ions are so suitable for most multivalent metal anodes, they have also brought about insurmountable limitations that could preclude most attractive high-voltage/-capacity cathodes for high-energy batteries. Both ethereal solvents and chloride ions bind strongly to multivalent metal ions, causing a large energy penalty desolvation/dissociation during intercalation reactions.⁷²⁻⁷³ Ethereal solvents have limited cathodic stability, being oxidized as early as 3.4 V vs Mg^{2+}/Mg on planar current collectors.³³ Chloride ions are also susceptible to oxidation, but their main limitation on electrochemical window of electrolyte solutions is through corrosion of most relevant current collectors at moderate to low potentials.⁷⁴ New electrolyte solutions are therefore still under intensive development for practical applications.

It is important to note that for rechargeable batteries, the cycling efficiency of the electrodes have to approach 100% with no compromise. Thereby, the development of new battery systems has to include rigorous studies of the electrodes surface chemistry, fully understanding possible side reactions and their completed mitigation. The electrochemical characteristics of a multivalent metal–electrolyte solutions system can be assessed by established methods, which will be discussed in section 6.2.3.

2.3 Cathode Storage Chemistry: The Devil is in the Details

Opposed to some early expectations that shifting from the monovalent lithium-ion to multivalent metal ions as the intercalants could lead to a higher number of electrons transferred per transition metal in intercalation-type cathode materials, intercalation hosts show largely the same valence change for storage of both monovalent and multivalent

metal ions.⁷⁵ Although the expectable specific capacities of intercalation hosts remain unchanged, multivalent metal ions do have the advantage that a fewer number of ions are required to balance the same valence change of the host, thus apparently giving rise to smaller volume change during cycling and, by extension, longer cycle life. For example, the unit cell volume of Mo_6S_8 increases by 11.2, 8.5, and 2.5% after intercalation of lithium, magnesium, and aluminium, respectively.⁷⁶ Likewise, lithiation and magnesiation of sulfur incurs 80 and 33–71% (depending on the formed MgS phase) of volume expansion, respectively.⁷⁷

Although the concept of replacing lithium with multivalent metal ions in cathode hosts appears straightforward, the development of multivalent metal-ion cathodes has been difficult. The dilemma originates from the high charge density of multivalent cations'. Their strong interactions with the electrolyte solution species (*e.g.*, tight solvation of Mg^{2+} ions by ether molecules) and the cathode materials make dissociation (de-solvation) and solid-state diffusion, the two essential events in an intercalation reaction, kinetically unfavorable. As a result, low current densities and elevated temperatures are employed in many studies (*e.g.*, in order to facilitate intercalation of Mg^{2+} ions into hosts like TiS_2),²⁰ under which conditions parasitic side reactions can contribute significantly to the observed capacities. The situation is further complicated by the complex composition and in some cases instability of any relevant metallic current collectors in multivalent metal-ion electrolyte solutions. Results from different studies were often inconsistent, as noted in a recent review article.¹² Characterizations were often not sufficiently rigorous for unambiguous conclusions. In this section, we highlight the latest understandings of alternative reaction pathways and side reactions in multivalent

metal-ion cathodes, based on which we have identified practices that could facilitate truthful cathode study.

The reaction at a multivalent metal-ion cathode is often more complicated than straightforward storage of the cations themselves. Transition metal oxides constitute a considerable body of literature on multivalent metal-ion cathodes, but recent studies revealed that proton intercalation was the dominant/sole reaction in many of these materials.^{49, 78-80} The presence of H₂O in the electrolyte solutions and in some cathodes' crystals structure is naturally responsible for such reactions, but even in systems involving anhydrous cathodes and thoroughly dried solvents, proton can still be generated via electrolyte solution decomposition.⁷⁹

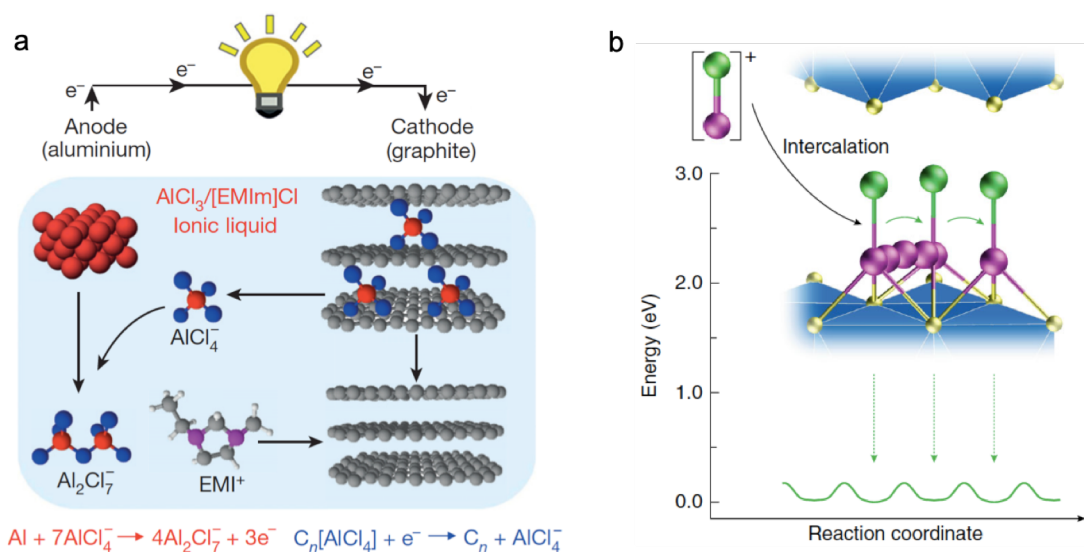


Figure 2.4 (a) Schematic of the Al/graphite cell. Reprinted with permission from Ref. 81. © 2015 Springer Nature. (b) Intercalation of MgCl⁺ cation. Reprinted with permission from Ref. 16. © 2017 Springer Nature.

For cells with chloride-containing electrolyte solutions, intercalation of Mⁿ⁺ would require cleavage of strong Mⁿ⁺–Cl⁻ solution interactions. This step is bypassed by some layered compounds such as transition metal sulfides and graphite and organic carbonyl

compounds such as small molecules and polymers through direct storage of the complex ions (MgCl^+ , AlCl_2^+ , AlCl_4^- , *etc.*) that intercalate smoothly instead of the bare M^{n+} ions (Figure 2.4).^{16, 30, 81-82} Besides M–Cl bond cleavage, desolvation in strongly coordinating solvents is also energy-intensive.⁷² Solvated ions sometimes can be inserted without stripping off the solvent molecules given that the cathode host can adapt to these large intercalants.²²

Due to the large variety of storage (ions insertion) chemistries, the proper evaluation of suitable cathodes for multivalent metal ion battery systems cannot be possible unless the reaction mechanisms have been unambiguously identified. Quantification of the elemental composition of possible discharged products is of utmost importance. Inductively coupled plasma spectroscopies provide such insight into the bulk material. Caution should be used where multivalent metal ions do not insert into the host but still form byproducts at the cathode and obscure bulk analysis.^{49, 80} Therefore, composition analysis often needs to be complimented by distributional observations at an adequate spatial resolution, such as elemental mapping by energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy in conjunction with scanning electron microscopy and transmission electron microscopy (TEM). Such mapping should also be quantitative, and the content of all relevant elements should be reported so as to be conclusive. Storage of complex ions and solvated ions is usually accompanied by considerable change in the cathode lattice spacing, which can be monitored by X-ray diffraction and high-resolution TEM. In addition to direct identification of discharged products, running control cells with no multivalent metal ions in the electrolyte solutions was proposed to rule out proton

reactions.⁸³⁻⁸⁵ However, accurately measuring and reproducing the pH in such reference experiments with the relevant non-aqueous solutions could be a great challenge.

The possibility to operate rechargeable batteries in which the metal anode releases upon discharge multivalent metal ions (M^{n+} cations) while the cathode host inserts complex species such as tightly solvated M^{n+} cations or $M^{n+}_xCl^-_y$ species complicates the situation in these systems compared to the lithium-ion batteries. In the latter systems, bare lithium ions are moving between the electrodes, while the solution concentration remains invariant (in the absence of side reactions). This situation enables to use a very small amount of electrolyte solution in the batteries that serves only as a lithium ions transfer medium. In contrast, rechargeable batteries based on multi-valent metal anodes may suffer from material imbalance during charging–discharging which alters the electrolyte solution concentration, pH value, ion species, *etc.* in solution, due to the difference between the ions produced upon discharge in the anode and the complex ions which are inserted into the cathode, as explained above. In a practical cell where the amount of electrolyte solution is limited, these changes could impact electrodes' reaction mechanisms, cell stability, and energy density.^{30, 86} Depending on the extent of electrolyte solution composition change, some of these batteries may no longer qualify as multivalent metal-ion batteries concerned herein, even though they may still be referred as multivalent metal batteries as long as a multivalent metal anode is involved. The characterization methodologies described above are important for identifying cathode materials capable of genuine reversible multivalent metal-ion storage, based on which the energy density estimates provided herein were made.

2.4 Cathode Material Development: Thinking Outside the Box

Among so many materials that can interact reversibly as cathode hosts with lithium ions, only a few cathode materials have shown potent performance in reversible multivalent metal-ions storage. For magnesium-ion batteries, Chevrel phase Mo_6S_8 (theoretical values: 1.15 V vs Mg^{2+}/Mg , 129 mAh g^{-1}) remains the cathode material to beat since 2000 when it marked the beginning of modern multivalent metal-ion battery studies (Figure 2.5).⁹

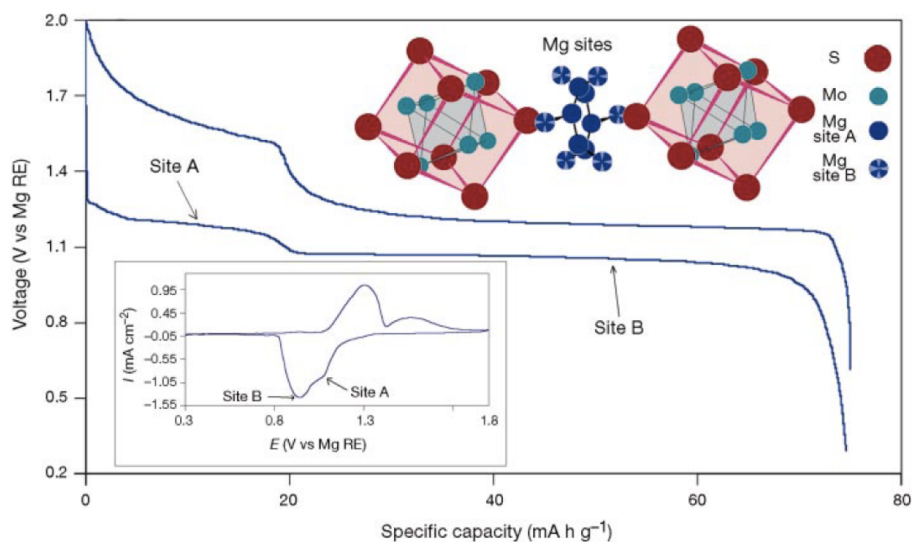


Figure 2.5 Typical electrochemical performances of Mo_6S_8 at room temperature. Reprinted with permission from Ref. 9. © 2000 Springer Nature.

Only a handful of materials, such as spinel Ti_2S_4 (1.2 V vs Mg^{2+}/Mg , 192 mAh g^{-1}) (Figure 2.6a), sulfur (1.1 V vs Mg^{2+}/Mg , 1247 mAh g^{-1}) (Figure 2.6b), and poly(1,4-anthraquinone) (1.37 V vs Mg^{2+}/Mg , 193 mAh g^{-1}), have shown higher energy densities than that of Mo_6S_8 , but they still fall short of stability.^{25-26, 30} Zinc-ion reversible intercalates into high-potential spinels $\text{ZnAl}_x\text{Co}_{2-x}\text{O}_4$ (1.8 V vs Zn^{2+}/Zn , 120 mAh g^{-1}) and $\text{ZnNi}_x\text{Mn}_x\text{Co}_{2-2x}\text{O}_4$ (~ 1.65 V vs Zn^{2+}/Zn , 180 mAh g^{-1}), representing a rare example of multivalent metal-ion storage in oxide hosts with evidenced naked cation storage,

relevant energy density, and decent cycling stability.⁸⁷⁻⁸⁸ Calcium- and aluminium-ion cathodes are most problematic, characterized by ill-shaped voltage profile, large polarization, and low energy. It has become evident that traditional cathodes design strategies for lithium ion are not readily transferable to multivalent technologies.

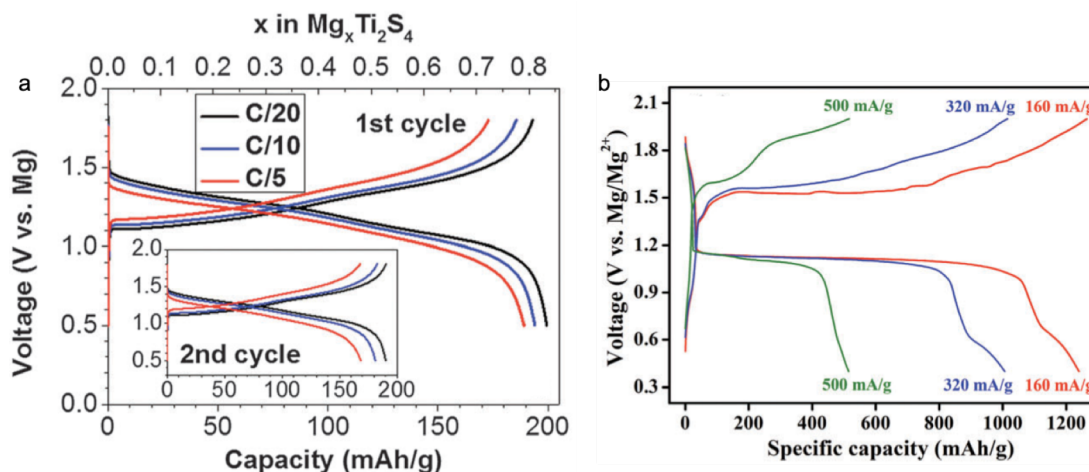


Figure 2.6 (a) Voltage profiles of Mg/Ti₂S₄ cell. Reprinted with permission from Ref. 25. © 2016 Royal Society of Chemistry. (b) Voltage profiles of Mg/sulfur cell. Reprinted with permission from Ref. 26. © 2017 Royal Society of Chemistry.

Valuable lessons have been learned from the success of Chevrel phases Mo₆X₈ (X = S, Se), which uniquely deliver nearly theoretical capacity when storing all multivalent metal ions discussed herein except for Ca²⁺, the size of which might be too close to the upper critical guest size for the host.⁸⁹⁻⁹¹ First, the surface atoms of Mo₆S₈ could catalyze cation dissociation from electrolyte species: the energy cost to break Mg–Cl is calculated to decrease from ~3 eV to 0.2–0.8 eV via concerted S coordination to Mg and Mo attraction to Cl (Figure 2.7a–d).¹⁷ Second, the anions S²⁻ and especially Se²⁻ are highly polarizable/soft and form relatively covalent bonds with the intercalated cations.⁹² Such bonding helps to stabilize the intermediate states during cation diffusion between coordination sites (Figure 2.7e–h) and is believed to be partly responsible for the

superionic conductivity of α -AgI and lithium thiophosphates.⁹³ Third, the Mo_6 cluster quickly delocalizes injected charges, accommodating up to four electrons by modifying the Mo–Mo distance and transitioning between metal and semiconductor states.⁹⁴ These features specifically address the dissociation and solid-state diffusion of multivalent metal ions. Although hardly necessary for lithium-ion storage, they may be put front and center when designing a multivalent metal-ion cathode. The unique behavior of Chevrel phase cathodes with multivalent cations that was studied very thoroughly⁹⁵⁻⁹⁶ may promote an intensive study of cluster compounds as cathode materials for these systems.⁹⁷

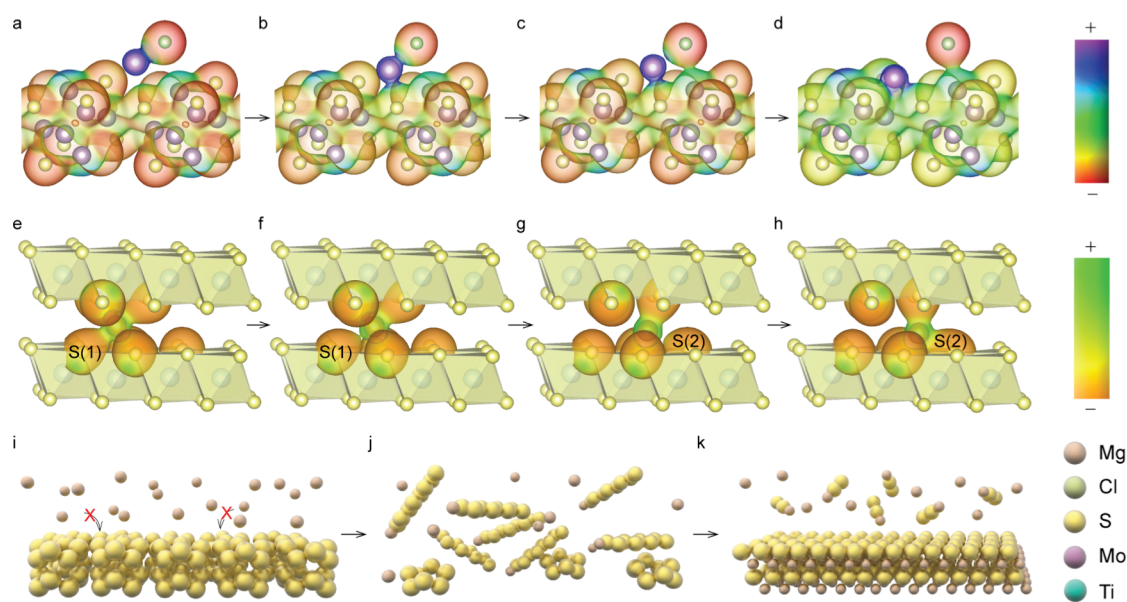


Figure 2.7 Mechanisms to enable multivalent metal-ion cathodes.

The option of facilitated de-solvation/de-complexation of magnesium ions by catalytic dissociation aided by the surface structure of the host material has been so far demonstrated only for Mo_6S_8 , but many other materials may share this function. For example, two-dimensional transition metal disulfides are known to catalyze a wide range of reactions initiated with surface adsorption on exposed metal atoms.⁹⁸ With more

theoretical insights and proper structure engineering, the exact same catalytic dissociation as seen for Mo_6S_8 could be expected for layered chalcogenides. Many more oxides have active surface sites for anion adsorption, though surface O may not be as strong a coordinating agent as S to multivalent metal ions. Metal-free materials such as organic compounds, chalcogens, and halogens have electron-rich anions to coordinate to multivalent metal ions, even though they may lack the metal centers to adsorb anions.

Construction of ion diffusion-friendly frameworks is reflected in a number of successful cathode designs. Spinel and layered Ti_2S_4 , for instance, have polarizable/soft anionic frameworks similar to that of Mo_6S_8 .^{20, 25} Layered chalcogenides, being semiconducting or metallic depending on the doping state, are also highly capable in charge delocalization. The challenge for these chalcogenides-based frameworks is the generally low redox potentials. Organic compounds with conjugated/delocalized building blocks may have similar functionalities.³⁰ Their relatively soft structures can also help to stabilize diffusion transition states following similar mechanisms in polymer electrolytes. A highly important advantage of organic cathode materials may be their softness. So, they can accommodate complex multivalent cations (either strongly solvated or coordinated with anions such as chloride moieties) that can be smoothly inserted into the soft structure upon compensating the negative charge which is accumulating during the discharge process.⁹⁹⁻¹⁰¹ Some oxide hosts allow multivalent metal-ion diffusion despite the less polarizable frameworks, probably due to water molecules within the structures shielding the cations.¹⁰²⁻¹⁰³ Due to the potential extraction by the intercalants from the host, the presence of water molecules as shielding agents in cathode materials may not be tolerable since the adverse effect of even trace amount of water contamination on the

negative electrodes (active metals like magnesium, calcium react with trace water and become fully passivated and blocked for any ions transport). However, there might be other polar-aprotic agents that can serve as charge shielding agents within rigid hosts (like oxides) that facilitate insertion of multivalent cations, without having adverse effect on the active metal anodes. This option is open for a further innovative research.

An alternative way to tackle solid-state ion diffusion is to bypass it altogether. Conversion-type cathode materials, notably sulfur, selenium, and iodine, undergo dissolution–precipitation reactions that do not involve solid-state ion transport (Figure 2.7i–k).^{29, 104–105} Magnesium–sulfur batteries have delivered reversible specific capacities of up to 1200 mAh g_{sulfur}⁻¹ at 1.1–1.4 V vs Mg²⁺/Mg with decent cycling stability (~100 cycles).²⁶ The capacity decay of these batteries has been attributed to the dissolution of polysulfides, but it remains unanswered why they show inferior stability compared to lithium–sulfur despite the relatively low solubility of magnesium polysulfides.¹⁰⁶ The reversibility of multivalent metal anodes in the presence of dissolved cathode species seems to vary from one system to another. The presence of even trace amounts of polysulfide species in the ethereal solutions used for magnesium batteries leads to precipitation of insoluble Mg-S species that fully block magnesium anodes.¹⁰⁷ Such passivation may explain the low voltaic efficiency observed for all multivalent metal–sulfur batteries.¹⁰⁸ Thereby, it seems that development of magnesium–sulfur batteries should include means to avoid infiltration of polysulfide moieties from the cathode to the solution phase. On the other hand, dissolved iodine was reported to reduce the magnesium deposition–stripping overpotential via surface film formation, although coulombic efficiency of the modified anode was not known.¹⁰⁹ Validation of the

practicality of conversion cathodes for multivalent metal-ion batteries would require detailed characterization of the metal anode in these cathode-contaminated electrolyte solutions. The 3 types of electrochemical measurements described schematically in section 6.2.3 allow a quick and effective assessment of electrolyte solutions that can be relevant for secondary battery systems based on various metal anodes. Screening tests can reveal easily which solutions are suitable via the most important parameter, namely, the cycling efficiency. Another critically important parameter that can be easily assessed is the anodic stability of each solution, which determines which cathodes can be paired to the metal anode under study.

2.5 Conclusions and Outlook

Multivalent metal-ion batteries may share the successful “rocking-chair” operating mechanism with lithium-based batteries but use much more abundant and affordable elements as ionic charge carriers. Early evidence suggests plausibility to directly use at least some multivalent metals as safe anodes due to their dendrite-free plating behavior. With metal anodes, calculations show that these batteries will deliver competitive energy densities even when compared to rechargeable lithium batteries with lithium metal anode, technologies that may enable affordable electric vehicles.¹¹⁰ As the metals of interest are quickly expanding from just magnesium to also calcium, zinc, and aluminium, factors that established magnesium-ion batteries as promising systems, notably compact plating and near-unity coulombic efficiency of the anode activity, will have to be validated for the new members using proven testing procedures. Cathodes development remains a major universal challenge for all multivalent metal-ions battery systems. Due to the strong cation–anion/solvent/host interactions and the resulted difficult ion dissociation,

intercalation, and solid-state diffusion, a considerable portion of reported cathodes store in fact complex ions and protons instead of the desired naked cations. Most cells based on these unintended alternative storage chemistries, namely the cases where the intercalating multivalent cations have complex structure (e.g., tight solvation shells) may not qualify as the multivalent metal-ion batteries defined herein. Although they may give nice results in lab cells in which there is no limitation of the electrolyte solutions, in practical batteries these systems may require too high amounts of electrolyte solution, in order to accommodate the changes in the solution composition during discharge/charge processes, what may limit their energy density and stability. Researchers would have to go the extra mile and make nontrivial characterization efforts to fully specify the mechanisms of ions insertion and the nature of the stored ion species in any cathode material of interest. Genuine multivalent metal-ion storage cathode materials, though still rare, do exist, from which useful design principles have been learned. Creative use of these tools combined with mechanisms scrutinization, would be the key for finding out successful cathodes.

Realization of competitive multivalent metal-ion batteries requires first of all the capability of using fully reversible multivalent metal anodes in very thin foils format. Here is the major advantage of these systems over any type of lithium metal or lithium-ion batteries. The possible operation of multivalent metal foils as fully reversible anodes depends on judicious selection/development of electrolyte solutions in which passivation of active multi-valent metals is fully avoided, which also possess wide enough electrochemical window (high anodic stability). Fortunately, this challenge has been fulfilled for multivalent metal anodes to varying extent. The major challenge remained for all of these systems the cathode side – availability of high voltage/high specific

capacity electro-active materials that can interact reversibly with the multivalent metal ions while being fully compatible with the electrolyte solutions in which the metal anodes are fully reversible. Electrolyte solutions plays a central role in this context: its composition subtly influences the morphology and coulombic efficiency of the metal anodes, and their anions and solvent species determine the electrochemical stability window and the ions dissociation energy which in turn limit the choice of cathode materials. Ethereal solvents, chloride, and borohydride anions are all essential ingredients for efficient multivalent metal-ion electrolyte solutions, but they are also associated with sluggish dissociation and limited anodic stability. Therefore, either cathode materials development should be directed to moderate-potential high-capacity types with strong dissociation capability, or electrolyte solutions with compositions vastly different from what we have today should be invented without compromising the metallic anodes performance. Besides fundamental chemical/electrochemical questions there are yet unexplored engineering challenges on the way to develop fully practical multivalent metal ions batteries. These include electrodes/cell design topics such as electrodes with high mass loading and optimal composite structure, cathode–anode mass balance, and optimization of the electrolyte solutions composition and content. Multivalent metal-ion batteries, as a whole, are at an early stage of development and there are a lot of roadblocks to clear, but the increasing interests from the energy community and the encouraging progress already made are forging a clear path towards a future success.

Chapter 3 Magnesium-Sodium Hybrid Batteries with High Operating Voltage

3.1 Introduction

The rapid growth of renewable energy from solar and wind power has created a strong demand for low-cost, safe, high-energy density energy storage systems to enable the integration of renewable energy into grid and peak shifting in energy demand. To meet the cost target of less than \$100 per kWh, earth-abundant materials have been actively explored for beyond-lithium-ion batteries. For example, Prussian blue analogues (PBAs) have attracted significant attention due to their unique open framework structures for Na and K ion storage in aqueous¹¹¹ and non-aqueous batteries.¹¹²⁻¹¹⁴ Recently, Lu et al. developed long cycle life Na-ion batteries using PBAs as the cathode.¹¹⁵ The large interstitial space in the framework allows rapid Na-ion diffusion. However, the full cell rate performance is limited by the choices of anode. It is well known that metallic sodium could not function as a practical anode due to the dendritic growth behavior.⁴⁵ Hard carbon is the most studied Na-ion anode.¹¹⁶ However, the voltage profile of hard carbon is too close to 0 V vs Na/Na⁺, making Na deposition possible during fast charging and could lead to battery shorting.¹¹⁷

Magnesium metal has recently attracted considerable attention as a safe anode due to that fact Mg has a low standard potential (-2.37 V vs. SHE), fast deposition-stripping kinetics, and planar hexagonal crystal growth instead of dendritic growth.⁹ However the challenge is the lack of stable high-voltage cathode material due to the slow solid-state diffusion of highly polarizing Mg²⁺ ions in host.¹⁹ The concept of an Mg-Li hybrid battery combining an Mg anode, a Li-insertion cathode, and a hybrid electrolyte is

attractive since the hybrid cell combines the safety and low cost feature of Mg anode and the fast kinetics and high voltage feature of Li-insertion cathode.¹¹⁸⁻¹²⁰ However, there has been very little study on a low-cost Mg-Na hybrid cell. Only one recent report from Kovalenko group used pyrite (FeS_2) as a cathode, Mg as an anode, and a hybrid electrolyte made of $\text{Mg}(\text{BH}_4)_2$ and NaBH_4 in diglyme.¹²¹ The electrolyte has low anodic stability that limits the selection of high-voltage cathode. The cell showed a sloping voltage profile from 0.4 to 1.6 V vs. Mg with the average discharge potential of 1.1 V. It is therefore important to find a compatible cathode and hybrid electrolyte combination to demonstrate a stable high-voltage Mg–Na-ion battery.

