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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · SEPTEMBER 2015

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Confession of a Magnesium Battery

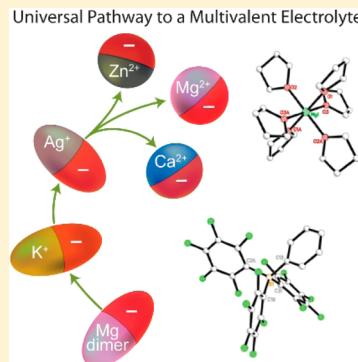
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ABSTRACT: Magnesium is an ideal metal anode that has nearly double the volumetric capacity of lithium metal with a very negative reduction potential of -2.37 vs SHE. A significant advantage of magnesium is the apparent lack of dendrite formation during charging, which overcomes major safety and performance challenges encountered with using lithium metal anodes. Here, we highlight major recent advances in nonaqueous Mg electrochemistry, notably the development of electrolytes and cathodes, and discuss some of the challenges that must be overcome to realize a practical magnesium battery.



One of the most far-reaching electrochemical success stories in recent years has been the development and commercialization of the lithium ion battery, which has changed the world in numerous ways. Lithium ion batteries now power cell phones, portable computers, power tools, and electric drive vehicles. However, consumer desire for cell phones that last longer and lower cost, longer range EVs fuel an ongoing thirst for higher energy density batteries. In particular, the volumetric energy density of the battery is highly important when considering applications where there is a limited space to accommodate it. This quest attracts interest toward enhancing the volumetric energy density of lithium ion batteries and toward finding a post lithium ion battery with 2–3 times the energy density of what lithium ion can offer. The banner of post lithium ion battery research is carried by lithium/sulfur, lithium/air, and multivalent metal batteries.

In order to increase the ratio of capacity to volume, innovative methods must be adopted without sacrificing cycling stability and safety. For example, an insertion graphite anode with a volumetric capacity of 777 mAh cm^{-3} could be upgraded to a lithium metal anode with a volumetric capacity of 2062 mAh cm^{-3} . However, attempts at commercializing a rechargeable battery containing a lithium metal anode have been hampered by the inherent stability limitations of lithium metal, especially during charging. Safety issues are associated with uneven Li plating, especially at higher rates that cause the formation of dendrites and powdery deposits, which can lead to thermal runaway.¹ In addition to the safety aspect, low Coulombic efficiency of deposition/dissolution hampers cycling due to incomplete recovery of lithium during charge.^{1–3} Solving the challenge of a lithium metal anode inspires valuable research and substantial attention.²

In contrast to a lithium metal anode, a magnesium anode is not plagued by dendrite formation.^{4,5} Magnesium also provides

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double the volumetric capacity of lithium; however, the standard reduction potential of magnesium (2.356 V vs NHE) is 700 mV less negative than that of lithium. Due to the highly electronegative nature of lithium metal, to our knowledge, there are no known electrolytes that are not reduced when in contact with lithium metal. However, the reduction products on the surface of the lithium metal anode form a solid electrolyte interface (SEI), which is blocking to electrons but not to the Li^+ ions. The reduction of magnesium analogs of commercial lithium electrolytes also occurs on the surface of metallic magnesium, but unfortunately Mg^{2+} cannot diffuse through the blocking layer formed by the reduced products.⁶ For this reason, the reductive stability of lithium electrolytes is not as crucial as it is for magnesium electrolytes that need to be reductively stable on magnesium metal to prevent the formation of a blocking film. Interestingly, effective magnesium deposition from ethereal solutions of Grignard reagents has been known since 1927, implying a lack of such blocking films in these electrolytes.⁷ These Grignards have limited oxidative stability, less than 2 V vs Mg. One approach to increasing the energy density of a battery is to increase its operating voltage; hence, there is great interest in magnesium electrolytes with electrochemical windows wider than those offered by Grignards.

Ongoing approaches to develop high voltage, noncorrosive electrolytes are detailed in this Perspective. Another strategy to

Received: June 8, 2015

Accepted: August 26, 2015



increase the energy density of lithium ion batteries is to increase the capacity of the cathode. Because Li^+ and Mg^{2+} have roughly the same ionic radius (0.9 Å vs 0.86 Å, respectively), assuming the same number of cations can be inserted into the same cathode host, intercalation of Mg^{2+} with double the charge of Li^+ would result in doubling the capacity of the cathode. Recently, research to double the energy density of lithium ion batteries has been aimed at inserting two Li^+ cations into the cathode, preferably accompanied by a two electron reduction at the same metal center.^{8–12} The challenge of inserting two lithium cations for every transition metal center is not trivial due to volume expansion of the intercalate, which can lead to severe distortions of the crystal lattice and pulverization of the host. Unfortunately, attempts to insert Mg^{2+} have been hampered by the higher ionic charge density that results in slow solid state diffusion. In this Perspective, we detail recent research aimed at discovering a high voltage insertion cathode or high capacity conversion cathodes.

Magnesium Electrolytes. The driving force for the development of magnesium electrolytes for battery applications has been the demand for voltage stabilities higher than those provided by Grignards. Original synthetic methods discovered in the mid to late 1900s are back in the spotlight with new twists aided by modern analytical techniques and wider availability of high grade starting materials. Understanding the foundation of these discoveries might encourage the reader to step beyond the current state of the art and solve challenges that still plague magnesium electrolytes. As early as 1957, Connor investigated the electrodeposition of magnesium from magnesium borohydride.¹³ In 2012, Mohtadi et al. demonstrated magnesium borohydride as a magnesium electrolyte.¹⁴ In contrast to Connor's findings, where boron and magnesium are codeposited in a ratio of 1 to 9, Mohtadi showed pure magnesium deposits by XRD analysis. In 1971, Brenner electroplated magnesium from magnesium boron clusters such as magnesium decaborane generated from the reaction of lithium decaborane with MgCl_2 in THF.¹⁵ More recently, in 2014, Carter et al. demonstrated a voltage stability of 3.2 V vs Mg for the magnesium decaborane cluster (1-(1,7-carboranyl)magnesium chloride) dissolved in THF.¹⁶ The first significant efforts for the development of magnesium electrolytes specifically for rechargeable battery applications were those of Gregory et al. from The Dow Chemical Company in the 1980s.^{17,18} His initial findings on magnesium organohalolaluminates and magnesium organoborates as battery electrolytes laid the foundation of the current magnesium electrolytes such as those reported by Aurbach, Muldoon, JCESR, Fichtner, NuLi, Wang and others.^{19–23} Magnesium organohalolaluminates are rooted in the discovery that spiking of alkyl Grignards with a Lewis acid such as aluminum trichloride enhances the electrochemical plating of Mg metal. Gregory also synthesized magnesium organoborates such as $\text{Mg}(\text{B}(\text{C}_4\text{H}_9)_4)_2$. In the 1990s, di Noto demonstrated a magnesium electrolyte generated from the reaction of $\delta\text{-MgCl}_2$ and aluminum trichloride. This approach was also used in 2013 to generate the magnesium aluminum chloride complex (MACC) electrolyte by Aurbach and Pellion Technologies.²⁴ A new approach has been proposed in 2013 by Muldoon to synthesize magnesium organoborates through an ion exchange pathway.²⁵ This methodology reaches far beyond magnesium toward a universal pathway for electrolyte synthesis.

Building on the premise that the addition of a Lewis acid enhances the oxidative stability offered by a Grignard, Aurbach investigated how different combinations/ratios of dialkylmagnesiums

Table 1. Mg Cycling Efficiency and Oxidation Potentials of THF Solutions Containing Different Combinations of R_2Mg and $\text{AX}_{3-n}\text{R}'_n$ Types of Lewis Bases and Lewis Acids, Respectively, at Different Ratios, As Indicated^a

Lewis base	Lewis acid	acid/base ratio	Mg cycling efficiency	electrolyte decomposition potential
Bu_2Mg	AlCl_2Et	1:2.00	95	2.10
Bu_2Mg	AlCl_2Et	1:1.75	95	2.05
Bu_2Mg	AlCl_2Et	1:1.50	97	2.00
Bu_2Mg	AlCl_2Et	1:1.25	94	1.90
Bu_2Mg	AlCl_2Et	1:1.00	96	1.80
Bu_2Mg	AlCl_2Et	1:0.75	95	1.65
Et_2Mg	AlCl_2Et	1:2.00	92	2.25
Ph_2Mg	AlCl_2Et	1:2.00	80	2.08
Bz_2Mg	AlCl_2Et	1:2.00	88	2.15
Bu_2Mg	AlCl_3	1:2.00	75	2.40
Bu_2Mg	AlCl_3	1:1.75	74	2.30
Bu_2Mg	AlCl_3	1:1.50	74	2.25
Bu_2Mg	AlCl_3	1:1.25	83	2.15
Bu_2Mg	AlCl_3	1:1.00	86	2.10
Bu_2Mg	AlCl_3	1:0.75	92	2.00
Bu_2Mg	BPh_3	1:1.50	86	1.77
Bu_2Mg	BPh_3	1:1.00	68	1.60
Bu_2Mg	BPh_3	1:0.66	91	1.40
Bu_2Mg	BPh_3	1:0.50	93	1.30
Bu_2Mg	BCl_3	1:1.00	80	1.20
Bu_2Mg	BCl_3	1:0.50	93	1.75
Bu_2Mg	BCl_3	1:0.20	71	1.50

^aThe electrolyte decomposition potential refers to oxidative decomposition of the electrolyte vs. Mg. Reprinted with permission from ref 19. Copyright 2003, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

to Lewis acids affected the Coulombic efficiency and oxidative stability of the in situ generated electrolyte. This work is summarized in Table 1.¹⁹

This comprehensive effort later yielded the DCC electrolyte of the given formula: $\text{Mg}(\text{AlCl}_2\text{BuEt}_2)_2$. This in situ generated magnesium organohaloaluminate is generated from the reaction of one equivalent of dibutylmagnesium and two equivalents of ethylaluminum dichloride. This electrolyte exhibits an oxidative stability of 2.2 V vs Mg and a Coulombic efficiency of 100% for Mg deposition/dissolution (Figure 1).

