A passivation-free solid electrolyte interface regulated by magnesium bromide additive for highly reversible magnesium batteries

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ABSTRACT:

Highly reversible Mg battery chemistry demands a suitable electrolyte formulation highly compatible with currently available electrodes. In general, conventional electrolytes form a passivation layer on Mg anode, requiring the use of MgCl₂ additives that lead to severe corrosion of cell components and low anodic stability. Herein, for the first time, we conducted a comparative study of a series of Mg halides as potential electrolyte additives in conventional magnesium bis(hexamethyldisilazide)-based electrolytes. A novel electrolyte formulation that includes MgBr₂ showed unprecedented performance in magnesium plating/stripping, with an average coulombic efficiency of 99.26% over 1000 cycles at 0.5 mA/cm² and 0.5 mAh/cm². Further analysis revealed the *in-situ* formation of a robust Mg anode-electrolyte interface, which leads to dendrite-free Mg deposition and stable cycling performance in Mg-Mo₆S₈ battery over 100 cycles. This study demonstrates the rational formulation of a novel MgBr₂-based electrolyte with high anodic stability of 3.1 V for promising future applications.

The increasing usage of electrochemical energy storage technologies in daily life drives the development of new battery systems to succeed existing Li-ion batteries.¹⁻³ Amongst these, rechargeable magnesium batteries (RMBs) using a bivalent Mg²⁺ charge carrier display great potential in meeting future battery needs, due to high earth abundance (1.94% for Mg vs. 0.002% for Li), high volumetric capacity (3833 mAh cm⁻³ for Mg vs. 2062 mAh cm⁻³ for Li), low reduction potential (-2.4 V vs. standard hydrogen electrode), low possibility of dendrite growth and low cost.⁴⁻⁶ Unlike in Li battery systems, conventional Mg battery electrolytes readily passivate on the Mg anode surface due to the spontaneous reduction of electrolyte components, resulting in low Mg-ion diffusion and high overpotential.⁷⁻¹¹ Constructing solid electrolyte interfaces (SEI) with high Mg conductivity and reversibility is a logical step to prevent passivation, either extrinsically¹²⁻¹⁶ or intrinsically¹⁷⁻²³. The most widely implemented strategy is the addition of inorganic chlorides (such as MgCl₂) in high concentrations with traditional salts.²⁴⁻²⁹ The addition of Cl⁻ ions forms electroactive species with Mg cations, while modifying the Mg anode surface with adsorbed chloride ions that regulate Mg diffusion. Even though this strategy is accepted as a working paradigm in Mg batteries, it is still limited by high corrosion behavior, low anodic stability, and low salt solubility in the electrolyte. Alternatively, borate and boron clusters can be used to produce corrosion-free electrolytes, but they suffer from poor batch reproducibility and non-dendrite short-circuiting.³⁰⁻³⁵ Another possible additive is a Mg halide other than MgCl₂ (i.e., MgI₂, MgF₂, MgBr₂), which remains unstudied as potential additives for Mg electrolytes. There have only been a few studies that fabricate ionically conductive Mg halide layers on Mg anode by using HF treatment and I₂ additives.^{17, 36-37} Canepa et al. used first principle calculations to explore possible protective layers for the anode, concluding that Mg(BH₄)₂ and Mg halide layers are the most suitable due to their reductive stability.³⁸ Although

they postulated MgBr₂ and MgI₂ to be the most ideal candidates among the Mg halides, this hypothesis awaits experimental verification.³⁹

Herein we investigate the performance of Mg halides as electrolyte additives in a conventional electrolyte, which consists of magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂) in 1,2dimethoxyethane (DME) with a small amount of tetrabutylammonium borohydride (TBABH₄). A novel MgBr₂-based electrolyte formulation was found to be the best with a cycle life exceeding 1000 cycles in both symmetric and asymmetric Mg cells. The robust inorganic SEI layer formed in situ (comprised of MgBr₂ and Mg(BH₄)₂ inorganic species) results in very high Mg-ion reversibility and prevents passivation on the anode surface. The BH₄⁻ ions also play a crucial role as a moisture scavenger which inhibit initial passivation of anode by contaminants and moisture present in the electrolyte.⁴⁰

