

Chapter 2

Magnesium Electrolytes

2.1 Liquid Electrolytes

2.1.1 History

The early history of magnesium electrolytes is vibrant and interesting because it uses modern synthetic routes but yields mediocre results may be due to inferior materials quality and equipment. The first electrochemical measurements of magnesium metal and/or attempts at magnesium plating start just as early as those for lithium metal. In 1899 Kahlenberg [1] followed by Lewis in 1913 [2] investigated the electrochemical reduction potential of lithium. Not far behind, Jolibois reports the deposition of magnesium from a solution of diethylmagnesium (Et_2Mg) and magnesium iodide (MgI_2) in diethyl ether (Et_2O) [3]. Fifteen years later, Gaddum et al. report the electrodeposition of magnesium on platinum electrodes from benzylmagnesium chloride (PhCH_2MgCl) solutions in ethers. They report superior deposition from PhCH_2MgCl compared to phenylmagnesium bromide (PhMgBr) and propose possible mechanisms [4]. Three years later, the same group reports the corrosive character of Grignards such as isoamylmagnesium chloride ($(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{MgCl}$) on anodes such as aluminum, zinc, and cadmium but stability on bismuth, gold, nickel, silver, and tin [5]. Interestingly, they report “brushy” deposits indicative of mossy, lithium-like deposition. Bismuth and tin have recently been reported to undergo reversible magnesiation from magnesium electrolytes and can be used as alloying anodes [6, 7]. In 1933, Overcash et al. perform an extensive investigation of solvents compatible with the process of magnesium deposition [8]. He reports that magnesium cannot be deposited from simple magnesium salts in nonaqueous solvents. Instead, “solutions of complex magnesium compounds similar to Grignard compounds” can plate magnesium with best results from dimethylaniline. This solvent supports the deposition of magnesium but not stripping. Among others, Overcash attempts to use dry formamides, nitriles, and pyridines without success and reports deposition in the form of “trees” in solvents such as benzene,

Fig. 2.1 Earliest published decomposition voltage for Grignards observed during a linear scan voltammogram experiment. Reproduced from Evans et al. [9]

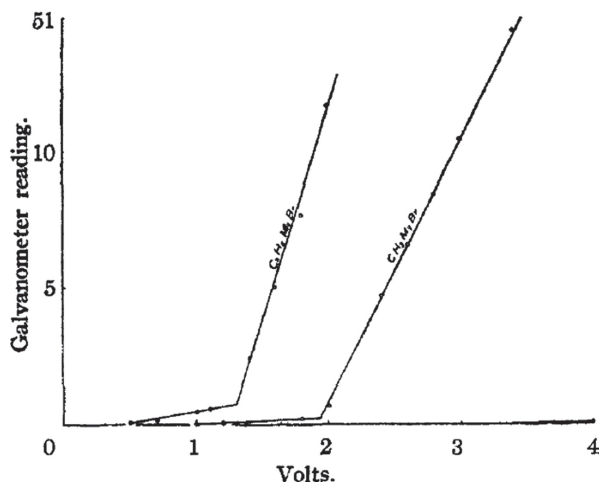


Table 2.1 Table of Grignard reagents and corresponding decomposition voltages

Reagent	Concentration		Decomposition voltage		Average
$\text{C}_6\text{H}_5\text{MgBr}$	1.02	1.04	2.21	2.13	2.17
CH_3MgBr	1.09		1.94		1.94
$\text{C}_3\text{H}_7\text{MgBr}$	1.01	0.92	1.41	1.43	1.42
$\text{C}_4\text{H}_9\text{MgBr}$	1.06	1.00	1.31	1.33	1.32
$\text{C}_2\text{H}_5\text{MgBr}$	1.56	1.03	1.27	1.29	1.28
$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHMgBr}$	1.03	1.00	1.23	1.25	1.24
$(\text{CH}_3)_2\text{CHMgBr}$	0.95	0.98	1.08	1.06	1.07
$(\text{CH}_3)_3\text{CMgBr}$	0.81	0.86	0.91	1.03	0.97
$\text{CH}_2=\text{CHCH}_2\text{MgBr}$	0.87	1.13	0.83	0.89	0.86

Reproduced from Evans et al. [9]

toluene, or xylene. He also investigates ethyl halides (e.g., ethyl iodide worked better than ethyl bromide) and reports a decomposition voltage between 1 and 1.5 V. Building on this work, Evans et al. compare the decomposition voltages of several Grignard reagents by linear scan voltammograms. The highest oxidative stability belongs to phenylmagnesium bromide (PhMgBr): 2.2 V (see Fig. 2.1) [9]. Evans also publishes the voltage stabilities of several Grignards (Table 2.1).

In 1942, Evans et al. perform an in-depth study on the ionic nature of Grignard reagents and measure the transference numbers and conductivity values of n-butyilmagnesium bromide (BuMgBr) and ethylmagnesium bromide (EtMgBr) [10]. For example, a 0.5 M solution of EtMgBr has a conductivity of 1.6×10^{-5} S/cm. Fifteen years later, Connor et al. make significant advances to the field. He publishes his efforts to plate magnesium from halides, aluminohydrides, and borohydrides in 1957 [11]. It is worthwhile to notice that these are the same synthetic methods which are currently hot topics in the synthesis of magnesium electrolytes. In his work, magnesium is electrodeposited from $\text{Mg}(\text{BH}_4)_2$ generated in situ from

MgBr₂ and LiBH₄ and Mg(AlH₄) obtained from Li(AlH₄) and MgCl₂. He also reports magnesium plating from concentrated solutions of MgBr₂. Interestingly, Xerox Corporation filed a patent in 1967 on the electrodeposition of magnesium from EtMgBr in THF [12].

The saga of magnesium plating electrolytes continues in 1967 [13] and 1971 [14, 15] with the published findings of Abner Brenner. The chief purpose for most of the magnesium electrolyte research so far had been the electrodeposition of light structural materials for lightweight components with complex shapes (which may be needed for satellites for example). Magnesium has a density of 1.74 g/mL and is even lighter than aluminum (2.7 g/mL). Brenner was interested in electrolytes for magnesium as well as beryllium. As far as magnesium electrolytes, Brenner published on deposition from solutions of Grignards in THF mixed with magnesium-boron complexes which are once again a great point of interest 45 years later [16, 17]. He prepared a plating bath by reaction of lithium decaborane (LiB₁₀H₁₂) with MgCl₂ in THF but did not believe that Mg(B₁₀H₁₂)₂ was obtained. Interestingly, he reports that analog beryllium reactions plate beryllium quite well. Brenner reports improvements in plating upon reaction of Grignards with the Lewis acid triethylboron (Et₃B). He notes that a ratio of 1:3 of Lewis acid to magnesium gave the best results which corresponds to the stoichiometric reaction $3R'MgX + R''_3B \rightarrow (Mg_2X_3)(R'X_3B) + R'_2Mg$. Now we know this reaction results in an electrochemically active magnesium dimer cation on which modern magnesium electrolytes such as GEN2 and GEN3 are based [17]. Even APC follows a similar synthetic strategy, albeit with an aluminum-based Lewis acid [18]. Brenner prefers an in situ electrolyte based on a three-molar solution of MeMgCl and one molar triethylboron in THF. We now know that this reaction may yield the following: $3MeMgCl + Et_3B \rightarrow (Mg_2Cl_3)(MeEt_3B) + Me_2Mg$. The (Mg₂Cl₃)(MeEt₃B) product would probably make a good electrolyte even in modern times with a voltage stability similar to that of DCC which is 2.5 V vs. Mg/Mg²⁺ and excellent coulombic efficiencies of deposition and stripping. Brenner looked at a variety of boron Lewis acids. For example, he investigated the plating properties of a solution composed of three parts Et₂MgCl and one part BF₃ and also reported 99% Mg deposited with high efficiencies. This electrolyte may have produced the following: $3Et_2MgCl + BF_3 \rightarrow (Mg_2Cl_3)(EtF_3B) + Et_2Mg$. Again, we now know that the active product (Mg₂Cl₃)(EtF₃B) may perform very well for battery applications. While the scope of Brenner's work was electroplating of magnesium, it is interesting to note that he filed a magnesium battery patent in 1996 [19].

In 1985, Genders et al. compare the reversible deposition of magnesium from Et₂MgBr solution in THF with solutions of MgBr₂ and Mg(ClO₄)₂ in THF or propylene carbonate (PC) [20]. He concludes that no deposition is observed from simple salts such as MgBr₂ and Mg(ClO₄)₂ in either solvent (partially contradicting the findings of Connor, who reports successful magnesium deposition from concentrated MgBr₂ solutions in ethers). Interestingly, Genders observes that MgBr₂ even inhibits the plating of lithium from a LiAsF₆ solution in PC, suggesting MgBr₂ is strongly passivating. Surprisingly, addition of MgBr₂ to a solution of Et₂MgBr enhances the rate of magnesium deposition. This report precludes modern reports of similar improvements when MgX₂ is added to Grignards or Hauser bases [21, 22].

Table 2.2 Early work of Gregory et al. solubility and conductivity of “naked” magnesium organoborates in THF

Compound	Solubility in THF	Specific conductance ($\Omega^{-1} \text{ cm}^{-1}$) (Sat'd. solution in THF)
$\text{Mg}(\text{BBu}_4)_2$	~1 M	1.0×10^{-3}
$\text{Mg}(\text{BBu}_3\text{Ph})_2$	0.45 M	2.3×10^{-3}
$\text{Mg}(\text{BBu}_2\text{Ph}_2)_2$	0.5 M	1.0×10^{-3}
$\text{Mg}(\text{BBuPh}_3)_2$	0.1 M	7.1×10^{-4}
$\text{Mg}(\text{BPh}_4)_2$	<0.01 M	1.7×10^{-6}

Reproduced from Gregory et al. [24]

In 1990, Mayer investigates the electrodeposition of magnesium from organometallic electrolytes [23]. The reaction of one equivalent of sodium fluoride (CsF) with two equivalents of Bu_2Mg does not yield an electroactive solution. However, addition of aluminum alkyls such as triethylaluminum (Et_3Al) to Bu_2Mg (or Et_2Mg) in ratios of 3.5:1 results in the active solutions which deposit pure magnesium. Interestingly, the plating solution was based on toluene which could be investigated further and may offer interesting properties to modern magnesium electrolytes. In many ways, the work of Mayer is complimentary to that of Brenner because Mayer introduced the use of aluminum-based Lewis acids resulting in organoaluminates, whereas Brenner concentrated on boron-based Lewis acids which resulted in organoborates.