In this work, we report such a hybrid battery combining a Berlin green (BG, $\text{FeFe}(\text{CN})_6$) cathode, an Mg metal anode, and a hybrid Mg–Na-ion electrolyte. Inspired by the remarkable activity of the recently reported dimagnesiumdichloro dimer complex cation electrolyte,³¹ we prepared 0.2 M $[\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2$ in dimethoxythane (DME), and then dissolved 0.4 M NaAlCl_4 in the electrolyte to form a clear and transparent solution. The hybrid electrolyte has high anodic stability (3.2 V vs. Mg^{2+}/Mg). The BG cathode shows reversible capacity of 143 mAh g^{-1} and stable cycling for 50 cycles.

3.2 Experimental Procedures

3.2.1 Synthesis of $\text{FeFe}(\text{CN})_6$ Nanoparticles

I used co-precipitation method to synthesize the Berlin green following reference.¹¹² Briefly, 50 mL of the 0.01 M FeCl_3 (Sigma-Aldrich, 97%) solution was added dropwise into 100 mL of the 0.005 M $\text{K}_3\text{Fe}(\text{CN})_6$ (Alfa Aesar, 98+%) under stirring in 2 hours. After the addition step was complete, the mixed solution was aged for another 6 hours at 60 °C. The mixed solution was cooled down naturally and then filtered. The obtained

dark green precipitate was washed with distilled water several times and dried in vacuum at 120 °C overnight.

3.2.2 Preparation of Electrolyte

The electrolyte synthesis was carried out inside an Ar filled glove box. In a typical synthesis of 20 ml 0.2M $[\text{Mg}_2\text{Cl}_2][\text{AlCl}_4]_2/\text{DME}$ electrolyte, 1.07 g AlCl_3 powder (Sigma Aldrich, 99.99%) was added slowly (exothermic reaction) to a suspension of MgCl_2 (Alfa Aesar, 99.999%, 0.76 g in 20 ml DME) in a 25 ml glass vial. The mixture was stirred at 60°C using a sand bath for 6 hours and was cooled to room temperature. A clear solution was obtained with no precipitants. The hybrid-ion electrolyte was prepared by dissolving appropriate amount of NaAlCl_4 (Alfa Aesar) into the above electrolyte. 1M NaPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC, 50:50% vol) was used as the electrolyte in Na-ion battery.

3.2.3 Electrochemical and Material Characterizations

Tubular sealed three-electrode cells or two-electrode Swagelok cells were fabricated inside an Ar-filled glovebox (M-Braun Co.) for electrochemical characterizations. The slurry of active material (75 wt %), Super-P carbon (15 wt %), and polytetrafluoroethylene (10 wt %) was spread on a piece of Mo foil (0.8 cm^2) and dried as the working electrode. The active material mass loading was 4 mg cm^{-2} . Freshly polished magnesium foils (0.2 mm thick, 99.95%, GalliumSource, LLC, Scotts Valley, CA) were used as both the counter and reference electrodes. For Swagelok cells, a glass fiber separator (0.68 mm thick, GF/D grade) was placed between a cathode and an Mg anode. 0.4 ml of hybrid $\text{Mg}^{2+}/\text{Na}^+$ electrolyte was added in the glass fiber. Electrochemical characterizations were conducted using a potentiostat (VMP-3, Bio-

Logic Co., Claix, France). The X-ray diffraction (XRD) spectra of the pristine BG nanoparticles were measured using a Rigaku diffractometer with Cu K α radiation (1.5405 Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy measurements were conducted using a JEOL JSM 6400 SEM and an EDAX with Octane Silicon Drift Detector (SDD). For the scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy characterizations, the Mg anode and BG cathode were taken out from the cell in the Ar-filled glove box. Afterwards, the electrodes were dipped in fresh anhydrous DME for 10 mins, and this procedure was repeated for three times. The washed electrodes were then dried in evacuated antechamber of Ar-filled glove box for 2 hours before further characterizations. Thermogravimetric analysis (TGA) test was performed using thermogravimetric analyzer of TA Instruments Q50.

X-ray absorption near edge structure (XANES) of the Fe K-edge (7112 eV) was measured in the transmission mode on the bending-magnet beamline of the Advanced Photon Source (APS, 20-BM-B). The incident beam was monochromatized using a Si (111) fixed-exit, double-crystal monochromator. Ex-situ samples at different states of charge were sealed in a Kapton tube. XANES data were processed following standard methods using the ATHENA software package. The HEXRD measurements were carried out at Beamline 11-ID-C at APS. The X-ray wavelength was 0.1174 Å (105.1 keV). The XRD patterns were collected using a Perkin-Elmer 2D X-ray detector. 2D images were converted into a 1D plot of 2 θ versus intensity using the FIT2D program calibrated against a CeO₂ standard.

3.3 Working Mechanism of the Mg-Na Hybrid Battery

Figure 3.1 shows the working mechanism of the proposed hybrid magnesium-sodium-ion battery. The electrolyte has complicated equilibrium among four electroactive species: charged species of $[\text{Mg}_2\text{Cl}_2]^{2+}$ and AlCl_4^- , and less dominant neutral species of MgCl_2 and AlCl_3 .³⁵ The cell is assembled in the charged state. During the discharge, metallic Mg reacts with AlCl_4^- to form $[\text{Mg}_2\text{Cl}_2]^{2+}$ dimer cations since AlCl_4^- is easier than MgCl^+ to lose Cl^- . Therefore no NaCl will form due to no free Cl^- available. Electrons are transferred through the external circuit from the Mg anode to the BG cathode, where a reduction reaction results in Na-ion insertion into the BG framework. During the charge, Na-ions are deinserted from the $\text{Na}_x\text{FeFe}(\text{CN})_6$ into electrolyte, and in the meantime $[\text{Mg}_2\text{Cl}_2]^{2+}$ dimer cations are reversibly reduced and deposited as Mg on the anode.

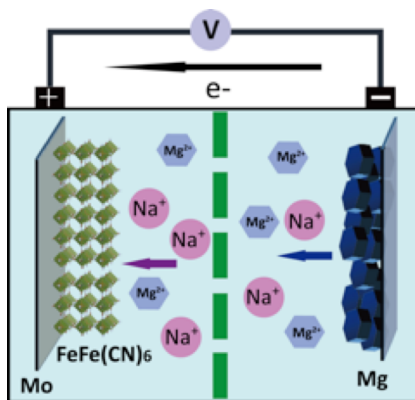


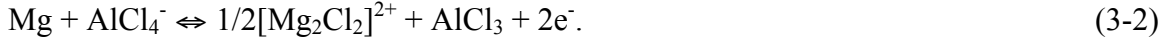
Figure 3.1 Schematic of the working mechanism of an Mg-Na hybrid battery.

Because the thermodynamic redox potential of Mg^{2+}/Mg is 0.36 V higher than that of Na^+/Na , reversible Mg deposition-dissolution should occur at the anode side before Na deposition-dissolution could take place. The following equations describe the reactions in the cell.

The positive electrode reaction is



The negative electrode reaction is



The overall reaction is



3.4 Electrochemical Performance of the Mg-Na Hybrid Battery

PBAs are used as the cathode material, which have the general formula $\text{A}_x\text{M1}_m\text{M2}_n(\text{CN})_z$ and an open framework (Figure 3.2) that facilitates reversible intercalation processes for alkali and alkaline earth ions (A_x). The PBA capacity is determined by the available A-sites in the compounds into which the alkali and alkaline earth ions can be intercalated reversibly in a range of working voltages. From the electric neutrality perspective, the valences and vacancies of M1 and M2 mainly contribute to the amount of the available A-sites. We used co-precipitation method to synthesize the BG nanoparticles.¹¹²

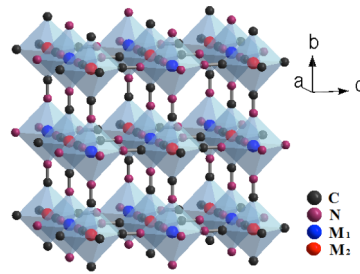


Figure 3.2 Framework of $\text{A}_x\text{M1}_n\text{M2}_m(\text{CN})_z$.

Figure 3.3 shows its X-ray diffraction (XRD) pattern, which can be indexed to a face-centered cubic structure (FCC, space group $\text{Fm}\bar{3}\text{m}$). Scanning electron microscopy (SEM) shows the cubic nanoparticles with average size of 400 nm.

Combining thermogravimetric analysis (TGA) (Figure 3.4) and Energy-dispersive X-ray (EDX) measurement, we obtained the chemical formula of our BG sample as $\text{K}_{0.07}\text{Fe}[\text{Fe}(\text{CN})_6]_{0.95} \cdot 0.61\text{H}_2\text{O}$.

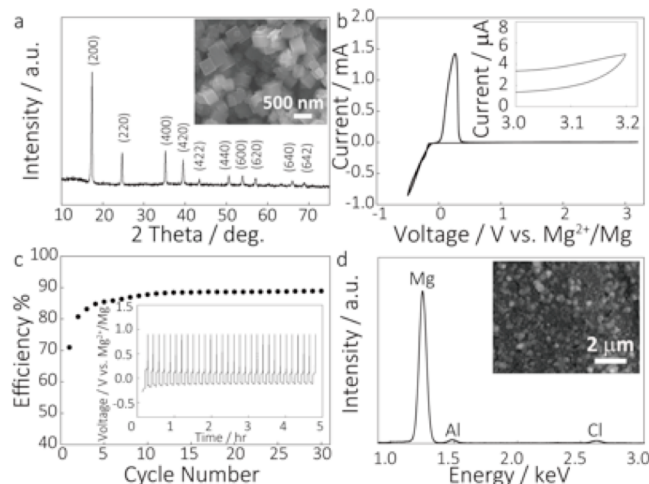


Figure 3.3 (a) XRD and SEM of BG nanoparticles. (b) Cyclic voltammogram of the hybrid electrolyte. (c) Chronopotentiometry of an asymmetric cell. (d) EDS and SEM of an Mg anode after 30 cycles of plating/stripping.

The hybrid electrolyte is the key to enable high capacity and stable cycling. As mentioned earlier, we used 0.2 M $[\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2$ and 0.4 M NaAlCl_4 in DME as the hybrid electrolyte due to the promise of high anodic stability. Figure 3.3b shows the cyclic voltammetry (CV) from -0.5 V to 3.2 V vs Mg/Mg^{2+} using a three-electrode setup. Molybdenum (Mo) foil is used as the current collector in a Swagelok cell due to its anti-corrosion property.¹²² A halogen-free magnesium monocarborane based electrolyte would be ideal for coin cells.³³

The overpotential for the magnesium deposition is 0.16 V and the Coulombic efficiency is ~87%. The electrolyte is stable up to 3.2 V, agreeing with the previous study. The Mg deposition and stripping behavior was further assessed via chronopotentiometry in a coin cell containing a stainless steel positive electrode and an

Mg negative electrode (Figure 3.3c). The Coulombic efficiency is 70% in the first cycle and increases to over 87% in following cycles. The Mg electrode was investigated after 30 cycles using EDX spectroscopy and SEM (Figure 3.3d). It is noteworthy that no Na deposition is observed, confirming the Mg-only deposition mechanism at the Mg electrode. The inset shows the SEM image of the electrode surface with an average Mg grain size of about 0.2 μm .

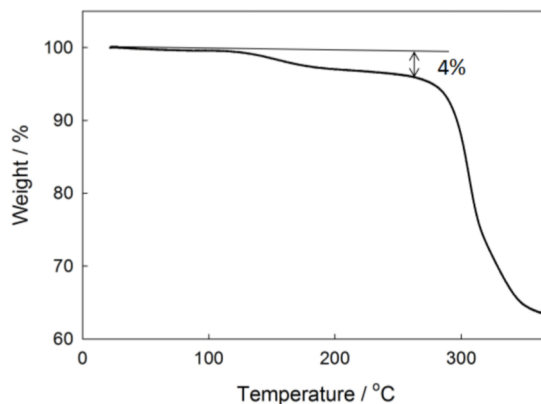


Figure 3.4 TGA profile of BG nanoparticles shows 4% weight loss due to crystalline H_2O .

Figure 3.5a shows the galvanostatic voltage profiles of BG cathodes in three cell configurations: (1) $\text{FeFe}(\text{CN})_6|\text{Na}^+|\text{Na}$ with 1M $\text{NaPF}_6/\text{EC}/\text{DEC}$ electrolyte; (2) $\text{FeFe}(\text{CN})_6|\text{Mg}^{2+}|\text{Mg}$ with 0.2M $[\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2/\text{DME}$ electrolyte; and (3) $\text{FeFe}(\text{CN})_6|\text{Mg}^{2+}, \text{Na}^+|\text{Mg}$ with 0.2M $[\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2/\text{DME}$ and 0.4 M NaAlCl_4 electrolyte. In cell configuration 1, the BG electrode exhibits two distinguishable plateaus during the discharge (2.9 and 3.5 V vs Na/Na^+) and the charge (3.0 and 3.7 V vs Na/Na^+), consistent with the results obtained by Lu et al.¹¹² According to previous study,¹¹⁵ the higher voltage plateau is attributed to the low-spin $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ bonded to the C atom of $\text{C}\equiv\text{N}^-$ and the lower voltage plateau to the high-spin $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ bonded to the N atoms of $\text{C}\equiv\text{N}^-$. The specific capacity of BG cathode reaches 145 mAh g^{-1} , higher than the previous

reported value of 120 mAh g^{-1} obtained by Wu et al.¹¹³ In cell configuration 2, BG delivers very low capacity around 10 mAh g^{-1} . For the cell configuration 3, we observed similar voltage profile and comparable capacity as those seen in configuration 1. The voltage difference of 0.8 V between configuration 1 and 3 is attributed to thermodynamic potential difference between Mg/Mg^{2+} and Na/Na^+ considering the electrolyte activity. This similarity in profile confirms the intercalation of Na^+ into BG as the dominant cathode reaction. This conclusion is also supported by EDX shown in Figure 3.5b. The intensity of Mg peak in the discharged sample is very small. This is not surprising given the observation of minimum Mg insertion in cell configuration 2. From the EDX spectra, we calculated the sodiated BG sample has 1.52 Na per formula of $\text{Fe}[\text{Fe}(\text{CN})_6]$, which agrees with the observed capacity of 143 mAh g^{-1} .

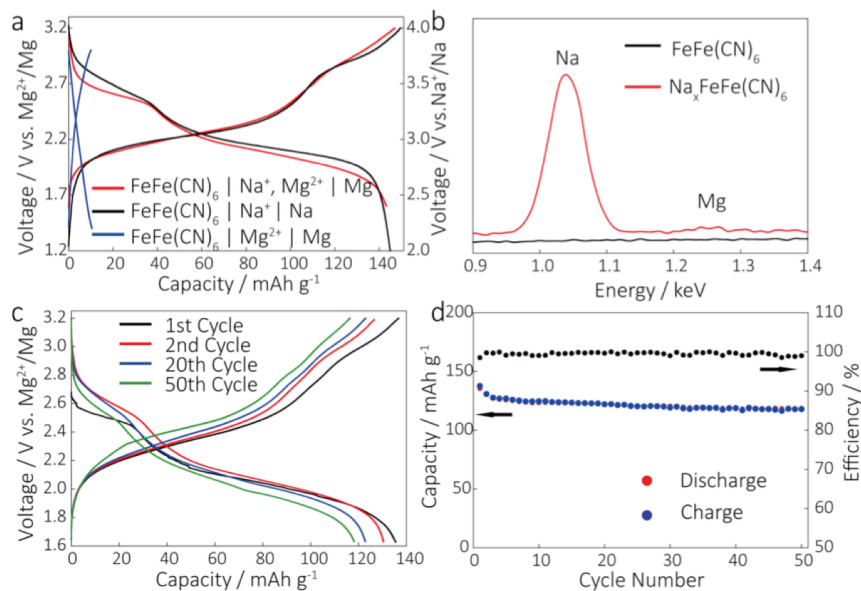


Figure 3.5 Electrochemical performances of Mg/Na hybrid batteries.

Figure 3.5c presents the galvanostatic voltage profiles of a $\text{FeFe}(\text{CN})_6|\text{Mg}^{2+}, \text{Na}^+|\text{Mg}$ hybrid cell at the 1st, 2nd, 20th and 50th cycles at a current density of 140 mA g^{-1} . The BG electrode shows two plateaus during the discharge (2.6 and $2.1 \text{ V vs Mg}/\text{Mg}^{2+}$)

and the charge (2.9 and 2.2 V vs Mg/Mg^{2+}). The 1st discharge and charge capacity reach 135 and 137 mAh g^{-1} , respectively, corresponding to an initial coulombic efficiency of 98.5%. The cell shows stable cycling for 50 cycles (Figure 3.5d) with 87% capacity retention of initial capacity. The Coulombic efficiency maintains a high level over 99% due to the high anodic stability of the hybrid electrolyte.

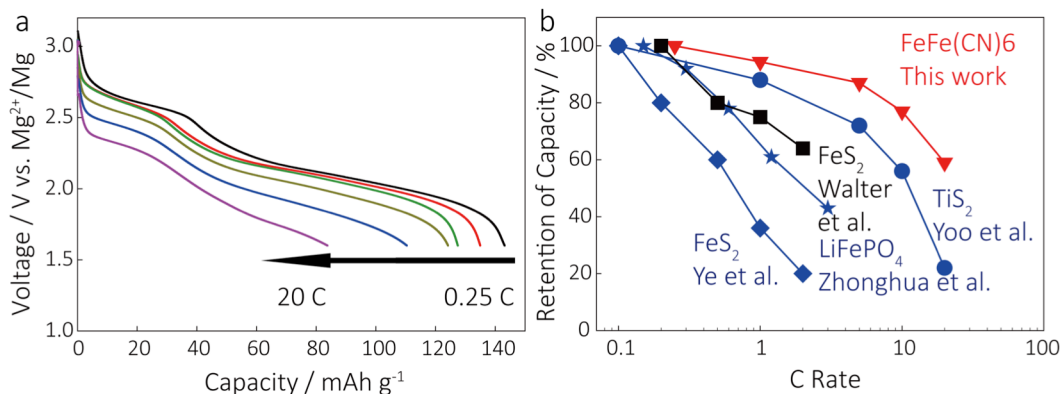


Figure 3.6 Rate performances for Mg/Na hybrid cells.

Figure 3.6a shows the discharge voltage profiles of the hybrid cell measured from 0.25C to 20C. The discharge capacity of the BG electrode decreases from 143 to 110 mAh g^{-1} when the current density increases from 0.25C (35 mA g^{-1}) to 10C (1400 mA g^{-1}). Even at 20C, more than 85 mAh g^{-1} can be retained. Note the capacity reported here is based on the mass of cathode active materials. Figure 3.6b shows the rate capability plot in comparison with hybrid cells reported in literatures. Black symbols indicate the reported Na-Mg hybrid cell¹²¹ and blue symbols indicate reported Li-Mg hybrid cells.^{8, 123-124} The excellent rate capability in this work compares favourably with previously reported hybrid cells. Such high power capability stems from the unique open framework structure of BG and agrees with previous reports on their fast rate capability. Since the salt in electrolyte participates the overall reaction, we calculated the theoretical specific

capacity for this battery reaction as 79 mAh g⁻¹ and theoretical specific energy density as 174 Wh kg⁻¹ considering 2.2 V as the average discharge voltage. Experimentally, we demonstrated the energy density of 135 Wh kg⁻¹ and power density of 1.67 kW kg⁻¹ at 20C (see supplementary information of reference 148 for the specific energy and power calculations).

3.5 Chemical Environment and Structural Change of FeFe(CN)₆ Cathode During Battery Cycling

To shed light on the chemical environment and structural change of BG during the Na insertion/deinsertion process, we carried out synchrotron radiation based X-ray absorption near edge structure (XANES) and high-energy X-ray diffraction (HEXRD) measurements. XANES is a powerful technique for detecting the average oxidation state of elements.

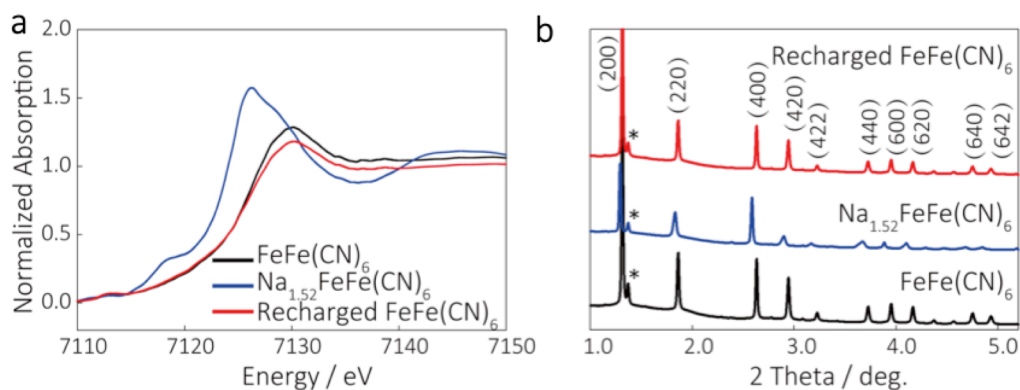


Figure 3.7 (a) Fe K-edge XANES and (b) HEXRD spectra of pristine, discharged, and recharged BG cathodes. (* indicates the diffraction peak from the PTFE binder)

Figure 3.7a shows XANES spectra for pristine, discharged, and recharged BG samples at the Fe K-edge. The pristine sample shows the main absorption peak at 7130 eV as the result of dipole-allowed Fe 1s to 4p transition.¹¹⁴ The pre-edge features

typically seen in most transition metal oxides are not discernible. With Na-ion insertion, the Fe K-edge showed a clear shift to lower energy of 7127 eV caused by the reduction of the oxidation state of Fe. A small hump around 7118 eV is also observed and could be explained by the ligand to metal charge transfer.¹²⁵ Since the LS-Fe(III) was reduced to LS-Fe(II), its t_{2g} orbitals were filled up. Therefore charges in CN molecular orbitals may be transferred to the empty E_g orbital of LS-Fe(II). The reduced symmetry of the sodiated BG framework may also be associated with the K-edge peak shift. As Na^+ ions are removed from the BG electrode, the K-edge absorption peak returned to the pristine peak position at 7130 eV.

Ex-situ HEXRD experiments were conducted for the same set of samples. The pristine BG sample has an FCC structure with the unit cell size of 10.215 Å calculated from its XRD pattern in Figure 3.7b. The shift of all peaks positions to smaller angle in the XRD patterns of $Na_{1.52}FeFe(CN)_6$ is indicative of an insertion mechanism. Calculation shows the increase of unit cell size to 10.394 Å, corresponding to ~5.3 % larger unit cell volume than that of the pristine compound due to Na-ion insertion. We also observed that the full width at half maximum (FWHM) for (220), (420), (422), (440), and (620) peaks reversibly increases during discharge and decreases during charge, while the FWHM of (200), (400), (600) peaks remains unchanged during the same processes. We ascribe such a phenomenon to the slight non-uniform structural distortion of BG in the b and c direction. Na insertion into BG framework can lead to a cooperative rotation of the FeN_6 and FeC_6 octahedral that retains straight CN^- anions and stabilizes the displacement of the Na^+ along the (111) axis towards the more negative FeN_6 site.¹¹⁴⁻

115, 126

3.6 Conclusions

In summary, we have demonstrated a low-cost high-power Mg/Na hybrid battery enabled by high-voltage Mg-Na dual salt electrolyte (3.2 V vs Mg/Mg²⁺), open framework cathode, and the fast-kinetic Mg metal anode. The full cell delivers an average discharge voltage of 2.2 V and stable cycling for 50 cycles. We obtained the high power density of 1.67 kW kg⁻¹. The unit cell of BG has only 5.3 % volume increases than the pristine compound and slight non-uniform structural distortion when 1.52 Na inserts into the framework. XANES study shows a clear reversible shift of Fe K-edge to lower energy and a small hump around 7118 eV. At the anode side, EDX and SEM confirm fast and reversible Mg-only deposition mechanism. Therefore this work opens the door to many Na-ion cathode materials for high voltage Mg-Na hybrid batteries that could become a viable candidate for stationary energy storage high.

Chapter 4 High-Energy Mg Batteries using Polymer Cathodes

4.1 Introduction

Magnesium metal has the high capacity (2205 mAh g^{-1} and 3833 mAh cm^{-3}), low redox potential (-2.37 V vs NHE), resource abundance, and non-dendritic deposition behavior to be qualified as an ideal anode for high-energy batteries.¹⁰ A major challenge for realizing viable Mg batteries is the hunt for high-performance cathode materials that are chemically compatible with electrolytes in which highly reversible Mg deposition/stripping occur.¹²⁻¹³ Magnesium ion has the radius of a Li ion but double the positive charge, hence strong electrostatic interaction with anionic species in both electrolytes and cathode materials.^{19, 35} Both cleavage of Mg^{2+} from solvated species such as Mg_xCl_y^+ before intercalation and solid-state Mg^{2+} diffusion through negatively charged intercalation sites involve high energy barriers as a result.^{16-18, 127} Intercalation-type Mg-storage materials Chevrel phase Mo_6S_8 and cubic Ti_2S_4 (c- Ti_2S_4) deliver state-of-the-art specific energies of 140 and 212 Wh kg^{-1} at elevated temperatures, respectively, but those values reduce to the less attractive 105 and 123 Wh kg^{-1} at room temperature, respectively (Figure 4.1).^{9, 25, 128} Other intercalation- and conversion-type compounds with high potential/specific capacity such as V_2O_5 ¹²⁹ and sulfur^{29, 104} may become interesting candidates if compatibility with Mg anode and a practical cell design becomes available.¹⁰⁷ Recently, multiple groups, including ours, have reported efficient Mg storage with organic electrode materials in both aqueous and non-aqueous electrolytes.^{100-101, 130-133} Some organic electrode materials, such as poly(1,4-anthraquinone) (P14AQ) and 2,5-dimethoxy-1,4-benzoquinone (DMBQ), deliver specific energies that match or exceed those by the best intercalation compounds even at room temperature in similar

Mg_xCl_y⁺-based electrolytes.^{101, 130} Such unique performance prompted us to scrutinize the Mg storage chemistry and, more importantly, the practicality of organic carbonyl compounds as cathode materials for Mg batteries.