Results and discussion

The effect of Mg halides on Mg plating/stripping was first investigated by the galvanostatic voltage profiles (Figure 1a) using electrolytes that include 20 mM of Mg halide additives $(MgX_2, X = Cl, I, F \text{ and } Br)$ in 0.1 M Mg(HMDS)₂ and 30 mM of TBABH₄ in dried DME. From the initial Mg plating voltage-time curve, the nucleation overpotential (Δ_n) and initial plating overpotential (Δ_p) of each system was calculated (Figure S1). The MgBr₂ formulation exhibited Δ_n of 0.39 V, which is much lower than MgCl₂ (0.71 V), MgI₂ (0.70 V), and MgF₂ (0.54 V), justifying the reduced energy barrier of Mg nucleation with MgBr₂ as the electrolyte additive (Figure 1b). The ionic conductivity in each electrolyte formulation measured at room temperature (Figure 1b) indicates that the MgBr₂-based electrolyte has the highest ionic conductivity (0.462 mS/cm) among the compared electrolyte systems which strengthen the observation from earlier part. Further, the enhanced deposition kinetics and ion transport

properties are investigated by electrochemical impedance spectroscopy (EIS). The Nyquist plots (Figure 1c and Figure S2a-b) yield the bulk resistance (R_b) and interfacial resistance (R_{int}=R_{SEI}+R_{ct}) which can be used to understand the ionic conductivity in electrolyte and interfaces, respectively.^{12, 17, 37, 41} Considering the Nyquist plots measured in RT (Figure 1c and **Table S1),** MgBr₂ system exhibited a R_b of only 28.47 Ω which is much lower than MgCl₂ $(44.89 \ \Omega)$, MgI₂ $(187.2 \ \Omega)$, and MgF₂ $(37.15 \ \Omega)$ formulations, which clearly elucidate that the MgBr₂ enables faster ion transport in electrolyte. The trend of R_b values precisely corresponds with the trend we observed in the ionic conductivity measurements. Further, the transport properties of Mg ion in the interface were investigated by temperature dependent electrochemical impedance spectroscopy (EIS) using symmetric Mg//Mg cells. The SEI established by the MgBr₂-based electrolyte has the lowest interface resistance at all the observed temperatures (Table S1), which results in improved Mg-ion reversibility through the interface with reduced overpotential. The Nyquist plots obtained at different temperatures shown in Figure S2a-d, indicate all four electrolyte systems to exhibit Vogel-Fulcher-Tamman temperature dependent ionic conductivity, suggesting thermal activation of interfacial ion transport.⁴²⁻⁴³ The calculated activation energy barrier for R_{int} (Figure S2e) and R_{ct} (Figure S2f) with MgBr₂ electrolyte is 27.18 kJ/mol and 30.92 kJ/mol, respectively, which is much lower than when using MgCl₂ and MgI₂-based electrolytes. Surprisingly, the MgF_2 exhibited the lowest activation energy but suffers from poor reversibility of Mg plating/stripping, showing only 5 cycles when cycled in an asymmetric cell (Table S2). Considering the measured values of activation energies, R_b, R_{ct} and R_{int}, the MgBr₂-based electrolyte is the best choice among all four systems.



Figure 1. (a) Voltage profile of the first cycle Mg plating/stripping in a 0.1 M Mg(HMDS)₂ + 30 mM TBABH₄ in DME + 20 mM of MgX₂ - X= Cl, I, F and Br on an Al/C electrode at 0.5 mA/cm² and 0.5 mAh/cm². (b) Graphical representation of ionic conductivity and nucleation overpotential (Δ_n). (c) EIS Nyquist plot measured at RT and the inset image shows the equivalent circuit model used to fit. (d) Coulombic efficiency of the magnesium plating and stripping

process with different halide electrolytes. (e) Galvanostatic cycling performance of Mg//Mg symmetric cells at 0.5 mA/cm² and 0.5 mAh/cm².