Gewirth has carried out a detailed electrochemical study of Mg deposition/dissolution from DCC and has shown that the Coulombic efficiency is considerably less than 100% for the early cycles.²⁶ More concerning is the fact that GC and NMR analysis of this electrolyte shows evidence of decomposition. Gewirth suggests that the DCC electrolyte is not ideal for use in a robust magnesium ion battery. In an attempt to characterize the structure of DCC, a single crystal was precipitated from THF solution by the addition of hexane. However, the redissolved crystal ($\text{Mg}_2(\mu\text{-Cl})_3\cdot6\text{THF}$) (EtAlCl_3) in THF showed no reversible magnesium deposition and dissolution.^{19,27,28} Contradictory to the findings of Aurbach, Muldoon reported that the crystallized DCC is indeed electrochemically active (Figure 2).²⁰ Aurbach demonstrated the first and to date only long cycle life rechargeable magnesium battery using the DCC electrolyte,²⁹ apparently contradicting the later reports of Gewirth on the stability of the DCC electrolyte.²⁶ However, this battery had low energy density comparable to that of nickel cadmium or lead acid batteries. One way of improving the energy density is to increase the operating voltage of the

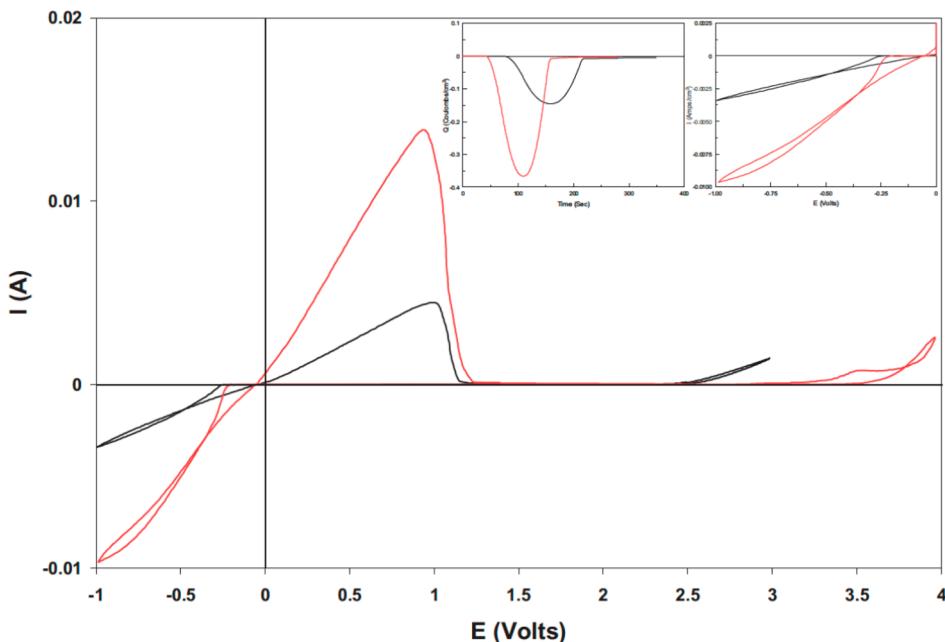


Figure 1. Comparison between the voltammetric behavior of THF solutions containing 0.25 M of the reaction product between 1:2 MgBu_2 and AlCl_2Et (DCC) (black line) and 0.4 M of the reaction product between 1:2 AlCl_3 and PhMgCl (designated APC) (red line) as indicated. Conditions: 25 mV s^{-1} , Pt wire working electrode, 25 $^{\circ}\text{C}$. Right insert: Enlargement of the cyclic voltammograms near 0 V vs Mg R.E., comparing the overpotential for Mg deposition in the two solutions. Left insert: Charge balance upon typical Mg deposition–dissolution cycles in these solutions (100% cycling efficiency of Mg deposition). Reprinted with permission from ref 30. Copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

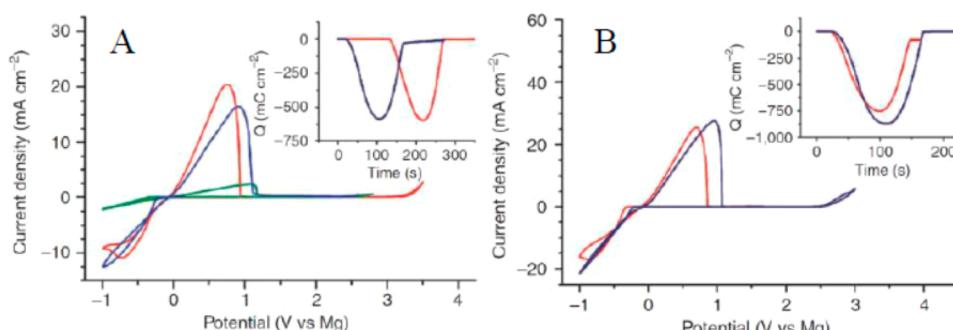


Figure 2. (A) Cyclic voltammograms of HMDSMgCl (green), the reaction product generated in situ from a 3:1 mixture of HMDSMgCl to AlCl_3 (blue), and the crystal obtained from a 3:1 mixture of HMDSMgCl to AlCl_3 (designated GEN1) (red). Inset shows the charge balance during the deposition and the subsequent dissolution of Mg. Reprinted with permission from ref 20. Copyright 2011, Nature Publishing Group. (B) Cyclic voltammograms of 0.4 M THF solution of the reaction product generated in situ from a 2:1 mixture of Bu_2Mg to EtAlCl_2 (DCC) (blue) and of the crystal obtained from a 2:1 mixture of Bu_2Mg to EtAlCl_2 (crystallized DCC) (red). Scan rate is 0.025 V s^{-1} . Reprinted with permission from ref 20. Copyright 2011, Nature Publishing Group.

battery, which requires magnesium electrolytes with a higher oxidative stability. Aurbach's second generation electrolyte APC enhanced the oxidative stability of DCC by substitution of the alkyl group with aromatic groups, which excludes β -H elimination as a possible route to oxidative decomposition.³¹ This electrolyte is readily generated in situ via the reaction of one equivalent of aluminum trichloride with two equivalents of phenyl magnesium chloride. This significantly enhances the reported oxidative stability from 2.2 to 3.2 V vs Mg on a platinum working electrode and attains a Coulombic efficiency of 100% (Figure 1).

In lithium ion batteries, electrolytes are prepared by dissolving a lithium salt such as LiPF_6 in organic solvents (ethers, carbonates or ionic liquids). The salts and the solvents are distinct components and this allows for electrolyte optimization

by varying the salt:solvent combination and ratios. This way, each and every component of the electrolyte can be individually selected for a particular purpose. Desirable magnesium electrolytes are those that share the strict level of control available in the design of lithium electrolytes. However, in situ generated magnesium organohaloaluminates are complex soup mixtures operating under dynamic equilibria that can result in formation of unwanted components. For example, the in situ generated electrolyte APC contains both corrosive and nucleophilic components that prohibit the use of aluminum current collectors³² or conversion cathodes such as sulfur.²⁰ One way to control the effects of unwanted components in magnesium electrolytes is to obtain simple magnesium salts that can be dissolved in the appropriate solvents. Recently, our group has demonstrated that in situ magnesium electrolytes purified by crystallization

