The Power of Stoichiometry: Conditioning and Speciation of MgCl₂/AlCl₃ in Tetraethylene Glycol Dimethyl Ether-Based Electrolytes

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Supporting Information

ABSTRACT: In many Mg-based battery systems, the reversibility of Mg deposition and dissolution is lowered by parasitic formation processes of the electrolyte. Therefore, high Coulombic efficiencies of Mg deposition and dissolution are only achieved after several “conditioning” cycles. As this phenomenon is especially reported for AlCl₃-containing solutions, this study focuses on the “conditioning” mechanisms of MgCl₂/AlCl₃ and MgHMDS₂/AlCl₃ (HMDS = hexamethyldisilazide) in tetraethylene glycol dimethyl ether (TEGDME)-based electrolytes. Electrochemical (cyclic voltammetry) and spectroscopic investigations (²⁷Al nuclear magnetic resonance spectroscopy, Raman spectroscopy, inductively coupled plasma optical emission spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy) reveal that cationic AlCl₃⁺ species in TEGDME-based electrolytes with an AlCl₃/MgCl₂ ratio higher than 1:1 corrode the Mg metal. According to a cementation reaction mechanism, the corrosion of Mg is accompanied with Al deposition. In effect, the consumption of Mg results in low Coulombic efficiencies of Mg deposition and dissolution during the electrolyte “conditioning”. After understanding the mechanism of this process, we demonstrate that a careful adjustment of the stoichiometry in MgCl₂/AlCl₃ and MgHMDS₂/AlCl₃ in TEGDME formulations prevents Mg corrosion and results in “conditioning”-free, highly efficient Mg deposition and dissolution.

KEYWORDS: magnesium battery, electrolyte, magnesium anode, conditioning, corrosion

INTRODUCTION

Because of the bivalency of the Mg²⁺ ion, rechargeable magnesium batteries have a great potential as beyond lithium-ion battery (LIB) systems.¹⁻³ Magnesium is by far more abundant⁴⁻⁵ and less expensive⁶ than lithium. At the anode, the Mg metal holds considerably higher theoretical volumetric and gravimetric specific capacities (3833 mAh/cm³ and 2202 mA h/g, respectively) than lithiated graphite LiC₆ (719 mAh/cm³ and 339 mA h/g, respectively), which is typically used in LIBs.⁷⁻¹⁰ The Li metal anode, which also holds high theoretical volumetric and gravimetric specific capacities (2062 mA h/cm³ and 3862 mA h/g, respectively), is thermodynamically instable against commonly used liquid organic electrolytes.⁷ Its kinetic protection by the formation of an effective solid electrolyte interphase and the effects on safe rechargeability have been and still are unsolved challenges.¹¹⁻¹⁵ In addition, Li deposition and dissolution is prone to the formation of high surface area lithium (HSAL) or even Li dendrites.¹³⁻¹⁷ In contrast, by careful choice of the electrolyte components, the Mg metal anode can show thermodynamic compatibility with several electrolyte systems, enabling Mg deposition and dissolution (dep./diss.) at close to 100% Coulombic efficiency.¹⁻¹³ In addition, Mg deposition/dissolution is more homogeneous and thus less prone to high surface area magnesium formation than in the case for Li with HSAL.¹⁶⁻¹⁸ At the cathode, many Mg insertion materials such as the Chevrel phase Mo₆S₈¹⁻³¹ and the transition-metal oxides such as MnO₂,²⁵ Co₃O₄,²⁶ and V₂O₅ have been proposed. However, apart from Mo₆S₈ and its selenide derivatives, most of these materials show slow kinetics and high capacity fading during Mg insertion and deinsertion.⁵⁻¹⁵,²⁵⁻³¹ On the basis of the high specific capacity (1675 mA h/g), very low price, and high abundance of elemental sulfur, the combination of Mg metal with a sulfur cathode is considered as a highly promising battery system.³⁶⁻⁴⁴ Despite some present concerns about practically realizable energy densities, Mg/S batteries are
considered as a potentially more economic and more sustainable alternative to LIBs. In order to couple the Mg metal anode with any of these or yet unknown cathode materials, the electrolytes need to fulfill the following requirements: a good Mg²⁺ transport and high ionic conductivity, sufficient electrochemical stability against reduction at the Mg anode and oxidation at the cathode, Mg dep./diss. at reasonably low overpotentials and very high Coulombic efficiency and energy efficiency, as well as chemical stability against the anode and cathode materials. In the case of a sulfur cathode, the electrolyte should thus be first and foremost non-nucleophilic in order to be stable with sulfur and the polysulfide intermediates.

