

An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries**

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Abstract: Unlocking the full potential of rechargeable magnesium batteries has been partially hindered by the reliance on chloride-based complex systems. Despite the high anodic stability of these electrolytes, they are corrosive toward metallic battery components, which reduce their practical electrochemical window. Following on our new design concept involving boron cluster anions, monocarborane $CB_{11}H_{12}^-$ produced the first halogen-free, simple-type Mg salt that is compatible with Mg metal and displays an oxidative stability surpassing that of ether solvents. Owing to its inertness and non-corrosive nature, the $Mg(CB_{11}H_{12})_2$ /tetraglyme (MMC/G4) electrolyte system permits standardized methods of high-voltage cathode testing that uses a typical coin cell. This achievement is a turning point in the research and development of Mg electrolytes that has deep implications on realizing practical rechargeable Mg batteries.

Currently, the prospect of attaining energy densities beyond those offered by current lithium-ion batteries is driving interest in rechargeable magnesium batteries. Mg metal offers high volumetric capacity (3833 mAh cm^{-3} vs. 2036 mAh cm^{-3} for Li metal) while being non-dendritic and abundant in the earth crust (fifth most abundant element).^[1] Since Aurbach et al. demonstrated the first and only rechargeable Mg battery prototype, challenges toward realizing Mg batteries still remain.^[2] These stem from the absence of practical electrolytes and high capacity/high voltage cathodes. For instance, the field demands electrolytes capable of operating at high voltages whilst being compatible with Mg metal and all other battery components.^[3]

Early studies suggested that simple-type salts widely used in Li-ion batteries, such as those based on ClO_4^- or PF_6^- , fail to work in Mg systems as they passivate the Mg metal surface.^[4] In contrast, ethereal solutions of Grignard reagents are compatible with Mg metal and are known to enable reversible Mg electrodeposition.^[1,3] Accordingly, electrolyte design focused on improving the low anodic stability of the Grignard carbanion by switching to amides, alkoxides, and aryloxides, usually in combination with chlorides or Lewis acids, to provide an acceptable ionic conductivity or improved anodic stability.^[3,5] These strategies successfully resulted in complex solutions with high anodic stability ($> 3.2 \text{ V vs. Mg}$), albeit at the expense of reduced compatibility with other battery components such as steel casings and current collectors.^[6] Recent studies linked the source of their corrosive nature to the presence of chlorides,^[6] which is an essential feature in these systems. Resolving this shortcoming on a material level calls for creating new platforms based on chloride-free designs.^[7] Galvanized by the magnitude and implications of realizing Mg battery technologies, the community is endeavoring to go beyond these complex systems and develop simple-type Mg salts compatible with Mg metal that possess high anodic stabilities and are not corrosive.^[7]

We initiated our efforts toward reaching this elusive goal by showing that $Mg(BH_4)_2$ electrolytes enabled reversible Mg deposition/stripping owing to high reductive stability of BH_4^- .^[8] However, this same reductive nature also resulted in low anodic stability (1.7 V vs. Mg). Drawing inspiration from the hydrogen storage properties of $Mg(BH_4)_2$, we proposed the highly stable *closo*-dodecaborate dianion, $B_{12}H_{12}^{2-}$, as potential “hydroborate-like” candidate with improved oxidative stability.^[9] Unfortunately, $MgB_{12}H_{12}$ was found to be unsuitable as the high charge density on both the cation and anion, exacerbated by the weakly coordinating nature of $B_{12}H_{12}^{2-}$, renders it insoluble in low-polarity solvents.