At the same time, Gregory et al. recognized that enough work has been reported on magnesium electrolytes to support a comprehensive effort for building a battery with a magnesium metal anode. His work jump-starts the quest for a rechargeable magnesium battery which is still ongoing today. After a decade of work, he reports the first manuscript on magnesium electrolytes for direct battery use in 1990 [24]. This report is unique because in addition to reporting electrolyte work, it also reports a multitude of cathodes which can magnesiate. These cathodes are screened with a rationally synthesized electrolyte which contains anions stable to high-voltage cathodes and R groups stable to magnesium metal. For the first time, Gregory reports the synthesis of the Hauser base *n*-methylaniline magnesium chloride ($\text{PhCH}_3\text{NMgCl}$) in THF. Building on the work of Brenner, Gregory reacts the Lewis acid Bu_3B with Bu_2Mg to yield $\text{Mg}(\text{Bu}_4\text{B})_2$ which is the first “naked” magnesium salt synthesized for magnesium battery (Table 2.2) and also spikes RMgCl Grignards with aluminum halides.

In 1998 Liebenow introduces a magnesium ion conducting polymer-gel electrolyte based on EtMgBr and poly(ethylene oxide) with 10^{-4} S/cm conductivity at room temperature [25]. Starting in 1999, Aurbach et al. make crucial contributions to the field of magnesium electrolytes [26]. He reports the di-chloro complex (DCC) electrolyte in 2000 [27] coupled with a Chevrel phase cathode and the all-phenyl chloro complex (APC) in 2011 which offers a 3.2 V stable window on a platinum electrode [18] and the magnesium aluminum chloride complex (MACC) in 2013 [28]. In 2011, Kim et al. introduce the GEN1 electrolyte coupled with a sulfur cathode [29]. The same group introduces a 3.7 V electrolyte (on Pt electrodes) the

following year (GEN3) [17]. Unfortunately all these electrolytes contain chlorides and are corrosive. The corrosion phenomenon was initially confused with cathode reduction, but it was brought into light by several publications from Toyota [17, 30]. For example, their voltage stability on aluminum or stainless steel is <2 V which renders them impractical for screening of high-voltage cathodes. In 2014, Nelson et al. report a very interesting tetraphenylaluminate magnesium salt obtained by replacing the Lewis acid AlCl_3 with $\text{Al}(\text{OPh})_3$ which has a wide 5 V voltage stability window on stainless steel [31]. Similar noncorrosive, wide windows are also reported by Tutusaus et al. from Toyota in 2015 [32], Herb et al. in 2016 [33], and [34] [34] with stabilities in excess of 4 V vs. Mg/Mg^{2+} on aluminum current collectors which is critical for efficient cathode screening.

2.1.2 “Naked” Magnesium Salts

2.1.2.1 Simple Halide Salts

The earliest reports of plating magnesium metal indicate that utilizing ethereal solutions of Grignards is required instead of simple magnesium salts with halide anions such as MgCl_2 , MgBr_2 , or MgI_2 . It is believed that these salts do not dissociate easily in solvents which are compatible with magnesium metal such as THF. There are a few divergent (and interesting) reports on successful magnesium deposition from magnesium halides. For example, MgI_2 was synthesized in a non-ethereal solvent, and magnesium deposition is reported with virtually zero overpotential (Fig. 2.2a) [35]. The low overpotential mirrors lithium electrolytes and may be solving one of the main challenges of magnesium batteries, namely, low energy efficiency between charging and discharging cycles.

Similarly, both Connor [11] and, recently, Shiraga et al. report reversible plating of magnesium from concentrated solutions of MgBr_2 solutions (3.5 M in Me-THF), but not from dilute solutions (Fig. 2.2) [36]. Sheha also reports reversibility of a magnesium-graphite battery with a “solvent-in-salt” 5.4 M MgBr_2 in DMSO electrolyte with a high conductivity of 10^{-2} S/cm at room temperature [37].

2.1.2.2 Complex Analogs of Salts Used in Lithium-Ion Batteries

More attention has been given to magnesium salts with complex anions which could offer improved dissociation and conductivity in nonaqueous solvents. These anions tend to accompany the lithium cation in lithium-ion battery electrolytes, so there has been a screening effort for their magnesium analogs [20, 24] (Table 2.3). It is interesting to note that $\text{Ca}(\text{BF}_4)_2$ has been shown to reversibly deposit calcium at elevated temperatures of 60°C , but no reports have been made regarding analogous magnesium salts [38]. However, most of such anions (BF_4^- , PF_6^- , AsF_6^- , ClO_4^-) result in thick passivating films on the magnesium anode which impede magnesium transport.

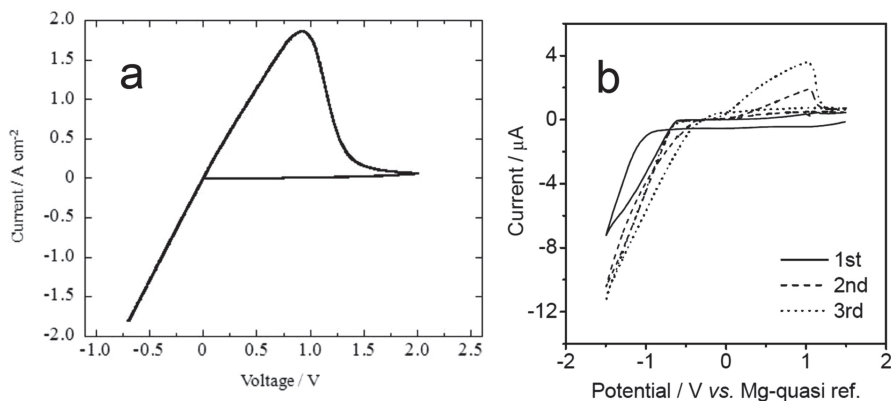


Fig. 2.2 (a) Cyclic voltammetry depicting the deposition/dissolution of magnesium from a MgI_2 electrolyte. Reproduced from Soeda et al. [35]. (b) Cyclic voltammograms depicting the reversible plating of magnesium from concentrated solutions of 3.5 M MgBr_2 in Me-THF. Reproduced from Shiraga et al. [36]

Table 2.3 Table shows the anodic stability of anions on magnesium metal with description of the films formed

Anion	Anodic current range, mA	Film on Mg anode
$\text{C}_2\text{H}_5\text{MgCl}_2^-$	10^0	None
AlCl_4^-	10^1	None
Br_3^-	10^0	None
BF_4^-	10^1	Light gray
PF_6^-	10^{-1}	Heavy gray
AsF_6^-	10^{-1}	Heavy gray
ClO_4^-	10^0	Heavy black
$\text{B}(\text{C}_4\text{H}_9)_4^-$	10^1	None

Reproduced from Gregory et al. [24]

It is interesting to note that recent reports on $\text{Mg}(\text{PF}_6)_2$ surprisingly suggest the opposite [39]. A 0.12 M solution of $\text{Mg}(\text{PF}_6)_2$ synthesized in 1:1 THF:ACN has a room temperature conductivity of 18.7 mS/cm, and it passivates aluminum well (as expected) to confer a wide voltage stability in excess of 4 V. The coulomb of deposition/stripping is poor on glassy carbon working electrode which corresponds to asymmetric deposition/stripping CV slopes on a magnesium electrode (Fig. 2.3). It should be noted here that Soeda et al. have similarly synthesized MgI_2 in a non-etheral solvent and were able to reversibly plate magnesium from a solution of MgI_2 [35]. Commercial MgI_2 has very low solubility in non-etheral solvents and does not plate or strip magnesium.

Once again ahead of his time, Connor compares the plating properties of $\text{Li}(\text{AlH}_4)$ to those of $\text{Mg}(\text{BH}_4)_2$ and reports successful magnesium plating [11]. More recently, superior results for the deposition of magnesium from $\text{Mg}(\text{BH}_4)_2$ were reported by Mohtadi et al. [40]. Another interesting analog of lithium salts is $\text{Mg}(\text{TFSI})_2$ which