The MgBr₂-based electrolyte exhibited a high cycling life of 274 cycles, with average CE of 99.00% and Mg plating/stripping overpotential of only 0.39 V when cycled in a Mg//Al asymmetric cell at 0.5 mA cm² and 0.5 mAh/cm² (Figure 1d and Figure S3a-b). In a long cycling scenario with Mg//Mg cells at 0.5 mA/cm² and 0.5 mAh/cm², the MgBr₂ electrolyte formulation was stable for up to 460 cycles (Figure 1e). The MgI₂ formulation is only stable for a few tens of cycles, and while the MgF₂-based formulation shows a moderate reversibility of 310 cycles, it suffers from higher overpotential. The MgCl₂ formulation had a lower overpotential initially, but this significantly increased over a cycle life of only 415 cycles. We benchmarked the performance of the MgBr₂ electrolyte formulation for high-energy applications by examining symmetric (Mg//Mg) and asymmetric (Mg//Al) cells under different current and areal capacities (Figure S4-6). The cells were able to cycle up at a higher current density of 4 mA/cm² and areal density of 6 mAh/cm² without short circuiting. They also exhibit flat voltage profiles, indicating homogeneous deposition of Mg with high reversibility. The MgBr₂ formulation was found to perform the best among the halide systems studied (Table S2), with the lowest nucleation overpotential (0.39 V), highest coulombic efficiency (99.00%) and longest cycling life (460 cycles in Mg//Mg and 274 cycles in Mg//Al).

We further studied the anodic stability of MgBr₂-based electrolyte in a three-electrode configuration using Mg as a reference and counter electrode (Figure S7a). With a Pt working electrode, the onset of electrolyte oxidation was observed at 3.1 V versus Mg/Mg²⁺, and an anodic stability of 2.61 V was achieved with a non-noble stainless steel (SS) working electrode, both of which are higher than the same electrolyte configuration with 20 mM MgCl₂ (1.95 V for

Pt and 2.38 V for SS) instead of MgBr₂.⁴⁴ This anodic stability up to 3.0 V on Pt was further confirmed with chronoamperometry over a prolonged period (Figure S7b).

The Mg anode-electrolyte interface in each electrolyte system was analyzed by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) using the Mg metal anodes retrieved from a symmetric cell after 20 cycles of plating/stripping. The deconvoluted C 1s spectra (Figure 2a) can be indexed as C-C (284.4 eV), O-C-O (285.5 eV), C=O (286.52 eV), O-C=O (287.09 eV), C₂O₄⁻/CO₃²⁻ (289.68 eV) and Si-C (283.25 eV) species. ²⁶ The organic species arises from both the decomposition of DME solvent and the polyether layer on the surface.^{40, 45} The presence of organic species on the surface is also confirmed from the O 1s spectra (Figure S8a). The anodes cycled in MgBr₂ electrolyte produced higher amount of surface organic species compared to the other three electrolyte systems. The deconvoluted Mg spectra (Figure 2b) peaks are indexed as Mg metal (49.8 eV), MgO/MgBr₂/MgF₂ (51.0 eV), MgCl₂ (51.8 eV), MgI₂ (52.5 eV) and Mg dangling bonds (48.4 eV).^{13, 24-25, 40, 44-47} The MgI₂-based electrolyte shows a substantially smaller amount of inorganic halide component, instead displaying higher Mg metal peaks on the surface revealing the minimal existence of SEI layers. The deconvoluted halide spectra in each system confirms the presence of MgCl₂ (199.1 eV)⁴⁸⁻⁴⁹, MgI₂ (618.5 eV)³⁷, MgF₂ (685.7 eV)^{12, 43, 46} and MgBr₂ (68.75 eV)^{41, 50} (Figure 2c). The Si 2p spectra (Figure S8b) indicated the formation of Si⁰ (99.2-99.5 eV) and Si-C (101-104 eV) on the anodes cycled in MgCl₂, MgF₂ and MgBr₂ electrolytes. The metallic Si^0 is a stable SEI component absent in anodes cycled in MgI₂ electrolyte (which displayed only the Si-C peaks). The B 1s spectra (Figure S8c) indicates that only MgBr₂ formulation produced boron-based components namely Mg-BH4 (188.7 eV) and B-oxides (192 eV).⁵¹



Figure 2. (a-c) The deconvoluted surface XPS spectra of C 1s, Mg 2p and halide (Br 3d, F 1s, I 3d and Cl 2p) in each electrolyte system. (d) TOF-SIMS 3D render images of the Mg anode after 20 plating/stripping cycles in Mg//Mg symmetric cells in plated state.