show improved oxidative stability, increased Coulombic efficiency of deposition and dissolution and can sustain higher current densities.²⁰ For example, the *in situ* generated electrolyte formed from the reaction of a 3 to 1 mixture of the Hauser base hexamethyldisilazide magnesium chloride (HMDSMgCl) and aluminum trichloride (AlCl_3) exhibits an oxidative stability of 2.5 V vs Mg (which is identical to the oxidative stability of the Hauser base). The crystallized electrolyte ($\text{Mg}_2(\mu\text{-Cl})_3 \cdot 6\text{THF}$) ($\text{HMDS}_n\text{AlCl}_{4-n}$) ($n = 1, 2$) shows an oxidative stability of 3.2 V vs Mg and columbic efficiency of 100% (Figure 2). Fichtner et al. have recently reported the formation of this electrolyte through the reaction of HMDS_2Mg with AlCl_3 .²² Similarly, the electrochemically active species of the crystallized reaction product between PhMgCl and AlCl_3 at a ratio of 2:1 (APC) was also confirmed. Grignard reagents are highly sensitive to air and moisture and must be handled under inert environments. The early work of di Noto has shown that $\delta\text{-MgCl}_2$ can be used as a substitute for Grignards in reactions with AlCl_3 . Recently Liu et al. have prepared electrolytes with an oxidative stability of up to 3.4 V vs Mg and Coulombic efficiencies of up to 100% by the reaction of MgCl_2 with aluminum Lewis acids such as AlEtCl_2 , AlPh_3 , and AlCl_3 .³³ Interestingly, the solvent can have a dramatic effect on the cation formed by the reaction of MgCl_2 with Lewis acids. If dimethoxyethane (DME) is used in place of THF, Cheng et al. has identified a unique cation complex $[\text{Mg}_2(\mu\text{-Cl})_2 \cdot 4\text{DME}]^+$ that undergoes reversible magnesium deposition and dissolution whereas if the analogous reaction is carried out in THF, the magnesium dimer $[\text{Mg}_2(\mu\text{-Cl})_3 \cdot 6\text{THF}]^+$ is observed.³⁴ Similarly, Doe et al. have also reported the *in situ* electrolyte (MACC) generated by the reaction of MgCl_2 and AlCl_3 .²⁴ The resulting electrolyte has an oxidative stability of 3.1 V vs Mg and a Coulombic efficiency of 100%. Gewirth examined the electrochemistry and composition of the MACC electrolyte and found that reversible magnesium deposition occurred after electrochemical conditioning.³⁵ More concerning was the codeposition of magnesium and aluminum; however, conditioned MACC shows no evidence of aluminum codepositing. All of the crystallized magnesium organohaloaluminate electrolytes comprise the same magnesium containing cation ($\text{Mg}_2(\mu\text{-Cl})_3 \cdot 6\text{THF}$)⁺ and their oxidative and reductive stability is therefore governed by the choice of unique anions. Extension of the oxidative stability of the magnesium organohaloaluminates could be achieved by simply functionalizing the aromatic groups of APC with electron withdrawing groups such as fluorine or $-\text{CF}_3$. However, based on literature reports and internal attempts, fluorinated aryl metal reagents and fluorinated

aluminates are explosive and should be handled with extreme caution or avoided altogether.³⁶ One other cause for concern is the triarylaluminum Lewis acids, which are highly reactive with air and water and can spontaneously result in uncontrollable fires. They should also be handled by experienced organometallic chemists. One way of overcoming these safety challenges associated with the preparation of fluorinated magnesium organohaloaluminates is to use fluorinated boron Lewis acids that can yield magnesium organoborates that are air and moisture stable.

DFT calculations have been demonstrated to be a very useful tool in estimating the oxidative and reductive stability of electrolytes.

DFT calculations have been demonstrated to be a very useful tool in estimating the oxidative and reductive stability of electrolytes.^{6,32} The oxidative stability of the electrolytes can be estimated by calculating the highest occupied molecular orbital energy (HOMO) as this involves the removal of an electron from this orbital. The oxidative stability determines the maximum cathode potential and thus applicable cathode materials. It is important to note the oxidative stability of the electrolyte increases as the HOMO energy becomes more negative. The reductive stability of the electrolyte is extremely important in a magnesium battery because it will determine if the electrolyte will decompose on the surface of the anode. Such a reaction may result in the formation of an insulating surface layer on the anode that will not permit transport of magnesium ions. The lowest unoccupied molecular orbital (LUMO) can be used to determine the reductive stability because it involves the addition of an electron to this orbital. On the basis of eq 1, the oxidative and reductive stability (U_{redox} vs NHE) can be calculated from the HOMO and LUMO energy (E_{redox}), given a finite elementary charge e (see Table 2)

$$E_{\text{redox}}[\text{eV}] = -(4.6 \pm 0.1) - eU_{\text{redox}}[\text{V vs NHE}] \quad (1)$$

Due to the electrolyte salts being ionic in nature, it is important to calculate the molecular orbitals by taking into consideration the polar solvents in which they are dissolved. Table 2 summarizes the HOMO/LUMO energies and the calculated/observed oxidative and reductive stabilities for a number of reported magnesium organohaloaluminates and magnesium organoborates. It is important to understand that in the case where the electrolyte has a number of anionic components such as APC (electrolyte 2 in Table 2), the oxidative

Table 2. Summary of HOMO and LUMO Energy Levels and the Corresponding Redox Potentials for the Anion Component of the Crystallized Electrolytes

magnesium electrolyte	anion	HOMO (eV)	$U_{\text{ox-expected}}$ (V vs Mg)	$U_{\text{ox-reported}}$ (V vs Mg)	LUMO (eV)	$U_{\text{red-expected}}$ (V vs Mg)
GEN1	$(\text{HMDS})_2\text{AlCl}_2^-$ ^a			3.2		
	$(\text{HMDS})\text{AlCl}_3^-$	-5.67	3.4		0.06	-2.3
	Ph_3Al^-	-5.38	3.1	3.2	0.02	-2.3
	Ph_2AlCl^-	-5.67	3.4		0.05	-2.3
	$\text{Ph}_2\text{AlCl}_2^-$	-6.05	3.8		0.06	-2.3
	PhAlCl_3^-	-6.40	4.2		-0.06	-2.2
APC	Cl_4Al^-	-6.74	4.5		-1.38	-0.9
	Ph_4B^-	-4.82	2.6	2.6	-0.54	-1.7
GEN2						
GEN3	$(\text{C}_6\text{F}_5)_3\text{BPh}^-$	-5.56	3.3	3.7	-0.42	-1.8

^aThe structural flexibility of $(\text{HMDS})_2\text{AlCl}_2^-$ makes its geometry difficult to optimize.

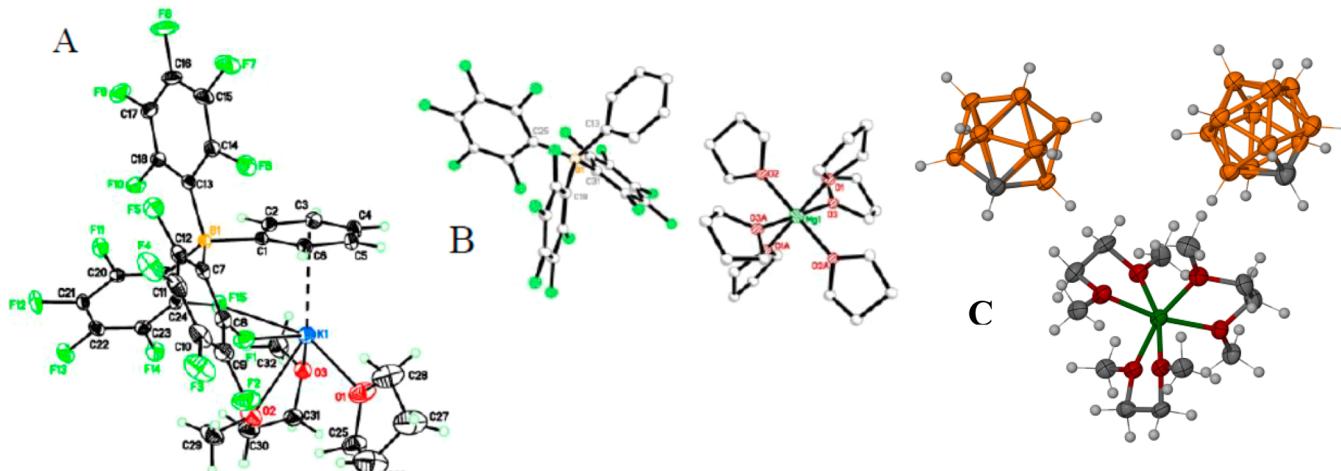


Figure 3. (A) ORTEP plot for potassium salt analog of $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})(\text{B}(\text{C}_6\text{F}_5)_3\text{Ph})$ (GEN3); (B) ORTEP plot for naked Mg salt analog of GEN3. Hydrogen atoms are omitted for clarity. There is a 25% thermal probability for the ellipsoids; (C) ORTEP for $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2/\text{tetraglyme}$ (MCC/G4). Reprinted with permission from ref 39. Copyright 2015, Wiley-VCH.

stability will be governed by the species with the most positive HOMO energy. The DFT calculations predict the following oxidative stability: GEN3 ($(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})(\text{B}(\text{C}_6\text{F}_5)_3\text{Ph})$) > APC, $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})(\text{Ph}_n\text{AlCl}_{4-n})$ ($n = 1$ to 4) > GEN1, $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})(\text{HMDS}_n\text{AlCl}_{4-n})$ ($n = 1,2$) > GEN2, $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})(\text{BPh}_4)$, which predicts that a fluorinated magnesium organoborate GEN3 (structure) can have a higher oxidative stability than magnesium organohaloaluminates. The experimental oxidative stability of these magnesium electrolytes was confirmed to be consistent with the DFT calculations, with the electrolytes GEN3, APC, GEN1, and GEN2 yielding oxidative stabilities of 3.7, 3.2, 3.2, and 2.6 V vs Mg, respectively. Interestingly, experimental results indicate that the aluminates have superior oxidative stability for the same organic functionality: $(\text{AlPh}_4)^-$ has an oxidative stability 0.7 V higher than $(\text{BPh}_4)^-$. Cheng et al. have recently demonstrated accelerated electrolyte discovery for magnesium batteries through high throughput calculations of the redox potential, solubility and stability of electrolyte candidates.³⁷ This approach may aid in the synthesis of novel magnesium battery electrolytes.

