



Recent Advances in Non-nucleophilic Mg Electrolytes

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High-performance electrolyte is still a roadblock for the development of rechargeable magnesium (Mg) batteries. Grignard-type electrolytes were once the only choice in the early stage of rechargeable Mg batteries research. However, due to their nucleophilic nature and high reactivity, Grignard-type electrolytes have inherent safety issues and low oxidation stability, which restrict the development of rechargeable Mg batteries in terms of practical application. Recently, emerging novel Mg battery systems such as Mg-S, Mg-O₂/air batteries also require non-nucleophilic electrolytes with high oxidation stability. This short review summarizes recent advances in non-nucleophilic Mg electrolytes and aims to provide insights into electrochemical properties and active Mg ion structure of such electrolytes.

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INTRODUCTION

After years of extensive research and evolution, rechargeable lithium-ion batteries (LIBs) have become the dominant secondary energy storage system. However, it is still a big challenge to meet the increasing demands for portable electronics and electric vehicles because of limited lithium resources. Rechargeable magnesium (Mg) batteries have been regarded as a promising candidate for novel LIBs technologies, owing to several considerable advantages (Liu et al., 2020) (Kim et al., 2020). Mg anode possesses a theoretical volumetric capacity of 3,833 mAh cm⁻² that is five times higher than graphite anode-based LIB (Zhang et al., 2018). Mg has a much higher abundance than Li, ranking 8th among the most 40 abundant elements in the Earth's crust. The nondendritic feature of Mg enables easy manufacturing of Mg metal batteries compared to Li-based battery systems. Additional clear advantages over Li-based batteries include lower cost and better safety. However, the superiority of rechargeable Mg battery has not been fully illustrated due to several inherent problems. Specifically, the actual energy density is still much lower than expected because of low discharge voltage and capacity; also, the cycle performance of the battery is extremely poor. An important reason for unsatisfying working voltage and poor cyclability of Mg-based battery is the passivation effect on Mg anode in electrolytes. Surface passivation film consists of ionic Mg compounds is formed during stripping/plating, even in nonaqueous electrolytes (Lu et al., 1999; Gofer et al., 2003). Unlike the situation in Li or Na battery, such passivation film hinders Mg²⁺ migration, thus resulting in high overpotential and irreversible stripping/plating (Aurbach, 1999; Attias et al., 2019).

In the early stage of rechargeable Mg batteries research, the electrolytes that allow high efficient stripping/plating were only limited to Grignard reagents and their analogs (Muldoon et al., 2012). Gregory et al. first developed Mg electrolyte with reversible deposition properties, which is based on a Grignard reagent activated by AlCl₃ (Gregory et al., 1990). Since then, many researchers have focused on Mg organohaloaluminate salts generated by the complexation of Grignard reagents RMgX with AlCl₃ in the ether solutions (Aurbach et al., 2002, 2003). The development of a novel rechargeable

Mg-S, Mg-O₂/air battery system promotes the demand for non-nucleophilic Mg electrolytes. Sulfur and oxygen are prone to be attacked by nucleophiles, making conventional nucleophilic electrolyte incompatible for Mg-S, Mg-O₂/air batteries. Even for Mg-ion battery based on intercalation chemistry, nucleophilic electrolyte has its shortcomings. Due to the use of organomagnesium precursors, most of the nucleophilic Mg electrolytes have limited oxidative stability, which restricts the use of high-voltage cathode materials. The highly sensitive and corrosive feature of Grignard-based electrolytes creates difficulties in manufacturing.

The development of Grignard reagent free, non-nucleophilic Mg electrolyte can not only meet the requirements of rechargeable Mg-S and Mg-O₂/air battery but also stepwise fulfill the requirements of practical rechargeable Mg ion battery manufacturing. In this minireview, we briefly summarized the development and recent advances of non-nucleophilic electrolytes (Table 1). Their electrochemical performance and ionic coordination structure were discussed to provide new insights for the future development of high-performance Mg-based electrolytes.