Many solvents such as carbonates and acetonitrile, as well as most of the commonly used anions in LIBs, such as BF₄⁻, ClO₄⁻, and PF₆⁻, are instable versus reduction at the Mg anode. Their decomposition products show extremely low Mg²⁺ conductivity and thus lead to a blocking passivation film on the Mg metal anode. In contrast, Grignard RMgX (R = alkyl or aryl group, X = Cl or Br) solutions in ethers show a very high reversibility of Mg dep./diss. Their reductive properties impede the formation of a passivation film. However, the low oxidative stability of Grignard species is incompatible with practically all cathode materials. To achieve a higher oxidative stability, organometallic Mg compounds R₂Mg or RMgCl can be combined with stoichiometric amounts of Lewis acids, such as AlCl₃, AlEt₂Cl, AlPh₃, and so forth. The resulting Mg organoaluminate-based electrolyte salts with the general formula of Mg(AlCl₄−xRₓ) reach oxidative stabilities of above 3 V versus Mg/Mg²⁺ and thus allow the operation of cathode materials, such as MoS₂. Similar oxidative stabilities can be achieved by combining the organometallic Mg compounds with boron-based Lewis acids. However, as organometallic Mg compounds are reactive toward the cathode and other cell components, non-Grignard electrolytes based on the combination of Mg amides or alkoxides (ROMgCl) with AlCl₃ have been developed. Especially for achieving compatibility with sulfur in Mg/S batteries, non-nucleophilic electrolytes, for example, based on HMDSmMgCl or MgHMDS₂ (HMDS = hexamethyldisilazide) in combination with AlCl₃, are required. By reaction with Al-based Lewis acids, also inorganic MgX₃ salts, such as MgCl₂, that are otherwise practically insoluble in ethers, form electrolytes with a high Coulombic efficiency of Mg dep./diss. of up to 100% and an oxidative stability of 3.1–3.4 V versus Mg/Mg²⁺.

In the electrolyte family of MgX₃/AlCl₃ [X = Cl, HMXDS, tetramethylazadisilolane, bis(dipropylamido) (i-Pr₂N)], etc.] in ethers, the Al-based Lewis acids are considered to be coordinated by an anion taken from the MgX₃ species to form AlCl₃−X⁻. In such anion, there is always a Cl⁻ species in combination with AlCl₃−X⁻. In the case of Mgx/AlCl₃-based electrolytes, the simplest members of this electrolyte family, the MgₓClₓ is considered to depend on the stoichiometry of MgClₓ and AlCl₄⁻ species (eq 1).

\[
\text{MgCl}_2 \cdot \text{AlCl}_3 \rightarrow \text{MgCl}^+ + \text{AlCl}_4^- \tag{1}
\]

In dimethoxyethane (DME), for instance, the MgCl⁺ monomers are partially stabilized as chloride-bridged MgClₓ₂ dimers. Depending on the solvent, further addition of MgCl₂ in the formation of Mg₃Cl₄ in tetrahydrofuran (THF) and Mg₃Cl₄ in DME. By the formation of these complexes, various Mgₓ/AlCl₃-based electrolytes support highly reversible Mg dep./diss. at reasonably low overpotentials. However, it is frequently reported that high Coulombic efficiencies and reasonably low overpotentials of Mg dep./diss. from Mgₓ/AlCl₃-based electrolytes are achieved only after the so-called “conditioning” cycles. The irreversible capacity losses during these cycles are related to reactions of electrolyte components at the Mg metal anode.