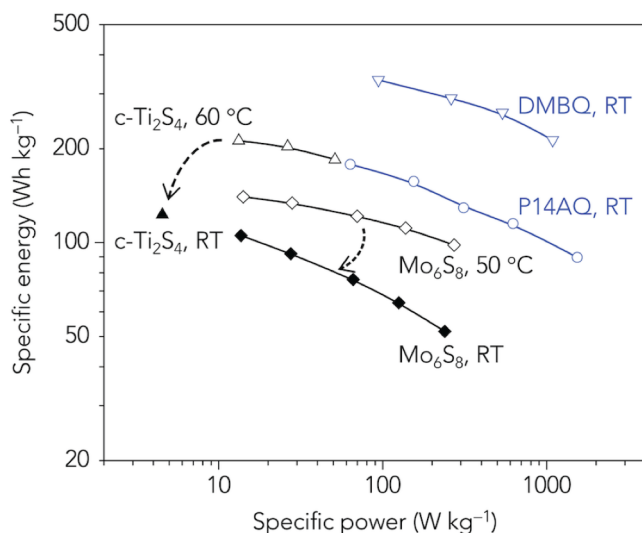


Figure 4.1 Ragone plot of representative Mg batteries.

Herein we report the Mg storage behavior of selected organic carbonyl compounds using a range of Mg metal-compatible electrolytes, based on which we propose a pathway towards high-energy organic Mg batteries. A vast library of organic carbonyl electrode materials are available thanks to active research on organic Li batteries,¹³⁴⁻¹³⁸ among which three compounds are selected as model compounds: the small-molecule quinone DMBQ which boasts high Li-storage specific capacity¹³⁹ and the highest specific energy for an Mg-storing organic cathode;¹³⁰ the polymeric quinone P14AQ which shows relatively high specific energy and great cycling stability as both organic Li¹⁴⁰ and Mg¹⁰¹ cathodes, and the conjugated redox polymer poly[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) (P(NDI2OD-T2)) which is a particularly fast and stable organic cathode for Li storage.¹⁴¹ Quantitative elemental analysis reveals that regardless of molecular structure or molecular weight, all three

compounds predominantly store MgCl^+ instead of the previously assumed Mg^{2+} when tested in Mg_xCl_y^+ -based electrolytes. Since the electrolyte is the sole supply of Cl, the MgCl-storage chemistry turns the electrolyte into an additional charge storage component alongside the cathode and anode. As such, this chemistry is not likely to allow for a lean-electrolyte cell design which is crucial for a high-energy cell. However, we manage to enable a Mg-storage chemistry by electing chloride-free electrolytes with weakly coordinating bis(trifluoromethane)sulfonimide (TFSI)¹⁴² and closo-carborane anions,³³⁻³⁴ in which little or no anion co-storage with Mg^{2+} is observed in our model polymers. The change from MgCl- to Mg-storage chemistry increases cell-level specific energy by multiple times, as explained theoretically by calculation and experimentally by cells using a limited amount of electrolyte (“lean electrolyte” conditions). Finally, through optimal combination of organic carbonyl polymer cathodes and Mg-storage-enabling electrolytes we are able to demonstrate high specific energy, power, and cycling stability that are rarely seen in Mg batteries.

4.2 Experimental Procedures

4.2.1 Fabrication of Organic Electrodes

Electrode compositions and preparation methods followed previous reports for DMBQ,¹³⁰ P14AQ,¹⁰¹ and P(NDI2OD-T2)¹⁴¹ for fair comparison. For lean electrolyte tests, we increased the ratio of the active material to avoid unnecessary electrolyte take-up by inactive components. The preparation of P(NDI2OD-T2) electrodes followed previous binder-free procedure for the same polymer.¹⁴¹ P(NDI2OD-T2) and Super-P carbon were hand-ground with pestle and mortar at a mass ratio of 6:4 with the aid of 1,2-dichlorobenzene without the use of binder. The resulted slurry was spread onto stainless

steel foil current collectors. The preparation of P14AQ and DMBQ electrodes followed a binder assisted procedure for quinone electrodes.¹³¹ P14AQ, Super-P carbon, and polytetrafluoroethylene (PTFE) binder were mixed in a 4:5:1 ratio with the aid of ethanol and pressed into stainless steel mesh. DMBQ, Super-P carbon, and PTFE binder were mixed in a 5:4:1 ratio with the aid of ethanol and pressed on a molybdenum (Mo) foil. Mo foils were used due to its anti-corrosion property at high charging potentials. The areal mass loading of active materials is 1 mg cm^{-2} in this work unless otherwise indicated. For the experiment on the effect of the electrolyte amount on the capacity, P14AQ, Super-P carbon, and PTFE binder were mixed in a 6:3:1 ratio and the areal mass loading of P14AQ in the electrode is 5 mg cm^{-2} . All electrodes were dried at 100°C under vacuum for 6 hours and used without being calendared.

4.2.2 Electrochemical and Material Characterizations

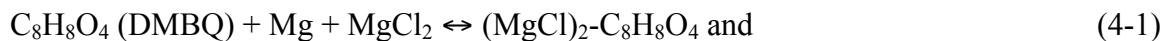
Tubular hermetically sealed three-electrode cells⁸ were used for all electrochemical characterizations except for lean electrolyte tests, for which two-electrode coin cells were used. The three-electrode cells require such a large amount of electrolyte (testing setup shown in Ref. 8) that we decided to use the affordable $\text{Mg}(\text{TFSI})_2/\text{diglyme}$ as a model electrolyte for the chloride-free scenario. Practical batteries are expected to be, instead, fabricated using two-electrode cells where a small amount of electrolyte is needed and the use of the optimal $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2/\text{tetraglyme}$ electrolyte, in which the overpotential for Mg plating/stripping is small,³³ becomes economically viable. The two electrolytes share high-efficiency Mg plating/stripping and chloride-free electrolyte with the only difference being the anode overpotential. All cells were assembled in an Ar-filled glovebox (M-Braun Co., Garching, Germany), and electrochemical characterizations

were conducted using a potentiostat (VMP-3, Bio-Logic Co., Claix, France). For three-electrode set-up, the electrodes of interest were used as working electrodes. Freshly polished magnesium foils (50 μm thick, 99.95%, GalliumSource, LLC, Scotts Valley, CA) were used as both counter and reference electrodes. The capacity of the Mg anode is greater than that of cathode. A trilayer polypropylene/polyethylene/polypropylene (PP/PE/PP) separator (25 μm thick, Celgard 2325, Celgard, LLC) was used in coin cells.

The electrodes at different discharge and charge states were characterized by XPS (Physical Electronics Model 5700), ICP-OES (Agilent Technologies, Model 725), and EDS. Energy-dispersive X-ray (EDX) spectroscopy measurement was conducted using a JEOL JSM 6400 SEM and an EDAX with Octane Silicon Drift Detector (SDD). The electrodes were taken out from disassembled cells in an Ar-filled glove box. The electrodes were dipped in anhydrous DME or THF for 3 min, and this procedure was repeated 3 times. The washed electrodes were then vacuum-dried at room temperature for 2 h before characterizations.

4.2.3 Specific Energy Calculations

For cells using chloride-containing electrolytes, the calculation is based on the following reaction equations:



The cell specific energy (E_s) is calculated as

$$E_s = E \times (C_c^{-1} + C_a^{-1} + C_e^{-1})^{-1}, \quad (4-3)$$

where E is the average discharge voltage, C_c is cathode specific capacity; C_a is anode specific capacity; C_e is the apparent specific capacity of the electrolyte defined as

$$C_e = z \times F \times (M_w \times c^{-1})^{-1}, \quad (4-4)$$

where M_w is the molecular weight of the solute that participates in the reaction (MgCl_2 here), z is the mole number of electrons transferred with the consumption of one mole of electrolyte solute molecule ($z = 2$ for both reactions), F is the Faraday constant, and c is the weight percentage of the solute (MgCl_2) in the electrolyte. For cells using chloride-free electrolytes, C_e is taken out of the equation, so the E_s is calculated as

$$E_s = E \times (C_c^{-1} + C_a^{-1})^{-1}. \quad (4-5)$$

Table 4.1 Performance parameters of bells based on MgCl -storage chemistry.

Cathode	Electrolyte	C_c (mAh g^{-1})	C_a (mAh g^{-1})	c (wt%)	C_e (mAh g^{-1})	E (V)	Specific energy (Wh kg^{-1})
DMBQ	MgCl_2 - $\text{Mg}(\text{TFSI})_2$ in DME	225	2205	4.5	25.3	1.63	36
P14AQ	MgCl_2 - $\text{Mg}(\text{HMDS})_2$ in THF	146	2205	10.3	58.1	1.30	53

Table 4.2 Performance parameters cells based on Mg-storage chemistry.

Cathode	Electrolyte	Temp. (°C)	C_c (mAh g^{-1})	C_a (mAh g^{-1})	E (V)	Specific energy (Wh kg^{-1})
Mo_6S_8	(tert- $\text{BuOMgCl})_6$ - AlCl_3 in THF	RT	100	2205	1.10	105
		50	129	2205	1.15	140
c- Ti_2S_4	PhMgCl- AlCl_3 in THF	RT	130	2205	1.00	123
		60	192	2205	1.20	212
P(NDI2OD- T2)	$\text{Mg}(\text{TFSI})_2$ in diglyme	RT	54	2205	1.44	76
P14AQ	$\text{Mg}(\text{TFSI})_2$ in diglyme	RT	193	2205	1.37	243

The values of E were taken from the corresponding reports which were typically obtained in two-electrode cells. For polymer cells based on Mg-storage chemistry, the E

values were taken from three-electrode cells. The use of cathode discharge potential obtained from three-electrode cells as discharge voltage omits the stripping overpotential of Mg metal; the latter is sufficiently small (e.g., 49 mV at 0.1 mA cm^{-2}) compared with the polymer cathode potential. The performance parameters of cells based on MgCl- and Mg-storage chemistries are summarized in Table 4.1 and 4.2, respectively.

4.2.4 Synthesis of Organic Electrode Materials

P(NDI2OD-T2) was obtained from Polyera Corp. as reported.¹⁴³ P14AQ was synthesized as reported.¹⁰¹ DMBQ was purchased from TCI America and used without further purification.

4.2.5 Preparation of Electrolyte

Mg(TFSI)₂ was dried under vacuum for 24 h at 250 °C. Solvents were pretreated with molecular sieves (Aldrich, 3 Å beads, 4-8 mesh) for two days before use unless otherwise specified.

Preparation of 0.25 M Mg(TFSI)₂ and 0.5 M MgCl₂ in DME electrolyte:

The electrolyte synthesis was carried out inside an Ar-filled glove box (M-Braun). In a typical synthesis of 5 ml 0.25 M Mg(TFSI)₂ and 0.5 M MgCl₂ electrolyte, 0.73 g Mg(TFSI)₂ powder (Solvionic, 99.5%) was added to a suspension of MgCl₂ (Alfa Aesar, 99.999%, 0.24 g in 5 ml DME) in a 10 ml glass vial. The mixture was stirred at 70 °C for 6 h in a sand bath and then cooled down to room temperature to afford a clear solution.

Preparation of 0.2 M Mg(TFSI)₂ in diglyme electrolyte:

In a typical synthesis of 5 ml 0.2 M Mg(TFSI)₂ electrolyte, 0.58 g Mg(TFSI)₂ powder (Solvionic, 99.5%) was added to 5 ml diglyme in a 10 ml glass vial under stirring at room temperature for 2 h to afford a clear solution.

Preparation of 0.3 M $\text{Mg}(\text{HMDS})_2$ and 1.2 M MgCl_2 in THF electrolyte:

In a typical synthesis of 5 ml 0.3 M $\text{Mg}(\text{HMDS})_2$ and 1.2 M MgCl_2 electrolyte, 0.52 g $\text{Mg}(\text{HMDS})_2$ powder (Sigma-Aldrich, 97%) was added to a suspension of MgCl_2 (Alfa Aesar, 99.999%, 0.57 g in 5 ml THF) in a 10 ml glass vial. The mixture was stirred at room temperature for 48 h to afford a clear solution.

Preparation of 0.3 M $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in tetraglyme and 0.5 mol kg^{-1} $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DOL/DME (1:1, w/w) electrolytes:

$[\text{Mg}(\text{DME})_3](\text{CB}_{11}\text{H}_{12})_2$ was synthesized as reported.¹⁴⁴ In a typical synthesis of 0.3 M $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in tetraglyme, $[\text{Mg}(\text{DME})_3](\text{CB}_{11}\text{H}_{12})_2$ (279.7 mg) was dissolved in anhydrous tetraglyme (1.542 ml, dried as reported³³) with stirring and the resulting clear solution was vigorously stirred under vacuum for 15 mins to remove DME solvent. In a typical synthesis of 1.5 ml 0.5 mol kg^{-1} $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DOL/DME (1:1, w/w), $[\text{Mg}(\text{DME})_3](\text{CB}_{11}\text{H}_{12})_2$ (379.5 mg) was added to 542.5 mg of DME and 717.8 mg of DOL and stirred at room temperature to afford a clear solution.

4.3 Charge Storage Mechanism of Organic Electrodes in Chloride-Containing Electrolytes

Since a large variety of electrolytes are involved in this work, we performed cathode evaluation in three-electrode cells so that their voltage profiles were not obscured by any difference in the overpotential for Mg plating/stripping in different electrolytes. We first studied the charge storage mechanism of carbonyl compounds DMBQ, P14AQ, and P(NDI2OD-T2), the molecular structures of which are shown in Figure 4.2, in typical chloride-containing electrolytes.^{14, 145} DMBQ was originally reported in $\text{Mg}(\text{ClO}_4)_2$ -

butyrolactone and $\text{Mg}(\text{TfSA})_2$ -sulfone electrolytes where DMBQ showed low potentials of ~ 1.1 V vs Mg/Mg^{2+} .⁹⁹ The low potentials were interpreted as the result of the two chloride-free electrolytes being incompatible with Mg metal. A recent reinvestigation of the molecule in $\text{Mg}(\text{TFSI})_2$ - 2MgCl_2 in dimethoxyethane (DME), an electrolyte capable of Mg metal plating/stripping,⁶⁹ revealed a clear discharge plateau at ~ 2 V vs Mg/Mg^{2+} with specific capacity slightly above 100 mAh g^{-1} followed by a slope with another 100 mAh g^{-1} .¹³⁰ Here we investigated the material in the same electrolyte for a fair comparison but used the inert Mo foil instead of stainless steel as the current collector for cleaner chemistry.¹²² Figure 4.2a shows well-defined plateaus for both charge and discharge with similar specific capacity (200 mAh g^{-1}) to reported values. The DMBQ electrodes composed of DMBQ, conductive carbon, and polytetrafluoroethylene (PTFE) at pristine, discharged, and charged states were subjected to energy dispersive X-ray spectroscopy (EDS) analysis. Strong Mg and Cl signals arose upon discharge, then both vanished when charged (Figure 4.2d). The simultaneous appearance and disappearance of both signals indicates co-storage of the two elements. The presence or absence of TFSI^- in the discharged sample cannot be confirmed due to the F signal arising from PTFE, but the possible TFSI^- storage can be ruled out as to be discussed later. The atomic ratio of Mg to Cl is 1:0.60 (with an error bar of $\pm 4.1\%$), i.e., a split of ca. 2:3 between Mg^{2+} and MgCl^+ . Therefore, the DMBQ | $\text{Mg}(\text{TFSI})_2$ - 2MgCl_2 | Mg battery is a hybrid-ion battery dominated by MgCl -ion storage rather than a Mg-ion battery.

Compared with molecular organic compounds, organic polymers are more popular cathode candidates due to their lower solubility in organic electrolytes. Therefore, we also studied P14AQ as a representative polymer cathode. Another Mg metal-compatible

electrolyte, $\text{Mg}(\text{HMDS})_2\text{-}4\text{MgCl}_2$ (HMDS = hexamethyldisilazide) in tetrahydrofuran (THF), was used following a previous report.¹⁴⁶ The polymer showed a sloping plateau during both charge and discharge with a specific capacity of 155 mAh g^{-1} at an average of $\sim 1.36\text{ V}$ vs Mg/Mg^{2+} (Figure 4.2b), agreeing well with previous report.¹⁰¹ Both Mg and Cl signals were again observed in the discharged electrode, with the atomic ratio of Mg:Cl being 1:0.97 (with an error bar of $\pm 4.3\%$), indicating almost exclusive MgCl^+ storage (Figure 4.2e).

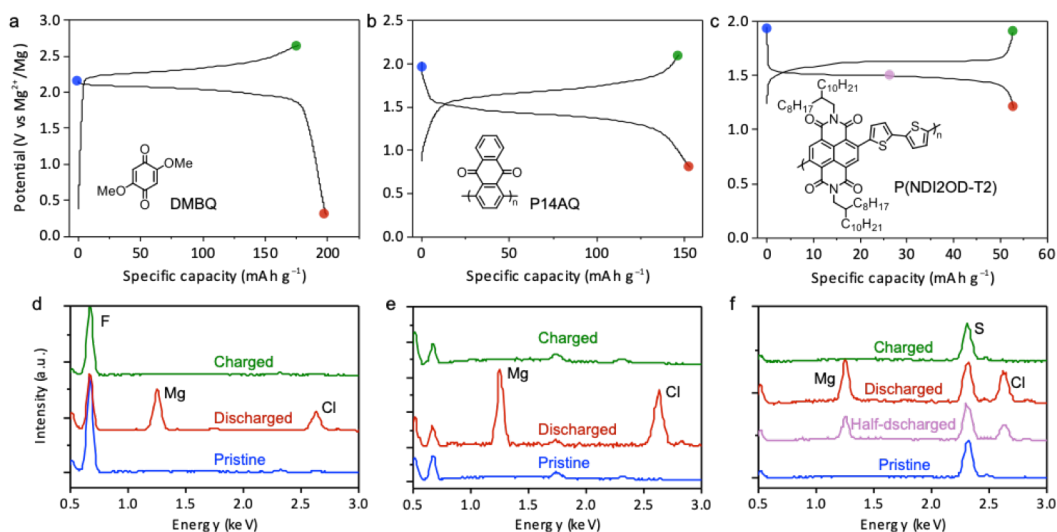


Figure 4.2 Charge storage mechanism of organic electrodes in chloride-containing electrolytes. (a and d) DMBQ. (b and e) P14AQ. (c and f) P(NDI2OD-T2).

The S-containing carbonyl polymer P(NDI2OD-T2) provides more insight into the electrode reaction. According to previous studies of the polymer for Li batteries, each repeating NDI2OD-T2 unit reversibly stores two electrons, corresponding to a theoretical capacity of 54.2 mAh g^{-1} .¹⁴¹ As shown in Figure 4.2c, the polymer showed flat plateaus for both charge and discharge with a small overpotential of 133 mV. The observed specific capacity of 52.8 mAh g^{-1} corresponds to 97% of its theoretical capacity. Such high level of material utilization is a major improvement from the previous reports

($<70\%$)¹⁰⁰ and implies that there is no fundamental limitation for an organic electrode material to achieve designed capacity. Binder-free electrodes composed of P(NDI2OD-T2) and conductive carbon were tested in a $\text{Mg}(\text{TFSI})_2\text{-}2\text{MgCl}_2$ electrolyte (same as that for DMBQ) and analyzed with EDS (Figure 4.2f). When half-discharged, the atomic ratio of Mg:Cl:S was 1:0.96:1.97 (with an error bar of $\pm 4.3\%$), i.e., each electron injected into the polymer is balanced by a MgCl^+ ion. As discharge completed, both Mg and Cl amount doubled, and the ratio became 1:0.96:0.99 (with an error bar of $\pm 3.2\%$). Upon charge, both Mg and Cl signal disappeared, leaving only S of the bithiophene moiety. No F signal was detected throughout the cycle even though there are TFSI⁻ ions in the electrolyte. We conclude that both polymers underwent MgCl^+ storage regardless of the redox active cores (quinone vs. imide), solvent (THF vs. DME) and the anion species (HMDS⁻ vs. TFSI⁻). On the basis of the fact that all previously reported organic Mg batteries use quinone and imide molecule/polymer cathodes and chloride-containing ethereal electrolytes, we believe what were assumed organic “Mg-ion” cathodes and batteries all involve MgCl -storage chemistry.

4.4 Charge Storage Mechanism of Organic Electrodes in Chloride-Free Electrolytes

A hybrid-ion cell design where the cathode and anode store different ions (MgCl^+ and Mg^{2+} in this case) offers plenty of flexibility in choice of electrode chemistry and has enabled many interesting types of batteries.^{51, 81, 147-148} However, the reliance on extra electrolytes dedicated to ion storage, as will be demonstrated later, makes such design unlikely to compete as a high-energy battery. We have therefore explored the plausibility of true organic Mg-ion batteries by using chloride-free Mg metal-compatible electrolytes.

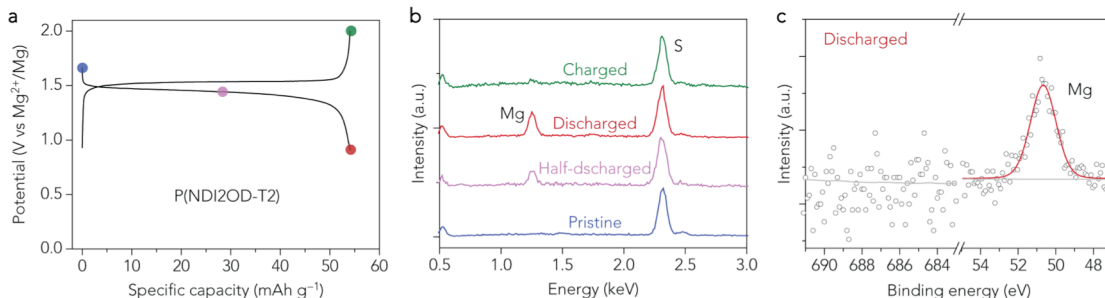


Figure 4.3 Charge storage mechanism of P(NDI2OD-T2) in chloride-free electrolytes. (a) Voltage profiles. (b) EDS of P(NDI2OD-T2) at different states of charge. (c) XPS of discharged P(NDI2OD-T2).

Figure 4.3a shows such an example using a P(NDI2OD-T2) cathode and an $\text{Mg}(\text{TFSI})_2/\text{diglyme}$ electrolyte. This very simple electrolyte, when dried thoroughly, allows reversible Mg plating/stripping with a surprisingly decent coulombic efficiency of 98.8% albeit a large overpotential for stripping (Figure 4.4). It makes for an economic model electrolyte for our three-electrode cells where a large amount of electrolyte is required and the anode overpotential does not obscure cathode profile. P(NDI2OD-T2) again showed flat plateaus with small polarization (91 mV) and 99.8% material utilization (54.1 mAh g^{-1}). EDS analysis showed Mg:S ratios of 1:3.81 (with an error bar of $\pm 4.4\%$) and 1:2.01 (with an error bar of $\pm 3.1\%$) for the half-discharged and fully discharged states, respectively, and no F signal throughout the cycle (Figure 4.3b). The results indicate no anion co-storage, and each Mg^{2+} balances two negative charges. X-ray photoelectron spectroscopy analysis of the discharged sample also confirmed the absence of F (689 eV) in Figure 4.3c.

Another example involved P(NDI2OD-T2) cathode and a $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2/\text{tetraglyme}$ electrolyte which showed efficient Mg plating/stripping.³³ The monocarborane anion $\text{CB}_{11}\text{H}_{12}^-$ is non-corrosive, chemically inert, and, most importantly, weakly coordinating. P(NDI2OD-T2) shows slightly larger polarization (151 mV) and lower specific capacity

(50.5 mAh g⁻¹) in this electrolyte, most likely due to the high viscosity of tetraglyme (Figure 4.5).

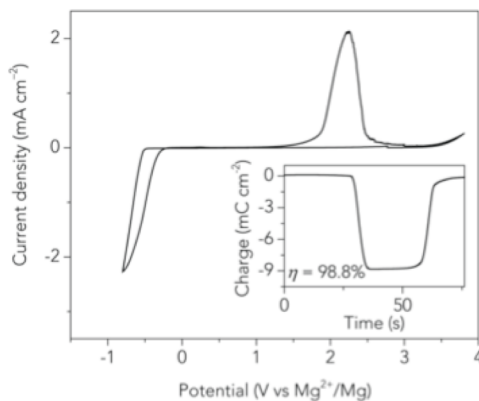


Figure 4.4 Cyclic voltammogram (5th cycle) for Mg metal plating/stripping in 0.2 M Mg(TFSI)₂ in Diglyme.

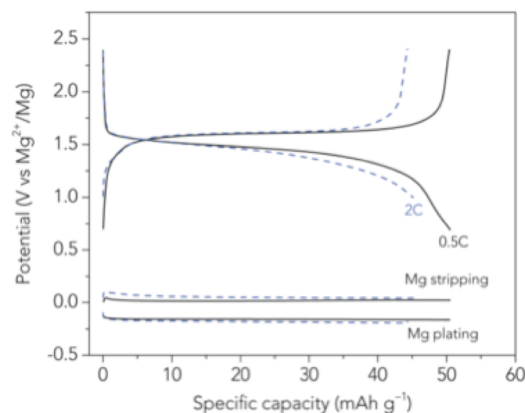


Figure 4.5 The voltage profiles of P(NDI2OD-T2) and Mg in 0.3 M Mg(CB₁₁H₁₂)₂ in tetraglyme.

The discharged electrode had a Mg:B:S ratio of 1:2.21:1.93 according to inductively coupled plasma (ICP) spectroscopy. The atomic ratio does not allow us to mathematically determine whether the B existed as the hybrid ion Mg(CB₁₁H₁₂)⁺ or residual solute Mg(CB₁₁H₁₂)₂. If all B entered the polymer as Mg(CB₁₁H₁₂)⁺, the ratio of Mg²⁺ and Mg(CB₁₁H₁₂)⁺ would be ca. 4:1, i.e., Mg²⁺ being the dominant storage species. However, considering the fact that the more strongly coordinating TFSI⁻ anions did not enter the

polymer as $\text{Mg}(\text{TFSI})^+$, the possibility of $\text{Mg}(\text{CB}_{11}\text{H}_{12})^+$ is less likely.^{142, 149} Instead, residual $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ is the more likely source of B due to the difficulty for thoroughly washing the very viscous electrolyte from the polymer electrode. The above two examples indicate the plausibility to have an Mg^{2+} -storing organic cathode in an Mg metal-compatible electrolyte.