ELECTROCHEMICAL PERFORMANCE OF NON-NUCLEOPHILIC MG ELECTROLYTES

Hexamethyldisilazide-Based Electrolytes

The first efficient non-nucleophilic Mg electrolyte was prepared by adding Lewis acid AlCl₃ to hexamethyldisilazide magnesium chloride (HMDSMgCl) in THF, demonstrating Coulombic efficiency (CE) of >95% with an increased Mg deposition current density by almost a factor of seven compared to HMDSMgCl-only electrolyte (Kim et al., 2011). Mg-S coin cell using HMDSMgCl-AlCl₃ electrolyte displayed discharge capacity of 1,200 mAh g⁻¹ initially; however, it decreased to 394 mAh g⁻¹ in the following cycle. Later on, stable, commercially available (HMDS)₂Mg was used to replace HMDSMgCl, which exhibited very high oxidative stability (3.5 V vs. Mg) and reversible Mg deposition up to 40 cycles with an overpotential of <150 mV (Zhao-Karger et al., 2013). To overcome the drawback of byproduct HMDSAlCl₂ formation in (HMDS)₂Mg-AlCl₃ electrolyte, MgCl₂ was introduced to convert HMDSAlCl₂ into active species (Zhao-Karger et al., 2015). Such novel electrolyte displayed a discharge potential of ~1.65 V in Mg-S battery, which was close to the theoretical thermodynamic value. Liao et al. further developed the strategy by preparing [(HMDS)MgCl₂-Mg₂Cl₃] via reverse Schlenk equilibrium from the reaction between (HMDS)₂Mg and MgCl₂. The substitution of MgCl₂ for Lewis acid AlCl₃ successfully avoided the possible Al deposition commonly observed in AlCl₃-containing electrolytes. It displayed comparable performance to HMDSMgCl-AlCl₃ in terms of ionic conductivity (0.5 mS cm⁻¹), oxidative stability (2.8 V vs. Mg), and Mg stripping/plating CE (99%) (Liao et al., 2015).

MACC Electrolytes

Using non-nucleophilic and cheap Mg²⁺ sources of MgCl₂, all-inorganic MgCl₂-AlCl₃ complex (MACC) electrolytes are of

particular interest due to their simplicity and low cost. Early research on MACC electrolyte was prepared in 2005; however, it showed poor electrochemical properties with 0.9 V deposition overpotential and 37% cycling efficiency (Viestfrid et al., 2005). Several years later, R. Doe et al. demonstrated a series of MACC electrolytes in dimethoxyethane (DME) with reversible Mg deposition capability by simply increasing the MgCl₂ concentration (Doe et al., 2014). One of the best among them can reach CE of at least 99%, overpotential of <200 mV, and anodic stability up to 3.1 V during 50 cycles. The MACC complex is formed based on acid-based reaction, generating solvated Mg₂Cl₃⁺ active cations, which is similar to that of the transmetalation process in Grignard-type complexes (Vestfried et al., 2007). Gewirth et al. (Barile et al., 2014) and Li et al. (Cheng et al., 2015) found that the overpotential of MACC electrolytes can be lowered by repeated CV scans or charge-discharge cycles, called the electrochemical conditioning process. Other inorganic chlorides, such as InCl₃, SnCl₂, SbCl₃, and BiCl₃, based binary chloride complex, were also investigated, which presented moderate Mg cycling performance (Barile et al., 2015). According to the retrosynthetic analysis of the Mg²⁺/Cl⁻/THF coordination cation formation process, Liu et al. developed a simple “mono-Cl abstraction” strategy to produce highly active MACC-derived electrolytes, which used MgCl₂ and Al-based Lewis acid (AlCl₃, AlPh₃, and AlEtCl₂) in THF solvent (Liu et al., 2014). The resulting electrolyte showed CE up to 100%, oxidation stability of 3.4 V, and improved electrophilic stability. A rechargeable Mg battery using Mo₆S₈ cathode and 0.3 M MgCl₂-AlEtCl₂ electrolyte delivered first discharge capacity of 104 mAh g⁻¹ and can remain at 95.1% of the initial value after 100 cycles. By adding 0.03 M magnesium bis(trifluoromethane sulfonyl)imide [Mg(TFSI)₂] to the MACC electrolyte, the electrochemical performance and water-tolerant property can be significantly improved (He et al., 2019). The CE of Mg(TFSI)₂-MACC electrolyte was increased to 97%, with Mg deposition potential of ~350 mV even without the conditioning process. A fascinating feature of the electrolyte is its moisture and impurity durability. A Mo₆S₈-Mg battery with such electrolyte can deliver a capacity of 92 mAh g⁻¹ at 0.2 C after 100 cycles.