In Al-free electrolytes, such as MgTFSI₂/MgCl₂ (1:2) in DME, for instance, the “conditioning” of the electrolyte primarily refers to an electrochemical removal of reductive impurities, for example, trace amounts of water. In these electrolytes, the “conditioning” can thus be circumvented by adding small amounts of chemically reducing species, such as Bu₂Mg.

In several Al-containing electrolytes, such as MgCl₂/AlCl₃-based solutions, it has been reported that the “conditioning” of the electrolyte is also associated with Al deposition. Thereby, a decrease of the Al/Mg ratio in the electrolyte due to Al depletion and additional Mg dissolution and the formation of free Cl⁻ anions is observed. As both the increase of the concentration of Mg species in the electrolyte and the presence of Cl⁻ at the Mg anode are considered beneficial for lowering the overpotentials for Mg dep./diss., such speciation is considered as an additional process during the “conditioning” of the electrolyte. However, as the depletion of Al linked to a dissolution of Mg has also been observed by stirring Mg powder in solutions of AlCl₃ or MgCl₂/AlCl₃ in ethers, the process might proceed already without applying an external voltage or current. In any case, it is discussed controversially, if Al deposition originates from cationic Al moieties, from anionic AlCl₄⁻ or from neutral AlCl₃ species. Accordingly, it remains unclear, how this parasitic process can be prevented.

So far, the MgCl₂/AlCl₃ system is mostly studied in THF, DME, dimethoxyethane (DME), and diglyme. Tetrahydrofuran glycol dimethyl ether (TEGDME, tetraglyme), which is used in MgHMDS₂/AlCl₃-based electrolytes, however, no reversible Mg dep./diss. from MgCl₂/AlCl₃-based electrolytes has been reported yet. Because of low volatility and high viscosity of TEGDME and moderate solubility and redox kinetics of Mg polysulfides in this glyme, it appears to be a promising and yet commonly used electrolyte solvent for Mg/S batteries and other Mg batteries.

This work thus studies the reversibility and overpotentials of Mg dep./diss. from MgCl₂/AlCl₃ in TEGDME-based electrolyte. By varying the MgCl₂/AlCl₃ ratio and examining the formed Al species, it is revealed that Al depletion during the electrolyte “conditioning” is linked to a spontaneous Mg corrosion process. After understanding the origin and fundamental mechanism of this process, it is demonstrated that Al depletion/Mg corrosion can be prevented by adjusting the stoichiometry of MgCl₂ and AlCl₃. Electrolytes with an optimized Al/Mg ratio, such as MgCl₂/AlCl₃ (1:1) or MgHMDS₂/AlCl₃/MgCl₂ (1:2:1) in TEGDME, yield in “conditioning”-free and much more efficient Mg dep./diss.
RESULTS AND DISCUSSION

Electrochemical “Conditioning”. The evolution of Coulombic efficiencies and overpotentials of Mg deposition/dissolution (dep./diss.) from MgCl2/AlCl3 in TEGDME electrolytes upon repetition was investigated in cyclic voltammetry experiments on a Pt foil working electrode (WE). To achieve a high resolution of this evolution during many cycles, the experiments were conducted in flooded cells (2 mL of electrolyte) and at high scan rates (25 mV/s). Figure 1 shows the trend of changes in the cyclic voltammograms (CVs) in MgCl2/AlCl3 (1:1) in TEGDME from the 1st cycle (red) to the 100th cycle (green). For these cycles, the onset potentials of Mg dep./diss. are also indicated. Furthermore, the CVs of every 10th cycle are highlighted in black.

The evolution of the onset potentials for Mg deposition (2) and dissolution (3), the current densities of these processes, and the resulting Coulombic efficiencies of Mg dep./diss. describe a typical “conditioning” behavior:

- In the first cycle (red), reductive currents (1) above the potential of Mg deposition (2) occur.65,66 As they diminish in the following cycles, they are considered to relate only to the electrochemical elimination of impurities in the electrolyte.
- During the whole experiment, a continuous decrease of the overpotentials for Mg deposition (2) is observed. Similarly, also the overpotentials for Mg dissolution (3) decrease. Both are reported for several Mg2+-based electrolyte systems.64–67
- Finally, because the reductive purification processes (1) only occur in the first cycles, the Coulombic efficiency of Mg dep./diss. increases from 51% (1st cycle) to 83% (100th cycle).