4.5 Impact of MgCl- and Mg-Storage Chemistries on Cell Specific Energy

The ion storage chemistry has an immense impact on the specific energy of a battery. Figure 4.6a and b compare the reaction and mass flux in Mg batteries based on MgCl- and Mg-storage chemistries, respectively. During the discharge of an MgCl-storage cell, an Mg atom in the Mg metal anode loses two electrons and enters the electrolyte as Mg^{2+} . Mg^{2+} then accepts a Cl^- from the MgCl_2 in the electrolyte and forms MgCl^+ , which enter the cathode as monovalent cations. Since the cathode stores both Mg^{2+} and Cl^- but the anode stores only Mg, the electrolyte has to double as a Cl^- reservoir (in addition to ion conduction), and the amount of Cl^- in the electrolyte must at least match the capacity of the cathode. The Mg-storage scenario is a much simpler rocking-chair mechanism where a flux of Mg^{2+} goes from the anode to the cathode during discharge and vice versa. Minimal electrolyte is needed to provide ionic conduction between the two electrodes.

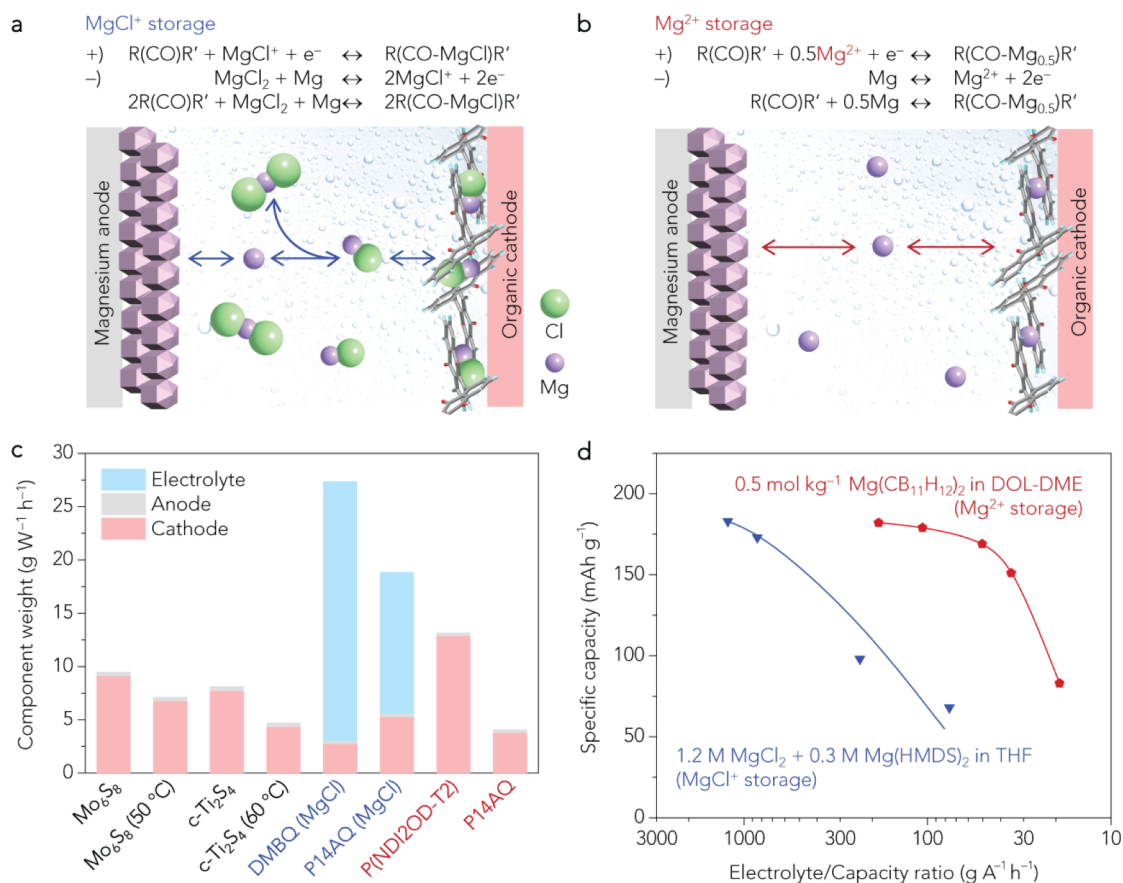


Figure 4.6 Working mechanism of organic cathodes in (a) Cl-containing and (b) Cl-free electrolytes. (c) Breakdown of weight of each component. (d) The effect of the amount of electrolyte on cell capacity.

One way to visualize the impact of the storage chemistry on cell energy is to look at the weight of materials needed to achieve a given energy. Figure 4.6c breaks down the weight of cathode material, anode material, and electrolyte (both solute and solvent) per watt hour for some representative Mg battery chemistries. The weight of anode material, i.e., Mg metal, is marginal in all cases due to its high specific capacity. Thiospinel Ti_2S_4 operated at 60 °C takes less than 5 grams of electrode materials to achieve 1 Wh. Previously reported organic cathodes P14AQ and DMBQ, when considering a solely MgCl -storage mechanism, suffer significantly from the massive weight of electrolyte. The situation is worse for DMBQ than for P14AQ due to a less concentrated MgCl_2

being used for the former (0.5 vs 1.2 M). While it is possible to reduce the electrolyte amount by increasing the MgCl_2 concentration, the limited solubility of MgCl_2 would eventually become the limiting factor. Similar discussions on the energy limitation by electrolyte had been made for hybrid-ion battery chemistries such as $\text{Mg}^{2+}\text{-Li}^+/\text{Na}^+$ hybrid batteries¹⁵⁰ and AlCl_4 -based Al batteries.⁸⁶ These batteries could theoretically use much more concentrated electrolytes, but the weight of electrolyte was still found to be the main limit on practical cell energy. Moving from MgCl - to Mg -storage chemistry trims the electrolyte from energy storage components, enabling P14AQ-Mg one of the highest-energy Mg batteries.

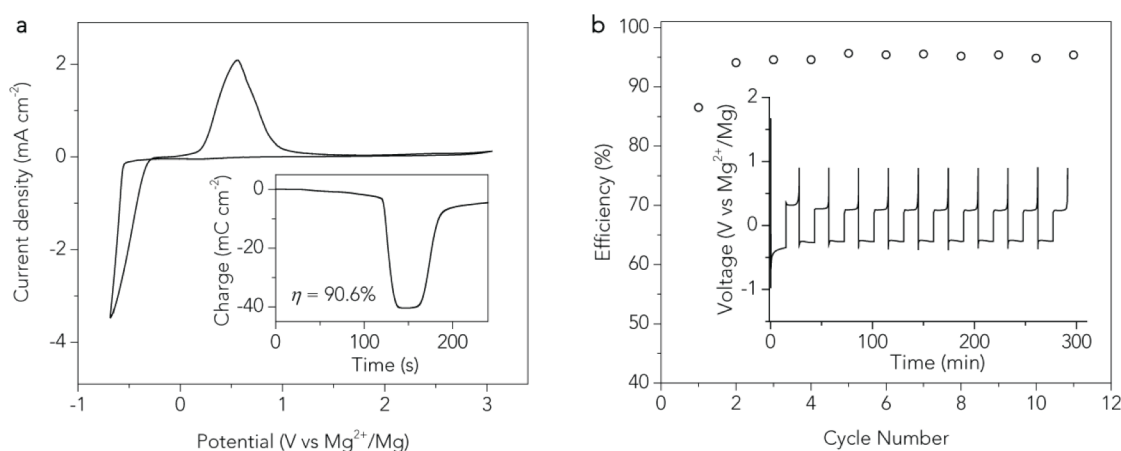


Figure 4.7 (a) CV for Mg metal plating/stripping in 0.5 mol kg^{-1} $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DOL-DME. (b) Electrochemical performances of an Mg/Cu asymmetric cell in 0.5 mol kg^{-1} $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DOL-DME.

The above analysis assumes the cell operation is sustained as long as the MgCl -storage chemistry is stoichiometrically satisfied. In practice, all Cl^- stored in the electrolyte cannot be consumed before the cell fails because an appropriate concentration of Cl^- is necessary to keep up the reversibility of Mg plating/stripping.¹⁵¹ To develop a more realistic understanding of the impact of the hybrid-ion chemistry on cell energy, we have compared P14AQ-Mg cells in electrolytes containing MgCl^+ and Mg^{2+} under “lean

electrolyte” conditions (Figure 4.6d). Electrodes with high areal loading (5 mg cm^{-2}) were used to better reflect a real-world application scenario. The $\text{Mg}(\text{HMDS})_2\text{-4MgCl}_2$ with a relatively high MgCl_2 concentration was used for the MgCl^+ cell. The Mg^{2+} cell employed a low-viscosity monocarborane electrolyte by replacing tetraglyme with a mixture of 1,3-dioxolane (DOL) and DME (Figure 4.7).

The polymer delivered the same maximum capacity of $\sim 180 \text{ mAh g}_{\text{P14AQ}}^{-1}$ in both electrolytes when the electrolyte is abundant. As we reduced the electrolyte–capacity ratio (E/C ratio, in $\text{g A}^{-1} \text{ h}^{-1}$) by decreasing the amount of electrolyte, the capacities of both cells dropped. To deliver 90% and 50% of the maximum capacity, the MgCl^+ cell required 620 and 142 $\text{g A}^{-1} \text{ h}^{-1}$ of electrolyte, respectively, while the Mg^{2+} cell 41 and 20 $\text{g A}^{-1} \text{ h}^{-1}$, respectively. That is, the Mg^{2+} cell needs about one order of magnitude less electrolyte to deliver the same capacity. To put it into context, a Li–S cell with an electrolyte–sulfur ratio (E/S ratio, in g g^{-1}) of 12, a common lean electrolyte condition, has a E/C ratio of 15 $\text{g A}^{-1} \text{ h}^{-1}$ considering a specific capacity of 800 mAh g^{-1} .¹⁵² To the best of our knowledge, this is the first report on an Mg battery operated with a limited amount of electrolyte. We expect higher capacity at lower E/C ratio when dedicated efforts are made to optimize electrode and cell fabrication.

4.6 Electrochemical Performance of Organic Mg-Ion Batteries

We have studied the rate capability and cycling performance of P(NDI2OD-T2) and P14AQ in greater detail. P(NDI2OD-T2) showed excellent fast charge–discharge performance with well-defined plateaus and 70% of theoretical specific capacity maintained at 50C ($1\text{C} = 54 \text{ mA g}^{-1}$) (Figure 4.8a). P14AQ showed two plateaus as opposed to one as observed in chloride-containing electrolytes; the polymer also showed

one plateau for Li^+ storage, therefore, the difference in plateau number may be intrinsic to the valence of ions stored. The performance of P14AQ is more sensitive to current density, but the maximum specific power of 553 W kg^{-1} is still appreciable especially considering this result is obtained at room temperature (Figure 4.8b).

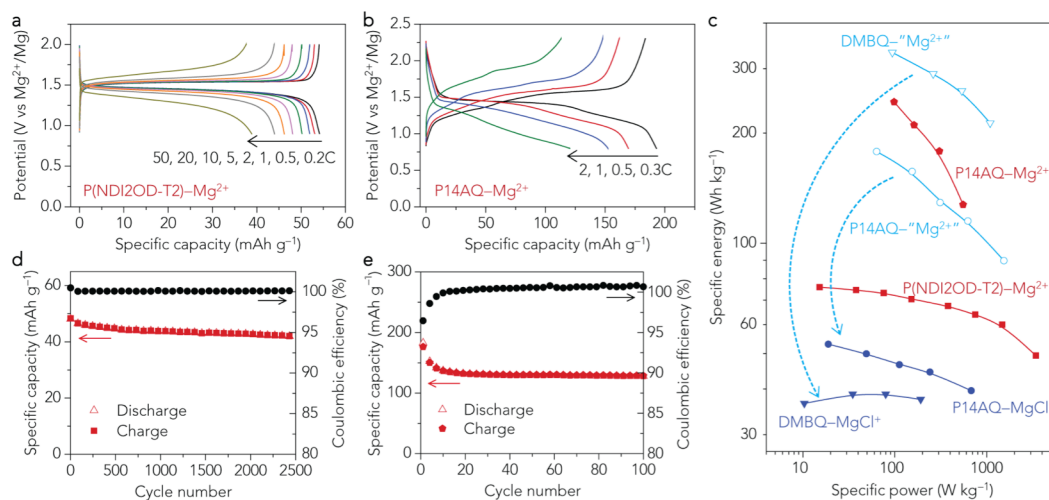


Figure 4.8 (a and b) Rate performances for P(NDI2OD-T2) and P14AQ. (c) Ragone plot of organic Mg batteries with different ion-storage mechanisms. (d) Cycling stability of P(NDI2OD-T2) and P14AQ.

Figure 4.8c compares the energy and power of cells operated on the two storage chemistries. When the specific capacities of cells obtained from electrolytes containing MgCl^+ are calculated based on the weight of the electrode materials, the specific energies of the DMBQ- Mg^{2+} and P14AQ- Mg^{2+} cells both appear pretty high (light blue). Once the MgCl -storage mechanism and the weight of the theoretically required amount of electrolyte are considered, the specific energies of DMBQ- MgCl and P14AQ- MgCl (deep blue) drop well below those achieved by inorganic intercalation compounds. The specific energies of the Mg -storage P(NDI2OD-T2)- Mg^{2+} and P14AQ- Mg^{2+} cells are not discounted by electrolytes (red). The P14AQ- Mg^{2+} cells show specific energies of up to 243 Wh kg^{-1} , while the P(NDI2OD-T2)- Mg^{2+} cells show specific powers of up to 3.4 kW

kg⁻¹. Both P(NDI2OD-T2) and P14AQ showed stable cycling performance. As shown in Figure 4.8d, P(NDI2OD-T2) maintained 87% of its initial capacity after 2500 deep cycles (> 700 hr; current density of 300 mA g⁻¹), representing one of the most stable cycling performance for a non-aqueous Mg battery. As shown in Figure 4.8e, P14AQ stabilized at ~130 mAh g⁻¹ after decay in the initial ~10 cycles at a current density of 130 mA g⁻¹. After 10 cycles, the average coulombic efficiency is slightly beyond unity at 100.5% which we ascribe to shuttle effect due to the slight dissolution of P14AQ.

4.7 Conclusions

In summary, we have evaluated the suitability of organic compounds as cathode materials for high-energy Mg batteries. We have identified that in typical chloride-containing electrolytes, storage of MgCl⁺ is dominant in probably all organic electrode materials, hence previously assumed organic “Mg-ion” electrodes/batteries are indeed hybrid-ion ones. The negative impact of the hybrid-ion-storage chemistry on the cell specific energy was elucidated through theoretical analysis and cell tests with controlled amount of electrolyte. We further showed that with the right combination of organic cathodes and chloride-free electrolytes, storage of Mg²⁺ in organic electrodes is possible without compromising the reversibility of Mg metal plating/stripping and the energy and power of the cell. Preliminary results from lean electrolyte cells indicate the plausibility for organic Mg batteries to be designed as practical high-energy storage devices. With the help of the Mg-storage chemistry, organic polymers have delivered some of the highest specific energy, power, and cycling stability for Mg batteries. Going forward, designing electrodes with higher mass loading, higher active material ratio, and lower electrolyte

demand would be just as important as developing better cathode materials for achieving truly high practical cell specific energy.

Chapter 5 High Power Mg-Organic Batteries

5.1 Introduction

Magnesium batteries are receiving increasing attention, since dendrite-free Mg metal can be directly used as anode.¹⁰ Although Mg dendrite was reported recently, this structure was only observed in the electrolytes with poor or unknown performances.⁴³ Non-dendritic plating behavior has been widely reported in efficient Mg electrolyte.⁸ Theoretically Mg battery has an absolute advantage over current Li-ion battery in terms of cost, safety, and energy, however, its development has been severely hindered due to the lack of appropriate cathodes and practical electrolytes.¹² It is impossible to deny that in recent years great progress has been made in cathodes (TiS₂, S, polymers)^{25-26, 30, 106} and electrolytes (non-nucleophilic and chloride-free electrolytes),^{32-33, 153} however, Mg battery based on Mo₆S₈ cathode still represents the benchmark Mg battery in terms of energy and cycling stability since it was demonstrated by Aurbach et al. 20 years ago.⁹

At the early stage, it was generally believed that the only hurdle for developing Mg cathode is the clumsy Mg²⁺ intercalation due to the sluggish solid-state diffusion of divalent Mg²⁺, but recently people gradually realized that how to overcome the high dissociation energy at the interphase between electrode and electrolyte is equally challenging.¹⁶⁻¹⁷ The dissociation energy includes the bond-breaking energy of MgCl⁻ complex and desolvation energy. Firstly, in most chloride-containing Mg electrolytes, Cl⁻ forms strong ionic bonds with Mg²⁺, and the Mg-Cl bond is hard to break before intercalation. Wan et al. estimated the Mg-Cl bond strength can easily exceed 3 eV.¹⁷ Secondly, even in chloride-free electrolytes, a high desolvation energy of 1 eV need to overcome.²² The magic of Mo₆S₈ lies in its surface catalysis capability to decrease the

dissociation energy to 0.1 eV, enabling Mg^{2+} ions to get rid of Cl^- ions and solvent easily. Most intercalation-type materials do not have this ability, resulting in failure of their application for Mg batteries. Besides, sluggish diffusion is definitely a serious problem, which cannot afford to overlook. Even representative Mo_6S_8 , $\text{s-Ti}_2\text{S}_4$ and V_2O_5 can only operate well at elevated temperature and small current density.^{9, 23, 25} To tackle above two challenges, two reliable approaches were proposed recently. The first alternative way is to use conversion materials, such as sulfur, which undergo dissolution-precipitation reactions that do not involve solid-state ion transport.^{26, 106} Although Mg-S batteries typically can release an ultrahigh energy at the first cycle, however, they decay very fast with cycling. The performance decay of these batteries has been attributed to the dissolution of polysulfides and formation of MgS passivation layer on Mg anode.¹⁰⁷ Moreover, the process of bond breaking during the reduction of sulfur leads all Mg-S even Li-S batteries to deliver a low capacity at high current density.¹⁵⁴ Secondly, instead of dealing with the problematic dissociation, intercalating solvated Mg_xCl_y -ions in certain hosts can bypass the most challenging step. This approach has been realized in intercalation compounds with open interstitial space and organic polymers.^{16, 30} This method seems to solve the problem, however, it actually sacrifices the cell energy, which is limited by the concentration of MgCl_2 in the electrolyte.³⁰ With the right combination of organic cathodes and chloride-free electrolytes, such as $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ (MMC) in tetraglyme (G4), storage of Mg^{2+} in organic electrodes is possible.³⁰ Some organic polymers deliver specific energies that exceed those by the best intercalation compounds even at room temperature.^{30, 101, 145} Nevertheless, Mg organic batteries are still at the early stage of the development, and the energy and power need to be further improved.

The advancements in Mg electrolytes have been remarkable in the most recent years, yielding a variety of new systems aim at overcoming the issues previously associated with classical Mg electrolytes, typically composed of complex chloride-containing solutions formed by combining a strong organic reducing agent and a strong Lewis acid.^{9,33} Among them, anions based on boron clusters stand out as they combine high reductive and oxidative stability and weakly coordinating nature arising from the negative charge delocalization within the electron-deficient cluster framework.³³ Such distinct features, combined with a benign nature (non nucleophilic, non electrophilic), prompted our study of $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ (MMC) as electrolyte for Mg batteries, which was later considered the third breakthrough in Mg battery electrolytes. In our previous work, we showed that a solution of MMC in tetraglyme (G4) is capable of Mg deposition and stripping with high coulombic efficiency, along with an extraordinary oxidative stability only limited by that of the solvent.³³ However, currently all MMC solvates were shown to dissolve in triglyme (G3) and tetraglyme (G4) beyond 0.5 M, and MMC ether solvates salts were found to be practically insoluble at room temperature in tetrahydrofuran (THF), dimethoxyethane (DME) or diglyme (G2). Despite the safety benefits reaped from the high flash point of long-chain glymes above G3, their increased viscosity and stronger coordination to Mg^{2+} may hinder ion mobility and render high solvation/desolvation barriers, respectively.¹⁵⁵ Ultimately, these may lead to increased overpotentials and lower battery rate capabilities. Therefore, the ability of the MMC salt to function in a less coordinating system, such as THF, DME, and G2, is highly desirable to enable much improved battery performance.¹⁵⁵

Herein, I report an Mg battery based on a molecule quinone, pyrene-4,5,9,10-tetraone (PTO), with a theoretical specific capacity of 408 mAh g⁻¹ and a high voltage of 2.1 V. Compared with intercalation-type materials, PTO can bypass the solid-state ion diffusion through dissolution-precipitation reaction. Compared with conversion-type materials, PTO does not involve bond-formation and -breaking in the process of coordination reaction. These two unique characteristics enable PTO to work under ultra-high current densities. Meanwhile, I report a solution that overcomes the solubility challenge of MMC in less coordinating ethers and produces a highly functioning Mg electrolyte, which is MMC in DME/G2. This electrolyte offers a path to discover an unexplored dimension of Mg metal behavior that further motivates research of Mg based energy storage devices. This has been manifested by unprecedented and extraordinary ability to cycle Mg at ultrahigh current densities in the order of 50 mA cm⁻² with dendrite-free morphology. Finally, by coupling PTO with MMC in DME/G2, we demonstrate a high-performance Mg-organic battery with a specific energy of 566 Wh kg⁻¹ and an ultra-high specific power of 30 kW kg⁻¹.

5.2 Experimental Procedures

5.2.1 Fabrication of Electrodes

PTO was synthesized as reported.¹³¹ PTO, Ketjenblack carbon (KB), and polytetrafluoroethylene (PTFE) binder were mixed in a 3:5:2 ratio with the aid of ethanol and pressed to form freestanding electrodes with the areal mass loading being 2.5 mg cm⁻². For the experiment of Mg anode study, sXAS, XPS, ICP, FTIR measurements, and the electrochemical test of high mass loading PTO electrodes, PTO, KB, and PTFE binder

were mixed in a 6:3:1 ratio and the areal mass loading of PTO in the electrode was 5 mg cm⁻². All electrodes were dried at 85 °C under vacuum for 24 hours.

P14AQ was synthesized as reported.¹⁰¹ P14AQ, KB, and PTFE binder were mixed in a 6:3:1 ratio and the areal mass loading of P14AQ in the electrode was 5 mg cm⁻². All electrodes were dried at 100 °C under vacuum for 6 hours.

Sulfur was purchased from Sigma-Aldrich and used without further purification. KB and sulfur were mixed in a 6:3 ratio and ground together in a mortar, and heated at 155 °C for 24h in a sealed tube furnace filled with Argon. After the calcination process, the sulfur loss was almost negligible. Later, S-KB composite and PTFE were mixed together at a weight ratio of 9:1 with the aid of ethanol and pressed to form freestanding electrodes with the areal mass loading being 5 mg cm⁻². The electrodes were dried at 50 °C under vacuum for 6 hours.

5.2.2 Preparation of Mg(CB₁₁H₁₂)₂ Based Electrolytes

[Mg(DME)₃](CB₁₁H₁₂)₂ was synthesized as reported.¹⁴⁴ In a typical synthesis of Mg(CB₁₁H₁₂)₂ in tetraglyme, [Mg(DME)₃](CB₁₁H₁₂)₂ was dissolved in anhydrous tetraglyme with stirring and the resulting clear solution was vigorously stirred under vacuum for 15 mins to remove DME solvent. In a typical synthesis of 0.5 mol kg⁻¹ Mg(CB₁₁H₁₂)₂ in DME/G2 (1:1, w/w), a weighed amount of [Mg(DME)₃](CB₁₁H₁₂)₂ solvate was added to tared 2 ml vial containing a stir bar and the vial was capped with a septum-lined cap. A weighed amount of DME was added with a syringe and the mixture was stirred for about 10 seconds. G2 was then added dropwise with a syringe while stirring until dissolution. All Mg(CB₁₁H₁₂)₂ based electrolytes were prepared in Toyota North America.

5.2.3 Preparation of 0.5M Mg(TFSI)₂ in DME Electrolyte

In a typical synthesis of 5 ml 0.5 M Mg(TFSI)₂ electrolyte, 1.46 g Mg(TFSI)₂ powder (Solvionic, 99.5%) was added to 5 ml DME in a 10 ml glass vial under stirring at room temperature for 24 h to afford a clear solution. This electrolyte was used for solvent-storage mechanism study.

5.2.4 Electrochemical and Material Characterizations

All experiments were conducted at 25 °C, using a potentiostat (VMP-3, Bio-Logic Co., Claix, France) or a battery tester (LAND CT-2001A). All cells were assembled and tested in an argon-filled glovebox (M-Braun Co., Garching, Germany, <0.5 ppm of water and oxygen). Mg foil (50 µm thick, 99.95%, GalliumSource, LLC, Scotts Valley, CA) was polished prior to use and Cu foil was washed with acetone prior to use. Two-electrode Swagelok cells (molybdenum rods as the current collectors) and glass fiber separators (170 µm thick, GF/D grade) were used for all batteries. For Mg|Mg symmetric cells, two Mg metal electrodes were used. For Mg|Cu asymmetric cells, Mg foil was used as counter electrode, and Cu foil served as the substrate for Mg metal deposition. The Cu substrate was preconditioned with 10 times Mg plating/stripping at a current density of 0.5 mA cm⁻² (30 minutes per cycle). Afterwards, Mg was deposited on Cu for another 15 minutes, and then cycling was continued for another 13 times with a fixed stripping/plating time (6 minutes per cycle) before a final complete stripping. The last half-cycle was galvanostatic oxidation with a cutoff voltage of 1.5 V. The coulombic efficiencies for the first 10 cycles are defined by the ratio of stripping capacity and plating capacity. The average coulombic efficiency is calculated by dividing the final stripping capacity by the first plating capacity. For full cells, Mg foil was used as anode,

and PTO or S or P14AQ electrode was used as cathode. All full cells using MMC/G4 electrolytes were tested under constant current/constant voltage charge and constant current discharge modes; the constant voltage charge process was initiated when the charge voltage reached the cut-off and terminated until the charge current density decayed to 0.2C (81.6 mA g⁻¹). All full cells using MMC in DME/G2 electrolytes were tested under constant current/constant voltage charge and constant current discharge modes; the constant voltage charge process was initiated when the charge voltage reached the cut-off and terminated until the charge current density decayed to 0.5C (204 mA g⁻¹). For GO-membrane-incorporated Mg/PTO cells, freestanding GO or GO/GN membrane was sandwiched between PTO electrode and a glass fiber separator. For the study of Mg plating/stripping behavior in MMC/G4 containing polysulfide and Mg₁PTO, we discharged a PTO or S electrodes with MMC/G4 in a Swagelok cell. After the PTO or S discharged to a fresh electrolyte, we replaced PTO electrode with a Cu electrode. We then conducted galvanostatic measurements using this two-electrode Mg|Cu asymmetric cells with polysulfide- or Mg₁PTO-containing solution. Cyclic voltammetric experiment of Mg electrolytes was conducted at a scan rate of 35 mV s⁻¹ in a three-electrode cell using a Pt disk as the working electrode, and Mg ribbons as reference and counter electrodes. Cyclic voltammetric experiments of 0.5 mM S or PTO in acetonitrile containing 0.1M tetra-n-butylammonium perchlorate at different scan rates were conducted in a three-electrode cell using a glassy carbon (GC) as the working electrode, a Pt wire as the pseudo-reference electrode and a Pt disk as the counter electrode. Prior to the measurements, the equivalent serial resistance of the test circuit was determined by EIS measurement in acetonitrile containing 0.1M tetra-n-butylammonium perchlorate. A

pretribulation of 7 mV was applied at the frequencies ranging from 1 MHz to 0.01 Hz. The first intersection with real axis was determined as the equivalent serial resistance. The iR drop in the CV test was then compensated. We used the redox potential of the ferrocene/ferricinium couple as an internal potential reference. We separately performed cyclic voltammetric experiments of 0.5 mM S or PTO with 2 mM ferrocene in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate so that the cyclic voltammograms for PTO or S were not obscured by ferrocene.