Mg(TFSI)₂ and Mg(CF₃SO₃)₂ Based Electrolytes

Mg(TFSI)₂ possesses high solubility in various solvents, good ionic conductivity, and high oxidative stability. However, electrolytes using single Mg(TFSI)₂ displayed large overpotential (>2.0 V) and low CE (<50%) even at high temperatures (Ha et al., 2014). Mg(TFSI)₂ electrolytes were very sensitive to the impurity species, thus strongly affecting their Mg stripping/plating properties (Connell et al., 2016). Cl⁻ can protect Mg surface from passivation by a trace amount of moisture via complex and dynamic interaction between Cl⁻ and H₂O (Connell et al., 2016). Therefore, the introduction of MgCl₂ into Mg(TFSI)₂ electrolytes was an effective strategy to achieve reversible stripping/plating and reduced overpotential. Li et al. first reported Mg(TFSI)₂-MgCl₂ combination in DME and presented improved performance of 80% CE, 400 mV

overpotential, and 3.5 V anodic stability limit (Cheng et al., 2015). In addition to the consumption of water impurities, MgCl_2 can also help to form $[\text{Mg}_x\text{Cl}_y]^{n+}$ electroactive species. Sa et al. confirmed that the active cation in $\text{Mg}(\text{TFSI})_2\text{-MgCl}_2/\text{THF}$ was dominated by the Cl^- component in electrolyte (Sa et al., 2016). When the $\text{Cl}^-/\text{TFSI}^-$ ratio increased from 1:5 to 1:2, CE was greatly improved from 12% to 93%; meanwhile, the average capacity in a $\text{Mo}_6\text{S}_8\text{-Mg}$ rechargeable battery increased by 15%. Of note, the performance of $\text{Mg}(\text{TFSI})_2$ based electrolytes is highly dependent on the purity of the Mg salt and can be improved by introducing scavenging reagent other than MgCl_2 (Shterenberg et al., 2015). By adding a trace amount of $\text{Mg}(\text{BH}_4)_2$ as moisture scavenger, reversible Mg stripping/plating cycling can be achieved in an $\text{Mg}(\text{TFSI})_2/\text{tetraglyme}$ (G4) electrolyte at onset potentials around -0.35 V (plating) and 0 V (stripping), with CE up to 84% over the initial cycles and ~75% for 500 cycles overall (Ma et al., 2017). Dimethylamine (DMA) was introduced as cosolvent to prepare a Cl-free, noncorrosive $\text{Mg}(\text{TFSI})_2$ based electrolyte, exhibited promising Mg stripping/plating. It showed polarization of 210 mV over 1,500 min in symmetric Mg cell cycling, which was equivalent to the performance in APC electrolyte. When using DMA-THF-G4 as mixed solvent, the CE was increased to 75% compared to 38% from an $\text{Mg}(\text{TFSI})_2\text{-G4}$ electrolyte (Fan et al., 2020).

Although MgCl_2 containing $\text{Mg}(\text{TFSI})_2$ electrolytes have already been extensively studied and demonstrated good stripping/plating properties, $\text{Mg}(\text{TFSI})_2$ for electrolyte still requires relatively high purity and low moisture level, which caused increased cost (Gao et al., 2017). As a relative “simple” Mg salt, low-cost trifluoromethanesulfonate [$\text{Mg}(\text{CF}_3\text{SO}_3)_2$, $\text{Mg}(\text{OTf})_2$] is commercially available with high purity and ultralow moisture, thus providing an alternative choice other than $\text{Mg}(\text{TFSI})_2$. A high-performance electrolyte was prepared by $\text{Mg}(\text{OTf})_2\text{-AlCl}_3\text{-MgCl}_2$ dissolved in THF and G4 mixed solvents with anthracene as a stabilizing agent, which exhibited low overpotential of 200 mV and high CE up to 98.5% without any conditioning process (Yang et al., 2019). Mg-S battery based on such electrolyte presented the highest capacity of 1,193.8 mAh g^{-1} and maintained a capacity of 420 mAh g^{-1} without fluctuations for 50 cycles. Later on, an improved $\text{Mg}(\text{OTf})_2$ based electrolyte was reported, by simply dissolving $\text{Mg}(\text{OTf})_2$, MgCl_2 , and AlCl_3 in DME (Huang et al., 2020). It showed high efficiency of 99.1% and good anodic stability up to 3.5 V, and also demonstrated excellent performance in Mg-S battery, with a high capacity of 866 mAh g^{-1} at 200 mA g^{-1} and power density of 550 W kg^{-1} .