Unfazed by this initial setback, we decided to shift our focus to enable a soluble salt that, while not necessarily simple, would allow us to investigate the feasibility of boron clusters. We turned to neutral isoelectronic and isostructural *m*-carborane ($1,7-C_2B_{10}H_{12}$) because of the availability of acidic protons amenable to yield Grignard-type compounds, which are known to be soluble in THF. Satisfyingly, the corresponding salt $[1-(1,7-C_2B_{10}H_{11})]MgCl$ (**1**) displayed reversible Mg deposition/stripping ($> 98\%$) and remarkably high anodic stability (ca. 3.2 vs. Mg).^[9] Having laid out the necessary foundation, we set out on a quest to exploit boron cluster anions to create the first all-around practical, simple Mg electrolyte. Achieving this goal would be akin to closing

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a critical gap and opening a new chapter in Mg battery development. Herein, we report how our efforts have culminated in the development of the first simple-type, ionic, halide-free, and non-corrosive Mg electrolyte that couples a wide electrochemical window with a benign character, as evident from its low volatility, high thermal stability, and chemical inertness.

Starting off at **1**, we considered the option of designing the desired electrolyte system by replacing Cl^- with $[\text{1}-(1,7\text{-C}_2\text{B}_{10}\text{H}_{11})]^-$. However, since most of the negative charge is localized on the carbon atom, the resulting compound $(\text{C}_2\text{B}_{10}\text{H}_{11})_2\text{Mg}$ was expected to display an analogous structure to alkyl/aryl MgR_2 compounds, which are known to be ionic insulators. Indeed, the crystal structure of the closely related $(2\text{-Me-1,2-C}_2\text{B}_{10}\text{H}_{10})_2\text{Mg}\cdot(\text{dioxane})\cdot(\text{PhMe})$ solvate confirms the formation of a non-dissociated contact ion pair.^[10] We therefore pursued a strategy to weaken the Mg–C bond association, while maintaining the electronic and structural features that make boron clusters highly stable.

The monoanionic icosahedral *closo*-carborane $\text{CB}_{11}\text{H}_{12}^-$ appeared as the perfect candidate because the anionic charge is part of the cage bonding and is fully delocalized over the cage. In fact, lacking of lone pairs of electrons, and basic or nucleophilic sites, some substituted $\text{CB}_{11}\text{H}_{12}^-$ anions are among the most weakly coordinating of all known anions.^[11] Furthermore, $\text{CB}_{11}\text{H}_{12}^-$ is more lipophilic than $\text{B}_{12}\text{H}_{12}^{2-}$ due to the charge reduction, and its salts are more soluble in low polarity solvents, such as ethers.^[11] We speculated that such solubility may be attainable in a yet to be prepared Mg salt. All these features, combined with the reported reductive and oxidative stability of $\text{CB}_{11}\text{H}_{12}^-$,^[12] presented a compelling motivation to synthesize the $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ salt (magnesium monocarborane, or MMC salt) and study its suitability as battery electrolyte.

To access anhydrous MMC salt, we initially prepared the hydrated analogue $[\text{Mg}(\text{H}_2\text{O})_6](\text{CB}_{11}\text{H}_{12})_2$ (**2**); however, as in the case of closely related $[\text{Mg}(\text{H}_2\text{O})_6](\text{B}_{12}\text{H}_{12})\cdot 6\text{H}_2\text{O}$, thermal dehydration was not possible (Supporting Information, Figure S47).^[13] Therefore, an alternative route consisting in salt metathesis of $\text{AgCB}_{11}\text{H}_{12}$ with MgBr_2 was explored. When carried out in THF, we were disappointed to find a precipitate composed of a mixture of AgBr and $[\text{Mg}(\text{THF})_6](\text{CB}_{11}\text{H}_{12})_2$ (**3**), arising from the insolubility of **3** in THF. Such a molecular composition is consistent with formation of an octahedrally coordinated magnesium ion $[\text{Mg}(\text{THF})_6]^{2+}$, and suggests the formation of an ion-separated and highly ionic salt. Having ruled out THF as solvent for **3**, we turned our attention to glymes owing to their ability to efficiently solvate cations. Although **3** initially dissolves in monoglyme (DME) and diglyme (G2), those solutions quickly precipitate $[\text{Mg}(\text{DME})_3](\text{CB}_{11}\text{H}_{12})_2$ (**4**) and $[\text{Mg}(\text{G2})_2](\text{CB}_{11}\text{H}_{12})_2(\text{G2})$ (**5**), respectively, as crystalline solids. X-Ray diffraction analysis (Figure 1) revealed the presence of Mg solvent-separated ion pairs, indicative of a high level of salt dissociation not commonly found in other simple Mg salts.^[14]