5.2.5 Preparation of GO and GO/GN Membranes

The GO film was prepared by dispersing 6 mg graphene oxide powder in 20 ml ethanol by a sonifier (450 Digital Sonifier, Branson) for 30 min. The suspension was filtrated through the Celgard separator to obtain a freestanding film and dried under vacuum at 80 °C overnight. The GO/GN film was prepared by first dispersing 2 mg graphene nano-plates (XG Science, Inc.) in 20 ml ethanol by a sonifier (450 Digital Sonifier, Branson) for 30 min. Then, 4 mg graphene oxide powder (ACS Material, LLC) was added into the suspension and ultrasonicated for another 30 mins. The suspension was filtrated through the Celgard separator to obtain a freestanding film and dried under vacuum at 80 °C overnight. The areal loading for both films was estimated to be 0.4 mg cm⁻².

5.2.6 Characterizations

The discharged and recharged PTO electrodes were characterized by XPS (Physical Electronics Model 5700), ICP-OES (Agilent Technologies, Model 725), sXAS and ATR-FTIR. sXAS was performed at Advanced Light Source in Lawrence Berkeley National Laboratory. IR spectra were performed as single reflection attenuated total reflectance

measurements with powder samples using a Thermo Scientific Nicolet iS 5 instrument and iD 5 ATR accessory. All electrodes were taken out from disassembled cells in an Ar-filled glove box, and ground in an agate mortar with pestle to avoid only surface of the electrodes being measured. The electrodes were dipped in anhydrous DME for 3 minutes, and this procedure was repeated 3 times. The washed electrodes were then vacuum-dried at room temperature for 30 min before characterizations. GO membrane and Cu substrate (with deposited Mg) were characterized by SEM (Gemini LEO 1525 microscopy). Before analysis, Cu electrode was first rinsed with DME solvent three times to remove residual electrolytes and vacuum-dried at room temperature. The cross-section of Cu electrode (with Mg deposition) was prepared by vertically cutting the electrode with a scissor, which led to a detachment of deposited Mg from Cu substrate, resulting in a gap between Mg and Cu.

5.3 Electrochemical Performance of Mg-PTO Batteries in $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2/\text{G4}$

Although conversion materials, such as sulfur, can bypass the issue of sluggish solid-state ion diffusion, it is well known that there are so many problems for Mg-S batteries. One of the greatest problems associate with the process of the bond-formation and -breaking during the reduction of S_8 .¹⁵⁴ Although the reduced sulfur, such as S_4^{2-} , can be re-oxidized, the process is considered as electrochemically irreversible, resulting in the limited rate capability. The cyclic voltammograms of S_8 are shown in Figure 5.1a. The first set of peaks is attributed to the reduction of S_8 to S_8^{2-} ,¹⁵⁶ and this step is considered irreversible, since at the scan rate of 100 mV s^{-1} , the peak separation width (ΔE_a) was 259 mV, which was significantly larger than 29.5 mV (for an electrochemical reversible process, ΔE_a should be less than $59/n$, $n=2$ here), and the peak potentials were scan-rate

dependent.¹⁵⁷ At more negative potentials, another 2-electron reduction step occurred (S_8^{2-} to $2S_4^{2-}$)¹⁵⁶. The peak separation width (ΔE_b) was 83.2 mV, also indicating an irreversible redox process. Therefore, the intrinsic irreversible redox process of S_8 enables Mg-S batteries to have poor performances at high current densities. In comparison, a high power-rate performance is expected for an organic material, because its intrinsic ion-coordination charge storage mechanism does not contain any bond-formation and – breaking, and hence the reaction process is expected to be very rapid.¹⁵⁸ PTO molecule theoretically undergoes a four-electron transfer that corresponds to a specific capacity of 408 mAh g⁻¹, and therefore four pairs of peaks are observed in Figure 5.1b. At the scan rate of 100 mV s⁻¹, the values of ΔE_a (78.4 mV), ΔE_b (54.9 mV), and ΔE_c (71.7 mV), were lower than 79 mV, which are indicative of reversible redox processes for the first three mono-electronic couples.¹⁵⁹ The value of ΔE_d (92 mV) is indicative of a quasi-reversible process for the last redox step.¹⁵⁹ Besides, the potentials of all peaks were independent with the scan-rate. The (quasi)-reversible electrochemically reversibility of PTO demonstrates that its ion-coordination redox process is sufficiently fast, and which can potentially be used as high power-rate electrode-active materials.

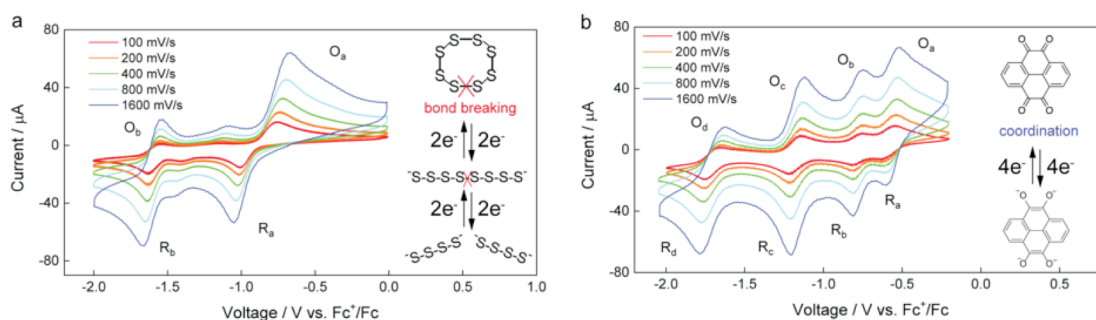


Figure 5.1 Cyclic voltammograms of 0.5 mM (a) sulfur and (b) PTO in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate.

The electrochemical performances of PTO were evaluated in MMC/G4 first. The typical galvanostatic charge-discharge profiles of Mg-PTO cell are shown in Figure 5.2a, which exhibited a specific capacity of 315 mAh g⁻¹, and an average discharge voltage of 2.0 V. Two well-defined plateaus were observed during discharge process, corresponding to solid-liquid and liquid-solid phase transitions. A series of characterizations were conducted to understand the reaction mechanism of the Mg/PTO battery. As shown in the inset of Figure 5.2a, the PTO electrodes were taken out from the cells at different states of discharge and were washed in DME. The pristine PTO electrode slightly dissolved into the electrolyte, leading to the color of the DME solution turned into light yellow. The transparent DME solution quickly changed to purple once PTO electrode taken out from the half-discharged cell at 2.0 V was put in, indicating the intermediate is soluble in the electrolyte. Whereas the electrode taken out from the fully discharged cell at 0.9 V has negligible solubility in electrolyte and the DME solution maintained transparent.

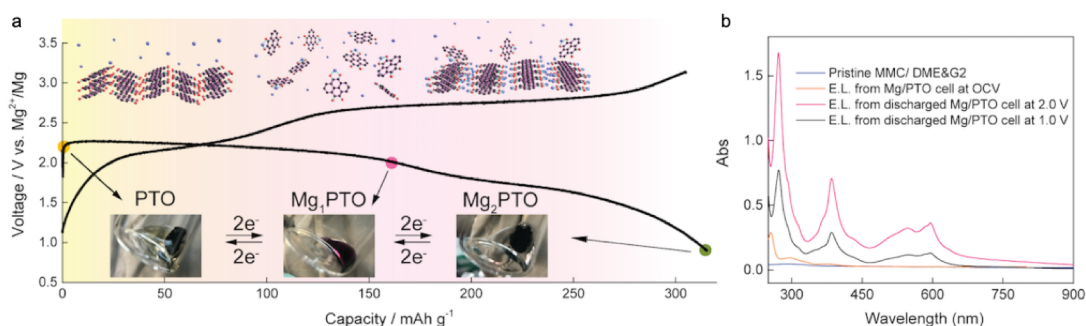


Figure 5.2 (a) Voltage profiles of PTO. Inset: liquid-solid two-phase reaction pathways of PTO. (b) UV-vis absorption spectra of electrolytes taken from the cells at different states of discharge.

To examine how many intermediates dissolved in the electrolyte during discharging, ultraviolet-visible spectroscopy (UV-vis) was used to monitor the change of electrolyte composition (Figure 5.2b). The samples were collected by immersing the PTO electrodes

and the separators at different discharged states in DME solutions. Apparently, the absorption spectra of the electrolyte from the half-discharged cell was the same as that of electrolyte from the fully discharged cell, however, was different from that of the electrolyte from the cell before discharge. This result indicates that only one soluble intermediate formed during discharge. Based on these observations, we proposed the following reaction pathways during the reduction of PTO:

Stage 1: A solid-liquid two-phase reduction from PTO to Mg_1PTO , which shows the first upper voltage plateau. In this region, PTO is partially reduced and forms a soluble intermediate, Mg_1PTO , through a coordination of one Mg^{2+} with two carbonyl groups at the same side of PTO. The reaction is



Stage2: A liquid-solid two-phase reduction from the soluble Mg_1PTO to insoluble Mg_2PTO through a coordination of 2nd Mg^{2+} with two carbonyl groups at the other side of PTO. This region forms the second lower voltage plateau. The reaction is

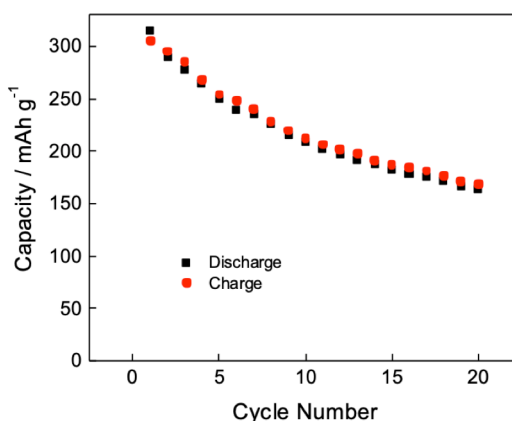
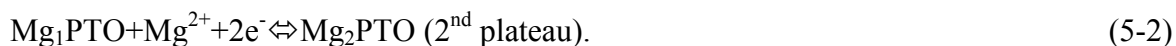


Figure 5.3 Cycling performance of Mg-PTO cell without GO membrane at a current density of 81.6 mA g^{-1} (0.2 mA cm^{-2} ; 0.2C).

Soluble intermediate, Mg_1PTO , led to the capacity decay (Figure 5.3). Therefore, we proposed a unique Mg-PTO battery configuration with an ultrathin graphene oxide (GO) membrane for high cycling stability (Figure 5.4a). It was reported that the carboxyl groups on the GO membrane acted as ion-hopping sites of positively charged species (Mg^{2+}) and rejected the transportation of negatively charged species due to the electrostatic interactions.¹⁶⁰ Hence, the GO membrane is expected to be permeable for Mg^{2+} ions but reject negatively charged species (PTO^{2-}), and which are expected to be confined at the cathode side. Moreover, the typical 2D structure of a GO flake can reduce the loading amount to form an effective shield layer.

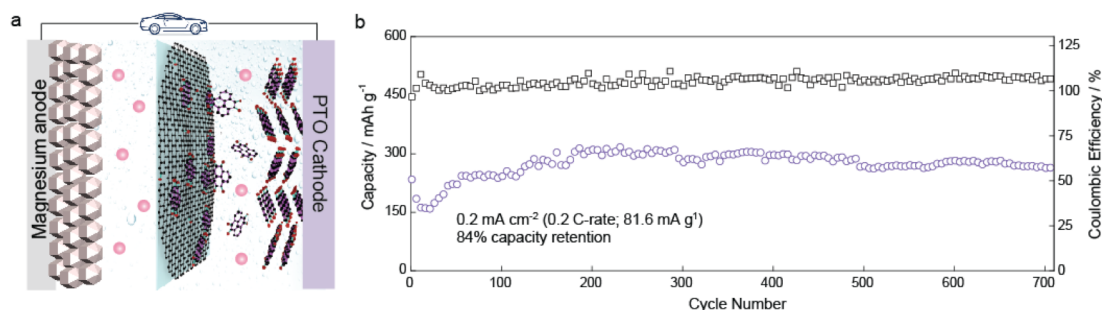


Figure 5.4 (a) Schematic of a GO-membrane-incorporated Mg-PTO cell. (b) Cycling performance of a GO-membrane-incorporated Mg-PTO cell.

As shown in Figure 5.5, the thickness of the freestanding GO membrane is only 2 μm with a light weight of 0.4 mg cm^{-2} , so the volume and weight of this thin layer are negligible compared to a commercial separator with 25 μm thickness and 2 mg cm^{-2} weight. The use of the GO membrane is of great significance in improving the cycling stability (Figure 5b). The capacity underwent a drop-then-climb phenomenon in first 200 cycles, which could be ascribed to the delayed electrolyte penetration into the electrode.¹⁶¹ After this activation process, the reversible capacity increased to 310 mAh g^{-1} and was stabilized therein for another 500 cycles with a high-capacity retention of 84%.

The contribution from carbon, PTFE, and GO membrane to the cell capacity was negligible. Such stable cycle performance for Mg batteries has rarely been reported. After first several cycles, the average coulombic efficiency is slightly beyond unity at 106.5%, which we ascribe to shuttle effect, since it is inevitable to have Mg_1PTO loss during discharge/charge and the GO membrane cannot fully block soluble Mg_1PTO at cathode side. The optimization of GO membrane in future could further improve the cycling stability, coulombic efficiency and voltage hysteresis.

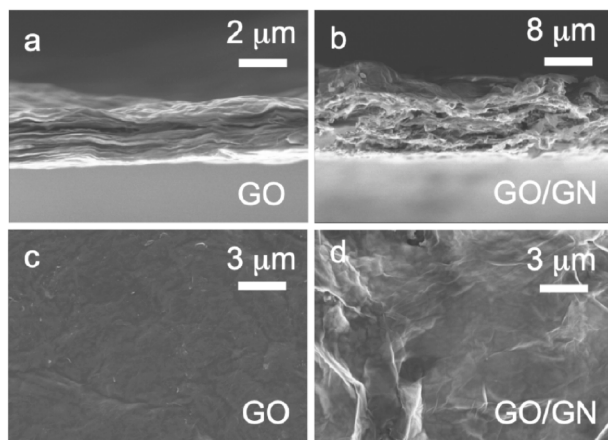


Figure 5.5 (a and b) Cross section morphology of graphene oxide (GO) and graphene oxide/graphene nanoparticle (GO/GN) hybrid membranes. (c and d) Surface morphology of GO and GO/GN membranes.

5.4 Characterizations of PTO Cathode and Mg Anode

Recent report showed that soluble discharged product could strongly affect the behavior of the Mg anode. For example, because of the high solubility of polysulfide (PS) and polyiodide, the inevitable shuttle effect can lead to the passivation of the Mg anode.^{105, 107} We found the Mg plating/stripping behavior was significantly affected in PS-containing MMC/G4. As shown in Figure 5.6a and Figure 5.6d, the coulombic efficiencies for Mg plating/stripping in PS-containing electrolyte were lower than that in pristine one, and meanwhile, a very large, spike-like, overpotential developed during

cycling. This observation is in accordance with Aurbach's results,¹⁰⁷ which has been attributed to the reduction of polysulfide species on the Mg anode surface, resulting in the formation of an insoluble passivation layer consisting of MgS. This layer possesses extremely low ionic and electronic conductivity. Similar with the soluble polysulfides, intermediate Mg_1PTO could also affect the behavior of the anode side.

To illustrate the effect of Mg_1PTO on Mg anode, we discharged a PTO electrode with MMC/G4 in a Swagelok cell. After the PTO discharged to a fresh electrolyte, we replaced PTO electrode with a Cu electrode. We then conducted galvanostatic measurement using this two-electrode asymmetric cell with Mg_1PTO -containing solution.

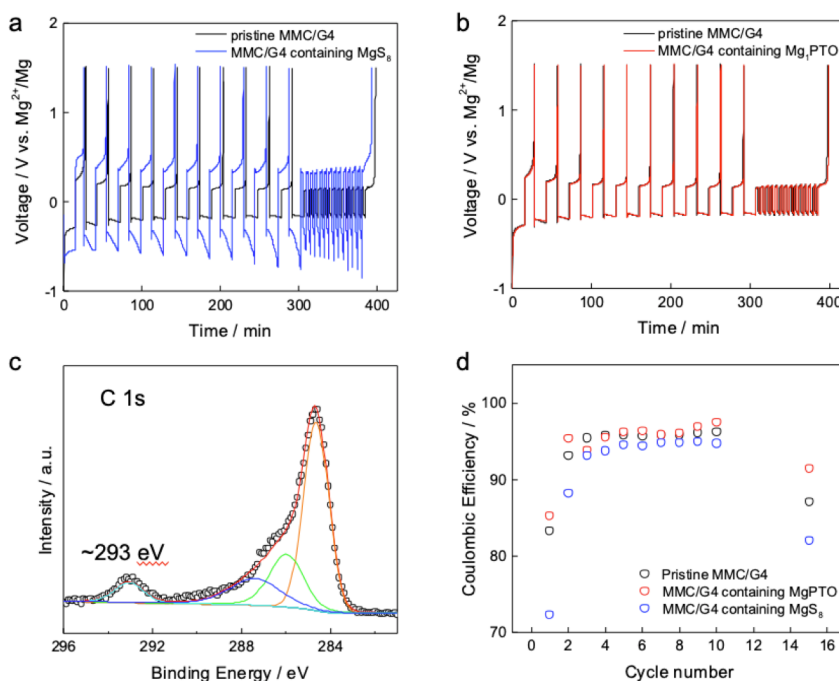


Figure 5.6 (a and b) Electrochemical performances of Mg|Cu asymmetric cells in MMC/G4 containing polysulfide and Mg_1PTO . (c) XPS for Mg anode (Mg_1PTO cell). (d) Coulombic efficiencies of above two cells.

As shown in Figure 5.6b and Figure 5.6d, the coulombic efficiencies and overpotentials for Mg plating/stripping in MMC/G4 containing Mg_1PTO were the same as those in pristine one. Mg anode later was taken out and investigated by high resolution

X-ray photoelectron spectroscopy (XPS), where the peak at 293 eV corresponding to π - π^* interaction was observed, which indicates that intermediate Mg_1PTO was further reduced and finally precipitated on Mg anode (Figure 5.6c). Even with an organic layer formed on Mg anode, the plating/stripping behavior was not affected. The addition of organic molecules in the electrolyte or on Mg anode is always regarded as an efficient way to enhance the reversibility of Mg plating/stripping.¹⁶²

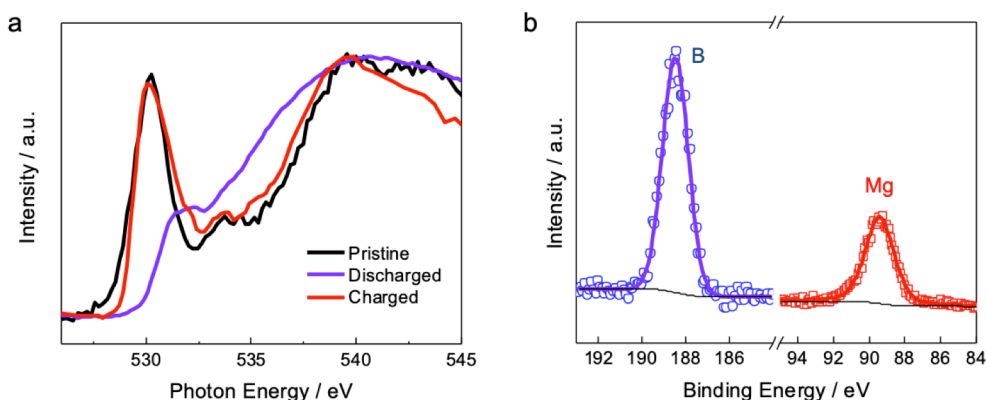


Figure 5.7 (a) O K-edge sXAS of pristine, discharged and recharged PTO electrodes. (b) XPS of B 1s and Mg 2p for discharged PTO electrode.

To shed light on the chemical environment change of PTO during Mg coordination/de-coordination process, we carried out synchrotron radiation based soft X-ray absorption spectroscopy (sXAS) measurement. Figure 5.7a shows sXAS for pristine, discharged, and recharged PTO electrodes at the O K-edge. The pristine sample showed the main absorption peak at 530.5 eV as the result of $\text{O } 1s (\text{C}=\text{O}) \rightarrow \pi^*_{\text{C}=\text{O}}$ transition.¹⁶³ With Mg^{2+} coordination, the main peak showed a clear shift to higher energy caused by the reduction of carbonyl groups of PTO. The $\text{O } 1s \rightarrow \sigma^*_{\text{C-O}}$ transition is always present at higher energy compared to $\text{O } 1s (\text{C}=\text{O}) \rightarrow \pi^*_{\text{C}=\text{O}}$ transition.¹⁶³ As Mg^{2+} were removed from the PTO electrode, the K-edge absorption peak returned to the pristine peak position, indicating a reversible redox reaction. The PTO electrode at discharged state

was subjected to XPS analysis. As shown in Figure 5.7b, both Mg and B signals were observed with the atomic ratio of Mg:B being 1:2.12. Inductively coupled plasma (ICP) spectroscopy of the discharged sample also showed the similar Mg:B atomic ratio of 1:2.54. There are two possibilities of the appearance of B signal. One is hybrid ion $\text{Mg}(\text{CB}_{11}\text{H}_{12})^+$, and the other is residual solute $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$. Even if all observed B coordinated with PTO as $\text{Mg}(\text{CB}_{11}\text{H}_{12})^+$, the ratio of Mg^{2+} and $\text{Mg}(\text{CB}_{11}\text{H}_{12})^+$ would be around 4:1, i.e., Mg^{2+} being the dominant storage species. However, based on the calculation of ICP result, the content of Mg^{2+} in the discharged PTO electrode was 3.02 wt%, when considering B was from residual solute $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$, which was very close to the theoretical Mg^{2+} content of 3.17 wt% in the discharged sample. Also, considering the fact that the anion $\text{CB}_{11}\text{H}_{12}^-$ is weakly coordinating to Mg^{2+} , the possibility of $\text{Mg}(\text{CB}_{11}\text{H}_{12})^+$ is less likely.

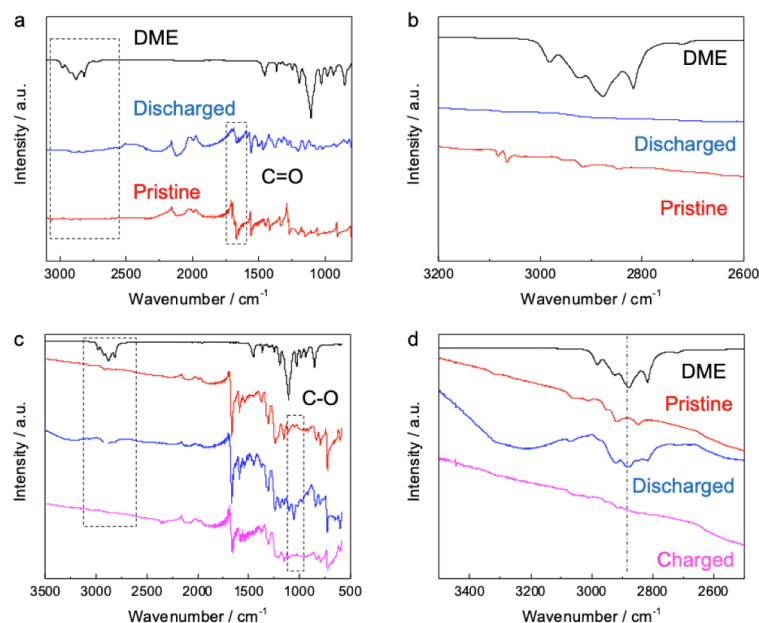


Figure 5.8 (a) The FTIR spectra of DME and PTO electrodes. (b) Magnified view of the region outlined in (a). (c) The FTIR spectra of DME and P14AQ electrodes. (d) Magnified view of the region outlined in (c).

Moreover, the discharged PTO electrode prepared in an Mg electrolyte based on pure DME, was analyzed with fourier-transform infrared spectroscopy (FTIR). Firstly, the intensity of the carbonyl vibration peak (1650 cm^{-1}) declined (Figure 5.8a), indicating a reduction reaction of carbonyl group. Besides, as shown in Figure 5.8b, no DME signal was detected, indicating no solvent co-storage. In contrast, for the polymer electrodes (P14AQ) at different states of charge, obvious DME signal arose upon discharge, and then vanished when recharged (Figure 5.8c and d). This result suggests co-storage of cations and solvent molecules in organic polymers. The different ion storage chemistries could be attributed to the different reaction mechanism. Although both of small molecule (PTO) and polymer (P14AQ) are rely on ion-coordination charge storage mechanism, the former is based on a dissolution/precipitation process, and later is based on swelling. Deeper mechanism study is ongoing.

5.5 Electrochemical Performance of $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DME/G2

As shown in Figure 5.9, PTO can deliver a capacity of 176 mAh g^{-1} at a high current density of 2040 mA g^{-1} . This rate performance has surpassed that of all previously reported Mg batteries, which confirms our hypothesis that the combination of liquid-solid two-phase reaction and ion-coordination charge storage mechanism can dramatically enhance the kinetics of Mg batteries. However, it is still far from of our expectation.

We later realized the rate performance could be limited by the G4 based electrolyte, since its high viscosity and stronger coordination to Mg^{2+} may hinder ion mobility and render high solvation/desolvation barriers. Ultimately, these may lead to increased overpotentials and lower battery rate capabilities. Therefore, the ability of the MMC salt to function in a less coordinating system, such as DME and G2, is highly desirable to

enable much improved battery performance. We report a solution that overcomes the solubility challenge of MMC in short-chain ethers and produces a highly functioning Mg electrolyte.

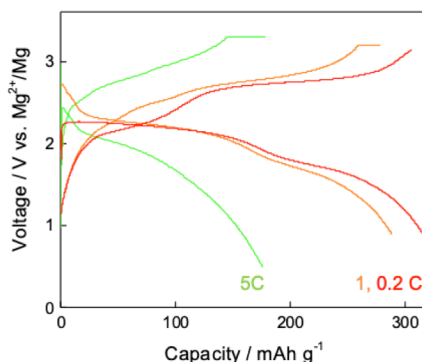


Figure 5.9 Rate performances of PTO in MMC/G4.