By increasing the AlCl3 concentration, MgCl2/AlCl3 in TEGDME solutions with stoichiometric ratios of 1:2 and 1:3 is prepared. In these electrolytes, the same characteristics of the “conditioning” behavior as described for the 1:1 sample are observed. However, with a higher AlCl3 content, such as the 1:2 ratio in Figure 2a, it takes more cycles until the onset potentials for Mg dep./diss. are minimized. In the 1:3 sample (Figure 2b), high overpotentials for Mg deposition (~0.5 V vs Mg/Mg2+) are still observed in the 100th cycle.

In addition, the finally achieved Coulombic efficiency of Mg dep./diss. is lower for solutions with a higher AlCl3 content. In the case of MgCl2/AlCl3 (1:2) in TEGDME, the Coulombic efficiency increases from 49% (1st cycle) to 78% (100th cycle) (Figure 2a). With the 1:3 sample, it increases from only 6% in the first to 39% in the 100th cycle (Figure 2b). Accordingly, the parasitic processes that hinder an efficient Mg dep./diss. are much more pronounced at higher AlCl3 contents.

As presented in Figure S1, a replacement of the Pt WE after the “conditioning” process does not change the electrochemical response. The electrochemical “conditioning” is thus solely related to the bulk electrolyte.

Electrolyte Speciation. When dissolving AlCl3 (0.2 M) in TEGDME, it completely dissociates into AlCl4− and AlCl26 (eq 2). Accordingly, the 27Al NMR spectra of this solution contain only AlCl4− (104 ppm) and AlCl26 species (25 ppm) (Figure 3a).64,69 In contrast to THF, in which AlCl4− is not observed, the chelate effect of TEGDME or other glymes is considered to stabilize the AlCl26 species.64,69,70

$$2\text{AlCl}_3 \leftrightarrow \text{AlCl}_2^6 + \text{AlCl}_4^{−} \quad (2)$$

In MgCl2/AlCl3 (1:1) in TEGDME, the AlCl26 species are completely converted into AlCl4− (eq 3). Therefore, the AlCl26-related signal at 25 ppm is not detected in the 27Al NMR spectrum of MgCl2/AlCl3 (1:1) in TEGDME (Figure 3a). In contrast to what is stated in the literature,23,66 the formulation of MgCl2/AlCl3 in glyme-based electrolytes should thus be written as follows

$$2\text{MgCl}_2 + \text{AlCl}_2^6 \rightarrow 2\text{MgCl}_3^+ + \text{AlCl}_4^{−} \quad (3)$$

When adding more AlCl3 and changing the MgCl2/AlCl3 ratio to 1:2 and 1:3, for instance, AlCl26 species are observed (Figure 3a). In these stoichiometries, the amount of MgCl3 is thus not sufficient to convert all AlCl26 into AlCl26 species.

In addition to 27Al NMR, also the FT-Raman spectra of solutions of MgCl2/AlCl3 (1:1), (1:2), and (1:3) in TEGDME
As AlCl$_4^-$ is formed by dissociation of AlCl$_3$ (eq 2), the intensity of these peaks is higher for solutions with higher AlCl$_3$ content (Figure 3b). Therefore, AlCl$_4^-$ is also detected solely in AlCl$_3$ in TEGDME solutions (Figure S3).

Furthermore, the high ionic conductivity of AlCl$_3$ (0.2 M) in TEGDME solutions [(0.66 ± 0.04) mS/cm, see Table 1] indicates the dissociation of AlCl$_3$ into AlCl$_4^-$ and AlCl$_2^+$ ions (eq 2). Adding equimolar amounts of MgCl$_2$ and thus replacing AlCl$_2^+$ ions by MgCl$_2^+$ and AlCl$_4^-$ (eq 3) do not increase the overall ionic conductivity. MgCl$_2$/AlCl$_3$ (1:1) in TEGDME solutions thus shows an ionic conductivity of (0.65 ± 0.03) mS/cm. In MgCl$_2$/AlCl$_3$ (1:2) and (1:3) in TEGDME solutions, the higher amount of (dissociated) AlCl$_3$ results in increased ionic conductivities of (0.90 ± 0.01) mS/cm and (1.10 ± 0.01) mS/cm, respectively.