Although the solubility challenge seemed initially daunting, we were pleased to find a high solubility of **3** (as well as **4** and **5**) in triglyme (G3) and tetraglyme (G4) ($> 1\text{M}$), which is maintained upon vacuum removal of the initial solvation

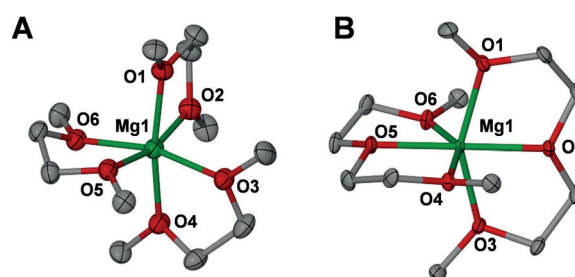


Figure 1. Mg cation coordination environment in **4** (A) and **5** (B). Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

molecules. In our pursuit of gaining further understanding of the Mg^{2+} -glyme interactions in G3 and G4 solutions, we turned to solid-phase structure analysis. While we were unable to obtain X-ray-quality single crystals from these solutions, crystals of $[\text{Mg}(\text{G4})_2(\text{H}_2\text{O})](\text{CB}_{11}\text{H}_{12})_2$ (**6**) suitable for X-ray analysis formed in the presence of a small amount of H_2O (< 50 ppm; Supporting Information, Figures S24 and S25). Similarly to **4** and **5**, the solid-phase structure of **6** reveals the presence of two glyme molecules per Mg atom, although in this case two or more adjacent oxygen atoms at one end of the tetraglyme are not involved in Mg coordination.^[15] We hypothesize that those non-coordinating solvent tails, only available in glymes larger than G2, may have provided a method for effective salt dissolution through cation–anion asymmetry.

Prior to initiating detailed electrochemical studies, we determined optimal electrolyte concentrations based on ionic conductivity profiles of MMC/G3 and MMC/G4. At room temperature, maximum values of 2.9 mS cm^{-1} between $0.65\text{--}0.85\text{ M}$ and 1.8 mS cm^{-1} between $0.55\text{--}0.75\text{ M}$, were obtained in G3 and G4 solutions, respectively (Supporting Information, Figure S26). This conductivity is comparable to other Mg electrolytes,^[3] and to solutions of Li salts such as LiPF_6 (2.1 mS cm^{-1}) and LiClO_4 (1.7 mS cm^{-1}) in G4.^[16] In subsequent studies, 0.75 M MMC salt solutions were used based on the optimal conductivity level in both solvents.

The electrochemical performances of MMC/G3 and MMC/G4 electrolytes were examined using cyclic voltammetry on a Pt working electrode (Figure 2A). Gratifyingly, starting from the first cycle, both solutions show Mg deposition/dissolution with very low overpotentials ($< 250\text{ mV}$) and high coulombic efficiencies (79.6% in G3, 94.4% in G4; Supporting Information, Figure S27),^[17] demonstrating anion compatibility with Mg metal.^[18] The anodic scan reveals high oxidative stabilities of about 3.4 V (G3) and 3.8 V (G4), representing the highest reported to date for Mg salts and consistent with those known for other $\text{CB}_{11}\text{H}_{12}^-$ salts.^[12a] Note that the measured oxidative limits are dictated by G3 and G4, as that of MMC measured in a solvent with high anodic stability such as CH_3CN , is at least 2.3 V vs Ag/Ag^+ (approximately 4.9 V vs. Mg; Supporting Information, Figure S30). The excellent coulombic efficiency found in G4 was valued over the higher conductivity provided by G3, thus MMC/G4 was used in further studies. The high coulombic efficiency of MMC/G4 does not degrade even with cycling