The oxidative stability of many magnesium electrolytes is reported to be in excess of 3 V vs Mg when tested by cyclic voltammetry on a Pt working electrode. However, their window of operation when assembled in coin cells and operated at constant current using typical aluminum or copper current collectors is rarely above 2.0 V. It has been proposed that the corrosive nature of magnesium electrolytes limits their window of operation to potentials less than what is observed on platinum working electrodes.^{25,32} In order to test this hypothesis, the removal of corrosive species such as chlorides from both the anion and the cation has been attempted. There is still an open question in our laboratory presently being investigated as to whether the magnesium dimer $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})^+$ is the cause of corrosion or whether the cause could be the purity of the starting materials. Synthetic attempts to make a chloride-free magnesium electrolyte represent valuable efforts toward development of noncorrosive electrolytes. It is worth noting that lithium electrolytes such as LiTFSI do not contain chlorides but are still corrosive toward aluminum current collectors. The magnesium organoborate $(\text{PhB}(\text{C}_6\text{F}_5)_3)_2\text{Mg}$, which is the naked magnesium analog of GEN3, was selected as a model candidate to test this hypothesis. The oxidative stability of GEN3 is 3.7 V vs Mg on a

platinum working electrode but due to its corrosive nature its window of operation is below 2.2 V on a stainless steel working electrode. Initial attempts at the synthesis of this electrolyte from the reaction of one equivalent of diphenylmagnesium and two equivalents of the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ yielded the desired product in addition to other products that are presumably reduced on the surface of the working electrode and precluded reversible deposition of magnesium. Mass spectrometry analysis showed exact mass and isotope patterns consistent with $\text{B}(\text{C}_6\text{F}_5)_4^-$ could be detected on the surface of the working electrode. The appearance of $\text{B}(\text{C}_6\text{F}_5)_4^-$ may be explained by aryl metathesis. This synthetic approach of reacting diaryl magnesium with boron based Lewis acids was abandoned due to the challenge of aryl metathesis, which results in scrambling of the aryl groups on the anion. These anions are often not compatible with magnesium anodes due to reduction.

It would be the holy grail of electrolyte development to have a universal synthetic method to readily convert the magnesium dimer $(\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF})^+$ into the corresponding naked magnesium analogue. Our approach to achieve this dream, which we deem universal, was based on an ion exchange pathway where the magnesium dimer of GEN3 is converted to the potassium salt (Figure 3a), which can be readily converted to the silver salt and then exchanged to the naked magnesium salt of GEN3 (Figure 3b).³⁸ There is one major challenge that must be overcome, which is the required high purity of the starting material, most notably obtaining anhydrous Lewis acid beyond what is commercially available. The universal aspect of this method relies on the use of the silver intermediate, which can

The universal aspect of this method relies on the use of the silver intermediate, which can be further exchanged with a wide variety of metal chlorides, which opens the gate to obtaining new electrolytes for sodium, potassium, calcium, aluminum, zinc, or even lithium batteries.

be further exchanged with a wide variety of metal chlorides, which opens the gate to obtaining new electrolytes for sodium, potassium, calcium, aluminum, zinc, or even lithium batteries. This method was used to obtain the model compound $Mg(BArF)_2$, which was used to evaluate the feasibility of magnesium organoborates as potentially noncorrosive electrolytes.²⁵ This electrolyte showed an oxidative stability greater than 4.0 V vs Mg but unfortunately it had limited reductive stability that precluded the reversible deposition of magnesium. Recently, Tutusaus et al. has used the ion exchange methodology to develop a magnesium electrolyte $Mg(CB_{11}H_{12})_2$ /tetraglyme (Figure 3C S21) that is compatible with magnesium metal and shows Coulombic efficiencies greater than 99% and an oxidative stability greater than 3.8 V vs Mg.³⁹ The electrolyte exhibits oxidative stabilities in excess of 3.5 V vs Mg on a stainless steel and aluminum working electrodes on a first CV scan. Hysteresis due to corrosion is not observed and a potential in excess of 3.0 V vs Mg can be maintained for 48 h without any visible (pitting) spikes in current. This magnesium electrolyte MCC/G4 is possibly the best current option for screening high voltage cathodes. In our laboratory there is significant interest in developing a one-step synthesis of naked magnesium electrolytes without the cumbersome multiple steps of the ion exchange pathway.

Although many hurdles have been cleared in efforts to develop practical magnesium electrolytes the quest for a suitable cathode for a magnesium battery is still ongoing. Currently, testing of new cathode materials in full cells is often hampered by high impedance exhibited by the magnesium metal anode. It is not uncommon for the magnesium metal anode impedance to reach $1\text{ M}\Omega\cdot\text{cm}^2$. This causes rapid voltage and capacity decay in the cell and can make currents pertaining to redox of cathode metal centers difficult to observe. One way to bypass this problem is to use an excess of electrolyte as a source of magnesium and high surface area carbon as the counter electrode (anode) in a half battery/half capacitor electrochemical cell. This approach has been reported in conjunction with a variety of cathodes in various studies⁴⁰ and has also been used in our laboratory. An additional advantage of this method is the ability to employ commercial magnesium electrolytes such as $Mg(TFSI)_2$ or $Mg(ClO_4)_2$ dissolved in solvents such as acetonitrile that are not compatible with magnesium metal. However, it is desirable to lower the resistance of magnesium metal such that new cathodes can be tested in full cells containing magnesium metal anodes. One common method to "activate" the magnesium anode is to scratch or abrade it under an inert atmosphere. Although this method works quite well for treating electrodes with a small surface area such as those used for three electrode cyclic voltammetry experiments, it still results in very high impedance for higher surface area magnesium foil used in coin cells or pouch cells. Borrowing from the early work of pioneers in Grignard organometallic chemistry who were highly skilled in activating magnesium for reactions with high thermodynamic thresholds, a highly active magnesium anode can be prepared with magnesium obtained from reduction of metal salts.⁴¹ The finely divided black powder can be generated in the laboratory or purchased commercially as a slurry in THF (Rieke active magnesium Mg*). An anode paste can be prepared under inert atmosphere with a 5% polymer solution of PVDF dissolved in THF. Some conductive carbon can be added if needed. The paste can then be coated onto a current collector such as carbon paper/graphite foil (for example, Grafoil) or aluminum and cut into disks to be used in battery cells. The impedance of

such electrodes in symmetrical cells has been measured in our laboratories to be in the $300\text{ }\Omega\cdot\text{cm}^2$ range, very much in line with lithium metal anodes. This approach opens the door toward practical testing of cathodes in cells with magnesium metal anodes.

Although batteries with a magnesium metal anode are highly desirable due to the high energy density offered by the metallic anode, promising efforts have been reported in the area of alloying anodes for magnesium ion batteries.^{42,43} The interest in metal anodes currently stems from the challenges related to the formation of passivation layers during magnesium plating and stripping and anode/electrolyte/cathode incompatibilities. One of the major driving forces for the use of such anodes is the use of conventional, commercially available magnesium salts such as $Mg(TFSI)_2$ or $Mg(ClO_4)_2$, which have been demonstrated to be compatible with alloy anodes such as tin or bismuth. The most impressive performance of alloying anodes was achieved by controlling their nanostructure. Shao et al. dramatically improved the discharge rates previously reported by Arthur et al.^{42,44} Figure 4 summarizes the cyclic voltammetry of the magnesium insertion and deinsertion of bismuth nanotubes as well as cycling and rate performance. Parent et al. has recently demonstrated exceptional performance for a nanostructured SnBi anode by limiting the particle size to less than 40 nm.⁴⁵ This work emphasizes the importance of nanotechnology to enhance both the cycling and rate performance of alloy anodes. Recently, Ha et al. have demonstrated the deposition and dissolution of $Mg(TFSI)_2$ in glyme.⁴⁶

Cathode Materials. A promising approach to reducing the cost and increasing the energy density of the conventional lithium ion battery is to identify cathode materials that can react with greater amounts of lithium than the 0.5–1 lithium ion per metal center in a typical intercalation cathode. For example, $VOPO_4$, which has a theoretical capacity of up to 2 lithium ions per $VOPO_4$ resulting in a theoretical specific capacity of 305 mAh/g (about 2 times that of existing commercial cathodes) has been identified as a possible component of higher capacity cells.⁴⁷ However, materials that electrochemically intercalate multiple lithium ions also tend to exhibit multiple voltage plateaus. In fact, $VOPO_4$ has been shown to deliver only about one-third of its theoretical capacity at voltages similar to existing Li-ion batteries and about another third at potentials over a volt lower. In addition, intercalation of $>1\text{ Li}^+$ ion has the potential to cause substantial structural strain on the host material and cause instability. However, it is likely that realization of high capacity Mg battery cathodes will also require development of materials that can undergo 2-electron reduction reactions involving one mole of Mg per mole of cathode material. This can be illustrated by assuming a hypothetical Mg/Mg_xVOPO_4 battery. Figure 5 shows the specific capacity of Mg_xVOPO_4 as a function of x and the volumetric energy density of the active materials in a Mg/Mg_xVOPO_4 cell assuming 50% excess Mg and a flat 2.5 V cell operating voltage.