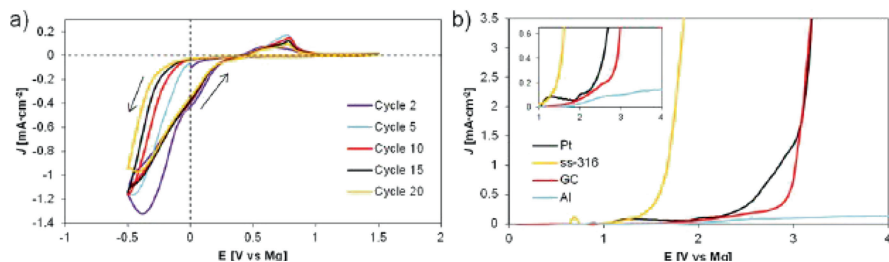


Fig. 2.3 (a) Cyclic voltammograms depicting the quasi-reversible plating of magnesium from a 0.12 M solution of $\text{Mg}(\text{PF}_6)_2$ in THF/ACN; (b) oxidative stability of this electrolyte on various current collectors. Reproduced from Keyzer et al. [39]

was long believed to reduce on the surface of magnesium and inhibit further magnesium diffusion and plating. However, Ha et al. reported in 2014 that $\text{Mg}(\text{TFSI})_2$ can plate magnesium in a glyme/diglyme solvent mixture [41]. 0.5 M $\text{Mg}(\text{TFSI})_2$ in 1:1 glyme:diglyme has a conductivity of 5.2 mS/cm and a voltage stability on aluminum of 4 V vs. Mg/Mg^{2+} on the first cycle. It is known however that the TFSI⁻ anion is corrosive toward aluminum and a stable passivating interface is not obtained. In lithium-ion systems, LiPF_6 is typically used to spike solutions of LiTFSI and passivate the aluminum cathode current collector. Since both salts have now been reported to be reversible with magnesium, it would be interesting to pursue this same strategy. Similar to $\text{Mg}(\text{PF}_6)_2$, $\text{Mg}(\text{TFSI})_2$ has a low coulombic efficiency when tested in our lab and exhibits high overpotentials (2 V) in galvanostatic plating mode at high current densities (1.5 mA/cm²). The electrochemistry of $\text{Mg}(\text{TFSI})_2$ is dramatically improved by the addition of MgCl_2 , but an in situ reaction is assumed which results in a dimer-type cation where the presence of chlorides increases the corrosive character of the electrolyte [42–44]. In our lab, we have also been able to improve the properties of $\text{Mg}(\text{TFSI})_2$ by reaction with AlCl_3 ; however, similar dimer yielding reactions are expected.

2.1.2.3 Novel “Naked” Magnesium Salts

“Naked” magnesium salts are magnesium salts where the magnesium cation, Mg^{2+} , coordinates directly to solvent molecules. This nomenclature is used to differentiate from magnesium salts where the magnesium cation (Mg_2Cl_3)⁺ coordinates to halides as well as to solvent molecules. The typical synthetic pathway to obtain new “naked” magnesium salts has been: $\text{R}'_2\text{Mg} + 2\text{R}''_3\text{A} \rightarrow \text{Mg}(\text{R}'\text{R}''_3\text{A})_2$, where R' and R'' can be the same ligands and A corresponds to boron (B) or (aluminum) Al. In the case of a boron-based anion, these “naked” magnesium salts may be stable in air or water. Another advantage of “naked” magnesium salts is their noncorrosive character due to a complete lack of halides in their structure. The first rationally designed magnesium salt where a “naked” magnesium cation is coordinated directly to the solvent has been Gregory’s synthesis of $\text{Mg}(\text{Bu}_4\text{B})_2$ by reacting the Lewis acid Bu_3B

with Bu_2Mg . He also noticed that by reacting Ph_2Mg with Bu_3B he could obtain $\text{Mg}(\text{Bu}_3\text{PhB})_2$ with a higher conductivity of 2.3 mS/cm. He dissolved this salt in THF:DME and cycled several cathodes with magnesium metal. Figure 2.4 shows several such novel “naked” magnesium salts. We were able to reproduce these findings in our lab.

The challenge of “naked” salts is that its solubility depends solely on the anion ligands and so does the voltage stability. For example, increasing the phenyl content in the borate anion improves the electrochemical stability but lowers the solubility and conductivity. The utility of R_2Mg reactions with a boron Lewis acid is limited by aryl metathesis which causes scrambling of the aryl groups on the borate anion. This results in a mixture of anionic products in cases where the R groups differ between $\text{R}'_2\text{Mg}$ and $\text{R}''_3\text{B}$. For example, instead of only obtaining the $(\text{R}'\text{R}''_3\text{B})^-$ species, one can obtain a proportion of the product as $(\text{R}''_4\text{B})^-$ due to scrambling. In many cases, there are undesired anionic components (e.g., $(\text{R}''_4\text{B})^-$) in the product mixtures which have inferior reductive stabilities, passivate the magnesium surface, and stop magnesium plating. Such products were confirmed by mass spectrometry and NMR in our lab. This phenomenon was first observed by [30] upon attempts to synthesize noncorrosive, high-voltage electrolytes based on the reaction of bis(cyclopentadienyl)magnesium ($(\text{C}_5\text{H}_5)_2\text{Mg}$ or Cp_2Mg) or fluorinated Cp_2Mg ($(\text{C}_5\text{F}_5)_2\text{Mg}$ or Cp^*_2Mg) with boron-based Lewis acids. Interestingly, a recent paper reports the compatibility of Cp_2Mg with magnesium metal [45]. Aryl metathesis precluded the yielding of the pure desired products due to scrambling, and the work was not published. A brilliant idea used to circumvent this problem has been proposed by Muldoon et al. from Toyota [30]. This ion exchange pathway of a magnesium dimer to a silver intermediate which can then be easily ion exchanged into the desired monovalent or divalent salt (Li, Na, K, Mg, Ca, or Zn) opens the door to a universal synthetic electrolyte pathway. Boron chemistry is required for this method because the resulting borate cations are water stable, whereas the aluminate analogs are not. Using this method, the new “naked” magnesium salts $\text{Mg}(\text{BAr}_\text{F})_2$ [30], $\text{Mg}(\text{BPh}_4)_2$, $\text{Mg}(\text{BPh}(\text{C}_6\text{F}_5)_3)_2$ [46], and $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ [32] have been reported from groups in Toyota with superior voltage stabilities and solubilities. All these salts have high solubilities >1 M and high voltage stabilities >4 V vs. Mg/Mg^{2+} . Crystal structures and cyclic voltammetry of these salts are shown in Fig. 2.4.

Aryl metathesis only becomes an issue for magnesium plating if R' and R'' are different in the reaction $\text{R}'_2\text{Mg} + 2\text{R}''_3\text{A} \rightarrow \text{Mg}(\text{R}'\text{R}''_3\text{A})_2$. Gregory’s original “naked” magnesium reaction, $\text{Bu}_2\text{Mg} + 2\text{Bu}_3\text{B} \rightarrow \text{Mg}(\text{Bu}_4\text{B})_2$, contained the same butyl (Bu) ligand in the organomagnesium reagent as well as in the Lewis acid, so scrambling did not result in undesired changes of the anion. Due to its electronic character, aluminum is below boron in the periodic table and forms stronger bonds which are more stable against oxidation than boron. Muldoon et al. have shown that magnesium electrolytes with aluminum-based anions have an oxidative stability 0.5 V higher than boron analogs. Thus, reacting organomagnesiums with aluminum Lewis acids which contain the same R groups may offer superior voltage stability. Herb et al. took this approach in 2016 with the following reaction: $\text{Mg}(\text{HFIP})_2 + 2\text{Al}(\text{HFIP})_3 \rightarrow \text{Mg}[(\text{HFIP})_4\text{Al}]_2$. When the product is dissolved in DME, a superior

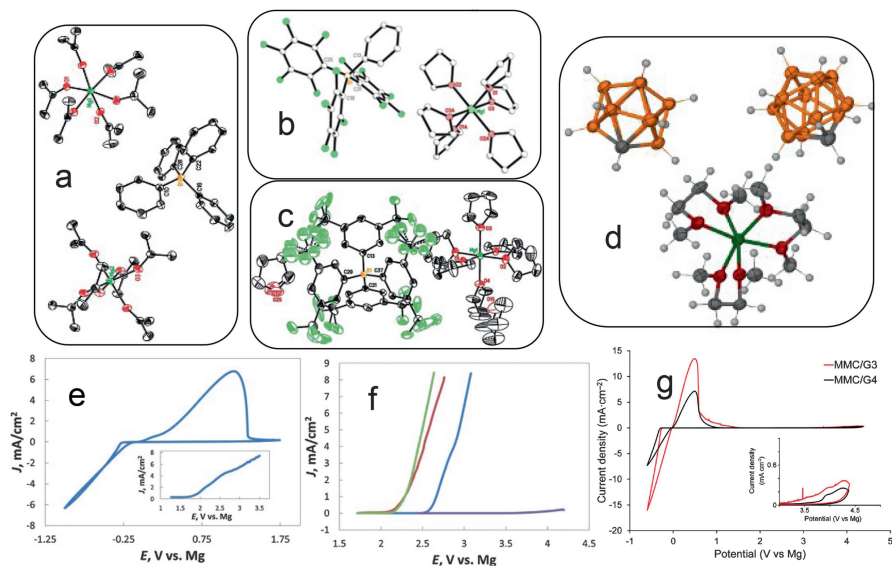


Fig. 2.4 Crystal structures of $\text{Mg}(\text{BPh}_4)_2/\text{acetone}$ (a). Reproduced from Muldoon et al. [30]; $\text{Mg}(\text{BPh}(\text{C}_6\text{F}_5)_3)_2$ (b). Reproduced from Muldoon et al. [17]; $\text{Mg}(\text{BArF})_2$ (c). Reproduced from Muldoon et al. [30]; $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ (d). Reproduced from Tutusaus et al. [32]. Deposition/dissolution and oxidative stability (inset) of $\text{Mg}(\text{Ph}_3\text{BuB})_2$ (e) (Reproduced from [30]), oxidative stability of $\text{Mg}(\text{BArF})_2$ on a stainless steel working electrode (Reproduced from Muldoon et al. [30]) (f), and the deposition/dissolution and oxidative stability (inset) of $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ (g). Reproduced from Tutusaus et al. [32]

magnesium electrolyte emerges which is stable on aluminum up to 5 V and has a coulomb efficiency of plating/stripping above 99% and a conductivity of 6.5 mS/cm. It should be mentioned however that aryl metathesis is not expected to occur in the case of aluminum Lewis acids which expand the degree of freedom for this class of reactions. $\text{R}'_2\text{Mg} + 2\text{R}''_3\text{Al}$ type of reactions should thus be explored further by the community. However, the stability gain comes at a cost. Unlike their boron-based analogs, the “naked” magnesium salts with aluminum-containing anions are not expected to be stable in air or water.