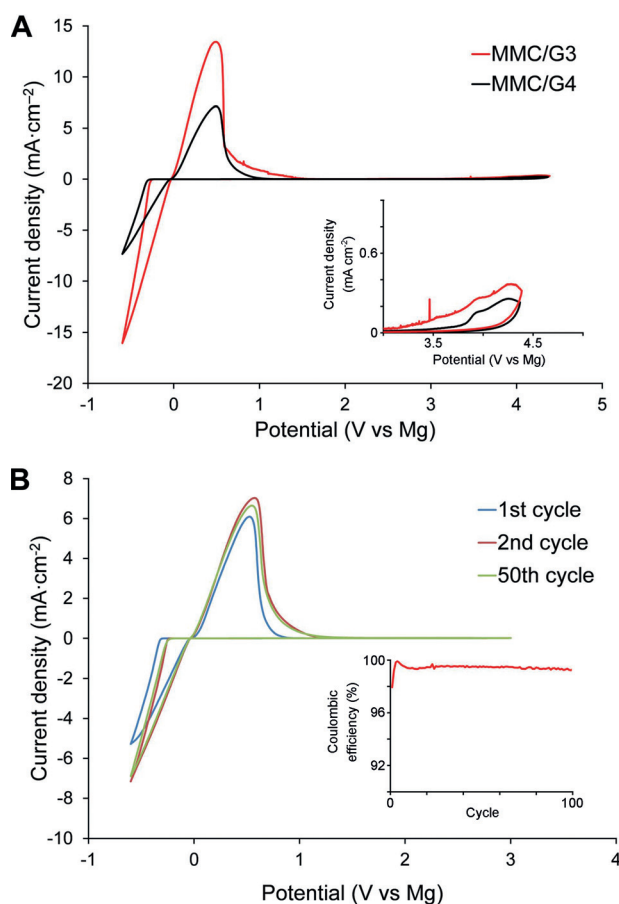


Figure 2. A) First scan of a cyclic voltammetry test of 0.75 M MMC/G3 and 0.75 M MMC/G4 on Pt electrode collected at 5 mVs^{-1} (inset: enlargement of 3.0–5.0 V region). B) Selected cyclic voltammograms of 0.75 M MMC/G4 electrolyte on Pt electrode collected within the potential range of -0.6 – 3.0 V (vs. Mg) at 5 mVs^{-1} (inset: cycling efficiencies of Mg deposition and dissolution).

over a wide electrochemical window (3.6 V), where a value of more than 99% per cycle is maintained for at least 100 cycles (Figure 2B). Such outstanding performance represents a breakthrough in Mg battery research as it unveils MMC/G4 as the first halogen-free simple-type salt based electrolyte that is both Mg compatible and can provide a wide electrochemical window.

The anodic stability of MMC/G4 was further studied by linear sweep voltammetry using inert and non-noble metal electrodes. Consistent with absence of corrosion, all of the electrodes display similar oxidation onset potential in a narrow range between 3.8–4.0 V (Figure 3), accompanied with current decrease on the reverse scan (Supporting Information, Figure S33). Since standard coin-type cells are constructed from stainless steel, we conducted in-depth studies on this substrate. Chronoamperometric experiments were carried out on 316-SS electrodes held at potentials of 3.0 and 3.5 V vs. Mg for 48 h in MMC/G4. A negligible current density ($<0.1 \mu\text{A cm}^{-2}$; Figure 3, inset), and absence of pitting in the SEM images (Supporting Information, Figure S35) corroborated non-existence of corrosion at 3.0 V. Meanwhile, a very small current (0.002 mA cm^{-2}) was noted