In addition to intercalation reactions, potential cathode reactions that may allow a two-electron reduction include conversion materials such as sulfur and oxygen as well as metal halides such as CuF_2 . Organic cathodes also hold promise in this area. Extensive reviews of Mg battery cathode materials are available in the literature;^{48,49} recent approaches toward high capacity cathodes are highlighted here.

Though the $VOPO_4$ cathode material has apparently not been evaluated in conjunction with Mg anodes to the best of our knowledge, V_2O_5 has received substantial attention as an

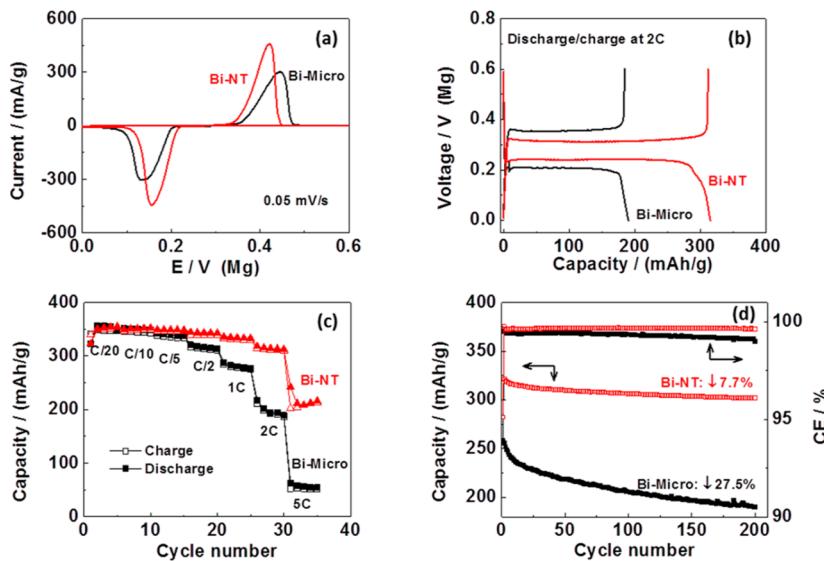


Figure 4. (A) Cyclic voltammograms of Mg insertion/deinsertion in bismuth; (B) discharge/charge profile of an Mg–Bi cell; (C) rate performance of an Mg–Bi cell; (d) cycling stability and Coulombic efficiency (CE) of bismuth electrode for reversible Mg insertion/deinsertion. Cell configuration: Mg/0.1 M $\text{Mg}(\text{BH}_4)_2$ –1.5 M LiBH_4 –diglyme/Bi. Reprinted with permission from ref 44. Copyright 2014, American Chemical Society.

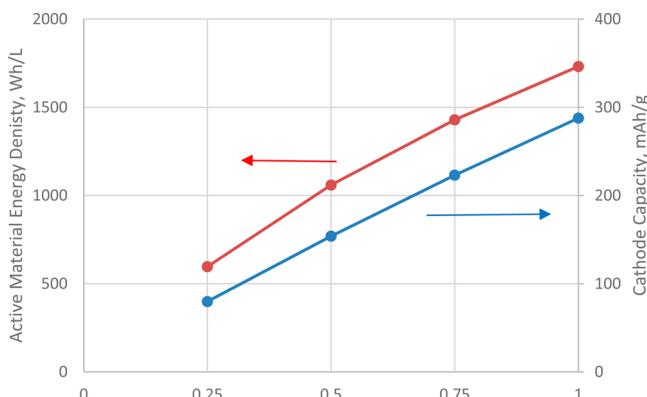


Figure 5. Specific Capacity of Mg_xVOPO_4 and Active Material Energy Density of $\text{Mg}/\text{Mg}_x\text{VOPO}_4$ vs x in Mg_xVOPO_4 .

intercalation cathode for Mg batteries. It has demonstrated a relatively high reversible specific capacity of about 150 mAh/g, suggesting intercalation of one equivalent of Mg rather than the desired two per unit formula. A recent theoretical study of Mg insertion into V_2O_5 sheds additional light on the behavior of this material. Density functional theory (DFT) calculations were used by Zhou et al.⁵⁰ to calculate an open circuit potential of 3.06 V vs Mg, which is actually 0.22 V higher than its potential vs Li, corroborating cyclic voltammetry results reported by Gershinsky et al.⁴⁰ However, the barrier to Mg^{2+} hopping in V_2O_5 was found to be substantially higher than that for Li^+ hopping, explaining observations of slow Mg^{2+} diffusion in this material. This ion hopping barrier was found to increase as a MgV_2O_5 phase forms via Mg intercalation, which would negatively impact the operation of a $\text{Mg}|\text{V}_2\text{O}_5$ battery and limit the extent of Mg intercalation that can be practically achieved at acceptable rates and cell voltages. Thus, further understanding of the phase behavior and ion transport pathways of the Mg–V–O system appears to be critical to potential improvement of this battery system. For example, doping V_2O_5 with another element may alter the phase behavior and ion transport

channels of the material and affect its electrochemical performance.

Prior studies that measured higher specific capacities for V_2O_5 involved use of aerogel material⁵¹ and addition of water to the electrolyte.^{52,53} The effect of water addition is particularly interesting, and its positive effect is believed to be due to shielding of the Mg^{2+} ion from direct interaction with lattice oxygen atoms;⁵⁴ however, the presence of water in the electrolyte is detrimental to electrolytes such as APC that are capable of Mg plating/stripping at the anode. Attempts to circumvent this by incorporating water into the cathode structure rather than in the electrolyte have achieved some success.^{55,56} Recently, Song et al. utilized a hybrid approach with MnO_2 nanowire (~ 200 nm diameter by $\sim 4.5 \mu\text{m}$ long) cathodes in an attempt to improve the performance of that material in Mg batteries.⁵⁷ Song et al. “activated” the cathode by first cycling it in water-containing electrolyte ($\text{Mg}(\text{ClO}_4)_2 \cdot \text{xH}_2\text{O}$ /propylene carbonate) before transferring it into a cell with a dry $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ /propylene carbonate electrolyte. It was observed that nonactivated electrodes in dry electrolytes exhibited an initial capacity of about 90 mAh/g (corresponding to intercalation of about 0.15 mol Mg per MnO_2), whereas use of electrolytes containing six molecules of water per magnesium perchlorate resulted in incorporation of about 0.7 mol Mg per MnO_2 (360 mAh/g). Cycling this electrode at a 1.6C rate in wet electrolyte vs a carbon cloth counter electrode resulted in an initial reversible capacity of about 160 mAh/g, which remained above 100 mAh/g for 200 cycles. The capacity dropped off substantially when the “activated” electrode was subsequently cycled in dry electrolyte at a reduced rate of 0.4C, but an initial capacity of about 120 mAh/g was measured, declining to about 80 mAh/g at 100 cycles. The behavior of the MnO_2 electrode in each of these scenarios (dry, wet, and wet then dry electrolytes) is illustrated schematically in Figure 6.

The behavior of the “activated” electrode after transfer to a dry electrolyte also depended on whether the electrode was in the charged or discharged state prior to transfer. Figure 7 shows cyclic voltammograms of “activated” electrodes after transfer

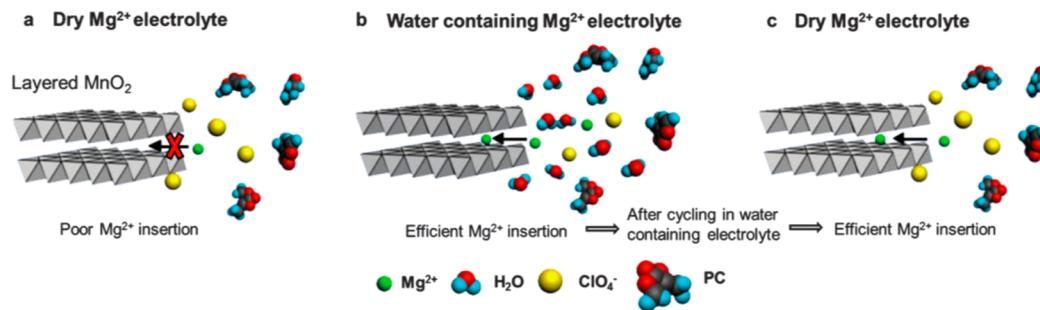


Figure 6. Schematic of Mg^{2+} insertion process in layered MnO_2 cathode. (a) Mg^{2+} insertion process in dry Mg^{2+} electrolyte ($Mg(ClO_4)_2$ /propylene carbonate). (b) Mg^{2+} insertion process in water containing Mg^{2+} electrolyte ($Mg(ClO_4)_2\cdot 6H_2O$ /propylene carbonate). (c) Mg^{2+} insertion process in dry Mg^{2+} electrolyte ($Mg(ClO_4)_2$ /propylene carbonate) after cycling in water containing electrolyte. Reprinted with permission from ref 57. Copyright 2015, Royal Society of Chemistry.