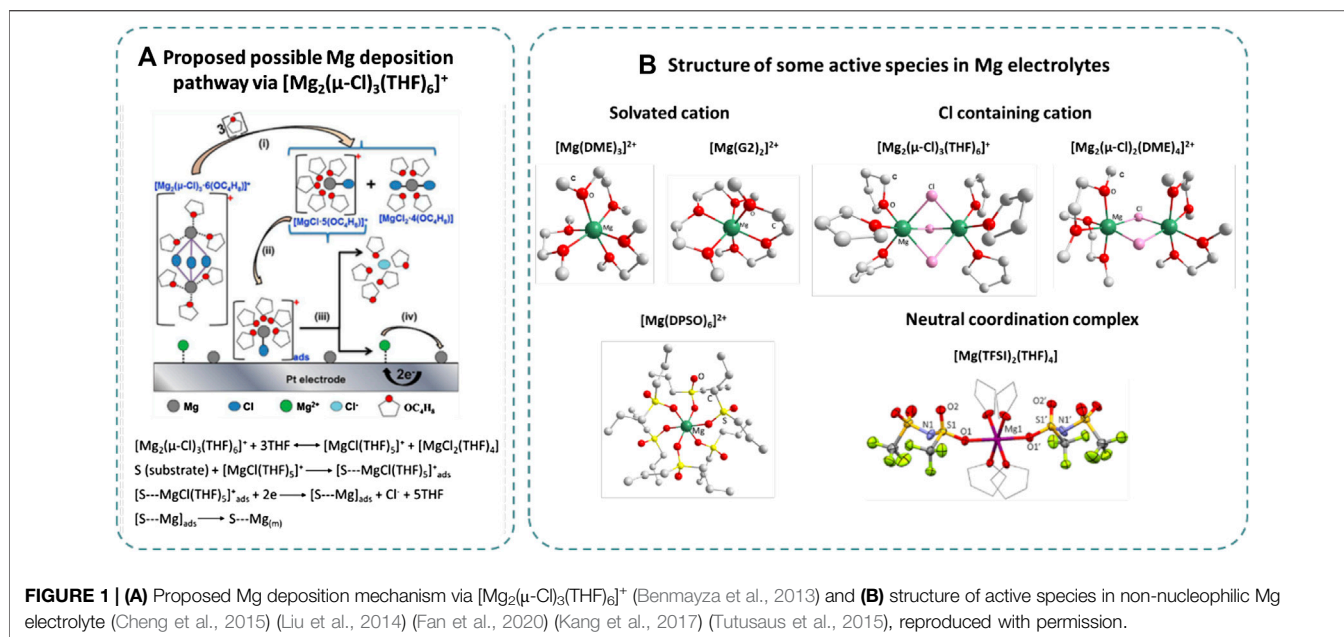
Other MgCl_2 -Containing Electrolytes

High-performance Mg electrolytes can be achieved using simple MgCl_2 salt only, with the help of proper sulfone as cosolvent. $\text{MgCl}_2\text{-sulfone-THF}$ electrolyte enabled highly reversible Mg stripping/plating, without the introduction of AlCl_3 , $\text{Mg}(\text{TFSI})_2$, or $\text{Mg}(\text{CF}_3\text{SO}_3)_2$. Dipropyl sulfone (DPSO) with a melting point of 29–33°C was selected, combined with THF cosolvent and solute, successfully lowered the melting point of the resulting electrolyte below 10°C. $\text{MgCl}_2/\text{DPSO-THF}$ electrolyte also presented a typical conditioning behavior

during consecutive 200 CV cycles and then underwent significant performance improvement with CE value raising from 76.2% to 92.3% (Kang et al., 2017). In the galvanostatic charge-discharge test, the CE value rapidly increased from 68.5% initially to >90% in the following 150 cycles. A $\text{Mo}_6\text{S}_8\text{-Mg}$ cell using the above-mentioned electrolyte displayed excellent cycle performance up to the 300th cycle with a constant specific capacity of 70–75 mAh g^{-1} and high CE value (98–99%).