In order to determine the Mg species in MgCl$_2$/AlCl$_3$ in TEGDME-based solutions, a mixture of MgCl$_2$/AlCl$_3$ (1:0.5) 0.2 M in TEGDME was prepared. As this mixture is found insoluble, the formation of MgCl$_2^{2+}$, which is observed for MgCl$_2$/AlCl$_3$ (2:1) in THF, does not occur. We hypothesize that MgCl$_2^{2+}$ is not stabilized in TEGDME. The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the supernatant solution detected an Al/Mg ratio of 0.72 ± 0.01 (Table 2). This ratio almost refers to a stoichiometry of 3 MgCl$_2$ to 2 AlCl$_3$. As found in MgCl$_2$/AlCl$_3$ in DME solutions, MgCl$_2$ is thus considered to form Mg$_3$Cl$_4^{2+}$ dimers which coordinate additional MgCl$_2$ to form Mg$_3$Cl$_4^{2+}$ clusters (eq 4).

$$\text{Mg}_2\text{Cl}_2^{2+} + \text{MgCl}_2 \leftrightarrow \text{Mg}_3\text{Cl}_4^{2+}$$  \hspace{1cm} (4)

The supernatant solution of MgCl$_2$/AlCl$_3$ (1:0.5) in TEGDME shows a low ionic conductivity of (0.30 ± 0.01) mS/cm (Table 1). This might be due to the lower AlCl$_4^-$ content.
of the Al species from the electrolyte is balanced by additional Mg\textsuperscript{2+} formation. These ions would coordinate most of the Cl\textsuperscript{−} anions liberated during Al depletion (eq 5).

\[
\text{AlCl}_2^+ + 3\text{e}^- \leftrightarrow \text{Al} + 2\text{Cl}^- \quad (5)
\]

\[
\text{Mg} + \text{Cl}^- \leftrightarrow \text{MgCl}^+ + 2\text{e}^-
\]

Apart from Al depletion during electrochemical Mg dep./diss. experiments, the Al/Mg ratio also decreases during stirring Mg powder (10 mg/mL) in MgCl\textsubscript{2}/AlCl\textsubscript{3} (1:2) in TEGDME. Similar to the observations by Luo et al.,\textsuperscript{68} the initial Al/Mg ratio of 1.86 diminishes to 1.40 in the Mg powder-treated sample (see Table S2).

Similarly, a decrease of the Al/Mg ratio to 1.69 is also found by storing a piece of Mg foil in this electrolyte for one week (see Table S2). When investigating the surface of the Mg foil, large pits and cracks are found (Figure 5a, see higher magnification in Figure S3). Energy-dispersive X-ray spectroscopy (EDS) analysis indicates that these structures are surrounded by Al deposits (Figure 5b) referring to (6) (as detected by EDS).

In Figure S4a, the Mg foil after storage for 1 week in MgCl\textsubscript{2}/AlCl\textsubscript{3} (1:2) 0.2 M in TEGDME is shown. Figure 5b shows a mapping of the Al species (red) (as detected by EDS). Figure 6 shows the proposed mechanism of Al cementation/Mg corrosion in AlCl\textsubscript{3}-containing electrolytes.

In contrast, in the case of MgCl\textsubscript{2}/AlCl\textsubscript{3} (1:2) in TEGDME, Al deposition occurs at very low overpotentials and shows a high Coulombic efficiency of 94%. Thereby, the addition of Bu\textsubscript{2}Mg-free sample (Figure 1), the Al/Mg ratio only slightly decreased from 0.97 to 0.96 (Table S1). Similar to MgCl\textsubscript{2}/AlCl\textsubscript{3}-based electrolytes in THF and DME,\textsuperscript{62,63} the difference between the onset potentials of Mg deposition and dissolution is only 160 mV.