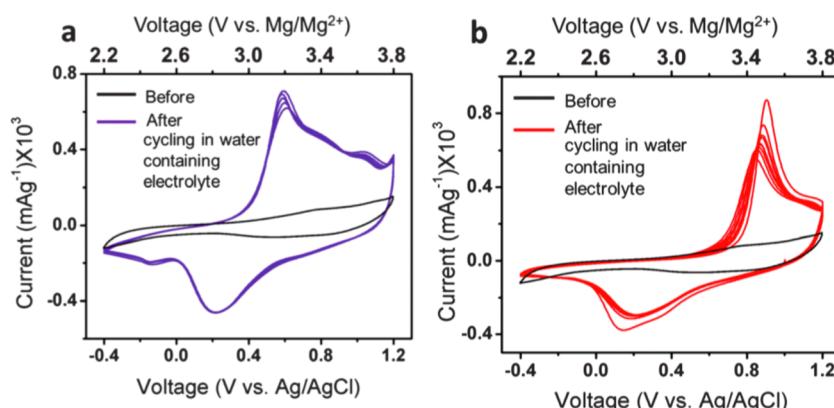


Figure 7. (a) CV of MnO_2 nanowire electrode measured in 0.1 M $Mg(ClO_4)_2/PC$ electrolyte before and after cycling in 0.1 M $Mg(ClO_4)_2\cdot 6H_2O/PC$. Measurement after cycling 0.1 M $Mg(ClO_4)_2\cdot 6H_2O/PC$ was started at (a) discharged state and (b) charged state. Reprinted with permission from ref 57. Copyright 2015, Royal Society of Chemistry.

from wet to dry electrolytes in both charged and discharged states vs “non-activated” electrodes.

Song et al. concluded that the water remaining in the discharged MnO_2 contributed to reducing ionic interaction between Mg^{2+} and MnO_2 and also had an impact on the structure of the cathode that was not resolved in this work. It is interesting to note that the improvement seen when “activated” MnO_2 was transferred to a dry electrolyte is in contrast to the behavior of V_2O_5 observed in previous work, where the improved performance of that material in wet electrolytes was not maintained upon transfer to dry electrolytes. A significant aspect that was lacking in the work of Song et al., however, was the fact that the electrolytes used were not capable of reversible Mg deposition/dissolution, nor were the MnO_2 cathodes cycled with Mg anodes in such electrolytes. Thus, it is not known at this point if the “activation” procedure described by Song et al. can be utilized in a practical Mg battery; this should be explored.

MnO_2 is an attractive cathode material for Mg batteries because of its high theoretical capacity of ~ 480 mAh/g for full reduction of $Mn(IV)$ to $Mn(II)$ and low cost but previously reported results for Mg intercalation into that material have been highly variable. For example, crystal structure was found to have a significant effect on electrochemical behavior of MnO_2 ,⁵⁸ and a wide range of capacities have been reported.⁴³ Zhang et al. attempted to clarify this situation by preparing or procuring and evaluating a variety of MnO_2 materials, including nanorods with various stabilizing additives and micron-sized aggregates, with BET surface areas ranging from 25 to 231 m²/g.⁵⁹ Electrochemical characterization of these materials was

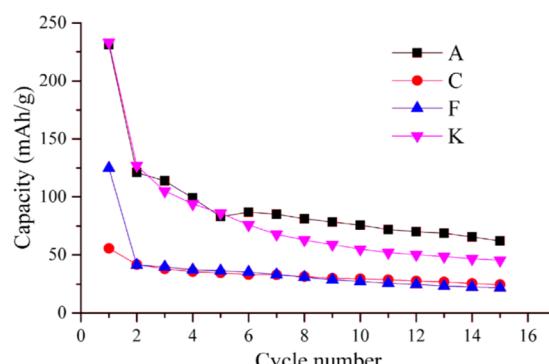


Figure 8. Cycling performance of a variety of MnO_2 cathodes in the cell $Mg|APC\text{-}THF|MnO_2$. Cathode materials are as follows: A = K^+ stabilized $\alpha\text{-MnO}_2$ nanorods, 231 m²/g; C = K^+ stabilized $\alpha\text{-MnO}_2$ nanorods, 30 m²/g; F = H_2O stabilized $\alpha\text{-MnO}_2$ nanorods, 28 m²/g; K = no stabilizer, $\gamma\text{-MnO}_2$ aggregates ($> 1 \mu\text{m}$), 70 m²/g. Reprinted with permission from ref 59. Copyright 2015, Elsevier.

accomplished in a cell using a Mg metal anode and 0.2 M APC/THF electrolyte, thus assuring reversibility of the Mg electrode. Figure 8 shows cycling performance of several of the MnO_2 materials.

As can be seen in Figure 8, both initial capacity and capacity after several cycles appears to be influenced by the BET surface area of the cathode material, whereas the type of stabilizer and the specific polymorph have little if any effect; capacity fade is substantial in all materials. Materials with BET surface area of at

least about $70 \text{ m}^2/\text{g}$ all exhibited first cycle capacity of about 250 mAh/g , indicative of reaction of about $0.45 \text{ mol Mg per mole MnO}_2$. XRD and TEM analyses of discharged cathodes revealed a largely amorphous surface layer containing Mn^{2+} as well as Mg and O. The authors also performed DFT calculations that, along with their analytical results, support a discharge mechanism involving a conversion reaction to form MgO and reduced Mn oxides rather than Mg-intercalated MnO_2 . Poor electrochemical reversibility of MgO and slow transport of Mg^{2+} through this amorphous layer are possible explanations for the rapid capacity fade seen in these materials, along with electrolyte decomposition and the well-known Mn dissolution phenomenon. Thus, this work indicates that if low-cost MnO_2 is to become a practical cathode for secondary Mg batteries a reversible pathway for MgO formation must be identified. A possible approach to this may involve the use of mediators, such as the use of an I_2/DMSO complex to create a reversible $\text{Mg}-\text{O}_2$ battery by Shiga.⁶⁰

Despite its obvious attractive properties, MnO_2 has not been successfully used as a cathode material in commercial rechargeable Li-ion batteries. Structural instability experienced with Li^+ intercalation into layered MnO_2 does not occur with spinel-phase LiMn_2O_4 and this compound is used in commercial Li-ion batteries. Electrochemical intercalation of Mg^{2+} into delithiated LiMn_2O_4 was evaluated by Cabana et al.⁶¹ Extensive electrochemical intercalation of Mg^{2+} into the tetrahedral sites of this cathode material was reported at a potential of $2.9 \text{ V vs Mg/Mg}^{2+}$ with concurrent reduction of Mn^{4+} to Mn^{3+} in the host material. A first cycle discharge capacity of $\sim 190 \text{ mAh/g}$ at a rate of $C/20$ was reported, which corresponds to a composition of about $\text{Mg}_{0.67}\text{Mn}_2\text{O}_4$. However, the experiments were conducted in an aqueous electrolyte ($1 \text{ M Mg}(\text{NO}_3)_2$), and although no apparent cointercalation of H_2O was detected, behavior in nonaqueous electrolytes that support reversible Mg electrochemistry would need to be demonstrated for this material to be considered for use in secondary Mg batteries. A few experiments utilizing $\text{Mg}(\text{TFSI})_2$ in diglyme or propylene carbonate were conducted and much lower levels of Mg^{2+} intercalation were detected, although reversibility was observed. Higher voltage hysteresis was also observed for nonaqueous vs aqueous electrolytes, suggestive of increased kinetic barriers for Mg^{2+} intercalation from nonaqueous electrolytes. Behavior in electrolytes reversible to Mg/Mg^{2+} was not evaluated. An interesting observation was that Mg^{2+} intercalation was primarily observed in nanoflakes created in the cathode material by the initial chemical delithiation procedure, whereas micron-sized particles largely retained the cubic spinel structure. This supports the hypothesis that slow Mg^{2+} diffusion has a substantial impact on the measured capacity of intercalation cathode materials. This may also indicate that techniques such as the use of nanoparticles, which are used instead of micron-sized particles to improve the electrochemical performance of cathode materials exhibiting slow cation diffusion such as LiFePO_4 , may promote improved performance of Mg intercalation cathodes.

The performance of layered vs spinel structured cathode materials was also investigated via a computational study of the behavior of Mg^{2+} intercalation into layered and spinel structure TiS_2 by Emly and Van der Ven.⁶² It was concluded that both Li_xTiS_2 and Mg_xTiS_2 are stable in similar structures, with the layered O1 structure being energetically preferred vs other layered structures and the spinel structure that was found to be metastable. Voltage curves were calculated for Mg_xTiS_2 vs Mg

in both the layered O1 and spinel structures over a composition range of $0 \leq x \leq 0.5$ at 300 K . The spinel material exhibited a sloping voltage curve, similar to that expected for a solid solution, over a range from about 1.5 to 0.7 V , whereas the layered O1 material exhibited voltage plateaus in the same voltage range, indicative of the formation of more stable intermediate phases. This calculated capacity is significantly higher than that measured in prior studies of Mg intercalation into TiS_2 , which may be explained by the differences in the behavior of different crystal structures and high polarization during electrochemical intercalation. Both Li^+ and Mg^{2+} were found to preferentially occupy the octahedral sites rather than the tetrahedral sites, although cation movement via hopping between octahedral sites was found to occur via passage through the intermediate tetrahedral sites. Mg mobility was also found to be substantially slower than Li mobility, similar to observations for other cathode materials. It was concluded that the size of the migration channel between adjacent sites had a substantial impact on cation mobility, and therefore, development of cathode materials with increased interlayer spacing such as by incorporation of large, immobile cations or molecules could increase Mg^{2+} mobility and thus improve electrochemical performance. This may also explain some of the positive effect noted above for water incorporation into Mg cathode materials. It was also speculated that choosing transition metals that more readily rehybridize upon Mg^{2+} insertion and deinsertion than Ti could lead to improved performance as well through reduction in ionic migration barriers.