Boron-Centered Mg Electrolytes

Chloride-based non-nucleophilic electrolytes are still corrosive to all cell parts to some extent. Boron- (B-) based anions are compatible with Mg anode and cell components; thus, they could be promising candidates for non-nucleophilic electrolytes (Zhang et al., 2017). The first B-based chloride-free electrolyte developed by Mohtadi et al. was $\text{Mg}(\text{BH}_4)_2$ in THF or DME (Mohtadi et al., 2012). The $\text{Mg}(\text{BH}_4)_2/\text{DME}$ showed better electrochemical performance with stripping/plating onset potential at 0.03 V/0.34 V and CE of 67%. Rechargeable Mg battery using $\text{Mg}(\text{BH}_4)_2/\text{DME}$ and Mo_6S_8 cathode delivered reversible cycling for 40 times at 128 mA g^{-1} . However, the reductivity of $\text{Mg}(\text{BH}_4)_2$ resulted in narrow electrochemical windows (1.7 V vs. Mg). A method for widening the electrochemical window of Mg electrolyte is to use weakly coordinating anions because the weakened coordination of anions to Mg^{2+} can mitigate the key step in the Mg^+ -mediated reductive decomposition (Lau et al., 2019). Hydroborates with B clusters with weak coordination ability, such as $\text{B}_{12}\text{H}_{12}^{2-}$, were predicted to possess improved anodic stability of 3.2 V compared to BH_4^{2-} , thus suitable for potential B-based electrolyte anion (Carter et al., 2014). Unfortunately, the weakly coordinating property of $\text{B}_{12}\text{H}_{12}^{2-}$ renders $\text{MgB}_{12}\text{H}_{12}$ insoluble in low-polarity, commonly used ether solvents for Mg batteries. Modified clusters of hydroborates $\text{CB}_{11}\text{H}_{12}^{2-}$ -based halogen-free, simple type electrolyte were prepared and exhibited high oxidative stability and improved solubility (Tutusaus et al., 2015). Due to charge reduction, $\text{CB}_{11}\text{H}_{12}^{2-}$ is more lipophilic than $\text{B}_{12}\text{H}_{12}^{2-}$, thus more soluble in low-polarity ethers such as triglyme (G3) and G4 (Keyzer et al., 2016). Magnesium monocarborane (MMC) salt/G4 electrolytes have a high CE of >94.4% and anodic stability up to 3.8 V (Tutusaus et al., 2015). A series of Mg salts containing weakly coordinating fluorinated alkoxyborate anions was prepared, which exhibited good solubility in aprotic solvents due to the high electronegativity of fluorine atoms. Among them, the $\text{Mg}[\text{B}(\text{hfip})_4]_2/\text{DME}$ electrolyte presented a high CE of >98% of Mg stripping/plating for over 100 cycles (Zhao-Karger et al., 2017). The anodic current density was as high as 45 mA cm^{-2} and oxidative voltage stability was 4.3 V. J. Luo et al. reported that magnesium fluorinated pinacolatoborate, $\text{Mg}[\text{B}(\text{O}_2\text{C}_2(\text{CF}_3)_4)_2]_2$ (Mg-FPB) based electrolyte, is noncorrosive, highly electrochemically active, and more chemically stable (Luo et al., 2019). The electrolyte delivered excellent electrochemical performance, with CE >95%, overpotential of <197 mV, and anodic stability up to 4.0 V. $\text{Mg}|\text{Mg-FPB}|\text{Mg}$ symmetric cell can cycle at 0.1 mA cm^{-2} for more than 500 h, with stable polarization.



ACTIVE MG CATIONS FOR REVERSIBLE DEPOSITION

It is still a big challenge to use simple Mg salts to obtain a high-performance Mg electrolyte. Ultrahigh purity is required because even residual moisture can cause the formation of a passivation layer that will inhibit reversible Mg stripping/plating. Of note, Cl-based electrolytes and most of the B-centered electrolytes exhibited good electrochemical performance without rigorous purification. It is believed that Mg-coordinated ions play a vital role in determining the performance of electrolytes (Shao et al., 2013).