In contrast, in the case of MgCl\textsubscript{2}/AlCl\textsubscript{3} (1:2) in TEGDME, the addition of Bu\textsubscript{2}Mg (10 mM) (Figure 7b) shows no improvement in comparison to the Bu\textsubscript{2}Mg-free sample (Figure 2a). Also in the Bu\textsubscript{2}Mg-containing sample, the Coulombic efficiency increases (from 42 to 67%) within the first 100 Mg dep./diss. cycles. For this Al/Mg ratio, a removal of the reducible impurities has thus no significant effect on the "conditioning". As indicated by a decrease in the Al/Mg ratio from 1.91 to 1.75 (Table S1), the "conditioning" of MgCl\textsubscript{2}/AlCl\textsubscript{3} (1:2) in TEGDME is mainly referred to Mg corrosion/Al cementation.

"Conditioning"-free MgCl\textsubscript{2}/AlCl\textsubscript{3}-Based Electrolytes.

In a broader context, the presence of cationic AlCl\textsubscript{2}\textsuperscript{+} and/or HMDSAlCl\textsubscript{3} species has also been reported in MgHMDS\textsubscript{2}/AlCl\textsubscript{3} (1:2) in TEGDME solutions.\textsuperscript{54} Similar to the electrolyte formulation in THF, the reaction of MgHMDS\textsubscript{2} and two equivalents of AlCl\textsubscript{3} in TEGDME is considered to form HMDSAlCl\textsubscript{3}\textsuperscript{−} anions and neutral HMDSAlCl\textsubscript{3} species (eq 6).\textsuperscript{22} However, as Mg\textsubscript{2}Cl\textsubscript{3} is not stabilized in TEGDME,
MgCl\(^+\) monomers as in diglyme\(^5\) (and/or Mg\(^{2+}\) dimers as in DME\(^6\)) are considered to be formed.

\[
\text{MgHMDS}\, 2\text{AlCl}_3 \leftrightarrow \text{MgCl}^+ \text{HMDSAlCl}_3 + \text{HMDSAlCl}^2- (6)
\]

Similar to AlCl\(^3\), HMDSAlCl\(^2\) dissociates to HMDSAlCl\(^+\) and HMDSAlCl\(^-\) species in TEGDME (eq 7).\(^5\)

\[
2\text{HMDSAlCl}_3 \leftrightarrow \text{HMDSAlCl}^+ + \text{HMDSAlCl}^- \quad (7)
\]

Because of the cationic Al species, Mg dep./diss. from Bu\(_2\)Mg-containing MgHMDS\(_2\)/AlCl\(_3\) (1:2) 0.2 M in TEGDME shows low Coulombic efficiencies of 14% (1st cycle) and 35% (100th cycle) (Figure 8a). Similar values are reported in the literature.\(^5\) As in the MgCl\(_2\)/AlCl\(_3\) (1:2) sample (Figure 7b), the increase in the Coulombic efficiency is considered to be due to the diminishing Mg corrosion/Al cementation process. In the Bu\(_2\)Mg-free sample, even lower Coulombic efficiencies of 4% (1st cycle) and 19% (100th cycle) are detected (Figure S7).

In order to prevent the formation of cationic Al species (eq 7), one equivalent of MgCl\(_2\) is added to the electrolyte solution. Thereby, HMDSAlCl\(_3\) attracts Cl\(^-\) from MgCl\(_2\) and forms anionic HMDSAlCl\(^3-\) and another equivalent of MgCl\(^+\) (eq 8).\(^5\),\(^6\)

\[
\text{MgHMDS}_2 + 2\text{AlCl}_3 + \text{MgCl}_2 \leftrightarrow 2\text{MgCl}^+ + 2\text{HMDSAlCl}^- \quad (8)
\]

Accordingly, MgHMDS\(_2\)/AlCl\(_3\)/MgCl\(_2\) (1:2:1) in TEGDME shows a "conditioning"-free behavior after the reducible impurities are removed by Bu\(_2\)Mg (Figure 8b). Thereby, low overpotentials and high Coulombic efficiencies of 94% (1st cycle) and 97% (100th cycle) are achieved.