Another example of the use of Li replacement with Mg in a Li-ion cathode material was reported by Oriksa et al.⁶³ An electrochemical ion exchange technique was used to anodically delithiate $\text{Li}_2\text{FeSiO}_4$ using 1 M LiClO_4 /propylene carbonate electrolyte, followed by magnesiation in $0.5 \text{ M Mg}(\text{TFSI})_2$ /acetonitrile. Subsequent cycling in the Mg electrolyte at 55°C demonstrated a high reversible capacity of about 330 mAh/g . The discharge curves exhibited two voltage plateaus at an average potential of about 2.4 and $1.8 \text{ V vs Mg/Mg}^{2+}$, respectively, with approximately equal capacities (Figure 9a).

These voltage plateaus apparently correspond to sequential reduction of MgFeSiO_4 to $\text{Mg}_{0.5}\text{FeSiO}_4$ and FeSiO_4 . XRD studies of the material at various states of magnesiation revealed that the material maintains an orthorhombic lattice with retention of the FeSiO_4 3-D structure. An attractive feature of this material is that it uses relatively inexpensive, abundant components. An attempt to construct a rechargeable Mg/MgFeSiO_4 battery using $\text{Mg}(\text{TFSI})_2$ /triglyme electrolyte resulted substantially reduced cathode capacity (166 mAh/g) and average potential vs Mg ($< 1.5 \text{ V}$) at 100°C (Figure 9b). The fact that only about half of the theoretical capacity was realized was attributed to high polarization in this electrolyte; the authors noted that this polarization behavior is similar to what is observed in $\text{LiTFSI}/$ triglyme electrolytes. This work clearly demonstrates the impact of electrolyte composition on cathode material behavior. Despite the performance reduction in a reversible Mg electrolyte, however, this work demonstrates that it may well be possible to prepare Mg intercalation cathode materials with high capacity.

Although intercalation of cations into transition metal chalcogenides typically involves reduction of the metal centers, an alternative intercalation reaction involving delocalization of electrons in a fullerene structure was recently reported by Zhang et al.⁶⁴ C_{60} fullerenes were evaluated for their ability to reversibly incorporate Mg^{2+} ions. Discharge at a low current density of $19 \mu\text{A/cm}^2$ exhibited two voltage plateaus at about

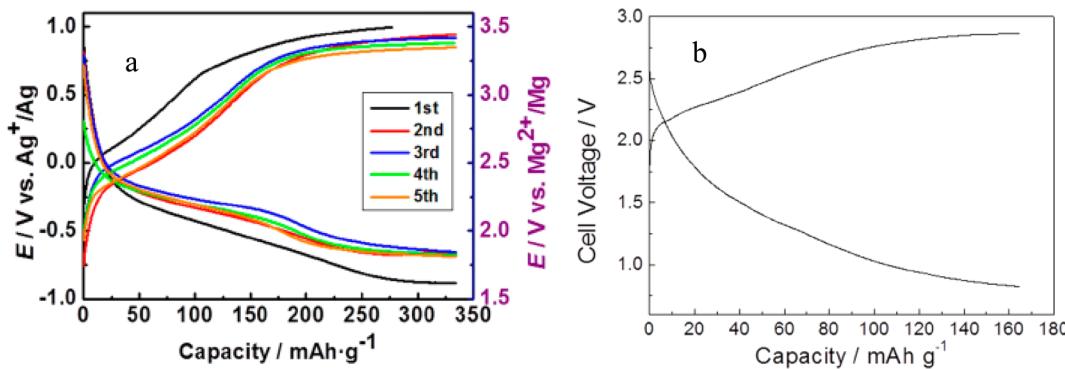


Figure 9. Charge–discharge curves for MgFeSiO₄ (current density 6.62 mA/g). a() 0.5 M Mg(TFSI)₂/AN electrolyte, 55 °C. (b) 0.5 M Mg(TFSI)₂/triglyme electrolyte, 100 °C. Reprinted with permission from ref 63. Copyright 2014, The Nature Publishing Group.

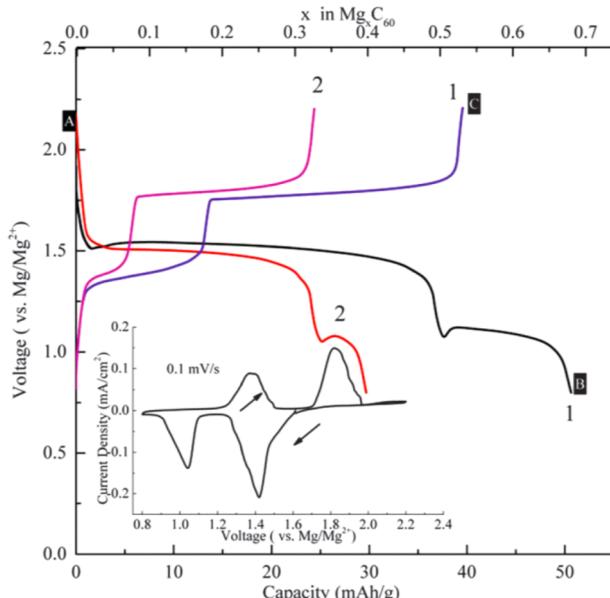


Figure 10. Galvanostatic charge/discharge curves for Mg incorporation into C₆₀ fullerenes cathodes at 19 μA/cm². Points A, B, and C represent pristine, fully discharged, and fully recharged electrodes, respectively. Peaks in the CV curve correspond to the two voltage plateaus. Reprinted with permission from ref 64. Copyright 2015, Royal Society of Chemistry.

1.5 and 1.0 V vs Mg, respectively. Figure 10 shows charge and discharge curves for this material along with a CV scan.

Improved Mg²⁺ mobility in this material vs other Mg cathode materials was inferred based on relatively low charge/discharge voltage hysteresis as well as rate capability and capacity retention at higher discharge rates as shown in Figure 11.

The primary drawback to these materials is their relatively low gravimetric capacity. The authors speculated that additional capacity may be expected at lower potentials, but such plateaus may occur at voltages too low to be of practical utility because they may lie below the deposition potential of Mg, making them electrochemically inaccessible. Therefore, addition of functional groups to the fullerene material to affect hybridization of the carbon atoms and increase the cell potential was proposed as a possible means to achieve higher capacity.

Intercalation reactions remain of interest for use in secondary Mg batteries due to their fundamental characteristics that can result in long cycle life, but achievement of high cell voltage, high capacity retention, and high Mg ion mobility remains

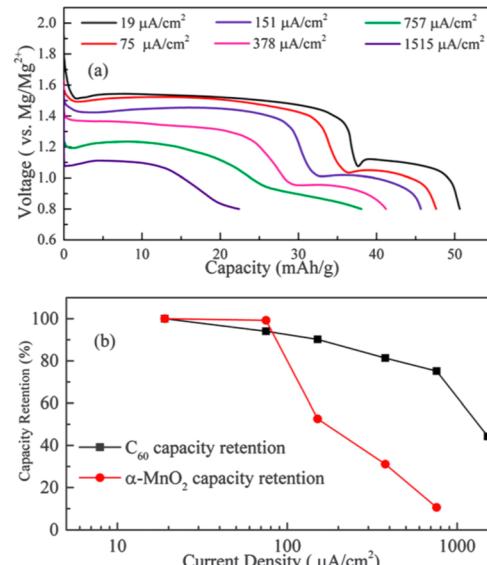


Figure 11. Rate capability and capacity retention for Mg incorporation into C₆₀ fullerenes. Reprinted with permission from ref 64. Copyright 2015, Royal Society of Chemistry.

challenging. The fact that some cathode materials that are useful in Li-ion batteries behave as conversion cathodes with poor reversibility in Mg batteries indicates that the number of suitable materials may be much lower for Mg batteries vs Li batteries. The impact of water on cathode performance is an interesting phenomenon that may be utilized to improve battery performance if potential impact on the Mg electrode reactions and electrolyte stability can be minimized. The development of insertion cathodes where charge balance is accomplished via electron delocalization rather than transition metal oxidation/reduction is an interesting development that deserves further attention.

Conversion reactions, such as oxygen, sulfur, or metal halide reduction, are receiving increasing attention for Li-based batteries due to the potential to achieve much higher capacities vs intercalation cathodes.