An early study on the mechanism of Grignard-type electrolytes suggested that the active cation was $[\text{MgCl}(\text{THF})_5]^+$ based on an electrochemical quartz crystal microbalance (EQCM) study (Aurbach et al., 2001). In the first reported HMDSAl-based non-nucleophilic electrolyte, $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6][\text{HMDSA}(\text{AlCl}_3)]$ crystal was isolated and determined by single-crystal X-ray diffraction. It is reasonable to presume that $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ was the active species because a similar cation has already been identified in previously reported Grignard-type electrolytes (Aurbach et al., 2003). The cation has two Mg octahedral coordination centers, three bridging Cl atoms ($\mu\text{-Cl}$), and six coordination O atoms from THF. Since then, $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ became the most commonly accepted active cation in the Cl-THF electrolyte system (Liao et al., 2015) (Barile et al., 2014). See et al. (2016) compared the ion structure in as-prepared and conditioned MACC electrolyte to identify the active species (See et al., 2016). Surface-enhanced Raman spectroscopy (SERS), 27Al and 35Cl NMR, and X-ray pair distribution function (PDF) were applied, indicating that the active specie in MACC electrolyte both before and after conditioning was $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$ (Esbenshade et al., 2015). $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$

also existed in $\text{Mg}(\text{TFSI})_2\text{-MgCl}_2$ electrolyte as confirmed by single-crystal XRD (Sa et al., 2016) and is predicted to be present in $\text{Mg}(\text{CF}_3\text{SO}_3)_2\text{-MgCl}_2$ electrolyte (Yang et al., 2019). One possible Mg deposition pathway via $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$, as proposed based on electrochemical and *in situ* X-ray absorption spectroscopy measurement, was shown in **Figure 1A** (Benmayza et al., 2013). Solvent molecule plays a vital role in forming the active Mg coordination ions. A $[\text{Mg}_2(\mu\text{-Cl})_2(\text{DME})_4]^{2+}$ complex cation was present in MACC/DME and $\text{Mg}(\text{TFSI})_2\text{-MgCl}_2/\text{DME}$, confirmed by single-crystal XRD (Cheng et al., 2015). The cation complex consists of two octahedrally coordinated Mg centers, each of which is bridged by two chlorine atoms and coordinated by four oxygen atoms from DME. The formation of solvated Mg_2Cl_3^+ is not thermodynamically favored in DME because of the difficulties in obtaining coordination number of six (Mizrahi et al., 2008). ESI-MS revealed that the coordination ion structure changed during the conditioning process in a $\text{Mg}(\text{CF}_3\text{SO}_3)_2\text{-MgCl}_2\text{-AlCl}_3$ electrolyte. Most of the $[\text{Mg}_2(\mu\text{-Cl})_2(\text{DME})_4]^{2+}$ cations were converted to $[\text{Mg}_3(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2(\text{DME})_7]^{3+}$ due to increase of Mg/Al ratio caused by Mg/Al codeposition (Huang et al., 2020).

Chloride-free B-centered electrolytes have very different electroactive cation structures, which are mainly solvated Mg cation paired with B-based anion. In the first reported $\text{Mg}(\text{BH}_4)_2\text{-DME}$ electrolyte, it was proposed that $\text{Mg}(\text{BH}_4)_2$ was present in the form of $\text{Mg}[(\mu\text{-H})_2\text{BH}_2]_2$, which could partially convert into $[\text{Mg}(\mu\text{-H})_2\text{BH}_2]^+$ and BH_4^- (Mohtadi et al., 2012). Then, further dissociation occurs to generate Mg^{2+} and BH_4^- . The electrochemical performance of $\text{Mg}(\text{BH}_4)_2$ electrolyte can be further enhanced by the addition of LiBH_4 , owing to weakened association within the ion pair as evidenced by IR spectrum. The CE was improved with increasing molar ratio of $\text{LiBH}_4/\text{Mg}(\text{BH}_4)_2$. The ion species in $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ electrolytes were more complicated. $[\text{Mg}(\text{THF})_6](\text{CB}_{11}\text{H}_{12})_2$, $[\text{Mg}(\text{DME})_3](\text{CB}_{11}\text{H}_{12})_2$, and $[\text{Mg}(\text{diglyme})_2](\text{CB}_{11}\text{H}_{12})_2$ can be

TABLE 1 | Performance of some non-nucleophilic Mg electrolytes.