According to the higher amount of MgCl\(^+\), higher current densities for Mg dep./diss. are recorded. In addition to the higher amount of electroactive Mg species that was intended by Zhao-Karger et al.,\(^3\)^\(^6\),\(^5\) it is demonstrated that adding one equivalent of MgCl\(_2\) to MgHMDS\(_2\)/AlCl\(_3\) (1:2)-based electrolytes also prevents Mg corrosion during the electrolyte "conditioning".

\section{CONCLUSIONS}

This work reports a latent Al cementation reaction leading to Mg corrosion in AlCl\(_3\)-based Mg electrolytes, suggests the presence of AlCl\(^2+\)-species as the origin of this deleterious reaction, and demonstrates that adjusted, AlCl\(^2+\)-free electrolyte formulations inhibit this process.

In a first step, reversible Mg deposition/dissolution from MgCl\(_2\)/AlCl\(_3\) in TEGDME electrolytes in different stoichiometries is presented. Thereby, as already reported for solutions of MgCl\(_2\)/AlCl\(_3\) in THF, DME, and other solvents, a "conditioning" of the electrolyte in parallel with a decrease of the Al/Mg ratio is observed.

To understand this phenomenon, the electrolyte speciation is investigated. As MgCl\(_2\)/AlCl\(_3\) at 2:1 ratio is not soluble in TEGDME, we conclude that the formation of Mg\(_2\)Cl\(_4\)^\(^z\)-, which is the main Mg\(_2\)Cl\(_4\)^\(^z\)- species in THF, is not stabilized in TEGDME. In contrast, as in DME, the formation of MgCl\(^-\) and/or Mg\(_2\)Cl\(_4\)^\(^z\) is strongly indicated. With MgCl\(_2\)/AlCl\(_3\) in a 1:1 ratio, MgCl\(^-\) and/or Mg\(_2\)Cl\(_4\)^\(^z\) and AlCl\(_4\)^\(^-\) are formed. When increasing the amount of AlCl\(_3\) to a ratio of 1:2, for instance, the excessive AlCl\(_3\) dissociates into AlCl\(_4\)^\(^-\) and AlCl\(_2\)^\(^+\). As the cationic Al species diminishes during the change of the
Al/Mg ratio upon "conditioning", the Al depletion is identified to originate from AlCl3+. Finally, when storing Mg foil in the AlCl3+-containing solutions of AlCl3 or MgCl2/AlCl3 (1:2) in TEGDME, Al deposition/Mg dissolution is observed as a spontaneous Al on the Mg cementation process.

As illustrated in Figure 9, the low Coulombic efficiency of electrochemical Mg deposition (1) and dissolution (3) in AlCl3+-containing electrolytes is deduced to be caused by the corrosion of freshly deposited Mg in parallel with Al cementation (2) at the WE. In CV experiments, the change of the Al/Mg ratio during "conditioning" might further relate to Al cementation/Mg corrosion also at the Mg counter and reference electrodes, but only to a lesser extent to electrochemical co-deposition of Al. This might differ in other solvents.

In contrast, AlCl3+-free solutions obtained with MgCl2/AlCl3 in a 1:1 ratio neither show corrosion of Mg foil during storage nor a significant change in the Al/Mg ratio during the "conditioning". The "conditioning" of MgCl2/AlCl3 (1:1) in TEGDME is thus only referred to the elimination of reducible impurities. Accordingly, a pretreatment with small amounts of Bu2Mg instantly results in a "conditioning"-free Mg dep./diss. behavior.