Clues to any possibility to dissolve the MMC salt in short-chain ethers were inconspicuous within the synthesis of MMC solvates reported in our initial study of MMC/G4 as electrolyte for Mg batteries. During searching for an optimal solvent to extract the resulting MMC-THF solvate from other solid-state reaction by-products, we discovered that although DME failed to dissolve MMC-THF solvate at room temperature, it succeeded upon addition of a slight amount of THF. The suspected cooperative effect between THF and DME to dissolve MMC was later successfully confirmed in a separate experiment, in which slow addition of THF to a suspension of MMC-DME solvate in DME eventually yielded a clear solution. These initial findings inspired the exploration of ether mixtures as a route to prepare MMC electrolytes in ethereal solvents beyond G3 and G4. Finally, we successfully dissolved $0.5 \text{ mol kg}^{-1} \text{ Mg}(\text{CB}_{11}\text{H}_{12})_2$ in a mixture of DME of G2.

Cycling efficiencies for MMC in DME/G2 were evaluated through macro reversibility measurements involving galvanostatic cycling of Mg plating/stripping on Cu

disk at 0.5 mA cm^{-2} (Figure 5.10a). The average coulombic efficiency can be up to 99.5%, demonstrating excellent electrolyte performance.

The availability of electrolyte systems capable of achieving ultrahigh rates offers a unique opportunity to probe the behavior of Mg metal under unexplored conditions, which pushes the boundaries of Mg metal cycling possibilities. As shown in Figure 5.10b, the Cu|Mg asymmetric cell was used to investigate the rate capability of Mg plating/stripping. Remarkably, although the polarization of the cell increased with increasing current density, Cu|Mg cell with MMC in DME/G2 can be cycled at different current densities with high coulombic efficiency of $\sim 99\%$, even at an ultrahigh current density of 50 mA cm^{-2} .

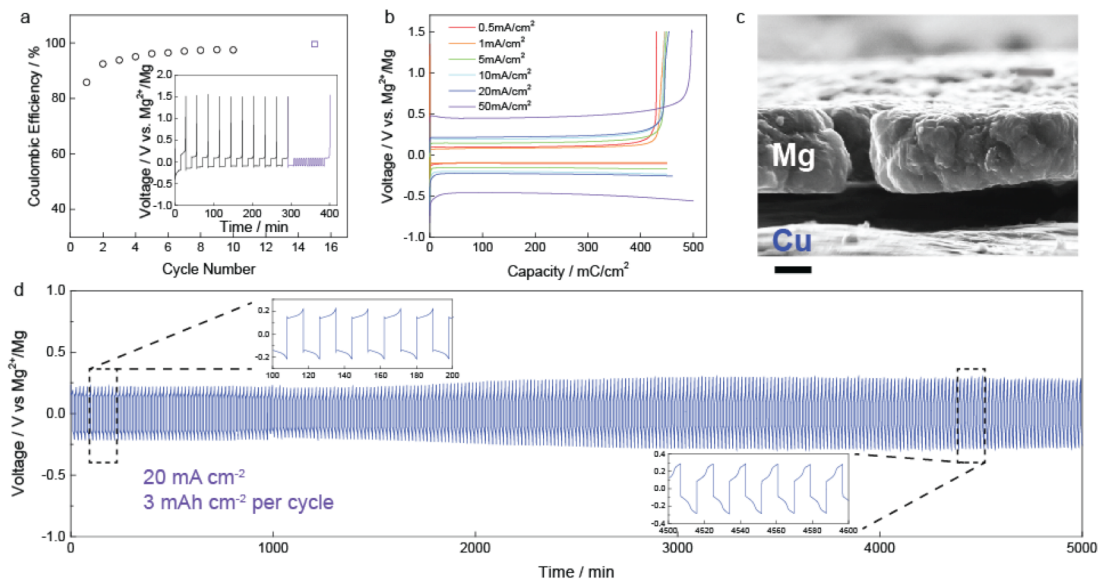


Figure 5.10 (a) Coulombic efficiencies of an Mg|Cu asymmetric cell. (b) Rate performance of an Mg|Cu asymmetric cell. (c) Morphology of deposited Mg on Cu. Scale bar: $3 \mu\text{m}$. (d) Cycling stability of an Mg|Mg symmetric cell.

Examination of the morphology of Mg deposited on Cu electrode (at a high current density of 20 mA cm^{-2} with an areal capacity of 3 mAh cm^{-2}) reveals a densely smooth dendrite-free morphology (Figure 5.10c). Observation of non-dendritic Mg deposition at

such high current densities is to our knowledge unprecedented, and consolidates Mg metal as promising anode for advanced batteries. A symmetric Mg|Mg cell was used to further investigate the stability of the Mg metal anode in MMC in DME/G2 (Figure 5.10d). An exceptionally high current density of 20 mA cm^{-2} was used and the cell was cycled for over 5000 minutes, which corresponded to almost 300 plating/stripping cycles. It is noteworthy that the per-cycle plating capacity was 3 mAh cm^{-2} , corresponding to a high cumulative capacity plated of 833 mAh cm^{-2} . This testing condition is markedly stricter than that used in previously reported Mg|Mg symmetric cells.^{153, 164} These results further demonstrate the unprecedented cycling stability of Mg metal anode with MMC in DME/G2 electrolyte at such a high current density. These findings not only point to the positive attributes of the reported electrolytes but also underscore the uniqueness of Mg metal in tolerating such high rates. Our results set a new precedence for possibilities achievable using energy dense metals and offered a new and important motivation towards research on Mg metal batteries.

5.6 Electrochemical Performance of Mg-PTO Batteries Based on $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DME/G2

By coupling PTO cathode with the electrolyte of MMC in DME/G2, finally I create a high-performance Mg battery. As shown in Figure 5.11a, at intermediate current densities of 204 and 408 mA g^{-1} (0.5 and 1 mA cm^{-2}), the two discharge plateaus became more obvious compared with those in MMC/G4, and the highest reversible capacity and average discharge voltage can be up to 312 mAh g^{-1} and 2.1 V , respectively. To the best of our knowledge, this is the highest voltage reported for Mg batteries so far. The high capacity and voltage enable the cell to deliver a specific energy of 566 Wh kg^{-1} .

Moreover, the rate capability was significantly improved. Even at the current density of 20 and 50 mA cm⁻², the capacity of 278 and 210 mAh g⁻¹ can be retained, respectively, which lead to an ultra-high specific power of 30 kW kg⁻¹.

The permeability of GO membrane for cations is important for its performance at high current density. In order to prevent the performance (voltage hysteresis, etc.) of Mg-PTO cell from being affected by GO membrane, we improved the permeability of the GO membrane with the addition of some graphene nanoparticles (Figure 5.5b and d). The hybrid graphene oxide/graphene nanoparticles (GO/GN) film can facilitate the Mg²⁺ diffusion in the membrane at the expense of having some intermediate Mg₁PTO loss. As shown in Figure 5.11b, with the help of GO/GN membrane, the cell underwent over 200 cycles with 82% capacity retention at a high current density of 2040 mA g⁻¹ (5 mA cm⁻¹). Again, this was a preliminary experiment to show the dissolution issue of intermediate (Mg₁PTO) can be greatly mitigated by using a GO membrane. Future work on tailoring the physical/chemical properties of the host for better intermediate (Mg₁PTO) entrapment is still ongoing. In theory, all effective methods used in Li/S batteries can be adopted in Mg/PTO batteries.

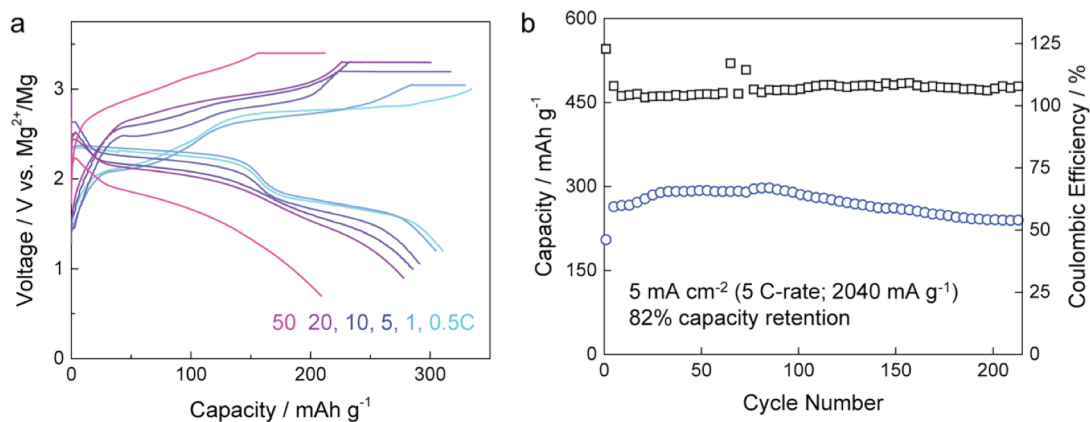


Figure 5.11 (a) Rate performances of PTO with MMC in DME/G2. (b) Cycling performance of a GO/GN-membrane-incorporated Mg-PTO cell.

5.7 Conclusions

In conclusions, firstly I overcame the solubility limitation of $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in the less coordinating ethers through the utilization of the mixture of DME and G2. This is the first time to certify that Mg metal is intrinsically resistant to dendrite formation even at ultra-high current density of 50 mA cm^{-2} . Thus, MMC in DME/G2 has set new high bar for Mg electrolytes, and paved the way to discover an unexplored dimension of Mg metal behavior that further motivate research of Mg batteries. Furthermore, I reported an organic molecule, PTO, can effectively circumvent the solid-state Mg^{2+} diffusion through a liquid-solid two-phase reaction. Also, the ion-coordination charge storage mechanism of PTO does not involve any bond-formation and -breaking, enabling it to work under ultra-high current density.

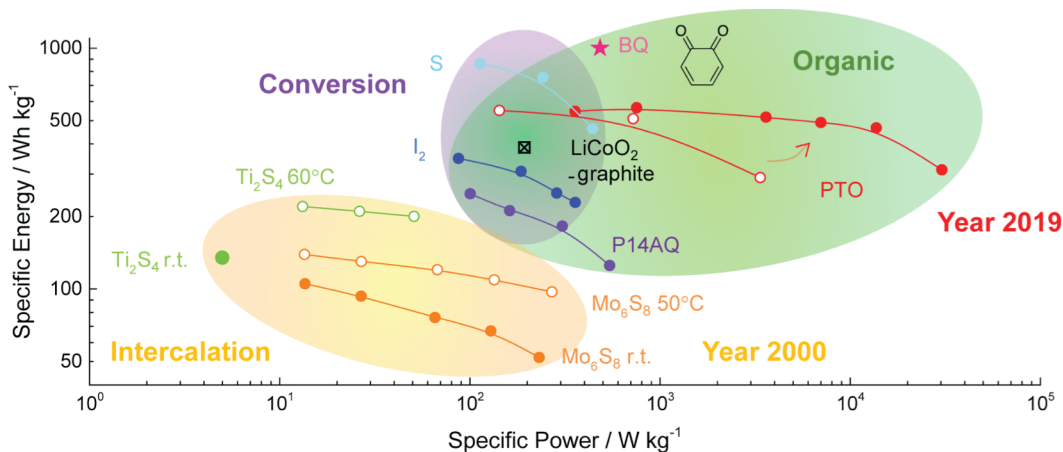


Figure 5.12 Ragone plot of a graphite/LiCoO₂ cell and representative Mg batteries based on intercalation-, conversion-type, and organic cathodes.

As shown in Figure 5.12, representative intercalation-type cathodes, such as Mo₆S₈ and s-Ti₂S₄, can only achieve moderate specific energy and power at elevated temperature, but which are still not comparable with those of current Li-ion technology. Conversion materials, such as S, can deliver a high specific energy in terms of its very high theoretical capacity, however, its specific power is still at a relatively low level due

to its intrinsic electrochemically irreversibility. Moreover, a limited cycle life due to the passivation layer on the Mg anode currently does not have any reliable solution. In contrast, PTO can achieve a specific energy of 566 Wh kg⁻¹ and an ultrahigh power of 30 kW kg⁻¹, which have surpassed current Li-ion technology.

The low density of organic materials is often criticized, however, in the case of Mg/PTO cell, the volumetric energy density of Mg-PTO cell is much higher than that of Mg batteries based on intercalation-type materials, and it has absolute advantage in volumetric power density (Figure 5.13).

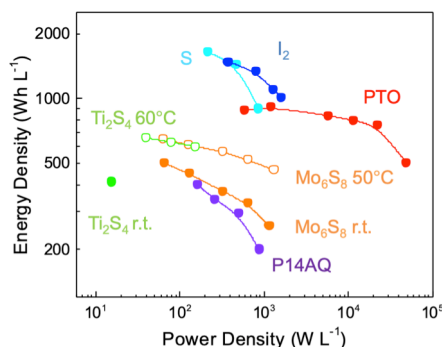


Figure 5.13 Ragone plot (volumetric energy density vs. volumetric power density) of representative Mg batteries based on intercalation-, conversion-type, and organic cathodes.

The structural diversity of organic compounds enables us to design molecules with higher capacity and voltage to fulfill higher energy Mg batteries, such as Benzoquinone (BQ), which with a theoretical capacity of 515 mAh g⁻¹ and a voltage of 2.4 V vs. Mg²⁺/Mg. Theoretically, the specific energy of Mg-BQ cell can be up to 1000 Wh kg⁻¹, even higher than Mg-S cell (Figure 5.12).¹⁶⁵

Nevertheless, the exclusive use of organic compounds as cathodes is sometimes regarded impractical in high mass-loading electrodes due to their poor electronic conductivity. In order to overcome the insufficient electronic conductivity, organic

electrodes frequently require a huge amount of carbon. In the case of Mg/PTO cell, as shown in Figure 5.14, the electrodes with 60% active materials (PTO) and high mass-loading of 5 mg cm^{-2} still can deliver a high capacity of 262 mAh g^{-1} and voltage of 2.1 V at a high current density of 408 mA g^{-1} . Even at 4080 mA g^{-1} , a decent capacity of 186 mAh g^{-1} was still retained.

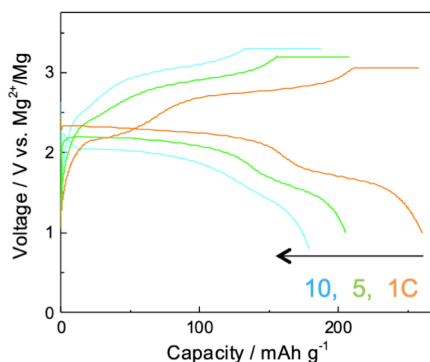


Figure 5.14 Electrochemical performances of Mg/TPO batteries with high mass loading PTO electrodes (5 mg cm^{-2} and the ratio of PTO/KB/PTFE is 6/3/1).

Moving forward, designing electrodes with higher mass loading, and higher active material ratio would be as important as developing better cathode materials for achieving truly high practical cell-level energy.¹⁶⁶ All in all, the prototype Mg-organic battery demonstrated the feasibility of combining liquid-solid two-phase reaction and ion-coordination charge storage mechanism to address the major challenges for the development of Mg cathode materials. This concept can significantly boost and promote the field of Mg batteries.

Chapter 6 Methodologies

6.1 Preparation of Efficient Mg Electrolytes

This section focuses on the details of the synthesis of various non-nucleophilic chloride-containing Mg electrolytes. All $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ based electrolytes were synthesized in Toyota North America as reported.³³

6.1.1 Synthesis of Various Mg Electrolytes

All experiments need to be conducted in an argon filled glove box (M-Braun). MgCl_2 (Alfa Aesar, 99.999%) and $\text{Mg}(\text{HMDS})_2$ (Sigma-Aldrich, 97%) can be used without drying. $\text{Mg}(\text{TFSI})_2$ (Solvionic, 99.5%) needs to be dried under vacuum for 24 h at 250 °C before use. Solvents (THF, DME, G2, G4) need to be pretreated with molecular sieves (Aldrich, 3 Å beads, 4-8 mesh) for two days before use unless otherwise specified. Molecular sieves need to be dried under vacuum for 24 h at 200 °C before use.

Preparation of 0.25 M $\text{Mg}(\text{TFSI})_2$ and 0.5 M MgCl_2 in DME electrolyte:

In a typical synthesis of 5 ml 0.25 M $\text{Mg}(\text{TFSI})_2$ and 0.5 M MgCl_2 electrolyte, 0.73 g $\text{Mg}(\text{TFSI})_2$ powder was added to a suspension of MgCl_2 (0.24 g in 5 ml DME) in a 10 ml glass vial. The mixture was stirred at 70 °C for 6 h in a sand bath and then cooled down to room temperature to afford a clear solution.

Preparation of 0.2 M $\text{Mg}(\text{TFSI})_2$ in diglyme electrolyte:

In a typical synthesis of 5 ml 0.2 M $\text{Mg}(\text{TFSI})_2$ electrolyte, 0.58 g $\text{Mg}(\text{TFSI})_2$ powder was added to 5 ml diglyme in a 10 ml glass vial under stirring at room temperature for 2 h to afford a clear solution.

Preparation of 0.3 M $\text{Mg}(\text{HMDS})_2$ and 1.2 M MgCl_2 in THF electrolyte:

In a typical synthesis of 5 ml 0.3 M Mg(HMDS)₂ and 1.2 M MgCl₂ electrolyte, 0.52 g Mg(HMDS)₂ powder was added to a suspension of MgCl₂ (0.57 g in 5 ml THF) in a 10 ml glass vial. The mixture was stirred at room temperature for 48 h to afford a clear solution.

6.1.2 Conditioning of MgTFSI₂-MgCl₂ Based Electrolytes

Some papers demonstrated a procedure termed “conditioning” to enhance the electrochemical performance of some Mg electrolytes, especially for MgTFSI₂-MgCl₂ based electrolytes.⁶⁹ Although till now people did not have enough evidence to determine why the process has such an enormous effect on the electrochemical performance, Aurbach et al. believed that the elimination of impeding impurities during the process is a major reason.⁶⁹ Later, Gewirth et al. proposed an additional mechanism for such “conditioning” processes, which has a chemical nature.¹⁴⁵

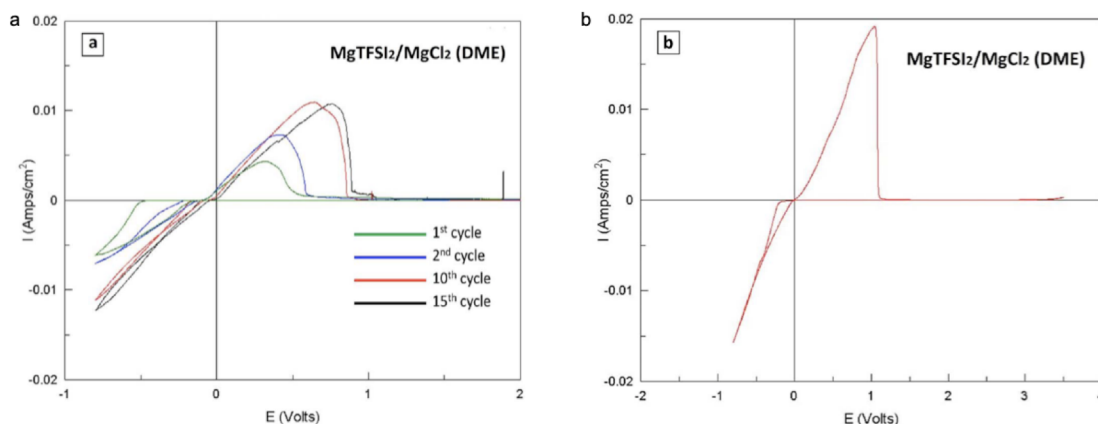


Figure 6.1 (a) Selected CV cycles during the conditioning procedure. (b) A typical cyclic voltammogram of a conditioned solution. Reprinted with permission from Ref. 69. © 2015 Electrochemical Society.

For example, Figure 6.1 shows consecutive voltammograms of a Pt wire in the electrolyte of MgTFSI₂/MgCl₂ in DME during the conditioning process.⁶⁹ The conditioning process consists of cycling at 1 mV s⁻¹ between -0.8V and 2.0 V. During

consecutive cycles, an enhancement in the reversibility of the Mg plating process is clearly observed, expressed by lower overpotential and higher coulombic efficiency. Following the conditioning process, the electrolyte retains its newly obtained enhanced electrochemical properties when introduced to a fresh cell with fresh electrodes. The post-condition electrolyte exhibits 98% reversibility, overpotential for plating of 0.2 V.

6.2 Electrochemical Measurements

6.2.1 Three-Electrode Cell Setup

Tubular hermetically sealed three-electrode cell set-up (Figure 6.2) is always used for evaluation of cathodes performances so that their voltage profiles of cathodes are not obscured by the overpotential for Mg plating/stripping. In the three-electrode tube cell, the electrodes of interest are used as working electrodes. Freshly polished magnesium foils (50 μm thick, 99.95%, GalliumSource, LLC, Scotts Valley, CA) are used as both counter and reference electrodes.

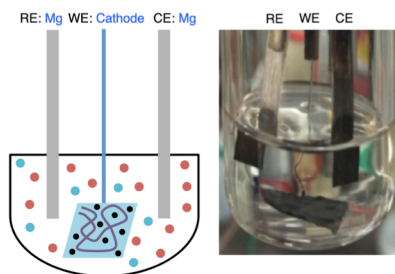


Figure 6.2 Schematic and optical image of a tubular hermetically sealed three-electrode cell.

6.2.2 Swagelok Cell Configuration

As shown in Figure 6.3, two-electrode Swagelok cells are always used for most Mg batteries, since molybdenum rods can be used as the current collectors due to its anti-corrosion property. A glass fiber separator (0.2 or 0.6 μm thick, GF/D grade) was placed between two electrodes.

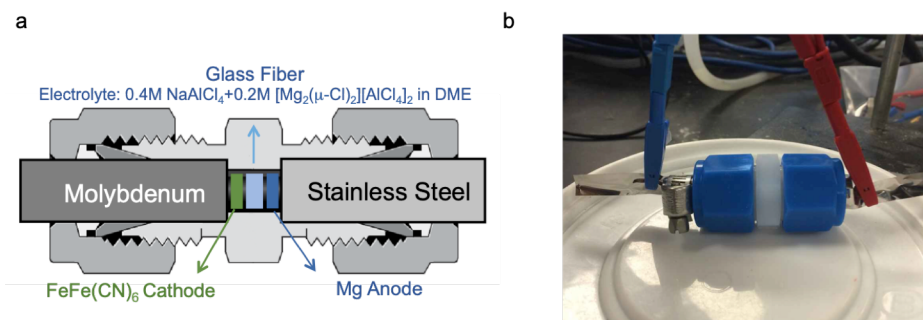


Figure 6.3 (a) Schematic and (b) Picture of a Swagelok cell.

6.2.3 Electrochemical Methods for Metal-Electrolyte Characterization

The electrochemical characteristics of Mg electrolytes can be assessed by established methods. Cyclic voltammetry performed on inert substrates using a three-electrode configuration provides rich information including coulombic efficiency, plating/stripping potentials and overpotentials, electrode kinetics, and even clues of nucleation/growth mechanism (Figure 6.4a). These information would be essential for validating novel systems, especially those where plating/stripping of multivalent metals were not considered possible.¹⁵ Galvanostatic measurements using two-electrode asymmetrical Mg|Cu cell and symmetrical Mg|Mg cell are gaining popularity due to the widespread use in lithium metal anode studies. These methods have the advantage of operating under conditions more akin to those for full cells tests. Measurements in asymmetric cells accurately indicate the reversible metal plating coulombic efficiency in any relevant electrolyte solutions (Figure 6.4b),¹⁶⁷ while measuring symmetrical cells can assess rate capability and cycle life (Figure 6.4c).

Typical cyclic voltammogram showing a cathodic loop and an anodic peak. Coulombic efficiency (C.E.) is defined by the ratio of passed charges during the cathodic

(*b*) and anodic (*a*) processes. Plating overpotential (*c*) is measured as the delay of cathodic current. Stripping overpotential is often negligible in efficient electrolyte solutions. (Figure 6.4a)

Galvanostatic measurement using two-electrode asymmetrical cells. A constant cathodic current is applied at the inert working electrode for a period of time (*d*), enough for plating a meaningful thickness of metal, before being reversed for complete stripping. The process is repeated for multiple times as a substrate preconditioning measure. After a final plating, cycling is continued with a fixed plating/stripping time *e* ($e < d$) before a final complete stripping that lasts for a period of *f*. C.E. is defined by the ratio of *f* and *d*. (Figure 6.4b)

Galvanostatic measurement of two-electrode symmetrical cells. Cycling is performed with a fixed plating/stripping time. The performance is gauged by overpotential *g*, the sum of plating and stripping overpotentials, and the total charge passed during the measurement. Increasing current densities may be used to probe the electrode kinetics and current tolerance. (Figure 6.4c)

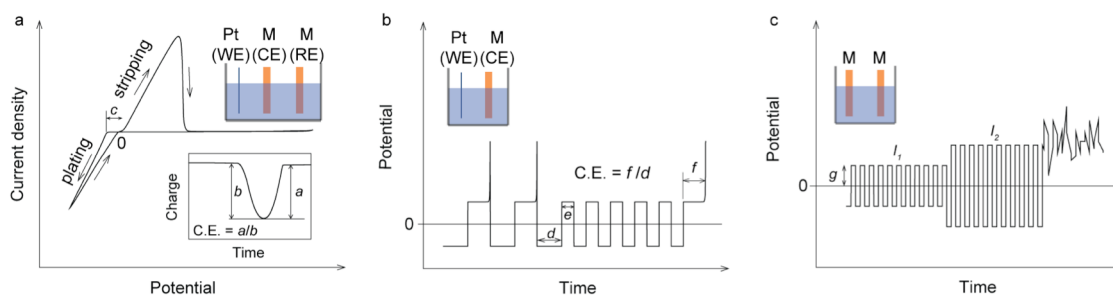


Figure 6.4 (a) Cyclic voltammetry of an electrolyte. (b) Galvanostatic measurement using an asymmetric cell. (c) Galvanostatic measurement using a symmetric cell.

Unlike the non-aqueous lithium electrochemistry which is relatively established in terms of the correlation between surface chemistry and electrochemical performance,

with multivalent metals surface chemical aspects which may be detrimental to any electrochemical activity are not yet fully understood. If there are side reactions that form surface species, they can fully obscure the electrochemical activity of the multivalent active metal electrodes.

6.2.4 Electrochemical Quartz Crystal Microbalance with Dissipation (EQCM-D)

Quartz crystal microbalance with dissipation monitoring (QCM-D) is a real-time, nanoscale technology for observing the surface phenomena including thin film formation, interactions and reactions.¹⁶⁸ QCM-D monitors the frequency and energy dissipation response of the freely oscillating sensor, thus generating results more accurately and faster. For rigid films, the mass of the adhering layer is calculated using the Sauerbrey equation, which is

$$\Delta m = -(C \times \Delta f)/n, \quad (6-1)$$

where m is the mass of the film, C is $17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ for a 5 MHz quartz crystal, and $n = 1, 3, 5, 7$ is the overtone number. However, in most applications, the films are not rigid and the Sauerbrey equation becomes invalid. A soft film (viscoelastic) will not completely couple to the oscillation of the crystal, so the Sauerbrey equation could underestimate the mass of the film. The energy dissipation (D) of the sensor's oscillation can reveal the films' softness or viscoelasticity. D is

$$D = E_{\text{lost}}/2\pi E_{\text{stored}}, \quad (6-2)$$

where E_{lost} is the energy lost (dissipated) during an oscillation cycle and E_{stored} is the energy stored.