The N 1s spectra (Figure S8d) measured in all the electrolytes show no apparent signal, indicating the high reductive stability of the TBA^+ ion against the Mg metal anode.⁴⁰ TOF-SIMS

3D render images (**Figure 2d**) showed that the anodes cycled in MgBr₂ electrolyte formed an organic-rich SEI which also included some native Mg oxides (MgO, Mg(OH)₂). Beneath the organic-rich SEI, an inorganic SEI layer consisting of MgBr₂, Mg(BH₄)₂, Mg oxides and Si as its major components can be found. The homogenous Mg deposition can be demonstrated from the consistent distribution of the Mg⁺ species. The anodes cycled in MgCl₂ and MgF₂ shows a low consistency in the distribution of surface organic-rich layer. Meanwhile the anode cycled in MgI₂-based electrolyte shows an uneven distribution of organic species and a larger agglomeration. The Mg halide species are present in all formulations studied except for the MgI₂ electrolyte, which is supported by data from the XPS Mg 2p spectra.

The SEM images of initial Mg deposits (Figure S9a) showed that MgBr₂ leads to a uniformly deposited Mg with a highly crystalline nature. This is due to the lowest nucleation potential of the MgBr₂ electrolyte system, which is supported by the SEM images of Mg deposit film on a carbon coated Al foil at 0.5 mA/cm² (0.5 mAh/cm²) for 3 cycles followed by 6 hours of deposition (Figure S9b). The Mg deposits are uniform, dendrite-free, and highly crystalline even at high areal capacity, with the cross-sectional image validating the denser deposits of Mg over the Al-C electrode. Mg deposition at high current density up to 4 mA/cm² in MgBr₂ electrolyte exhibits the lowest nucleation overpotential (only 0.39 V) which lowers the energy barrier for Mg nucleation and increases the rate of Mg deposition. The XRD pattern of initial Mg deposits on Al/C in each electrolyte (Figure S12) indicates that the presence of MgBr₂ allowed for better crystallization of Mg deposits, which agrees with the arguments from SEM. The XRD pattern (Figure S9c) of Mg deposits coated on Al/C confirmed that the deposit is polycrystalline pure Mg (PDF card no. 00-001-1141).⁴⁶

To understand the better reversibility of Mg deposition/dissolution, the composition of SEI formed in situ on the Mg metal anodes in MgBr₂-based electrolyte is examined by a depthprofiling XPS study of recovered Mg anodes from Mg//Mg cells. The C 1s spectra (Figure 3a) indicates the formation of higher amounts of organic species on the anode surface, which is substantially reduced only after 5 minutes of etching. This observation is supported by the O 1s spectra (Figure S13a) in which the O-C-O is progressively reduced with increased etching time. The Mg spectra (Figure 3b) indicates that the $MgO/MgBr_2$ increases from the surface to the point after 0.5 minutes of etching, being reduced substantially only after 5 minutes of etching and exhibiting strong Mg⁰ peaks thereafter. This verifies the homogenous deposition of pure Mg metal in bulk, a process regulated by an SEI layer formed in situ. The B 1s (Figure 3c) and Br 3d (Figure 3d) spectra confirms the thick inorganic layer of SEI to be comprised of Mg(BH₄)₂ and MgBr₂ species. Both species have been predicted computationally as a robust protecting layer that can inhibit the surface passivation of Mg anode.³⁸⁻³⁹ The Si 2p spectrum demonstrates the presence of Si⁰ along with residual Si-C originating from HMDS^{-,40} The schematic representation of the passivation in traditional Mg(HMDS)₂ electrolyte and the in situ formed bilayer SEI in a MgBr₂-based electrolyte is given in Figure 3e. Generally, in a Mg(HMDS)₂based electrolyte the anode surface suffers from passivation, which arises mainly from the moisture content of the electrolyte and interactions of electrolyte species to the anode surface. Our proposed electrolyte plays two key roles in inhibiting the anode surface from passivation: (1) a minimal amount of BH_4^- ions serves as a moisture scavenger and (2) the robust in situ formed SEI acts as a protecting layer enables highly reversible Mg ion transport.