Electrolytes	Concentration (M)/solvents	Conductivity (mS cm ⁻¹)	CE (%)	Mg plating potential (mV)/scan rate (mV S ⁻¹)	Anodic stability (V vs. Mg)	Battery type/capacity (mAh g ⁻¹)/current density (mA g ⁻¹)	Ref.
HMDSMgCl-AlCl ₃	0.4/THF	--	95	-250/20	2.5	--	Kim et al., (2011)
(HMDS) ₂ Mg-AlCl ₃	0.25-0.75/THF	1.72	98	-400/25	3.3	Mo ₆ S ₈ -Mg/95/10	Zhao-Karger et al., (2013)
(HMDS) ₂ Mg-AlCl ₃ -MgCl ₂	1.8-3.6-1.8/G2	--	--	-350/25	3.2	Mg-S/550/20	Zhao-Karger et al., (2015)
(HMDS) ₂ Mg-MgCl ₂	1.25-5/THF	0.5	99	-240/20	2.8	Mo ₆ S ₈ -Mg/86/12.8	Liao et al., (2015)
MgCl ₂ -AlCl ₃	0.25-0.125/DME	2	99	-200/25	3.1	Mo ₆ S ₈ -Mg/80/64	Doe et al., (2014)
MgCl ₂ -AlCl ₃	0.04-0.02/THF	0.26	90	-290/25	3.4	Mo ₆ S ₈ -Mg/99/12.8	Barile et al., (2014)
MgCl ₂ -AlEtCl ₂	0.4/DME	3.9	95	-220/20	3.5	Mo ₆ S ₈ -Mg/100/12.8	Liu et al., (2014)
Mg(TFSI) ₂ -AlCl ₃ -MgCl ₂	0.03-0.03-0.06/THF	--	97	-350	2.6	Mo ₆ S ₈ -Mg/92/25.6	He et al., (2019)
Mg(TFSI) ₂ -MgCl ₂	0.4/DME	--	80	-400/20	3.5	--	Cheng et al., (2015)
Mg(TFSI) ₂ -MgCl ₂	0.5-0.25/THF	--	72	-500/20	3.2	Mo ₆ S ₈ -Mg/67/6.4	Sa et al., (2016)
Mg(TFSI) ₂ , 6 mM Mg(BH ₄) ₂	0.5/G4	--	75	-350/25	--	--	Ma et al., (2017)
Mg(TFSI) ₂	0.5/DMA-THF-G4	--	75	-500/50	3.0	--	Fan et al., (2020)
Mg(OTf) ₂ -AlCl ₃ -MgCl ₂	0.125-0.25-0.25/THF-G4	1.88	95.5	-250/50	3.25	Mg-S/420/84	Yang et al., (2019)
Mg(OTf) ₂ -AlCl ₃ -MgCl ₂	0.2-0.4-0.4/DME	--	99	-250/50	3.5	Mg-S/844/200	Huang et al., (2020)
MgCl ₂	0.8/DPSO-THF	1.1	92.3	-430/20	3.0	Mo ₆ S ₈ -Mg/75/0.016 mA cm ⁻²	Kang et al., (2017)
Mg(BH ₄) ₂	0.5/THF	--	40	-200/20	2.2	Mo ₆ S ₈ -Mg/55/128	Mohtadi et al., (2012)
Mg(CB ₁₁ H ₁₂) ₂	0.75/G4	1.8	94.4	-250/5	3.8	MnO ₂ -Mg/195/0.2 mA cm ⁻²	Tutusaus et al., (2015)
Mg[B(hfip) ₄] ₂	0.6/DME	6.8	98	-250/25	4.3	Mg-S/500/167	Zhao-Karger et al., (2017)
Mg-FPB	0.5/G2	3.95	95	300/50	4.0	MnO ₂ -Mg/150/0.01mA cm ⁻²	Luo et al., (2019)