In a broader context, the formation of the electroactive MgCl22+ cations in MgHMDS2/AlCl3-based23,54 and similar55 electrolyte formulations requires two equivalents of AlCl3. Thereby, HMDSAlCl2 is formed as a side product. As for excessive AlCl3 in the MgCl2/AlCl3 (1:2) sample, also HMDSAlCl2 dissociates and forms cationic Al species.45 Accordingly, a MgHMDS2/AlCl3 (1:2) in the TEGDME electrolyte shows a low Coulombic efficiency of Mg dep./diss. Finally, as for MgCl2/AlCl3 (1:1) in TEGDME, the occurrence of cationic Al species (and thus Mg corrosion) can be prevented by adjusting the stoichiometry of Mg and Al species and adding one equivalent of MgCl2. As a proof-of-concept, MgHMDS2/AlCl3/MgCl2 (1:2:1) in TEGDME shows "conditioning"-free Mg dep./diss. with high initial Coulombic efficiencies.

This work thus emphasizes that Al depletion/Mg corrosion processes in Al-containing electrolytes can be prevented by adjusting the stoichiometry of Mg and Al species. In solvents different than TEGDME, the desired stoichiometries are considered to vary according to the solvent-dependent MgCl22+ speciation.60

EXPERIMENTAL SECTION

The investigated electrolytes were prepared by adding MgCl2 (99.99%, Alfa Aesar) and/or MgHMDS2 (97%, Sigma-Aldrich) to solutions of AlCl3 (99.99%, Strem Chemicals) in TEGDME (99%, Sigma-Aldrich). To avoid harmful exothermic reactions, the solutions of AlCl3 in TEGDME were prepared by slowly adding AlCl3 to the glyme. The concentration of MgCl2 or MgHMDS2 was always 0.2 M, whereas the AlCl3 concentration was varied between 0.2, 0.4, and 0.6 M for the 1:1, 1:2, and 1:3 ratios, respectively. The Bu2Mg (10 mM)-containing samples were prepared by adding Bu2Mg (0.050 mmol, 50 μL, 1.0 M in heptane, Sigma-Aldrich) to the electrolyte (5 mL). TEGDME was dried over Na and distilled, whereas the other chemicals were used as received.

Cyclic voltammetry experiments were performed in a flooded cell with 2.5 mL of electrolyte. The spectra were recorded between −1.5 and +2.5 V versus Mg/Mg2+ at a scan rate of vs = 25 mV/s. The Pt WE (0.5 cm2, 25 μm, 99.95%, Goodfellow) was boiled in HNO3 (conc) (65%, PENTA) for several minutes, washed in water and ethanol, and dried in vacuo prior to each measurement. The Mg foil CE (0.5 cm2, 250 μm, 99.9%, Goodfellow) and the Mg rod reference electrode (1.6 mm, 99.9%, Goodfellow) were scratched with a glass microscope slide before each measurement. The conductivity of the samples was determined in potentiostatic electrochemical impedance spectroscopy (PEIS) measurements (1 MHz to 1 Hz) on Pt blocking electrodes with an amplitude of 5 mV. The Ohmic resistance of the electrolytes was determined by the x-intercept of the impedance spectra in the Nyquist plot. Cyclic voltammetry and the PEIS experiments were conducted with a Solartron SI 1287 potentiostat in combination with a Solartron SI 1260 impedance/gain phase analyzer.

SEM images of the Pt and Mg electrode surface (3 kV acceleration voltage) were obtained with an Auriga field emission scanning electron microscope (Zeiss) with an in-lens secondary electron detector. To determine the element distribution on the electrode surface, EDS was conducted using an X-Max 80 mm2 EDS detector. To determine the presence of Mg and Al species and thus Mg corrosion can be prevented by adjusting the stoichiometry of Mg and Al species and adding one equivalent of MgCl2. As a proof-of-concept, MgHMDS2/AlCl3/MgCl2 (1:2:1) in TEGDME shows "conditioning"-free Mg dep./diss. with high initial Coulombic efficiencies.

This work thus emphasizes that Al depletion/Mg corrosion processes in Al-containing electrolytes can be prevented by adjusting the stoichiometry of Mg and Al species. In solvents different than TEGDME, the desired stoichiometries are considered to vary according to the solvent-dependent MgCl22+ speciation.60

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b05307.
Additional cyclic voltammograms, FT-Raman spectra, SEM/EDS images/mappings, and AI and Mg concentrations (as detected by ICP-OES) (PDF)

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