2.1.3 “Dimer” Magnesium Salts

“Dimer” magnesium salts refer to the dimer structure of their magnesium cation where two magnesiums are coordinated to three halides and six solvent molecules such as THF. For simplicity, this will be referred to as $(\text{Mg}_2\text{Cl}_3)^+$. The dimer cation carries two magnesiums per cation which doubles the transference number of magnesium at the same concentration. In addition, it increases the solubility of its salt in organic solvents. However, the magnesium dimer is not stable in air or water where

it quickly decomposes into MgCl_2 . It is also interesting to observe that most dimer-based magnesium salt electrolytes do not have a voltage stability in excess of 3.2 V Mg/Mg^{2+} on platinum electrodes, regardless of very different anions which should add a much greater degree of variability in voltage stability. A common disadvantage of “dimer”-based magnesium salts is their corrosive character due to the presence of halides in the dimer cation or in the aluminate cation.

There are two modern schools of thought when it comes to reactions yielding “dimer” magnesium salts. One school uses Lewis acids to spike solutions of Grignard reagents in nonstoichiometric ratios (typically deficient amounts of Lewis acid). Here the Lewis acid has the purpose of pushing the Schlenk equilibrium one way or another depending on the reaction occurring at the cathode or anode during electrodeposition. In addition, products of these reactions are not typically purified by crystallization, and the reaction mixture is used as is, as an in situ magnesium electrolyte. In addition, due to the lack of purification, these electrolytes are complex mixtures which often contain reactive nucleophile species which react with highly desirable cathodes such as sulfur or oxygen. Electrolytes proposed by Gregory or Aurbach (DCC, APC) are obtained from nonstoichiometric mixtures of Grignards and Lewis acids. These types of electrolytes are in situ mixtures and differ from currently commercial electrolytes used in lithium-ion batteries where synthetic salts are purified and distributed as dry powders in large quantities and can be later blended at will with a variety of solvent mixtures and additives to modify the property of the electrolyte. The other school of thought uses stoichiometric mixtures of Grignards or Hauser bases and Lewis acids to obtain specific electrochemically active ionic products. Recent examples are the electrolytes proposed by Muldoon (GEN1, GEN2, and GEN3) or Bartlett [47]. These reactions follow the general formula: $3\text{R}'\text{MgX} + \text{R}''_3\text{A} \rightarrow (\text{Mg}_2\text{X}_3)(\text{R}'\text{R}''_3\text{A}) + \text{R}'_2\text{Mg}$. Purification by crystallization can remove the $\text{R}'_2\text{Mg}$ nucleophile and recover only the desired active salt $(\text{Mg}_2\text{X}_3)(\text{R}'\text{R}''_3\text{A})$ which can be redissolved in a solvent of choice and used to electroplate magnesium in magnesium batteries with magnesium metal anodes. Due to the purification step and removal of the nucleophile, these electrolytes are compatible with high-capacity post-lithium-ion cathodes such as sulfur. Such compatibility with sulfur was first proposed by Kim et al. from Toyota [29].

Some of the earliest successful electrodeposition of magnesium has been reported from Grignard solutions. This may suggest the marked effect of the common cation in the oxidation stability observed. In 1912, Jolibois proposes that magnesium can be electrodeposited from an in situ solution of MgEt_2 and MgI_2 which formed the Grignard $\text{MgEt}_2 \cdot \text{MgI}_2$ in Et_2O solvent. In 1927, Gaddum et al. used the Grignard PhMeMgCl [4] to electroplate magnesium. It has been recently reported that Grignard solutions form crystals with magnesium-containing dimers [48], so it is correct to state that the first successful deposition of magnesium occurred from dimer magnesium salts. A very interesting variation of a Grignard (RMgX , where the R-Mg bond is a C-Mg bond) for the electroplating of magnesium is the work of Carter et al. [16]. It is well known that RMgCl can be partially ionized in solution to RMg^+ and Cl^- . However, Carter et al. were able to control the equilibrium of the Grignard solution by a clever juggling of solvents and obtain the $(\text{R}_2\text{MgX})^-$ anion

paired with the dimer $(\text{Mg}_2\text{Cl}_3)^+$ cation. In this unique version of the Grignard, both the cation and anion contain magnesium (Fig. 2.5). Surprisingly, this electrolyte with an anion containing a coordinated magnesium has the same voltage stability as salts with anions containing boron and aluminum a voltage stability of 3.2 V vs. Mg/Mg^{2+} . Other than Grignards, the Hauser base *n*-methylaniline magnesium chloride was prepared from the reaction of *n*-methylaniline (PhNHCH_3) and ethylmagnesium chloride as follows: $\text{PhNHCH}_3 + \text{EtMgCl} \rightarrow \text{PhCH}_3\text{NMgCl}$ [24].

The first synthetic improvements of Grignards with the goal of enhanced electroplating of magnesium have been reported by Brenner in 1970 [14]. Effectively, he runs the stoichiometric reaction $3\text{MeMgCl} + \text{Et}_3\text{B} \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{MeEt}_3\text{B}) + \text{Me}_2\text{Mg}$ which improves the plating of magnesium. Brenner does not mention the reaction, but he reports that the best results are obtained from a bath where three parts of MeMgCl are mixed with one part of Et_3B . We now know this may be due to the active product $(\text{Mg}_2\text{Cl}_3)(\text{MeEt}_3\text{B})$. In 1990, Gregory proposes [24] substituting hazardous and expensive boron-based Lewis acids with aluminum Lewis acids. He reports several enhanced electroplating baths when small ratios of AlCl_3 are added to Grignard solutions (Table 2.4). None of the resulting in situ electrolytes have the required voltage stability for use with high-voltage cathodes (>2 V vs. Mg/Mg^{2+}). Gregory resorts to synthesizing a more stable “naked” magnesium salt $\text{Mg}(\text{Bu}_x\text{Ph}_{4-x}\text{B})_2$.

Advances are made by Aurbach et al. by reporting the in situ generated electrolytes DCC [27] and APC [18]. DCC can reportedly cycle a magnesium metal/Chevrel phase cathode battery for 4000 cycles, and APC has a high voltage stability of 3.2 V vs. Mg/Mg^{2+} on a platinum electrode but no long cycling full battery reports. DCC is obtained by the nonstoichiometric reaction of $\text{Bu}_2\text{Mg} + 2\text{EtCl}_2\text{Al}$ and has similar ligands to those used by Gregory. It is a very elegant, simple, and transferable reaction which yields precipitated solids due to the THF/heptane solvent reaction mixture. The solids can be redissolved in a solvent of choice. The high cycle life with the Chevrel phase cathode is due to the low voltage of the battery which is charged to 2 V vs. Mg/Mg^{2+} . The conductivity of a 0.25 M solution of DCC based on magnesium has a conductivity in the mS/cm at room temperature. APC improves upon the voltage stability of DCC by using more stable ligands and is obtained by the nonstoichiometric reaction of $2\text{PhMgCl} + \text{AlCl}_3$ and has a conductivity of 1.8 mS/cm and voltage stability of 3.2 V vs. Mg/Mg^{2+} on a platinum electrode. Unfortunately, APC is corrosive on aluminum and stainless steel with voltage stabilities <2 V vs. Mg/Mg^{2+} . The long cycling stability of DCC and APC has been recently scrutinized [49–51]. In 2016, Bucur prepared a magnesium electrolyte from a simple reaction which yields solids due to the THF/heptane solvent mixture by mixing three parts PhMgCl with one part BCl_3 (which comes in heptane from Sigma). The electrolyte is corrosive and has an oxidative stability of ~ 2.5 V vs. Mg/Mg^{2+} . Due to the low oxidative stability, this finding was not reported.

A similar dimer-based magnesium electrolyte containing more stable ligands was proposed by Kim et al. (GEN1) by the stoichiometric reaction of $3\text{HMDSMgCl} + \text{AlCl}_3 \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{HMDS}_n\text{Cl}_{4-n}\text{Al}) + \text{HMDS}_2\text{Mg}$, where $n = 1$ or 2 [29]. The crystallized active compound is $(\text{Mg}_2\text{Cl}_3)(\text{HMDS}_n\text{Cl}_{4-n}\text{Al})$, where $n = 1$ or 2. This

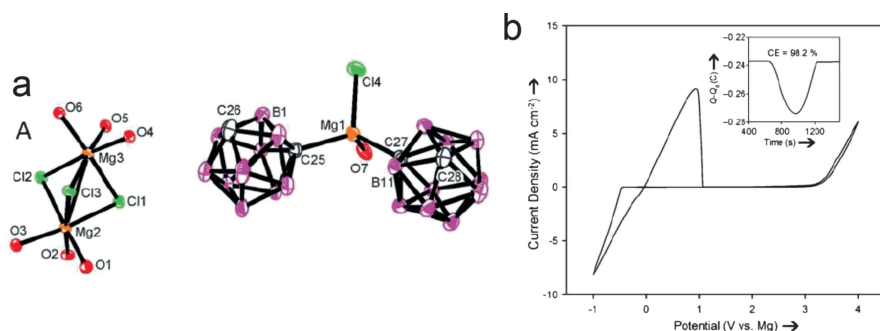


Fig. 2.5 Crystal structure of the magnesium salt $[\text{Mg}_2\text{Cl}_3][\text{R}_2\text{MgCl}]$ (a) and its electrochemistry in THF (b). Reproduced from Carter et al. [16]

Table 2.4 Various early magnesium electrolytes prepared by Gregory et al. from Grignards and different ratios of AlCl_3