Figure 3. (a-d) XPS depth profiling analysis of Mg anode retrieved from a Mg//Mg cell in 0.1 M $Mg(HMDS)_2 + 30 \text{ mM TBABH}_4 + 20 \text{ mM MgBr}_2$ after 20 cycles. (e) Schematic representation of the passivation in traditional Mg(HMDS)₂ electrolyte and the evolution process of SEI in a MgBr₂-based electrolyte.

The performance of the Mg//Al cells cycled in electrolytes at fixed concentrations of MgBr₂ (20 mM) and TBABH₄ (30 mM) with varying concentrations of Mg(HMDS)₂ (0.1 to 1 M) suggest that 0.1 M Mg(HMDS)₂ is optimal (**Figure S14 a-b**). Next, the cells were cycled in 0.1 M Mg(HMDS)₂, 30 mM TBABH₄ and different molar concentrations of MgBr₂ at 0.5 mA/cm² and 0.5 mAh/cm² (**Figure 4a**). The initial Mg plating/stripping overpotential at 10 mM MgBr₂ is 0.89 V, which was reduced to 0.81 V at 20 mM, and further reduced substantially to 0.54 V when the MgBr₂ concentration was increased to 50 mM. A further increase in concentration (to

100 mM) resulted in a slight increase in the overpotential (0.64 V). The cycling life and average coulombic efficiency increases with increasing amount of MgBr₂ additive in the electrolyte (Figure 4b and Table S3). The electrolytes with 50 mM and 100 mM MgBr₂ displayed low Mg plating/stripping overpotentials of 0.37 V and 0.34 V, and high average coulombic efficiencies of 99.10% and 99.26% over 575 and 1000 cycles, respectively (Figure 4c and Figure S15). With this in mind, we further explored electrolytes with 50 mM of MgBr₂ for its low-cost and high-energy applications.

The voltage profiles of Mg//Al cell at different current densities (0.5 to 4.0 mA/cm² at 1 mAh/cm²) in 50 mM MgBr₂ electrolyte displays remarkably high reversibility even at high current densities (Figure 4d and Figure S16a). Particularly even after the current density switched twice from 4 mA/cm² to 0.5 mA/cm², the cells were showing steady Mg plating/stripping profiles confirming the robustness of the electrolyte towards dendrite growth. The voltage profile of Mg//Al cell measured at different areal capacities (up to 10 mAh/cm² at 0.5 mA/cm²) exhibits flat voltage profiles demonstrating homogenous Mg deposition even at high areal capacities (Figure 4e and Figure S16c). In both the benchmarking tests the CE remained high (Figure S16b and d), suggesting that the proposed electrolyte is favorable for high-power applications. To ensure Mg plating/stripping reversibility, a series of Mg//Al cells were cycled at different areal capacities at a fixed current density of 1 mA/cm² (Figure S17). We found the cycle life to be more than 2000 cycles at 0.1 mAh/cm²; the cells remained highly reversible even at 1 mAh/cm², working for up to 150 cycles. Still at 3 and 12 mAh/cm², the cycle life were 40 and 3 cycles, respectively. We point out that the overpotential is consistent and the CE remained high (98.32-99.38%) throughout all cycling conditions.



Figure 4. (a) First cycle voltage profile of Mg//Al cells in 0.1 M Mg(HMDS)₂ + 30 mM TBABH₄ with different MgBr₂ concentration. (b) Coulombic efficiency vs cycle numbers. In (c-g), studies are measured with 0.1 M Mg(HMDS)₂ + 30 mM TBABH₄ + 50 mM MgBr₂ in DME electrolyte (c) Voltage profile of Mg//Al cells measured at 0.5 mA/cm² and 0.5 mAh/cm². (d) Voltage profile of Mg//Al cells measured at different current densities at 1 mAh/cm². (e) Voltage profile of Mg//Al cells measured at different areal capacities at 0.5 mA/cm². (f) Cycling profile of Mg//Mg symmetric cell at 0.5 mA/cm² and 0.5 mAh/cm². (g) Voltage profile of Mg//Mg cells measured at different areal capacities at 0.5 mA/cm².