collected as precipitates and were unfortunately unable to be redissolved (Tutusaus et al., 2015). The above solids could only be redissolved in larger glymes such as G3 and G4. The successful isolation of [Mg(G4)₂(H₂O)](CB₁₁H₁₂)₂ characterized by single-crystal XRD indicates that [Mg(Gx)₂]²⁺ (x = 3, 4) is highly possible to be the active Mg ion. Similarly, [Mg(DME)₃]²⁺ paired by counterion [B(hfip)₄]²⁻ was isolated and verified in Mg[B(hfip)₄]/DME electrolyte (Zhao-Karger et al., 2017). It can be redissolved in DME to allow highly efficient Mg stripping/plating. [Mg(G2)₂]²⁺ was determined by single-crystal XRD in a noncorrosive magnesium fluorinated pinacolatoborate Mg[B(O₂C₂(CF₃)₄)₂]-G2 electrolyte (Luo et al., 2019).

Employing cosolvents can tune the Mg coordination ion formation, thus affecting the electrolyte properties. In a MgCl₂/DPSO-THF electrolyte, [Mg(DPSO)₆]²⁺ cation complex was identified as active Mg ion, coupled by two [MgCl₃(THF)]⁻ anions (Kang et al., 2017). The cosolvent THF can help form more stable anion [MgCl₃(THF)]⁻ with weakened coordinating ability, thus allowing Mg²⁺ to be solvated solely by DPSO. The unique structures of such novel active ion enabled highly efficient reversible Mg deposition/dissolution. Mg(HMDS)₂-MgCl₂ based on certain sulfone/THF mixed solvent exhibited comparable Mg deposition reversibility and much higher thermal stability than that of pure THF-based counterparts (Merrill and Schaefer, 2018). The solvated Mg₂Cl₃⁺/MgCl⁺ ratio, which is affected by

cosolvent type, was the key factor in anode reversibility. Butyl sulfone-/THF-based electrolyte with higher Mg₂Cl₃⁺/MgCl⁺ presented facilitated reversible Mg deposition than that of sulfolane/THF electrolyte. When dimethylamine (DMA) was introduced into a Mg(TFSI)₂/THF-G4 electrolyte, the CE can be significantly improved. A neutral coordination compound Mg(TFSI)₂(THF)₄ was identified, which successfully reduced the effective charge and accelerated the kinetics for reversible Mg deposition (Fan et al., 2020). It was suggested that the cosolvent DMA participated in the formation of the ion pair in the solvation shell by Mg...N interaction.

CONCLUSION REMARKS

Non-nucleophilic electrolytes have become new trends in Mg electrolyte research, especially considering the rapid development of Mg-S and Mg-O₂/air battery in recent years. Although many of the drawbacks in conventional Grignard-based electrolytes have been overcome by emerging non-nucleophilic electrolytes, it is still very challenging to prepare Mg electrolytes for practical application. Cl-based electrolytes including MACC, Mg(TFSI)₂-MgCl₂, and (HMDS)₂Mg-MgCl₂ have good processability and excellent performance but are still corrosive to many current collectors and cell components, especially when

strong Lewis acid AlCl_3 was involved. In Cl-free B-centered electrolytes, $\text{Mg}(\text{BH}_4)_2$ suffered from low anodic stability and limited solubility. Magnesium carbaborate and alkoxyborate originating from $\text{Mg}(\text{BH}_4)_2$ precursor have a wide electrochemical window, albeit with a complicated synthetic procedure. There are some common disadvantages of most Mg electrolytes, such as high raw materials price, moisture sensitivity, and long-term preconditioning behavior. Another key issue in the Mg electrolyte research is understanding the mechanism of Mg stripping/plating, including anode-electrolyte interfacial chemistry, Mg coordination chemistry, and Mg cation electrochemistry. Although there have already been rational hypotheses presented with support from theoretical simulation and experimental results, researchers still need to explore the chemical and electrochemical process during reversible Mg deposition in-depth.

In summary, developing non-nucleophilic, noncorrosive, less air-/moisture-sensitive electrolyte with wide electrochemical window and high Mg deposition reversibility is preferred to promote the development of practical rechargeable Mg batteries. It is highly recommended to prepare Mg electrolyte from low-cost, commercially available materials via a facile procedure. Further investigation is also needed to better

understand the ion structure of electrolyte, electrode-electrolyte interface, and their effect on the electrochemical performance.

AUTHOR CONTRIBUTIONS

All authors have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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