Organic group	[RMgCl] (M)	[AlCl ₃] (M)	Cell voltage	Current efficiency, %		Mg deposit quality
				Anodic	Cathodic	
Methyl	1.5	0.10	0.5	100	101	Dendritic
Ethyl	0.8	0.10	1.5	98.9	100	Excellent, small grain
Ethyl	1.5	0.10	0.6	99.5	100	Excellent, large grain
Ethyl	2.0	0.20	0.6	90.1	—	Very dendritic
Butyl	1.0	0.1	1.0	104	98.4	Excellent, small grain

Reproduced from Gregory et al. [24]

electrolyte is also corrosive on aluminum and stainless steel <2 V vs. Mg/Mg^{2+} . Interestingly, Zhao-Karger et al. have reported a similar crystallized active product of $(\text{Mg}_2\text{Cl}_3)(\text{HMDSCl}_3\text{Al})$ [52] yielded by the stoichiometric reaction $\text{HMDSCl}_2\text{Mg} + 2 \text{AlCl}_3 \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{HMDSCl}_3\text{Al}) + \text{HMDSCl}_2\text{Al}$. This crystallized electrolyte has a conductivity of 1.7 mS/cm and a voltage stability of 3.2 V on a platinum electrode. It is corrosive to aluminum. Muldoon et al. have later proposed the “dimer” boron-based magnesium electrolytes GEN2 and GEN3 [17]. GEN2 has reduced corrosivity, has a voltage of 2.7 V on stainless steel, and is obtained from the stoichiometric reaction $3\text{PhMgCl} + \text{Ph}_3\text{B} \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{Ph}_4\text{B}) + \text{Ph}_2\text{Mg}$. The crystallized active compound is $(\text{Mg}_2\text{Cl}_3)(\text{Ph}_4\text{B})$. To improve the voltage stability, GEN3 uses a fluorinated analog of Ph_3B as follows: $3\text{PhMgCl} + (\text{C}_6\text{F}_5)_3\text{B} \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{Ph}(\text{C}_6\text{F}_5)_3\text{B}) + \text{Ph}_2\text{Mg}$. The crystallized active compound is $(\text{Mg}_2\text{Cl}_3)(\text{Ph}(\text{C}_6\text{F}_5)_3\text{B})$. GEN3 has voltage stability of 3.7 V vs. Mg/Mg^{2+} on a platinum electrode, but it is corrosive on stainless steel <2.2 V vs. Mg/Mg^{2+} . GEN3 provides a stable fluorinated anion which improves the voltage stability by 1 V over the non-fluorinated analog (GEN2).

Crowe et al. have also investigated the effect of a fluorinated alkoxide-based aluminum-based anion obtained from the nonstoichiometric reaction of $6(\text{CF}_3)_2\text{CH}_3\text{OMgCl} + \text{AlCl}_3$ [53]. The fluorinated alkoxide shows a high conductivity of 3.5 mS/cm at room temperature and the typical voltage stability of 3.2 V vs. Mg/Mg^{2+} . The molar ratio of Grignard to Lewis acid is controlled here to maximize conductivity, similar to the work of Gregory. A unique “dimer”-based magnesium electrolyte which does not contain the R_2Mg nucleophile in situ is the MACC electrolyte proposed by Doe et al. from Pellion Technologies (in collaboration with Aurbach) [28]. Interestingly, this electrolyte does not use a Grignard reagent and is obtained by the stoichiometric reaction of $2\text{MgCl}_2 + \text{AlCl}_3 \rightarrow (\text{Mg}_2\text{Cl}_3)(\text{AlCl}_4)$. MACC was not crystallized in its original report, but even so it is compatible with nucleophilic cathodes such as sulfur and has a conductivity of 2 mS/cm and voltage stability of 3 V vs. Mg/Mg^{2+} . This electrolyte requires many conditioning [54] cycles before high coulombic efficiency is observed between plating/stripping and is corrosive on aluminum and stainless steel <2 V vs. Mg/Mg^{2+} . A recent report from Ha et al. suggests that a CrCl_3 additive acts as a “promoter” and activates MACC without any need for conditioning [55]. A year later, Liu expanded [56] on this organomagnesium-free chemistry and evaluated the reaction of MgCl_2 with the Lewis acids AlCl_3 , AlEtCl_2 , and AlPh_3 in the same stoichiometries as Doe et al. The resulting electrolytes contain the dimer cation and the corresponding anions $(\text{AlCl}_4)^-$, $(\text{AlEtCl}_3)^-$, and $(\text{AlClPh}_3)^-$ with voltage stabilities of 3.2 V, 2.9 V, and 3.1 V vs. Mg/Mg^{2+} on platinum electrodes. They are all corrosive on aluminum and stainless steel due to chlorides in both the cation and anion. An interesting recent report is of an electrolyte prepared from the reaction of MgF_2 with a large excess of a halide-free boron Lewis acid tris(2H-hexafluoroisopropyl) borate $[(\text{CF}_3)_2\text{CHO}]_3\text{B}$ (20× molar excess) [34]. This is another example of the nonstoichiometric approach which yields in situ electrolyte mixtures without purification. The reported results are stellar, with a very good passivation of aluminum and 4 V voltage stability on aluminum current collectors. The deposition/stripping of magnesium however seems sluggish with large overpotentials (>0.5 V on CV) and may require conditioning cycles. The coulombic efficiency reported is 1.1 mS/cm. A reaction utilizing a halide-free aluminum Lewis acid was reported by Nelson et al., in an effort to reduce corrosivity of dimer-based magnesium electrolytes. She reported the reaction of Grignards with aluminum phenoxide $((\text{PhO})_3\text{Al})$ [31]. According to mass spectrometry, the nonstoichiometric reaction $4\text{PhMgCl} + \text{Al}(\text{OPh})_3$ yields several cations such as $(\text{Mg}_2\text{Cl}_3)^+$ as well as $[\text{Mg}_2(\text{OPh})_3\text{Cl}]^+$ and anions such as $(\text{AlPh}_4)^-$ and $[\text{AlPh}_3(\text{OPh})]^-$. However, the crystallized product only shows the neutral species $\text{Mg}_2(\text{OPh})_2\text{Cl}_2$ and $\text{Mg}_4(\text{OPh})_6\text{Cl}_2$ as seen in Fig. 2.6. Muldoon ran a similar reaction in 2012, $3\text{PhMgCl} + \text{Al}(\text{OPh})_3$, which upon crystallization also resulted in the neutral species $\text{Mg}_2(\text{OPh})_2\text{Cl}_2$; however, the electrochemistry as performed by Bucur was far inferior (and not published) to that reported by [31]. Grignard chemistry is however temperamental, and the results of Nelson et al. are encouraging toward largely unexplored halide-free chemistry between organomagnesiums and halide-free Lewis acids. Surprisingly, the voltage stability of Nelson’s electrolyte is in excess of 4 V and is not corrosive. It has a conductivity of 1.2 mS/cm.

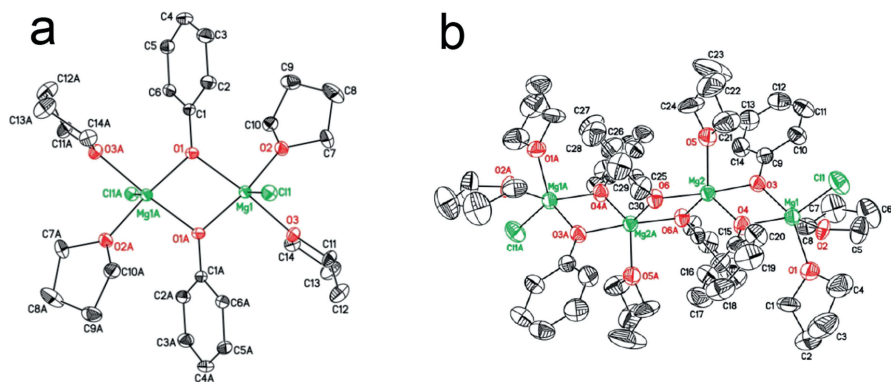


Fig. 2.6 Crystal structures of the neutral species $\text{Mg}_2(\text{OPh})_2\text{Cl}_2$ (a) and $\text{Mg}_4(\text{OPh})_6\text{Cl}_2$ (b) from the electrolyte prepared by Nelson et al. Reproduced from Nelson et al. [31] (Supporting info)

Liquid magnesium electrolytes have come a long way over the last 100 years. More importantly, in the past 3 years, several electrolytes have been reported with stabilities in excess of 4 V vs. Mg/Mg^{2+} which are stable on aluminum and are not corrosive [31–34, 39]. They have high conductivities around 5 mS/cm which are in line with commercial lithium-ion battery electrolytes. However, there still exists the challenge of ease of synthesis and reproducibility by untrained organometallic chemists. On paper, these electrolytes have all the desired properties for use with high-voltage cathodes. The litmus test will be whether they are easily prepared by nonspecialists such that suitable cathodes can be discovered for a viable magnesium battery. As of 2017, most of the magnesium cathode work which uses magnesium metal anodes is still reported with electrolytes such as DCC, APC, or GEN1. More recently $\text{Mg}(\text{TFSI})_2$ has gained some attention due to the option of purchasing it from suppliers, but its use is not without fundamental hurdles on the anode side. Appendix A.4 contains a table with properties of relevant magnesium electrolytes which are (or may be) compatible with magnesium metal.