Electrochemical QCM-D (EQCM-D)-based methodology can help people to quantify the real-time mass and shear modulus change of the thin film electrode during

the reduction and oxidation processes (discharge-charge process). Recently, Lutkenhaus et al. quantified the real-time mass transfer of anions and solvent during the reduction and oxidation of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl) (PTMA) with 0.5 M LiCF_3SO_3 in propylene carbonate using EQCM-D during cyclic voltammetry.¹⁶⁹

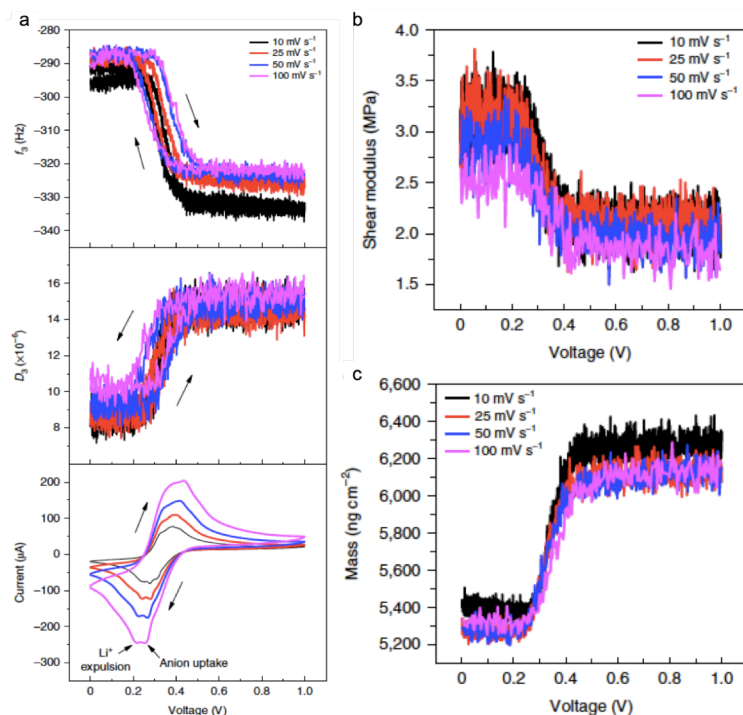


Figure 6.5 (a) Frequency and dissipation responses from EQCM-D of PTMA electrode. (b and c) shear modulus and mass from EQCM-D of PTMA electrode. Reprinted with permission from Ref. 169. © 2017 Springer Nature.

As shown in Figure 6.5a, as voltage increased from 0 to 1 V, PTMA oxidation occurs and frequency (f_3) decreases, indicating a qualitative increase in the mass of the electrode. An anion (in this case CF_3SO_3^-) diffuses into the PTMA electrode, so the electrode mass increases. Meanwhile, dissipation (D_3) increases upon oxidation, resulting from a softening of the PTMA electrode. During a reduction process, the frequency increases and dissipation decreases, indicating a reversible reaction. Changes in mass and viscoelastic properties of the PTMA thin film electrode can be extracted using a Voigt

model applied to the EQCM-D data. As shown in Figure 6.5b and c, the mass of the PTMA electrode increases and the shear modulus decreases upon oxidation process. To achieve further insight into the charge and mass transfer process, the mass change per electron (m.p.e.) transferred can be calculated as $\Delta m/\Delta Q$. The theoretical m.p.e. value of 0.073 mg C⁻¹ for Li⁺, 0.123 mg C⁻¹ for Mg²⁺, and 2.37 mg C⁻¹ for Li⁺ with three dioxolane.

6.3 Preparation of Electrodes at Different States of Charge for EDS and XPS

The electrodes at different discharge and charge states can be characterized by X-ray photoelectron spectroscopy (XPS), and Energy-dispersive X-ray (EDX) spectroscopy. For the fully discharged and fully charged electrodes, the cells can be tested under constant current/constant voltage discharge/charge modes. The constant voltage discharge/charge process is initiated when the voltage reaches the cut-off and terminated until the current density decays to a low C-rate (0.1 C or 0.05 C). For other states of discharge/charge, stop the cells once they reach the cut-off. The electrodes need to be taken out from disassembled cells in an Ar-filled glove box, and ground in an agate mortar using pestle to avoid only surface of the electrodes being measured. The electrodes need to be dipped in anhydrous solvent (DME or THF, etc.) for 3 minutes, and this procedure need to be repeated 3 times. This washing step is essential, which can effectively avoid the elemental signal of the residual salts from electrolytes. The washed electrodes need to be then vacuum-dried at room temperature for 30 min before characterizations. Some elements originally in the material structure can be used as reference elements. For example, the S-containing carbonyl polymer P(NDI2OD-T2) (refer to section 4.3 for the details of analysis). When half-discharged, the atomic ratio of

Mg:Cl:S was 1:0.96:1.97 (with an error bar of $\pm 4.3\%$), i.e., each electron injected into the polymer is balanced by a MgCl^+ ion. As discharge completed, both Mg and Cl amount doubled, and the ratio became 1:0.96:0.99 (with an error bar of $\pm 3.2\%$). Upon charge, both Mg and Cl signal disappeared, leaving only S of the bithiophene moiety. EDS can be used to determine which chemical elements are present in a sample, and can be used to estimate their relative abundance. The accuracy of this quantitative analysis of sample composition is affected by the nature of the sample. Based on my experience, the signals of metallic elements are more accurate than those of non-metallic elements. The electrode achieved using above method can also be characterized by inductively coupled plasma spectrometry (ICP) to identify the content of element in the electrode. In most routine ICP analyses, the sample is introduced as a liquid. Thus, the electrode is typically digested in 2% nitric acid, and needs to be diluted. Dilution factor is based on the theoretical content of the element in the sample.

Chapter 7 Summary and Outlook

7.1 Summary

This dissertation has successfully identified and demonstrated new research directions that can effectively address major challenges for development of high-performance Mg batteries and eventually led to high energy and high power Mg batteries.

I first clarified the definition, key strengths, as well as common misconceptions of Mg batteries. I also clearly discussed two major barriers, which limit the development of Mg cathodes. One is high dissociation energy of solvated MgCl^+ at the interphase between electrode and electrolyte, and the other one is sluggish Mg^{2+} diffusion due to the extremely high-energy barrier for Mg^{2+} migration in host materials.

I then proposed and demonstrated two new research directions to overcome these two barriers. I first demonstrated a low-cost high-power Mg-Na hybrid battery enabled by high-voltage Mg-Na dual salt electrolyte (3.2 V vs Mg/Mg^{2+}), open framework cathode, and the fast-kinetic Mg metal anode. The full cell delivered an average discharge voltage of 2.2 V and stable cycling for 50 cycles. I obtained the high power density of 1.67 kW kg^{-1} . The unit cell of BG had only 5.3 % volume increases than the pristine compound and slight non-uniform structural distortion when 1.52 Na inserts into the framework. XANES study showed a clear reversible shift of Fe K-edge to lower energy and a small hump around 7118 eV. At the anode side, EDX and SEM confirmed fast and reversible Mg-only deposition mechanism. Therefore this work opened the door to many Na-ion cathode materials for high voltage Mg-Na hybrid batteries that could become a viable candidate for stationary energy storage. However, as a matter of fact that the cathode and anode employ different charge carriers, the whole was actually a Daniel

cell, and the cell energy was limited by the concentration of Na^+ in the electrolyte rather than electrodes.

The second strategy was to utilize organic compounds as cathode materials for Mg batteries. I have evaluated the suitability of organic compounds as cathode materials for high-energy Mg batteries. I have identified that in typical chloride-containing electrolytes, storage of MgCl^+ is dominant in probably all organic electrode materials, hence previously assumed organic “Mg-ion” electrodes/batteries were indeed hybrid-ion ones. The negative impact of the hybrid-ion-storage chemistry on the cell specific energy was elucidated through theoretical analysis and cell tests with controlled amount of electrolyte. I further showed that with the right combination of organic cathodes and chloride-free electrolytes, storage of Mg^{2+} in organic electrodes was possible without compromising the reversibility of Mg metal plating/stripping and the energy and power of the cell. Preliminary results from lean electrolyte cells indicated the plausibility for organic Mg batteries to be designed as practical high-energy storage devices. With the help of the Mg-storage chemistry, organic polymers have delivered some of the highest specific energy, power, and cycling stability for Mg batteries.

Finally, I reported a molecule quinone, pyrene-4,5,9,10-tetraone (PTO), can circumvent sluggish Mg^{2+} diffusion through a liquid-solid two-phase reaction pathway, and its intrinsic ion-coordination charge storage mechanism does not involve bond-breaking and –formation, making it has potential to achieve high power. By coupling PTO cathode with a highly functioning electrolyte, $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ in DME/G2, I created an Mg battery with a specific energy of 566 Wh kg^{-1} and an ultra-high power of 30 kW kg^{-1} , which surpassed all previously reported Mg batteries and current Li-ion technology.

7.2 Outlook and Future Directions

The work in this dissertation has evaluated the suitability of organic compounds as cathode materials for high energy and high power Mg batteries. The structural diversity of organic compounds enables us to design molecules with higher capacity and voltage to fulfill higher energy Mg batteries, such as BQ with a theoretical capacity of 515 mAh g⁻¹ and a voltage of 2.4 V vs. Mg²⁺/Mg. Theoretically, the specific energy of Mg-BQ cell can be up to 1000 Wh kg⁻¹, even higher than Mg-S cell. Secondly, the exclusive use of organic compounds as cathodes is sometimes regarded impractical in high mass-loading electrodes due to their poor electronic conductivity. In order to overcome the insufficient electronic conductivity, organic electrodes frequently require a huge amount of carbon. Moving forward, designing electrodes with higher mass loading, and higher active material ratio would be as important as developing better cathode materials for achieving truly high practical cell-level energy.

Another potential strategy to bypass the high desolvation energy is to utilize ionic liquids, which are good candidates for replacing ether solvents (DME, G2, etc.) in Mg electrolytes. Recently, people reported layered V₂O₅ was capable of reversibly intercalating Mg²⁺ in ionic liquid Mg electrolyte, where high-energy desolvation is unnecessary before intercalation.²³ V₂O₅ can deliver a reversible capacity of 280 mAh g⁻¹ and an average discharge voltage of 2 V vs. Mg²⁺/Mg in MgTFSI₂/PY14TFSI at 110 °C. However, current ionic liquid Mg electrolyte is not capable of reversible Mg plating/stripping, so if the compatibility of the pure ionic liquids with Mg metal can be realized, this approach could be a promising way to accomplish high-energy Mg batteries.

References

1. Liu, C.; Neale, Z. G.; Cao, G., "Understanding electrochemical potentials of cathode materials in rechargeable batteries." *Materials Today* **2016**, *19* (2), 109-123.
2. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D., "Challenges in the development of advanced Li-ion batteries: a review." *Energy & Environmental Science* **2011**, *4* (9), 3243-3262.
3. Nowak, S.; Winter, M., "The role of sub- and supercritical CO₂ as “processing solvent” for the recycling and sample preparation of lithium ion battery electrolytes." *Molecules* **2017**, *22* (3).
4. Winter, M.; Barnett, B.; Xu, K., "Before Li ion batteries." *Chemical Reviews* **2018**, *118* (23), 11433-11456.
5. Choi, J. W.; Aurbach, D., "Promise and reality of post-lithium-ion batteries with high energy densities." *Nature Reviews Materials* **2016**, *1*, 16013.
6. Ji, X.; Lee, K. T.; Nazar, L. F., "A highly ordered nanostructured carbon–sulphur cathode for lithium–sulphur batteries." *Nature Materials* **2009**, *8*, 500.
7. Xia, C.; Kwok, C. Y.; Nazar, L. F., "A high-energy-density lithium-oxygen battery based on a reversible four-electron conversion to lithium oxide." *Science* **2018**, *361* (6404), 777.
8. Yoo, H. D.; Liang, Y.; Li, Y.; Yao, Y., "High areal capacity hybrid magnesium–lithium-ion battery with 99.9% coulombic efficiency for large-scale energy storage." *ACS Applied Materials & Interfaces* **2015**, *7* (12), 7001-7007.

9. Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E., "Prototype systems for rechargeable magnesium batteries." *Nature* **2000**, 407 (6805), 724-727.
10. Yoo, H. D.; Shterenberg, I.; Gofer, Y.; Gershtinsky, G.; Pour, N.; Aurbach, D., "Mg rechargeable batteries: an on-going challenge." *Energy & Environmental Science* **2013**, 6 (8), 2265-2279.
11. Muldoon, J.; Bucur, C. B.; Gregory, T., "Quest for nonaqueous multivalent secondary batteries: magnesium and beyond." *Chemical Reviews* **2014**, 114 (23), 11683-11720.
12. 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.
13. Muldoon, J.; Bucur, C. B.; Gregory, T., "Fervent hype behind magnesium batteries: an open call to synthetic chemists—electrolytes and cathodes needed." *Angewandte Chemie International Edition* **2017**, 56 (40), 12064-12084.
14. He, S.; Nielson, K. V.; Luo, J.; Liu, T. L., "Recent advances on MgCl_2 based electrolytes for rechargeable Mg batteries." *Energy Storage Materials* **2017**, 8, 184-188.
15. Attias, R.; Salama, M.; Hirsch, B.; Goffer, Y.; Aurbach, D., "Anode-electrolyte interfaces in secondary magnesium batteries." *Joule* **2019**, 3 (1), 27-52.
16. Yoo, H. D.; Liang, Y.; Dong, H.; Lin, J.; Wang, H.; Liu, Y.; Ma, L.; Wu, T.; Li, Y.; Ru, Q.; Jing, Y.; An, Q.; Zhou, W.; Guo, J.; Lu, J.; Pantelides, S. T.; Qian, X.; Yao, Y., "Fast kinetics of magnesium monochloride cations in interlayer-

- expanded titanium disulfide for magnesium rechargeable batteries." *Nature Communications* **2017**, 8 (1), 339.
17. Wan, L. F.; Perdue, B. R.; Apblett, C. A.; Prendergast, D., "Mg desolvation and intercalation mechanism at the Mo₆S₈ chevrel phase surface." *Chemistry of Materials* **2015**, 27 (17), 5932-5940.
 18. Sun, X.; Duffort, V.; Mehdi, B. L.; Browning, N. D.; Nazar, L. F., "Investigation of the mechanism of Mg insertion in birnessite in nonaqueous and aqueous rechargeable Mg-ion batteries." *Chemistry of Materials* **2016**, 28 (2), 534-542.
 19. Liang, Y.; Yoo, H. D.; Li, Y.; Shuai, J.; Calderon, H. A.; Robles Hernandez, F. C.; Grabow, L. C.; Yao, Y., "Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage." *Nano Letters* **2015**, 15 (3), 2194-2202.
 20. Sun, X.; Bonnick, P.; Nazar, L. F., "Layered TiS₂ positive electrode for Mg batteries." *ACS Energy Letters* **2016**, 1 (1), 297-301.
 21. Zhang, R.; Ling, C., "Unveil the chemistry of olivine FePO₄ as magnesium battery cathode." *ACS Applied Materials & Interfaces* **2016**, 8 (28), 18018-18026.
 22. Li, Z.; Mu, X.; Zhao-Karger, Z.; Diemant, T.; Behm, R. J.; Kübel, C.; Fichtner, M., "Fast kinetics of multivalent intercalation chemistry enabled by solvated magnesium-ions into self-established metallic layered materials." *Nature Communications* **2018**, 9 (1), 5115.
 23. Yoo, H. D.; Jokisaari, J. R.; Yu, Y.-S.; Kwon, B. J.; Hu, L.; Kim, S.; Han, S.-D.; Lopez, M.; Lapidus, S. H.; Nolis, G. M.; Ingram, B. J.; Bolotin, I.; Ahmed, S.; Klie, R. F.; Vaughey, J. T.; Fister, T. T.; Cabana, J., "Intercalation of magnesium

- into a layered vanadium oxide with high capacity." *ACS Energy Letters* **2019**, 1528-1534.
24. Mao, M.; Ji, X.; Hou, S.; Gao, T.; Wang, F.; Chen, L.; Fan, X.; Chen, J.; Ma, J.; Wang, C., "Tuning anionic chemistry to improve kinetics of Mg intercalation." *Chemistry of Materials* **2019**, *31* (9), 3183-3191.
 25. Sun, X.; Bonnick, P.; Duffort, V.; Liu, M.; Rong, Z.; Persson, K. A.; Ceder, G.; Nazar, L. F., "A high capacity thiospinel cathode for Mg batteries." *Energy & Environmental Science* **2016**, *9* (7), 2273-2277.
 26. Du, A.; Zhang, Z.; Qu, H.; Cui, Z.; Qiao, L.; Wang, L.; Chai, J.; Lu, T.; Dong, S.; Dong, T.; Xu, H.; Zhou, X.; Cui, G., "An efficient organic magnesium borate-based electrolyte with non-nucleophilic characteristics for magnesium–sulfur battery." *Energy & Environmental Science* **2017**, *10* (12), 2616-2625.
 27. Yu, X.; Manthiram, A., "Performance enhancement and mechanistic studies of magnesium–sulfur cells with an advanced cathode structure." *ACS Energy Letters* **2016**, *1* (2), 431-437.
 28. 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.
 29. Zhao-Karger, Z.; Zhao, X.; Wang, D.; Diemant, T.; Behm, R. J.; Fichtner, M., "Performance improvement of magnesium sulfur batteries with modified non-nucleophilic electrolytes." *Advanced Energy Materials* **2015**, *5* (3), 1401155.

30. Dong, H.; Liang, Y.; Tutusaus, O.; Mohtadi, R.; Zhang, Y.; Hao, F.; Yao, Y., "Directing Mg-storage chemistry in organic polymers toward high-energy Mg batteries." *Joule* **2019**, 3 (3), 782-793.
31. 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 $[\text{Mg}_2(\mu\text{-Cl})_2]^{2+}$ cation complex in dimethoxyethane." *Physical Chemistry Chemical Physics* **2015**, 17 (20), 13307-13314.
32. Zhao-Karger, Z.; Gil Bardaji, M. E.; Fuhr, O.; Fichtner, M., "A new class of non-corrosive, highly efficient electrolytes for rechargeable magnesium batteries." *Journal of Materials Chemistry A* **2017**, 5 (22), 10815-10820.
33. 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.
34. Hahn, N. T.; Seguin, T. J.; Lau, K.-C.; Liao, C.; Ingram, B. J.; Persson, K. A.; Zavadil, K. R., "Enhanced stability of the carba-closo-dodecaborate anion for high-voltage battery electrolytes through rational design." *Journal of the American Chemical Society* **2018**, 140 (35), 11076-11084.
35. 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.

36. 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." *Chemical Communications* **2014**, 50 (2), 243-245.
37. Liu, M.; Rong, Z.; Malik, R.; Canepa, P.; Jain, A.; Ceder, G.; Persson, K. A., "Spinel compounds as multivalent battery cathodes: a systematic evaluation based on ab initio calculations." *Energy & Environmental Science* **2015**, 8 (3), 964-974.
38. Salama, M.; Rosy; Attias, R.; Yemini, R.; Gofer, Y.; Aurbach, D.; Noked, M., "Metal–sulfur batteries: overview and research methods." *ACS Energy Letters* **2019**, 4 (2), 436-446.
39. Matsui, M., "Study on electrochemically deposited Mg metal." *Journal of Power Sources* **2011**, 196 (16), 7048-7055.
40. Crowe, A. J.; DiMeglio, J. L.; Stringham, K. K.; Bartlett, B. M., "Kinetics of magnesium deposition and stripping from non-aqueous electrolytes." *The Journal of Physical Chemistry C* **2017**, 121 (38), 20613-20620.
41. Ta, K.; See, K. A.; Gewirth, A. A., "Elucidating Zn and Mg electrodeposition mechanisms in nonaqueous electrolytes for next-generation metal batteries." *The Journal of Physical Chemistry C* **2018**, 122 (25), 13790-13796.
42. Ding, M. S.; Diemant, T.; Behm, R. J.; Passerini, S.; Giffin, G. A., "Dendrite growth in Mg metal cells containing Mg(TFSI)₂/Glyme electrolytes." *Journal of The Electrochemical Society* **2018**, 165 (10), A1983-A1990.
43. Davidson, R.; Verma, A.; Santos, D.; Hao, F.; Fincher, C.; Xiang, S.; Van Buskirk, J.; Xie, K.; Pharr, M.; Mukherjee, P. P.; Banerjee, S., "Formation of

- magnesium dendrites during electrodeposition." *ACS Energy Letters* **2019**, *4* (2), 375-376.
44. Ling, C.; Banerjee, D.; Matsui, M., "Study of the electrochemical deposition of Mg in the atomic level: Why it prefers the non-dendritic morphology." *Electrochimica Acta* **2012**, *76*, 270-274.
 45. Jäckle, M.; Groß, A., "Microscopic properties of lithium, sodium, and magnesium battery anode materials related to possible dendrite growth." *The Journal of Chemical Physics* **2014**, *141* (17), 174710.
 46. Jäckle, M.; Helmbrecht, K.; Smits, M.; Stottmeister, D.; Groß, A., "Self-diffusion barriers: possible descriptors for dendrite growth in batteries?" *Energy & Environmental Science* **2018**, *11* (12), 3400-3407.
 47. Ponrouch, A.; Frontera, C.; Bardé, F.; Palacín, M. R., "Towards a calcium-based rechargeable battery." *Nature Materials* **2015**, *15*, 169.
 48. Wang, D.; Gao, X.; Chen, Y.; Jin, L.; Kuss, C.; Bruce, P. G., "Plating and stripping calcium in an organic electrolyte." *Nature Materials* **2017**, *17*, 16.
 49. Pan, H.; Shao, Y.; Yan, P.; Cheng, Y.; Han, K. S.; Nie, Z.; Wang, C.; Yang, J.; Li, X.; Bhattacharya, P.; Mueller, K. T.; Liu, J., "Reversible aqueous zinc/manganese oxide energy storage from conversion reactions." *Nature Energy* **2016**, *1*, 16039.
 50. Zhao, Q.; Huang, W.; Luo, Z.; Liu, L.; Lu, Y.; Li, Y.; Li, L.; Hu, J.; Ma, H.; Chen, J., "High-capacity aqueous zinc batteries using sustainable quinone electrodes." *Science Advances* **2018**, *4* (3), eaao1761.

51. Wang, F.; Borodin, O.; Gao, T.; Fan, X.; Sun, W.; Han, F.; Faraone, A.; Dura, J. A.; Xu, K.; Wang, C., "Highly reversible zinc metal anode for aqueous batteries." *Nature Materials* **2018**, *17* (6), 543-549.
52. Han, S.-D.; Rajput, N. N.; Qu, X.; Pan, B.; He, M.; Ferrandon, M. S.; Liao, C.; Persson, K. A.; Burrell, A. K., "Origin of electrochemical, structural, and transport properties in nonaqueous zinc electrolytes." *ACS Applied Materials & Interfaces* **2016**, *8* (5), 3021-3031.
53. Qian, J.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J.-G., "High rate and stable cycling of lithium metal anode." *Nature Communications* **2015**, *6*, 6362.
54. Pradhan, D.; Reddy, R. G., "Dendrite-free aluminum electrodeposition from AlCl_3 -1-ethyl-3-methyl-imidazolium chloride ionic liquid electrolytes." *Metallurgical and Materials Transactions B* **2012**, *43* (3), 519-531.
55. Amalraj, S. F.; Aurbach, D., "The use of in situ techniques in R&D of Li and Mg rechargeable batteries." *Journal of Solid State Electrochemistry* **2011**, *15* (5), 877-890.
56. Woods, J.; Bhattarai, N.; Chapagain, P.; Yang, Y.; Neupane, S., "In situ transmission electron microscopy observations of rechargeable lithium ion batteries." *Nano Energy* **2019**, *56*, 619-640.
57. Chen, X.; Lai, J.; Shen, Y.; Chen, Q.; Chen, L., "Functional scanning force microscopy for energy nanodevices." *Advanced Materials* **2018**, *30* (48), 1802490.

58. Chen, H.; Xu, H.; Zheng, B.; Wang, S.; Huang, T.; Guo, F.; Gao, W.; Gao, C., "Oxide film efficiently suppresses dendrite growth in aluminum-ion battery." *ACS Applied Materials & Interfaces* **2017**, *9* (27), 22628-22634.
59. Aurbach, D.; Skaletsky, R.; Gofer, Y., "The electrochemical behavior of calcium electrodes in a few organic electrolytes." *Journal of The Electrochemical Society* **1991**, *138* (12), 3536-3545.
60. Yu, J.; McMahon, B. W.; Boatz, J. A.; Anderson, S. L., "Aluminum nanoparticle production by acetonitrile-assisted milling: effects of liquid- vs vapor-phase milling and of milling method on particle size and surface chemistry." *The Journal of Physical Chemistry C* **2016**, *120* (35), 19613-19629.
61. Lu, Z.; Schechter, A.; Moshkovich, M.; Aurbach, D., "On the electrochemical behavior of magnesium electrodes in polar aprotic electrolyte solutions." *Journal of Electroanalytical Chemistry* **1999**, *466* (2), 203-217.
62. Peled, E.; Menkin, S., "Review—SEI: past, present and future." *Journal of The Electrochemical Society* **2017**, *164* (7), A1703-A1719.
63. Mohtadi, R.; Mizuno, F., "Magnesium batteries: Current state of the art, issues and future perspectives." *Beilstein J Nanotechnol* **2014**, *5*, 1291-311.
64. 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.
65. Pour, N.; Gofer, Y.; Major, D. T.; Keinan-Adamsky, K.; Gottlieb, H. E.; Aurbach, D., "Multinuclear magnetic resonance spectroscopy and density function theory

- calculations for the identification of the equilibrium species in THF solutions of organometallic complexes suitable as electrolyte solutions for rechargeable Mg batteries." *Organometallics* **2013**, 32 (11), 3165-3173.
66. 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." *Angewandte Chemie International Edition* **2014**, 53 (12), 3173-3177.
 67. Zhao-Karger, Z.; Liu, R.; Dai, W.; Li, Z.; Diemant, T.; Vinayan, B. P.; Bonatto Minella, C.; Yu, X.; Manthiram, A.; Behm, R. J.; Ruben, M.; Fichtner, M., "Toward highly reversible magnesium–sulfur batteries with efficient and practical $\text{Mg}[\text{B}(\text{hfip})_4]_2$ electrolyte." *ACS Energy Letters* **2018**, 3 (8), 2005-2013.
 68. Lipson, A. L.; Han, S.-D.; Pan, B.; See, K. A.; Gewirth, A. A.; Liao, C.; Vaughey, J. T.; Ingram, B. J., "Practical stability limits of magnesium electrolytes." *Journal of The Electrochemical Society* **2016**, 163 (10), A2253-A2257.
 69. Shterenberg, I.; Salama, M.; Yoo, H. D.; Gofer, Y.; Park, J.-B.; Sun, Y.-K.; Aurbach, D., "Evaluation of $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (TFSI) based electrolyte solutions for Mg batteries." *Journal of The Electrochemical Society* **2015**, 162 (13), A7118-A7128.
 70. Liu, T.; Shao, Y.; Li, G.; Gu, M.; Hu, J.; Xu, S.; Nie, Z.; Chen, X.; Wang, C.; Liu, J., "A facile approach using MgCl_2 to formulate high performance Mg^{2+} electrolytes for rechargeable Mg batteries." *Journal of Materials Chemistry A* **2014**, 2 (10), 3430-3438.
 71. 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.
72. Attias, R.; Salama, M.; Hirsch, B.; Gofer, Y.; Aurbach, D., "Solvent effects on the reversible intercalation of magnesium-ions into V_2O_5 electrodes." *ChemElectroChem* **2018**, *5* (22), 3514-3524.
 73. 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.
 74. Yagi, S.; Tanaka, A.; Ichikawa, Y.; Ichitsubo, T.; Matsubara, E., "Electrochemical stability of magnesium battery current collectors in a grignard reagent-based electrolyte." *Journal of The Electrochemical Society* **2013**, *160* (3), C83-C88.
 75. Whittingham, M. S.; Siu, C.; Ding, J., "Can multielectron intercalation reactions be the basis of next generation batteries?" *Accounts of Chemical Research* **2018**, *51* (2), 258-264.
 76. Lee, B.; Lee, H. R.; Yim, T.; Kim, J. H.; Lee, J. G.; Chung, K. Y.; Cho, B. W.; Oh, S. H., "Investigation on the Structural Evolutions during the Insertion of Aluminum Ions into Mo₆S₈ Chevrel Phase." *Journal of The Electrochemical Society* **2016**, *163* (6), A1070-A1076.
 77. Robba, A.; Vizintin, A.; Bitenc, J.; Mali, G.; Arčon, I.; Kavčič, M.; Žitnik, M.; Bučar, K.; Aquilanti, G.; Martineau-Corcos, C.; Randon-Vitanova, A.; Dominko, R., "Mechanistic study of magnesium–sulfur batteries." *Chemistry of Materials* **2017**, *29* (21), 9555-9564.