Conversion reactions, such as oxygen, sulfur, or metal halide reduction, are receiving increasing attention for Li-based batteries due to the potential to achieve much higher capacities vs intercalation cathodes. Nonaqueous lithium–oxygen (air) and lithium–sulfur batteries represent systems that involve two electron reductions when the cell is completely discharged to Li_2O_2 and Li_2S , respectively. The current state of the art in $\text{Li}-\text{O}_2$ (air) batteries and challenges to be solved to create a practical battery system for demanding applications such as electric vehicles are summarized in a recent review paper.⁶⁵ A large charge–discharge voltage hysteresis that leads to low roundtrip energy efficiency, electrolyte decomposition promoted by formation of superoxide species at the cathode, and the negative impact of impurities in air (for an air breathing system) that may require the use of a self-contained oxygen supply onboard a vehicle are all significant roadblocks for Li –air batteries. Lithium–sulfur batteries appear to face fewer problems of this nature, but substantial R&D is being devoted to resolving issues such as the sulfur redox shuttle mechanism that results in reduced capacity and cycle life. Despite the fact that magnesium–oxygen (air) and magnesium–sulfur batteries would likely face these same issues, these cathode materials do represent an opportunity for achieving two electron reductions. Mg – S and Mg – O_2 battery development has been summarized in a recent review.⁴⁸ Relatively low cell voltages and rapid capacity fade were typically observed in these systems. The apparent electrochemical irreversibility of MgO discharge product is a significant barrier to the successful development of secondary Mg – O_2 batteries, although the use of a mediator by Shiga et al. cited above appears to be an interesting approach. Overall, however, pursuit of Mg – O_2 and Mg – S batteries appears to be challenging with substantial barriers to success.

Metal halide conversion cathodes have received renewed attention for high energy density Li batteries, but have received much less attention with respect to Mg batteries. One issue for such cathode materials is the fact that many metal halides exhibit significant solubility in Mg battery electrolytes that would result in parasitic reactions between dissolved cathode material and the anode, reducing practical cell capacity and efficiency. One potential metal halide conversion cathode material with relatively low solubility in THF is AgCl , and this cathode material was evaluated in a recent study by Zhang et al.⁶⁶ Figure 12 shows charge and discharge curves for a Mg/AgCl battery using 0.2 M APC–THF electrolyte at a rate of 0.12C.

The XRD data shows that the cathode exhibited nearly complete conversion of Ag back to AgCl in the charge cycle, although some morphological changes were seen in the material. In addition, replating of Mg metal at the anode was confirmed after recharging the cell, indicating that the desired electrochemical reactions were indeed taking place. The first cycle discharge capacity of 178 mAh/g is very close to the theoretical value of 186 mAh/g. The cell showed excellent rate capability and was able to deliver >100 mAh/g after one activation cycle at a discharge rate of 10C. However, substantial capacity fade to about 60 mAh/g after 100 cycles was also observed. An additional issue for this cell is the need to use substantial electrolyte volume to ensure complete solubility of the MgCl_2 discharge product. Thus, the theoretical energy density of this cell was estimated to be only about 30 Wh/L. The cost of AgCl is of course an additional barrier, so replacement of Ag with a more abundant and economical metal would be necessary to achieve practicality. Nevertheless, these results are encouraging and

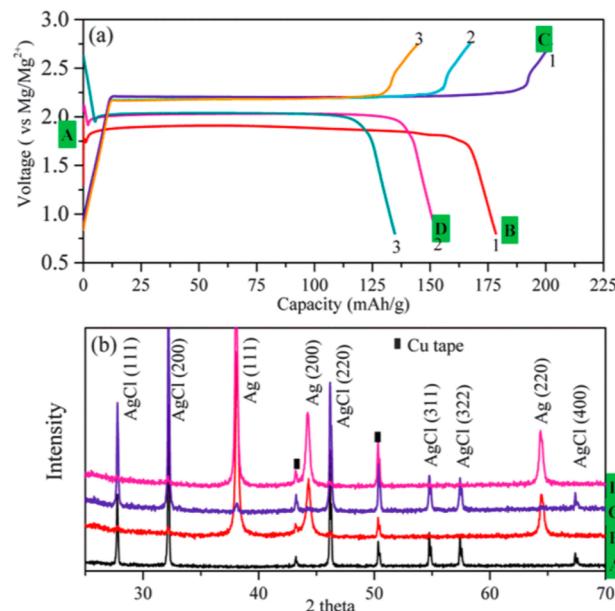


Figure 12. Charge/discharge curves for Mg/AgCl battery at 0.12C and XRD patterns for cathode material at different stages: A = Prior to first discharge, only AgCl peaks in XRD; B = end of first discharge, only Ag peaks in XRD; C = end of first charge, AgCl peaks with minor Ag peaks in XRD; D = end of second discharge, only Ag peaks in XRD. Reprinted with permission from ref 66. Copyright 2015, Royal Society of Chemistry.

appear to indicate that conversion cathodes may hold significant potential for high energy density Mg batteries given suitable electrolytes.

A high voltage, high capacity cathode material for secondary Mg batteries remains elusive, but recent work provides some clues as to potential directions to pursue. Intercalation cathodes capable of achieving two electron reduction and intercalating one Mg^{2+} ion per metal center have yet to be identified, but certain vanadium oxides appear to have some promise, as do certain polyanion cathodes. The ability of water molecules to shield the Mg^{2+} cation and ameliorate Coulombic interactions in the intercalate is an interesting phenomenon that may prove useful in improving the capacity and rate capability of intercalation cathodes. Understanding and improving Mg^{2+} mobility within intercalation cathode materials, perhaps through modification of ionic transport channels, appears to be a key to improving both rate capability and effective capacity. The use of materials that can accommodate Mg^{2+} ions with charge compensation via electron delocalization rather than metal center reduction provides an alternative approach to developing suitable cathode materials. Although much of the effort in this area continues to concentrate on intercalation cathodes, some progress has been reported with respect to conversion cathodes. As with intercalation cathodes, the situation with respect to Mg-conversion cathode cells appears to be more complex and problematic vs Li analogs. Mg – O_2 , Mg – S , Mg –metal halide, and Mg –organic redox cells have all been investigated but face substantial hurdles to successful development.

Magnesium has major advantages over a lithium metal anode such as double the volumetric capacity and the apparent lack of dendrite formation during charging. Unfortunately, there are challenges associated with the solid state diffusion of Mg^{2+} ions into and within cathode hosts. Although there has been significant progress in the area of electrolyte and anodes there has

been no reported work on the development of a magnesium battery with energy densities comparable to lithium ion. From our point of view, the major stumbling block is cathode development. One of our major concerns in developing high voltage cathodes is the formation of blocking films by oxidation of the electrolyte that may be catalyzed by extremely electro-positive cathodes. Ether solvents, which have been used in most successful Mg electrolytes to date, typically exhibit good reductive stability but their oxidative stability tends to be inferior to that of carbonate solvents used in Li-ion battery electrolytes. With this concern in mind, it may worthwhile for the community to evaluate lower voltage but higher capacity conversion cathodes that will not catalyze the oxidation of magnesium electrolytes on the surface of the cathode to form blocking films.

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Notes

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Claudiu B. Bucur obtained his Ph.D. in 2008 from The Florida State University under the mentorship of Prof. Schlenoff. Bucur attempted to understand the manner in which polyelectrolyte multilayers assemble and how doping them with ions changes their mechanical and thermodynamic properties. Several manuscripts and a book were published with his findings. In 2010, he completed his postdoctoral studies at the USDA Agricultural Research Service, where he investigated corrosion inhibition by biomembranes. Currently, he is a research associate for the post-lithium-ion research group at the Toyota Research Institute of North America. Bucur is fascinated by the synthesis and characterization of innovative materials for batteries with multivalent anodes or sulfur cathodes.

Thomas Gregory received his B.S. and M.S. degrees in Chemical Engineering in 1978 and 1979, respectively, from Case Western Reserve University. He spent 34 years in a variety of R&D roles at The Dow Chemical Company in Midland, Michigan, retiring in 2013 as a Principal Research Scientist in Dow's Energy Materials Business. His work at Dow encompassed a wide variety of technology areas, including electrochemical engineering, process development and scale-up, polymer processing, and process economic analysis. He is widely recognized for his pioneering work in rechargeable magnesium battery electrochemistry. He is currently the owner of Borealis Technology Solutions LLC and consults in the areas of electrochemical energy generation and storage and chemical and electrochemical process technology.

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chemistry to discover HIV protease inhibitors and acceleration for chemical reactions on water. He is currently a senior principal scientist at Toyota Research Institute of North America. His research interests include future energy solutions such as multivalent batteries, lithium/sulfur batteries, Li-ion batteries, and fuel cells. He has numerous patents in the area of new battery chemistry and fuel cell.

ACKNOWLEDGMENTS

We would like to thank our colleagues and collaborators for their support: Dr. Gary D. Allred, Dr. Timothy S. Arthur, Dr. William C. Boggess, Dr. Jack Chen, Dr. Paul Fanson, Dr. Hideki Iba, Mr. Toshihiko Inoue, Mr. Yasutoshi Jagawa, Prof. Noboru Kikuchi, Dr. Hee Soo Kim, Dr. Angela Knapp, Mr. Yukinari Kotani, Mr. Takashi Kuzuya, Dr. Chen Ling, Dr. Masaki Matsui, Dr. Fuminori Mizuno, Dr. Rana Mohtadi, Dr. John G. Newman, Dr. Alexander E. Rodnyansky, Mr. Kazuaki Sato, Dr. Nikhilendra Singh, Mrs. Wei Song, Mr. Tsuyoshi Sugimoto, Dr. Kensuki Takechi, Dr. Oscar Tutzus, Dr. Ruigang Zhang, and Dr. Jaroslav Zajicek. We would also like to thank the Toyota Motor Corporation for funding this research.

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