2.2 Ionic Liquids

Ionic liquids (or room temperature molten salts) have a dual role in electrolyte mixtures. Typically they act as a solvent or cosolvent with improved stability, extended electrochemical stability window, and the promise of improved safety due to their inability to burn. Since they are ionic mixtures of cations and anions, they can also act as active co-salts in the battery system. Challenges of ionic liquid electrolytes include high viscosity and low transference numbers for the desired cation which often results in inferior conductivities. With respect to magnesium battery applications, ionic liquid electrolytes require stability with the magnesium metal anode. Any reduction materials on the surface at the anode result in blocking of the battery

due to the impermeable nature to magnesium cations. Blends of certain organic solvents and ionic liquids have been shown to substantially improve the conductivity of magnesium ions in these electrolytes due to better coordination of the mobile magnesium cation. Efforts to dissolve magnesium compatible salts in ionic liquids have been first reported by [57]. A series of papers describe the use of ionic liquids such as 1-*n*-butyl-3-methylimidazoliumtetrafluoroborate (BMIMBF₄) and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI) to dissolve Mg(TFSI)₂. Interestingly, while solutions of Mg(TFSI)₂ in liquid glyme offer very low coulombic efficiencies with high overpotentials (>2 V vs. Mg/Mg²⁺), an optimized ionic liquid solution of Mg(TFSI)₂ can cycle magnesium metal galvanostatically for over 200 cycles at low currents of 0.1 mA/cm² (Fig. 2.7a) [57, 59]. It is unclear why the overpotentials drop near zero past the 275 cycle mark, but the observed decomposition of the TFSI⁻ anion may contribute.

In 2008, Cheek et al. report that 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm BF₄) does not possess the required reductive stability to be compatible with magnesium; however, 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (BMP TFSO) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP TFSI) do and can plate/strip magnesium when mixed with a 2 M solution of PhMgCl in THF [58]. Both the pyrrolidinium ionic liquids allow for the deposition of magnesium when mixed with the Grignard. BMPTFSO can deposit magnesium at room temperature and offers no advantage in voltage stability; however, BMPTFSI requires 100 °C temperatures to plate magnesium in a 1:2 mixture of the 2 M Grignard in THF with BMPTFSI. This THF-BMPTFSI solvent mixture gives a voltage stability in excess of 2 V vs. Mg/Mg²⁺ (Fig. 2.7b).

The same approach was also developed by the group of Morita. In 2005, Morita et al. dissolve Mg(TFSI)₂ in the liquid/solid solvent mixture of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI)/PEO-PMA, where the ionic liquid acts as plasticizer for the polymer [60]. No deposition/dissolution is reported, but conductivities around 0.1 mS/cm are obtained at room temperature. Such an approach combines the safety of ionic liquids with the stability of the polymer solvent electrolyte. However, the use of newer salts which are compatible with magnesium metal is required. In 2010, Yoshimoto et al. (same group) report the Grignard/THF/ionic liquid *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium-bis(trifluoromethanesulfonyl)imide (DEMETFSI) mixture EtMgBr/THF:DEMETFSI (3:1 by volume ratio) with a conductivity of 7.4 mS/cm at room temperature which is 22× higher than that of the Grignard in THF [61]. This increase in conductivity results in a ten times improvement in current density for the deposition/dissolution CV and a 200 mV overpotential for the plating/stripping galvanostatic curves. There is no apparent improvement in voltage stability over the EtMgBr/THF solution. Kakibe et al. (same group) optimize imidazolium-based ionic liquids based on conductivity and current densities for the reversible plating of magnesium [62]. The AC₁C₂O₁ImTFSI ionic liquid where A is an allyl group, C₁ is methyl, and C₂O₁ is methoxenyl has a room temperature conductivity of 3.5 mS and highest current densities when mixed with MeMgBr/THF. Again, it is not discussed whether there are oxidative stability gains. Further improvements were made in

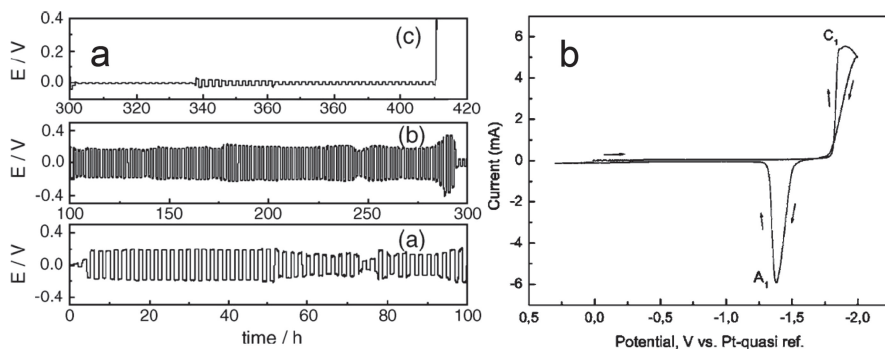


Fig. 2.7 (a) The chronopotentiograms of Mg deposition/dissolution for different stages in mixed ionic liquid system with volume ratio of 4:1 for BMIMBF₄ and PP13-TFSI in the presence of 0.3 M Mg(TFSO)₂. Reproduced from NuLi et al. [57]. (b) Cyclic voltammogram recorded at Pt substrate in the upper phase of the 1:2 mixture of Grignard reagent (2.0 M phenylmagnesium chloride in THF) and 1-butyl-1-methylpyrrolidinium TFSI ionic liquid at 100 °C. The scan rate was 10 mV/s. Reproduced from Cheek et al. [58]

2012 when Kakibe et al. improved the conductivity (>7 mS/cm) and current densities when a MeMgBr/THF was dissolved in an ionic liquid of DEME⁺ cations and a mixture of FSI⁻ and TFSI⁻ anions (Fig. 2.8) [63].

It is interesting that Narayanan et al. have reported in 2009 the reversible plating of magnesium from an acetamide/Mg(ClO₄)₂ solution with conductivities of 1.7 mS at room temperature [65]. The paper even cycles a Mg/acetamide/Mg(ClO₄)₂/δ-MnO₂ cathode for several cycles. Mg(ClO₄)₂ has not successfully cycled magnesium from any liquid organic solvent. Cheek et al. also suggest that Mg(ClO₄)₂ may reversibly plate magnesium (figure 2 in his manuscript, [58]). No study has yet proposed an explanation regarding reports of Mg(ClO₄)₂ plating of magnesium from ionic liquids but no such plating from organic solvents. However, an attempt to clarify and debunk recent reports regarding the reversibility of magnesium plating from ionic liquids has been published in 2014 by Vardar et al. [64]. The authors test several ionic liquids with voltage stability windows which should enable the plating of magnesium (Fig. 2.8). Unfortunately, attempts to plate magnesium from solutions of simple salts such as Mg(BH₄)₂, Mg(TFSI)₂, and Mg(TFSO)₂ are all unsuccessful.

Bertasi et al. published a series of papers on the conductivity of MgCl₂ dissolved in EMImBF₄ as well as the reversible plating of magnesium from EMImCl/AlCl₃/MgCl₂ (Fig. 2.9) [66, 67]. This body of work offers a detailed account of ionic association processes responsible for the migration and electrochemical activity of magnesium in ionic liquids.

Reversible plating of magnesium has also been reported by Kar et al. with the aim of coupling a magnesium metal anode with the oxygen cathode [68]. The authors demonstrate a novel ionic liquid composed of a 0.1 M solution of Mg(BH₄)₂ dissolved in [N₂(20201)(20201)(20201)]⁺[TFSI]⁻ which can reversibly plate magnesium without the addition of an organic solvent. In 2016, Huie et al. reported a systematic

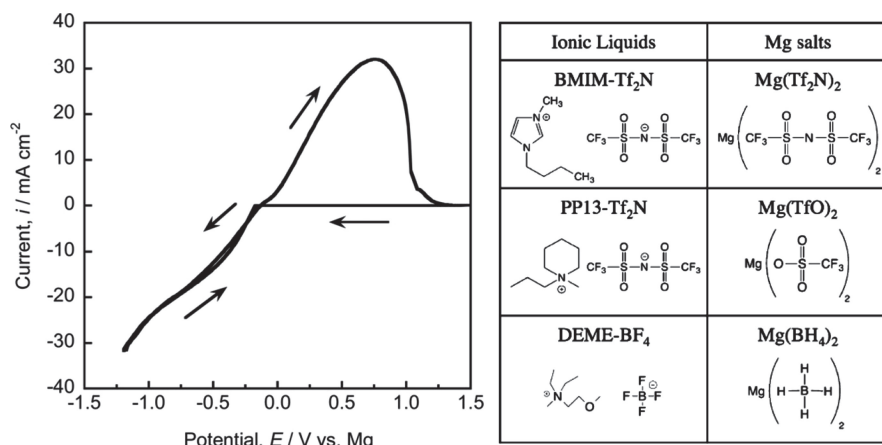
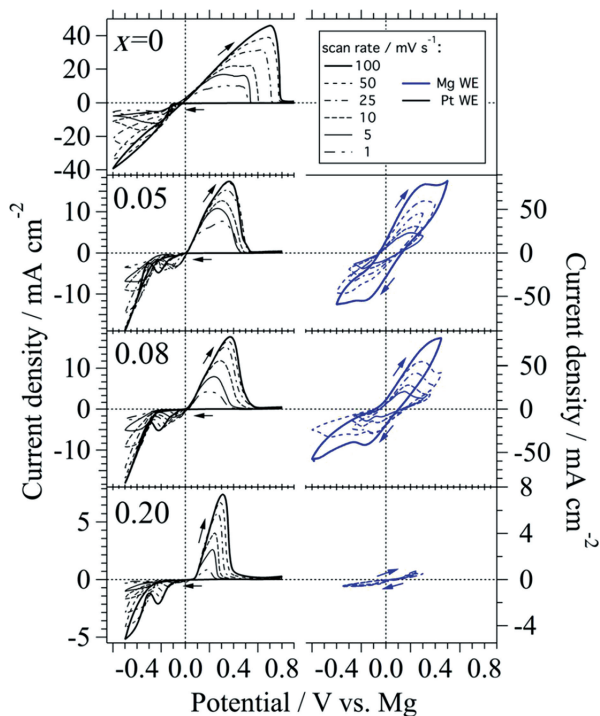