Testing the stability and reversibility of the electrolyte in a typical Mg//Mg cell at 0.5 mA/cm² and 0.5 mAh/cm² (Figure 4f) indicated the cells to show a superior cycle life of more than 1000 cycles (2000 h). The SEI layer established in initial cycles shields the anode surface from the passivation and parasitic reactions, which enable highly reversible Mg deposition and dissolution on Mg anode. These observations were supported by the cycling data measured at 1 mA/cm² at areal capacities of 0.1 mAh/cm² and 1 mAh/cm² (Figure S18). The symmetric cells performed well even at a current density of 4 mA/cm² (Figure S19a-b) and an areal capacity of 15 mAh/cm² (Figure S19c-d). The flat voltage profile curves indicate homogeneous Mg plating/stripping regulated by a dendrite-free surface and passivation-preventing SEI layers.⁴⁶ Our proposed MgBr₂-based electrolyte thus outperforms others in terms of cycling life and coulombic efficiency (Fig. 5a-b; Table S4-S5).^{22-25, 27, 29-30, 32, 35, 40, 43-46, 48, 52-62}

We measured the anodic stability and reversibility of Mg plating and dissolution on different current collectors in a three-electrode cell in 50 mM MgBr₂ electrolyte. Cyclic voltammograms (**Figure 5c and Figure S20a-c**) obtained with different metals as the working electrode and Mg as both reference and counter electrodes, clearly demonstrates highly reversible Mg plating/stripping in all cases (Pt, SS, Ni and Mo). The electrolyte displayed a high anodic stability with Pt (onset potential of 3.1 V), and non-noble metals like SS, Ni, Mo appearing with onset potentials at 2.51 V, 2.58 V and 2.78 V, respectively (**Figure 5d**). The multistep chronoamperometry data obtained validates the high anodic stability up to 3.0 V, 2.5 V, 2.5 V and 2.75 V on Pt, SS, Ni and Mo, respectively (**Figure 5e and Figure S20d-f**). Although Mg plating/stripping is reversible on Al current collector, there is still some corrosion due to the presence of halide Br⁻ ions (**Figure S21**). To determine the applicability of MgBr₂ with other conventional Mg salts, we investigated its voltage profiles with magnesium triflate (Mg(OTF)₂)

and magnesium bis(trifluoromethanesulfonimide) (Mg(TFSI)₂) (**Figure S22**), which indicates that the initial overpotential is low for both, with a lower cycling life and a lower CE. We also studied the MgBr₂-based electrolyte formulation in a prototype Mg//Mo₆S₈ full cell in the potential window of 0.2-2.0 V using a Ni foil as current collector (**Figure 5 f and g**). The cell exhibited a reversible capacity of around 53 mAh/g over 100 cycles with an average coulombic efficiency of 95.87% at 0.1 C, showing promise for future applications.



Figure 5. (a) The comparison of coulombic efficiency vs cycling life of Mg asymmetric cells performance at 0.5 mA/cm^2 of our work with previous reports. (b) Comparison of current density

vs cycling life of symmetric Mg//Mg cell performance with previous reports. In (c-g), electrochemical studies are measured with 0.1 M Mg(HMDS)₂ + 30 mM TBABH₄ + 50 mM MgBr₂ in DME electrolyte. (c) Cyclic voltammetry in a three-electrode cell at 5 mV/s with Ni as the working electrode. (d) Linear sweep voltammetry at 5 mV/s in three electrode cells with different metals as working electrodes. (e) Chronoamperometry measured at different potentials with Ni as the working electrode. (f) Cycling voltage profile of Mg//Mo₆S₈ full cell at 0.1 C and voltage window of 0.2–2 V. (g) Capacities and coulombic efficiency versus cycle number for Mg//Mo₆S₈ full cell.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, three electrode CV, LSV and CA graphs, Nyquist plots, SEM images, XRD patterns, and galvanostatic charge–discharge profiles.

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D.C and Z.W.S conceived the idea. D.C performed the experiments and wrote the manuscript.

W.Y.L conducted the XPS experiments. S.K and Z.W.S revised the manuscript. G.Y contributed

to SEM experiments. Y.L contributed in TOF-SIMS measurements.

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