78. Sa, N.; Wang, H.; Proffit, D. L.; Lipson, A. L.; Key, B.; Liu, M.; Feng, Z.; Fister, T. T.; Ren, Y.; Sun, C.-J.; Vaughey, J. T.; Fenter, P. A.; Persson, K. A.; Burrell, A. K., "Is α - V_2O_5 a cathode material for Mg insertion batteries?" *Journal of Power Sources* **2016**, *323*, 44-50.
79. Verrelli, R.; Black, A. P.; Pattanathummasid, C.; Tchitcheкова, D. S.; Ponrouch, A.; Oró-Solé, J.; Frontera, C.; Bardé, F.; Rozier, P.; Palacín, M. R., "On the strange case of divalent ions intercalation in V_2O_5 ." *Journal of Power Sources* **2018**, *407*, 162-172.
80. Zhao, Q.; Zachman, M. J.; Al Sadat, W. I.; Zheng, J.; Kourkoutis, L. F.; Archer, L., "Solid electrolyte interphases for high-energy aqueous aluminum electrochemical cells." *Science Advances* **2018**, *4* (11), eaau8131.
81. Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen, C.; Yang, J.; Hwang, B.-J.; Dai, H., "An ultrafast rechargeable aluminium-ion battery." *Nature* **2015**, *520*, 324.
82. Kim, D. J.; Yoo, D.-J.; Otley, M. T.; Prokofjevs, A.; Pezzato, C.; Owczarek, M.; Lee, S. J.; Choi, J. W.; Stoddart, J. F., "Rechargeable aluminium organic batteries." *Nature Energy* **2019**, *4* (1), 51-59.
83. Kundu, D.; Hosseini Vajargah, S.; Wan, L.; Adams, B.; Prendergast, D.; Nazar, L. F., "Aqueous vs. nonaqueous Zn-ion batteries: consequences of the desolvation penalty at the interface." *Energy & Environmental Science* **2018**, *11* (4), 881-892.
84. Wu, C.; Gu, S.; Zhang, Q.; Bai, Y.; Li, M.; Yuan, Y.; Wang, H.; Liu, X.; Yuan, Y.; Zhu, N.; Wu, F.; Li, H.; Gu, L.; Lu, J., "Electrochemically activated spinel

- manganese oxide for rechargeable aqueous aluminum battery." *Nature Communications* **2019**, *10* (1), 73.
85. Wang, R. Y.; Wessells, C. D.; Huggins, R. A.; Cui, Y., "Highly reversible open framework nanoscale electrodes for divalent ion batteries." *Nano Letters* **2013**, *13* (11), 5748-5752.
 86. Kravchyk, K. V.; Wang, S.; Piveteau, L.; Kovalenko, M. V., "Efficient aluminum chloride–natural graphite battery." *Chemistry of Materials* **2017**, *29* (10), 4484-4492.
 87. Pan, C.; Zhang, R.; Nuzzo, R. G.; Gewirth, A. A., "ZnNi_xMn_xCo_{2-2x}O₄ spinel as a high-voltage and high-capacity cathode material for nonaqueous Zn-ion batteries." *Advanced Energy Materials* **2018**, *8* (22), 1800589.
 88. Pan, C.; Nuzzo, R. G.; Gewirth, A. A., "ZnAl_xCo_{2-x}O₄ spinels as cathode materials for non-aqueous Zn batteries with an open circuit voltage of ≤ 2 V." *Chemistry of Materials* **2017**, *29* (21), 9351-9359.
 89. Geng, L.; Lv, G.; Xing, X.; Guo, J., "Reversible electrochemical intercalation of aluminum in Mo₆S₈." *Chemistry of Materials* **2015**, *27* (14), 4926-4929.
 90. Cheng, Y.; Luo, L.; Zhong, L.; Chen, J.; Li, B.; Wang, W.; Mao, S. X.; Wang, C.; Sprenkle, V. L.; Li, G.; Liu, J., "Highly reversible zinc-ion intercalation into chevrel phase Mo₆S₈ nanocubes and applications for advanced zinc-ion batteries." *ACS Applied Materials & Interfaces* **2016**, *8* (22), 13673-13677.
 91. Schöllhorn, R., "Reversible topotactic redox reactions of solids by electron/ion transfer." *Angewandte Chemie International Edition in English* **1980**, *19* (12), 983-1003.

92. Levi, M. D.; Lancry, E.; Levi, E.; Gizbar, H.; Gofer, Y.; Aurbach, D., "The effect of the anionic framework of Mo_6X_8 Chevrel Phase ($\text{X}=\text{S}, \text{Se}$) on the thermodynamics and the kinetics of the electrochemical insertion of Mg^{2+} ions." *Solid State Ionics* **2005**, 176 (19), 1695-1699.
93. Adelstein, N.; Wood, B. C., "Role of dynamically frustrated bond disorder in a Li^+ superionic solid electrolyte." *Chemistry of Materials* **2016**, 28 (20), 7218-7231.
94. Richard, J.; Benayad, A.; Colin, J. F.; Martinet, S., "Charge transfer mechanism into the chevrel phase Mo_6S_8 during Mg intercalation." *The Journal of Physical Chemistry C* **2017**, 121 (32), 17096-17103.
95. Levi, E.; Lancry, E.; Mitelman, A.; Aurbach, D.; Isnard, O.; Djurado, D., "Phase diagram of Mg insertion into chevrel phases, $\text{Mg}_x\text{Mo}_6\text{T}_8$ ($\text{T} = \text{S}, \text{Se}$). 2. The crystal structure of triclinic MgMo_6Se_8 ." *Chemistry of Materials* **2006**, 18 (16), 3705-3714.
96. Levi, E.; Aurbach, D., "Chevrel phases, $\text{M}_x\text{Mo}_6\text{T}_8$ ($\text{M} = \text{Metals}, \text{T} = \text{S}, \text{Se}, \text{Te}$) as a structural chameleon: changes in the rhombohedral framework and triclinic distortion." *Chemistry of Materials* **2010**, 22 (12), 3678-3692.
97. Levi, E.; Gofer, Y.; Aurbach, D., "On the way to rechargeable Mg batteries: the challenge of new cathode materials." *Chemistry of Materials* **2010**, 22 (3), 860-868.
98. Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I., "Identification of active edge sites for electrochemical H_2 evolution from MoS_2 ." *Science* **2007**, 317 (5834), 100.

99. Senoh, H.; Sakaebe, H.; Sano, H.; Yao, M.; Kuratani, K.; Takeichi, N.; Kiyobayashi, T., "Sulfone-based electrolyte solutions for rechargeable magnesium batteries using 2,5-dimethoxy-1,4-benzoquinone positive electrode." *Journal of The Electrochemical Society* **2014**, *161* (9), A1315-A1320.
100. Bitenc, J.; Pirnat, K.; Bančič, T.; Gaberšček, M.; Genorio, B.; Randon-Vitanova, A.; Dominko, R., "Anthraquinone-based polymer as cathode in rechargeable magnesium batteries." *ChemSusChem* **2015**, *8* (24), 4128-4132.
101. Pan, B.; Huang, J.; Feng, Z.; Zeng, L.; He, M.; Zhang, L.; Vaughey, J. T.; Bedzyk, M. J.; Fenter, P.; Zhang, Z.; Burrell, A. K.; Liao, C., "Polyanthraquinone-based organic cathode for high-performance rechargeable magnesium-ion batteries." *Advanced Energy Materials* **2016**, *6* (14), 1600140.
102. Rastgoo-Deylami, M.; Chae, M. S.; Hong, S.-T., "H₂V₃O₈ as a high energy cathode material for nonaqueous magnesium-ion batteries." *Chemistry of Materials* **2018**, *30* (21), 7464-7472.
103. VahidMohammadi, A.; Hadjikhani, A.; Shahbazmohamadi, S.; Beidaghi, M., "Two-dimensional vanadium carbide (MXene) as a high-capacity cathode material for rechargeable aluminum batteries." *ACS Nano* **2017**, *11* (11), 11135-11144.
104. Zhang, Z.; Cui, Z.; Qiao, L.; Guan, J.; Xu, H.; Wang, X.; Hu, P.; Du, H.; Li, S.; Zhou, X.; Dong, S.; Liu, Z.; Cui, G.; Chen, L., "Novel design concepts of efficient Mg-ion electrolytes toward high-performance magnesium–selenium and magnesium–sulfur batteries." *Advanced Energy Materials* **2017**, *7* (11), 1602055.

105. Tian, H.; Gao, T.; Li, X.; Wang, X.; Luo, C.; Fan, X.; Yang, C.; Suo, L.; Ma, Z.; Han, W.; Wang, C., "High power rechargeable magnesium/iodine battery chemistry." *Nature Communications* **2017**, *8*, 14083.
106. Gao, T.; Hou, S.; Wang, F.; Ma, Z.; Li, X.; Xu, K.; Wang, C., "Reversible S0/MgSx redox chemistry in a MgTFSI₂/MgCl₂/DME electrolyte for rechargeable Mg/S batteries." *Angewandte Chemie International Edition* **2017**, *56* (43), 13526-13530.
107. Salama, M.; Attias, R.; Hirsch, B.; Yemini, R.; Gofer, Y.; Noked, M.; Aurbach, D., "On the Feasibility of practical Mg–S batteries: practical limitations associated with metallic magnesium anodes." *ACS Applied Materials & Interfaces* **2018**, *10* (43), 36910-36917.
108. Gao, T.; Ji, X.; Hou, S.; Fan, X.; Li, X.; Yang, C.; Han, F.; Wang, F.; Jiang, J.; Xu, K.; Wang, C., "Thermodynamics and kinetics of sulfur cathode during discharge in MgTFSI₂–DME electrolyte." *Advanced Materials* **2018**, *30* (3), 1704313.
109. 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." *Advanced Energy Materials* **2018**, *8* (7), 1701728.
110. Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham, M. S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X.-Q.; Zhang, J.-G., "Pathways for practical high-energy long-cycling lithium metal batteries." *Nature Energy* **2019**, *4* (3), 180-186.

111. Wessells, C. D.; Huggins, R. A.; Cui, Y., "Copper hexacyanoferrate battery electrodes with long cycle life and high power." *Nature Communications* **2011**, *2*, 550.
112. Lu, Y.; Wang, L.; Cheng, J.; Goodenough, J. B., "Prussian blue: a new framework of electrode materials for sodium batteries." *Chemical Communications* **2012**, *48* (52), 6544-6546.
113. Wu, X.; Deng, W.; Qian, J.; Cao, Y.; Ai, X.; Yang, H., "Single-crystal $\text{FeFe}(\text{CN})_6$ nanoparticles: a high capacity and high rate cathode for Na-ion batteries." *Journal of Materials Chemistry A* **2013**, *1* (35), 10130-10134.
114. You, Y.; Yu, X.; Yin, Y.; Nam, K.-W.; Guo, Y.-G., "Sodium iron hexacyanoferrate with high Na content as a Na-rich cathode material for Na-ion batteries." *Nano Research* **2015**, *8* (1), 117-128.
115. Wang, L.; Song, J.; Qiao, R.; Wray, L. A.; Hossain, M. A.; Chuang, Y.-D.; Yang, W.; Lu, Y.; Evans, D.; Lee, J.-J.; Vail, S.; Zhao, X.; Nishijima, M.; Kakimoto, S.; Goodenough, J. B., "Rhombohedral prussian white as cathode for rechargeable sodium-ion batteries." *Journal of the American Chemical Society* **2015**, *137* (7), 2548-2554.
116. Bommier, C.; Surta, T. W.; Dolgos, M.; Ji, X., "New mechanistic insights on Na-ion storage in nongraphitizable carbon." *Nano Letters* **2015**, *15* (9), 5888-5892.
117. Stevens, D. A.; Dahn, J. R., "The mechanisms of lithium and sodium insertion in carbon materials." *Journal of The Electrochemical Society* **2001**, *148* (8), A803-A811.

118. Gofer, Y.; Chusid, O.; Gizbar, H.; Viestfrid, Y.; Gottlieb, H. E.; Marks, V.; Aurbach, D., "Improved electrolyte solutions for rechargeable magnesium batteries." *Electrochemical and Solid-State Letters* **2006**, 9 (5), A257-A260.
119. Yagi, S.; Ichitsubo, T.; Shirai, Y.; Yanai, S.; Doi, T.; Murase, K.; Matsubara, E., "A concept of dual-salt polyvalent-metal storage battery." *Journal of Materials Chemistry A* **2014**, 2 (4), 1144-1149.
120. Cheng, Y.; Shao, Y.; Zhang, J.-G.; Sprenkle, V. L.; Liu, J.; Li, G., "High performance batteries based on hybrid magnesium and lithium chemistry." *Chemical Communications* **2014**, 50 (68), 9644-9646.
121. Walter, M.; Kravchyk, K. V.; Ibáñez, M.; Kovalenko, M. V., "Efficient and inexpensive sodium–magnesium hybrid battery." *Chemistry of Materials* **2015**, 27 (21), 7452-7458.
122. Cheng, Y.; Liu, T.; Shao, Y.; Engelhard, M. H.; Liu, J.; Li, G., "Electrochemically stable cathode current collectors for rechargeable magnesium batteries." *Journal of Materials Chemistry A* **2014**, 2 (8), 2473-2477.
123. Zhang, Z.; Xu, H.; Cui, Z.; Hu, P.; Chai, J.; Du, H.; He, J.; Zhang, J.; Zhou, X.; Han, P.; Cui, G.; Chen, L., "High energy density hybrid $\text{Mg}^{2+}/\text{Li}^{+}$ battery with superior ultra-low temperature performance." *Journal of Materials Chemistry A* **2016**, 4 (6), 2277-2285.
124. Zhang, Y.; Xie, J.; Han, Y.; Li, C., "Dual-salt Mg-based batteries with conversion cathodes." *Advanced Functional Materials* **2015**, 25 (47), 7300-7308.
125. Nam, K.-W.; Bak, S.-M.; Hu, E.; Yu, X.; Zhou, Y.; Wang, X.; Wu, L.; Zhu, Y.; Chung, K.-Y.; Yang, X.-Q., "Combining in situ synchrotron X-ray diffraction and

- absorption techniques with transmission electron microscopy to study the origin of thermal instability in overcharged cathode materials for lithium-ion batteries." *Advanced Functional Materials* **2013**, 23 (8), 1047-1063.
126. Wang, L.; Lu, Y.; Liu, J.; Xu, M.; Cheng, J.; Zhang, D.; Goodenough, J. B., "A superior low-cost cathode for a Na-ion battery." *Angewandte Chemie International Edition* **2013**, 52 (7), 1964-1967.
 127. Zhou, L.; Liu, Q.; Zhang, Z.; Zhang, K.; Xiong, F.; Tan, S.; An, Q.; Kang, Y.-M.; Zhou, Z.; Mai, L., "Interlayer-spacing-regulated VOPO₄ nanosheets with fast kinetics for high-capacity and durable rechargeable magnesium batteries." *Advanced Materials* **2018**, 30 (32), 1801984.
 128. Liao, C.; Guo, B.; Jiang, D.-e.; Custelcean, R.; Mahurin, S. M.; Sun, X.-G.; Dai, S., "Highly soluble alkoxide magnesium salts for rechargeable magnesium batteries." *Journal of Materials Chemistry A* **2014**, 2 (3), 581-584.
 129. Andrews, J. L.; Mukherjee, A.; Yoo, H. D.; Parija, A.; Marley, P. M.; Fakra, S.; Prendergast, D.; Cabana, J.; Klie, R. F.; Banerjee, S., "Reversible Mg-ion insertion in a metastable one-dimensional polymorph of V₂O₅." *Chem* **2018**, 4 (3), 564-585.
 130. Pan, B.; Zhou, D.; Huang, J.; Zhang, L.; Burrell, A. K.; Vaughey, J. T.; Zhang, Z.; Liao, C., "2,5-dimethoxy-1,4-benzoquinone (DMBQ) as organic cathode for rechargeable magnesium-ion batteries." *Journal of The Electrochemical Society* **2016**, 163 (3), A580-A583.

131. Liang, Y.; Jing, Y.; Gheytani, S.; Lee, K.-Y.; Liu, P.; Facchetti, A.; Yao, Y., "Universal quinone electrodes for long cycle life aqueous rechargeable batteries." *Nature Materials* **2017**, *16*, 841.
132. Fan, X.; Wang, F.; Ji, X.; Wang, R.; Gao, T.; Hou, S.; Chen, J.; Deng, T.; Li, X.; Chen, L.; Luo, C.; Wang, L.; Wang, C., "A universal organic cathode for ultrafast lithium and multivalent metal batteries." *Angewandte Chemie International Edition* **2018**, *57* (24), 7146-7150.
133. Chen, L.; Bao, J. L.; Dong, X.; Truhlar, D. G.; Wang, Y.; Wang, C.; Xia, Y., "Aqueous Mg-ion battery based on polyimide anode and prussian blue cathode." *ACS Energy Letters* **2017**, *2* (5), 1115-1121.
134. Liang, Y.; Tao, Z.; Chen, J., "Organic electrode materials for rechargeable lithium batteries." *Advanced Energy Materials* **2012**, *2* (7), 742-769.
135. Poizot, P.; Dolhem, F., "Clean energy new deal for a sustainable world: from non-CO₂ generating energy sources to greener electrochemical storage devices." *Energy & Environmental Science* **2011**, *4* (6), 2003-2019.
136. Song, Z.; Zhou, H., "Towards sustainable and versatile energy storage devices: an overview of organic electrode materials." *Energy & Environmental Science* **2013**, *6* (8), 2280-2301.
137. Zhao, Q.; Zhu, Z.; Chen, J., "Molecular engineering with organic carbonyl electrode materials for advanced stationary and redox flow rechargeable batteries." *Advanced Materials* **2017**, *29* (48), 1607007.
138. Liang, Y.; Yao, Y., "positioning organic electrode materials in the battery landscape." *Joule* **2018**, *2* (9), 1690-1706.

139. Yao, M.; Senoh, H.; Yamazaki, S.-i.; Siroma, Z.; Sakai, T.; Yasuda, K., "High-capacity organic positive-electrode material based on a benzoquinone derivative for use in rechargeable lithium batteries." *Journal of Power Sources* **2010**, *195* (24), 8336-8340.
140. Song, Z.; Qian, Y.; Gordin, M. L.; Tang, D.; Xu, T.; Otani, M.; Zhan, H.; Zhou, H.; Wang, D., "Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage." *Angewandte Chemie International Edition* **2015**, *54* (47), 13947-13951.
141. Liang, Y.; Chen, Z.; Jing, Y.; Rong, Y.; Facchetti, A.; Yao, Y., "Heavily n-dopable π -conjugated redox polymers with ultrafast energy storage capability." *Journal of the American Chemical Society* **2015**, *137* (15), 4956-4959.
142. 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.
143. Chen, Z.; Zheng, Y.; Yan, H.; Facchetti, A., "Naphthalenedicarboximide- vs perylenedicarboximide-based copolymers. synthesis and semiconducting properties in bottom-gate N-channel organic transistors." *Journal of the American Chemical Society* **2009**, *131* (1), 8-9.
144. Singh, N.; Arthur, T. S.; Tutusaus, O.; Li, J.; Kisslinger, K.; Xin, H. L.; Stach, E. A.; Fan, X.; Mohtadi, R., "Achieving high cycling rates via in situ generation of

- active nanocomposite metal anodes." *ACS Applied Energy Materials* **2018**, *1* (9), 4651-4661.
145. 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.
 146. 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 $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2$ complex as a magnesium electrolyte for rechargeable magnesium batteries." *Journal of Materials Chemistry A* **2015**, *3* (11), 6082-6087.
 147. Yu, X.; Manthiram, A., "Electrochemical energy storage with mediator-ion solid electrolytes." *Joule* **2017**, *1* (3), 453-462.
 148. Dong, H.; Li, Y.; Liang, Y.; Li, G.; Sun, C.-J.; Ren, Y.; Lu, Y.; Yao, Y., "A magnesium–sodium hybrid battery with high operating voltage." *Chemical Communications* **2016**, *52* (53), 8263-8266.
 149. Strauss, S. H., "The search for larger and more weakly coordinating anions." *Chemical Reviews* **1993**, *93* (3), 927-942.
 150. Cheng, Y.; Chang, H. J.; Dong, H.; Choi, D.; Sprenkle, V. L.; Liu, J.; Yao, Y.; Li, G., "Rechargeable Mg–Li hybrid batteries: status and challenges." *Journal of Materials Research* **2016**, *31* (20), 3125-3141.
 151. 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.
152. Chung, S.-H.; Chang, C.-H.; Manthiram, A., "progress on the critical parameters for lithium–sulfur batteries to be practically viable." *Advanced Functional Materials* **2018**, 28 (28), 1801188.
153. Luo, J.; Bi, Y.; Zhang, L.; Zhang, X.; Liu, T. L., "A stable, non-corrosive perfluorinated pinacolatoborate Mg electrolyte for rechargeable Mg batteries." *Angewandte Chemie International Edition* **2019**, 58 (21), 6967-6971.
154. Levillain, E.; Gaillard, F.; Leghie, P.; Demortier, A.; Lelieur, J. P., "On the understanding of the reduction of sulfur (S₈) in dimethylformamide (DMF)." *Journal of Electroanalytical Chemistry* **1997**, 420 (1), 167-177.
155. Rajput, N. N.; Seguin, T. J.; Wood, B. M.; Qu, X.; Persson, K. A., "Elucidating solvation structures for rational design of multivalent electrolytes—A review." *Topics in Current Chemistry* **2018**, 376 (3), 19.
156. Lu, Y.-C.; He, Q.; Gasteiger, H. A., "Probing the lithium–sulfur redox reactions: A rotating-ring disk electrode study." *The Journal of Physical Chemistry C* **2014**, 118 (11), 5733-5741.
157. Huang, X.; Wang, Z.; Knibbe, R.; Luo, B.; Ahad, S. A.; Sun, D.; Wang, L., "Cyclic voltammetry in lithium–sulfur batteries—challenges and opportunities." *Energy Technology* **2019**, 0 (0).
158. Suga, T.; Pu, Y.-J.; Oyaizu, K.; Nishide, H., "Electron-transfer kinetics of nitroxide radicals as an electrode-active material." *Bulletin of the Chemical Society of Japan* **2004**, 77 (12), 2203-2204.

159. Martínez-Cifuentes, M.; Salazar, R.; Ramírez-Rodríguez, O.; Weiss-López, B.; Araya-Maturana, R., "Experimental and theoretical reduction potentials of some biologically active ortho-carbonyl para-quinones." *Molecules* **2017**, *22* (4).
160. Huang, J.-Q.; Zhuang, T.-Z.; Zhang, Q.; Peng, H.-J.; Chen, C.-M.; Wei, F., "Permselective graphene oxide membrane for highly stable and anti-self-discharge lithium–sulfur batteries." *ACS Nano* **2015**, *9* (3), 3002-3011.
161. Tian, J.; Zhou, X.; Wu, Q.; Li, C., "Li-salt mediated Mg-rhodizonate batteries based on ultra-large cathode grains enabled by K-ion pillaring." *Energy Storage Materials* **2019**.
162. Hebié, S.; Alloin, F.; Iojoiu, C.; Berthelot, R.; Leprêtre, J.-C., "Magnesium anthracene system-based electrolyte as a promoter of high electrochemical performance rechargeable magnesium batteries." *ACS Applied Materials & Interfaces* **2018**, *10* (6), 5527-5533.
163. Urquhart, S. G.; Ade, H., "Trends in the carbonyl core (C 1S, O 1S) $\rightarrow \pi^*C=O$ transition in the near-edge X-ray absorption fine structure spectra of organic molecules." *The Journal of Physical Chemistry B* **2002**, *106* (34), 8531-8538.
164. 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.
165. Miao, L.; Liu, L.; Shang, Z.; Li, Y.; Lu, Y.; Cheng, F.; Chen, J., "The structure–electrochemical property relationship of quinone electrodes for lithium-ion batteries." *Physical Chemistry Chemical Physics* **2018**, *20* (19), 13478-13484.

166. Hatakeyama-Sato, K.; Wakamatsu, H.; Katagiri, R.; Oyaizu, K.; Nishide, H., "An ultrahigh output rechargeable electrode of a hydrophilic radical polymer/nanocarbon hybrid with an exceptionally large current density beyond 1 A cm⁻²." *Advanced Materials* **2018**, 30 (26), 1800900.
167. Adams, B. D.; Zheng, J.; Ren, X.; Xu, W.; Zhang, J.-G., "Accurate determination of coulombic efficiency for lithium metal anodes and lithium metal batteries." *Advanced Energy Materials* **2018**, 8 (7), 1702097.
168. Shpigel, N.; Levi, M. D.; Sigalov, S.; Daikhin, L.; Aurbach, D., "In situ real-time mechanical and morphological characterization of electrodes for electrochemical energy storage and conversion by electrochemical quartz crystal microbalance with dissipation monitoring." *Accounts of Chemical Research* **2018**, 51 (1), 69-79.
169. Wang, S.; Li, F.; Easley, A. D.; Lutkenhaus, J. L., "Real-time insight into the doping mechanism of redox-active organic radical polymers." *Nature Materials* **2019**, 18 (1), 69-75.