Fig. 2.8 Cyclic voltammogram for an Ni substrate in the electrolyte solution of MeMgBr/THF/[DEME⁺][TFSI⁻]_{0.5}[FSI⁻]_{0.5}. Reproduced from Kakibe et al. [63]. Table shows formulae and structures of ionic liquids and salts which could be compatible with magnesium metal. Reproduced from Vardar et al. [64]

Fig. 2.9 Cyclic voltammograms of the ionic liquid electrolytes hosting Mg ions, (EMImCl)/(AlCl₃)_{1.5}/ (δ-MgCl₂)_x; voltammograms in *black* (left side) were obtained with Pt working electrodes; voltammograms in *blue* (right side) were obtained with Mg working electrodes. Mg pseudo-reference electrodes and counter electrodes were used in all experiments, and measurements were recorded at scan rates in the range 1–100 mVs⁻¹. Reproduced from Bertasi et al. [66]



approach to optimizing hybrid ionic liquid solutions of $\text{Mg}(\text{TFSI})_2$ and dipropylene glycol dimethyl ether (DPGDME) or acetonitrile (ACN) with high voltage stabilities of 5.5 V vs. Mg/Mg^{2+} or high conductivities 50 mS/cm [69]. Unfortunately, while these classes of electrolyte solutions enable screening of high-voltage cathodes, they are not reductively stable on a magnesium metal anode and preclude their application in a battery with a magnesium anode. This study finds a correlation of higher conductivity with unsaturated rings and short carbon chain lengths, but by contrast, these ionic liquids also exhibited lower oxidation voltage limits. An interesting report was that of Pan et al. which shows the beneficial effect of adding the ionic liquid DEMETFSI to a liquid electrolyte of $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2$ in THF [70]. A current density and conductivity improvement is generated by the addition. Appendix A.5 contains a table with properties of relevant ionic liquid-based magnesium electrolytes which are (or may be) compatible with magnesium metal.

2.3 Polymeric Conductors

Polymer electrolytes have the advantage of softness and conforming interfaces with irregular electrodes when compared to stiffer solid electrolytes. Polymeric electrolytes typically consist of mixtures of salts and polymers which have low glass transition points and mobile ligands used to transfer ions of choice. These mixtures can be prepared by ball milling/hot pressing or by solution mixing, followed by evaporation of the solvent over a flat glass substrate which results in a thin and uniform polymer/salt solid solution. In polymer electrolytes, the salt is dissolved in a polymeric solid or gel matrix. As such, the system stability can be increased since polymers have higher stabilities than (ethereal) solvents. Polyethylene oxide (PEO) complexes with monovalent alkali metals were shown to have high conductivity in 1973 [71]. The first reports of Mg^{2+} conductivity in polymer electrolytes have been those by Patrick et al. [72] and Yang et al. [73] in 1986. They reported blends of 12PEO: $\text{Mg}(\text{ClO}_4)_2$ with conductivities of 10^{-6} S/cm and 16PEO: MgCl_2 with conductivities of 10^{-9} S/cm at room temperature. Sequeira published tables with conductivities of several divalent cations in PEO polymers in 1990 [74] (Table 2.5). The best conductivity belonged to the PEO: $\text{Mg}(\text{ClO}_4)_2$ complex. In 1998, di Noto et al. reported a 10^{-5} S/cm conductivity for PEG400: δ - MgCl_2 at room temperature [75]. Unfortunately, all the salts used so far are not compatible with magnesium metal which would render the PEO:salt complex incompatible with a magnesium anode. The first effort of complexing an ionically conductive polymer with a magnesium compatible salt was reported by Liebenow in 1998 [25]. Liebenow mixed 4PEO:EtMgCl which has a $10^{-4.5}$ S/cm conductivity at 50 °C. The use of magnesium compatible EtMgCl allows the deposition/dissolution of magnesium from this electrolyte. In 1999, Ikeda et al. used a cross-linked polyethylene glycol diacrylate (PEGDA) polymer mixed with magnesium trifluoromethanesulfonate ($\text{Mg}(\text{TFSO})_2$). The complex PEGDA:1% $\text{Mg}(\text{TFSO})_2$ has a room temperature conductivity of 0.2 mS/cm [76]. The same salt was used the same year by Kumar et al. mixed with

Table 2.5 Table shows $-\log \sigma$ conductivity values in S/cm for several PEO/magnesium salt complexes

Salt	Temperature (°C)		
	20	30	40
Ca(ClO ₄) ₂ ·6H ₂ O	8.0	7.2	6.2
Ca(SCN) ₂ ·3H ₂ O	8.8	8.2	7.5
Cu(ClO ₄) ₂	4.7	4.3	4.0
MgCl ₂	9.4	8.8	8.0
Mg(ClO ₄) ₂ ·6H ₂ O	6.4	5.6	5.0
Mg(SCN) ₂ ·4H ₂ O	9.2	8.3	7.0
PbBr ₂	9.0	8.6	8.2
Sr(ClO ₄) ₂ ·6H ₂ O		7.5	6.8
ZnCl ₂	5.3	4.7	4.4
Zn(ClO ₄) ₂ ·6H ₂ O	7.6	6.7	5.8
PbI ₂		9.6	9.2
PbCl ₂	9.4	9.1	8.7

Reproduced from Martins and Sequeira [74]

PAN and plasticized by propylene carbonate (PC) and ethylene carbonate (EC). This polymer-gel electrolyte had a room temperature conductivity of 1.8 mS/cm. The magnesium trifluoromethanesulfonate may be compatible with magnesium metal; however the PC/EC solvent component is not and will render a magnesium metal inactive [77]. Liebenow reported his findings again in 2000 on the PEO-DEE:EtMgBr complex which had a 0.1 mS/cm conductivity at 40 °C. Once again, the EtMgBr Grignard is natively compatible with magnesium metal and deposition/dissolution cyclic voltammetry is shown in the manuscript [78]. Another magnesium compatible salt, Mg(TFSI)₂, was mixed with PEO-polymethacrylate (PMA) by Morita et al. in 2001. The complex PEO-PMA:50%Mg(TFSI)₂-EMITFSI had a conductivity of 0.1 mS at room temperature, and a Mg/gel/V₂O₅ battery is reported [79].

Starting in 2003, the reported conductivities of magnesium polymer electrolytes start to match those of liquid electrolytes by making a one order of magnitude improvement into the mS/cm range. The highest reported conductivity surpasses liquid electrolytes and is reported by Pandey in 2011: 10 mS/cm. In 2003, Saito achieves a 0.51 transference number for Mg²⁺ in a polymer/salt mixed with a Lewis acid which may interact akin to the common reaction of liquid electrolytes by coordinating into a strong anion. Thus, the complex PEG150/B₂O₃/Mg(ClO₄)₂ has a conductivity of 1 mS/cm [80]. Taking the use of Lewis acids a step further and in line with liquid electrolytes, in 2004, a patent by Aurbach et al. is accepted and reports the complexing of DCC (which is a nonstoichiometric mixture of Bu₂Mg and the Lewis acid EtCl₂Al) with the polymer polyvinylidene fluoride (PVDF) plasticized by tetraglyme (TDME). PVDF-TDEM/DCC has a conductivity of 3.7 mS/cm (the same conductivity as DCC in liquid state) and cycles the Chevrel phase cathode Mo₆S₈ just as well as DCC in the liquid state [81]. It is interesting to note

that the patent was filed in 1999, at the same time with the submission of the first report on DCC and the Chevrel phase cathode [27, 82]. PVDF-HFP was also used by Oh et al. and mixed with $\text{Mg}(\text{ClO}_4)_2$ to yield a conductive complex [83]. The PVDF-HFP matrix was however plasticized by EC:PC (1:1 ratio) and imparted a porous structure by incorporation of 12% SiO_2 . A voltage stability of 4.3 V was reported and a conductivity of 3.2 mS/cm. A $\text{Mg/gel/V}_2\text{O}_5$ was reported with limited cycle life due to instability of $\text{Mg}(\text{ClO}_4)_2$ on the magnesium anode. Pandey et al. also used a PVDF-HFP with 3% SiO_2 complexed with $(\text{MgClO}_4)_2$ but reported a higher conductivity of 10 mS/cm at room temperature. A $\text{Mg-MWCNT/PVDF-HFP/MoO}_3$ battery reportedly had a 200 mAh/g capacity [84]. It would be very interesting to investigate the electrochemistry of recent high-voltage magnesium salts with stabilities in THF or glyme of >4 V vs. Mg/Mg^{2+} such as $\text{Mg}(\text{Al}(\text{HFIP})_4)_2$ [33], $\text{Mg}(\text{PF}_6)_2$ [39], the nonstoichiometric in situ electrolyte reported by Nelson et al. [31] obtained by the reaction of 4PhMgCl and $\text{Al}(\text{OPh})_3$, or $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ [32] with PVDF-HFP- SiO_2 polymer templates. It is highly probable that the oxidative stability of the salts enumerated above is limited by the ethereal solvents and a more stable polymer solvent may extend that limit. In addition, all these magnesium salts can reversibly plate magnesium. An in-depth study for the mechanism of Mg^{2+} transfer via GHz broadband electrical spectroscopy in a model PEO polymer electrolyte has been published by Piccolo et al. in 2013 [85]. $\text{Mg}(\text{BH}_4)_2$ is a salt which has been reported to reversibly plate magnesium and has also been complexed with a PEO-MgO matrix to yield a magnesium conductive polymer electrolyte which cycles well with the Chevrel phase cathode Mo_6S_8 and deposits magnesium reversibly (Fig. 2.10) [86, 87]. Appendix A.6 contains a table with properties of relevant polymeric magnesium electrolytes which are (or may be) compatible with magnesium metal.

2.4 Solid-State Conductors

In lithium-ion batteries, solid conductors provide improvements in the energy density of the cell by allowing better balancing between anode and cathode capacities. If the battery has liquid electrolytes, a solid electrolyte interphase (SEI) is formed at the anode by reduction products. The formation of this SEI occurs on the initial charging step, and it irreversibly consumes capacity from the cathode. As a result, battery cells with liquid electrolytes require additives as well as cathode active material in excess of the reversible anode capacity to account for the SEI formation. With a solid electrolyte which is stable on the anode, no SEI is formed, and no excess cathode active material is required for balance. Solid electrolytes can improve the energy density without any changes in anode/cathode materials. Magnesium batteries with a magnesium metal anode do not form an SEI at the anode, so solid electrolytes do not offer the same energy density benefit. However, since compatible magnesium electrolytes have so far used ether-based solvents which are known for a limited oxidative stability, solid electrolytes may provide a more stable alternative.

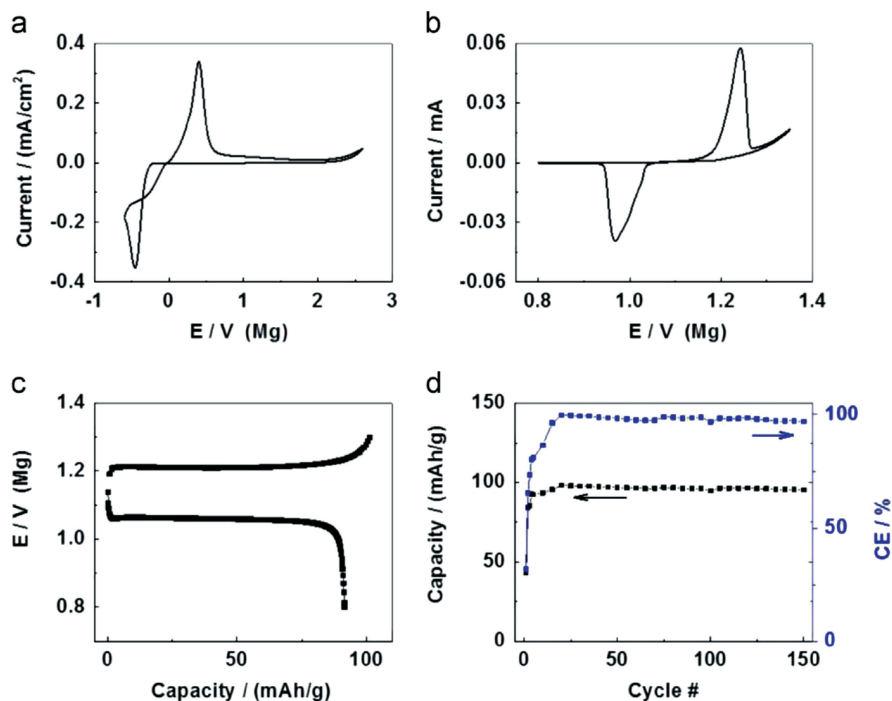


Fig. 2.10 Figures show electrochemistry of $\text{Mg}(\text{BH}_4)_2$ complexed with PEO:MgO. (a) Cyclic voltammogram depicting the deposition/dissolution of magnesium and oxidative stability; (b) the reduction/oxidation of the Chevrel phase Mo_6S_8 cathode in this electrolyte; (c) discharge/charge plateaus for the magnesium/ $\text{Mg}(\text{BH}_4)_2$:PEO:MgO/ Mo_6S_8 battery; (d) cycle life of this battery. Reproduced from Shao et al. [86]

The requirements of solid electrolytes for magnesium battery are high conductivities (mS/cm range or higher at room temperature), high transference numbers for the magnesium-containing cation (closer to 1 is better), and stability against the magnesium metal anode as well as against the cathode. One of the main challenges for practical solid electrolytes for lithium batteries is stability against the very reductive lithium metal. Since magnesium is 0.7 V more positive than lithium, the anode stability requirement should be easier to meet.

In the lithium-ion field, solid electrolytes currently surpass polymer electrolytes with conductivities as high as 10–20 mS at room temperature for lithium-potassium-sulfide (LPS) and Li_3OCl -based solid electrolytes [88, 89]. However, reports of magnesium conducting solid electrolytes with useful room temperature conductivities do not abound. The highest magnesium conductivity in a solid electrolyte has been reported by [90] in metal-organic framework (MOF): $\text{Mg}(\text{TFSI})_2$ or $\text{Mg}(\text{OPhCF}_3)_2$ mixtures, 0.25 mS/cm at room temperature [90]. The first efforts of finding magnesium conductivity in solids were taking place at the same time Gregory and Mayers were doing their investigations on liquid electrolytes. In 1987, Ikeda et al. reported that the system $\text{MgZr}_4(\text{PO}_4)_6$ (MZP) had a conductivity similar to $\text{NaZr}_2(\text{PO}_4)_3$:

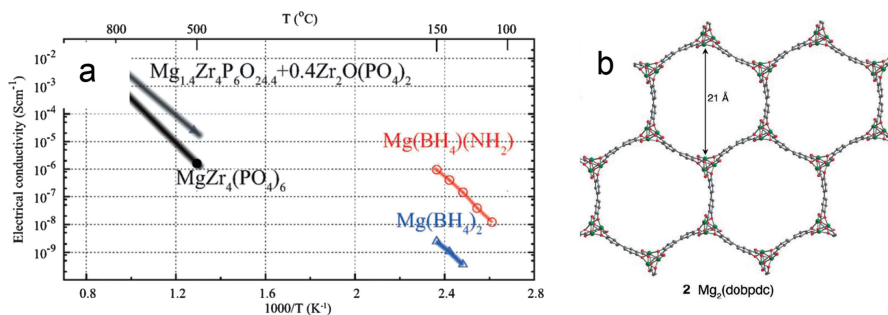


Fig. 2.11 (a) Conductivities of several magnesium solid electrolytes. Reproduced from Higashi et al. [95]. (b) Structure of MOF Mg₂(4,4'-dioxidobiphenyl-3,3'-dicarboxylate) with high magnesium conductivity at room temperature. Reproduced from Aubrey et al. [90]

Table 2.6 Table shows the conductivities of several guest salts in the MOF matrix

Guest salt(s) per mole of framework	Equivalents triglyme	Electrolyte concentration (M)	[Framework]	Conductivity log ₁₀ (S cm ⁻¹)	Molar conductivity log ₁₀ (S M ⁻¹ cm ⁻¹)
			[Solution]		
0.22Mg(TFSI) ₂	3.3	0.45	1.0	-3.9	-3.6
0.21Mg(OPhCF ₃) ₂ and 0.46Mg(TFSI) ₂	4.8	1.37	2.4 (Mg(TFSI) ₂)	-3.6	-3.7

Reproduced from Aubrey et al. [90]

10⁻⁶ S/cm at 350 °C [91, 92]. In 1999 and 2000, Imanaka et al. reported a new structure, Zr₂O(PO₄)₂, which had twice the conductivity of MZP [93, 94] but at higher temperatures of 500 °C. In 2001, Kawamura used ³¹P NMR as a guide to optimize the conductivity of MZP by doping. Mg_{1.1}(Zr_{0.85}Nb_{0.15})₄(PO₄)₆ had a conductivity one order of magnitude higher than MZP. Unfortunately, the measurements were done at high temperatures of 800 °C (Fig. 2.11) [96]. A new, sol-gel synthetic method was reported for MZP in 2016 which increased its conductivity at 725 °C (7.23 mS/cm) [97]. A unique salt which conducts magnesium in solid state is the magnesium salt reported by [40] for liquid electrolytes. Higashi et al. from Toyota have improved the conductivity by reporting the Mg(BH₄)(NH₄) derivative in 2014 with a conductivity of 10⁻⁶ S/cm at 150 °C (Fig. 2.11) [95]. Departing from the MZP class of materials, Aubrey et al. have reported in 2014 that a MOF Mg₂(2,5-dioxidobenzene-1,4-dicarboxylate) and Mg₂(4,4'-dioxidobiphenyl-3,3'-dicarboxylate) has a conductivity of 0.25 mS/cm at room temperature (Fig. 2.11) [90]. Table 2.6 shows the conductivities obtained when the MOF is impregnated with several magnesium salts. In 2014, Yamanaka et al. have prepared the magnesium analog (MgS-P₂S₅-MgI₂) of the highly conductive lithium solid conductor LPS by a simple, mechanochemical technique [98]. Unfortunately, the material had a low conductivity of 2.1 × 10⁻⁷ S/cm at 200 °C. Another magnesium analog of the highly solid lithium conductor LiPON was prepared by Nishitani et al. from Panasonic. He showed in 2017 that MgPON

also has a conductivity of 10^{-6} S/cm at 210 °C [99]. While low conductivities and high temperatures are still the norm for magnesium solid conductors, the future is bright as more groups become active in this field. Appendix A.7 contains a table with properties of relevant solid magnesium electrolytes which are (or may be) compatible with magnesium metal.

While most lithium-ion batteries require an SEI stabilizing electrolyte, the higher reduction potential of magnesium does not require the formation of an SEI. Stable electrolytes which are compatible with magnesium have been reported for a long time; however, they have been corrosive and had low oxidative stabilities. However, in the past few years, there have been several reports of noncorrosive high-voltage liquid electrolytes with oxidative stabilities above 4 V vs. Mg/Mg^{2+} . Once these types of electrolytes are embraced and reproduced by the community, progress will be made toward finding suitable cathodes for the rechargeable magnesium battery. Advanced solid electrolytes represent the next stage of electrolyte development but are not required in the cathode search. There are interesting recent reports of carborate-based [100, 101] and closo-borate-based [102] solid conductors for sodium with very high conductivities (70 mS/cm at room temperature) which are higher than those for liquid electrolytes. Since liquid magnesium electrolytes containing carborane anions have already been reported [32], it would be very attractive to investigate the Mg^{2+} conductivities of analogous solid-state magnesium closo-borates which may be similarly high.

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