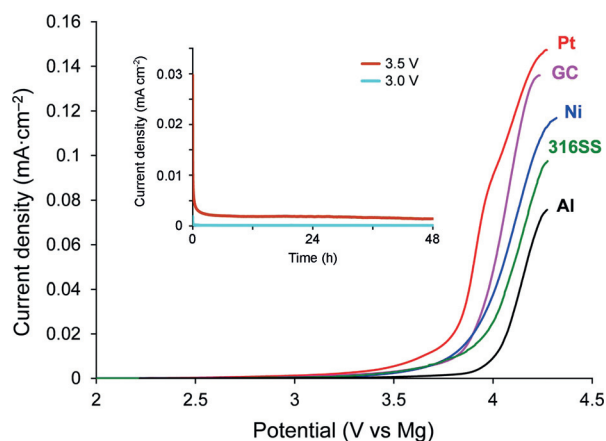


Figure 3. Linear sweep voltammograms of 0.75 M MMC/G4 electrolyte on different electrode materials with a scan rate of 5 mVs^{-1} (inset: chronoamperometry of 0.75 M MMC/G4 electrolyte on 316SS disk electrodes (area = 1.33 cm^2) at 3.0 V (light blue) and 3.5 V (brown) vs. Mg).

at 3.5 V (Figure 3, inset), consistent with initiation of electrolyte solvent decomposition as seen in the LSV experiment. At that voltage, we found no pitting (see the Supporting Information, Figure S37 for SEM images), no change in the composition of electrode surface (see the Supporting Information, Figure S37 for EDS analysis), nor presence of dissolved Fe, Cr or Ni in the electrolyte solution following electrolysis (Supporting Information, Table S2), all supporting the non-corrosivity of MMC/G4.

Along with an exceptional performance, MMC/G4 also displays beneficial properties with regards to supporting safe battery operation. At the outset, G4 is an inherently safer solvent compared to THF and lower glymes owing to its high boiling (275°C) and flash points (141°C). Specifically, thermal gravimetric analysis of 0.75 M and 1.0 M MMC/G4 solutions reveal high thermal stability with loss of tetraglyme starting at about 190°C , followed by decomposition of the residual MMC:G4 (1:2) at 270°C (Supporting Information, Figures S48–S51). Another property pertaining to safety relates to hazards accompanying exposure to moisture such as violent/rapid outgassing and/or smoking. Addition of water to 0.75 M MMC/G4 was uneventful (Supporting Information, Figure S52), where the absence of any chemical reactivity during and following addition of water underscores the benign nature of MMC/G4. The chemical inertness of $\text{CB}_{11}\text{H}_{12}^-$ was further probed using high voltage organic redox-active molecules prone to chemical attacks from strong Lewis acids or bases, such as the TEMPO derivative 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl radical (**7**). A stable performance of the $7/7^+$ redox couple (0.3 V vs Fc/Fc^+ , 2.8 V vs. Mg) in MMC/G4 electrolyte marks high compatibility evident from hundreds of overlapping CV cycles (Supporting Information, Figure S38), as well as from an electrochemical performance consistent with the reversibility of TEMPO reported in other inert aprotic solutions (Supporting Information, Figures S39–S42).^[19]

Access to non-corrosive, oxidatively stable electrolytes also opens avenues to explore a variety of potential cathodes

for Mg batteries in standardized battery cells, such as coin cells, which has not been possible so far. At first, we examined the ability of MMC/G4 electrolyte to support reversible Mg insertion/extraction in a Chevrel phase (Mo_6S_8) which, despite its low voltage (<1.5 V), has a stable and known performance.^[3a] The results showed that MMC/G4 electrolyte supports reversible Mg^{2+} insertion/extraction (Supporting Information, Figures S43–S45) and the battery performance is consistent with previous reports. Next, we examined the coin cell performance of the previously reported 3 V class cathode material $\alpha\text{-MnO}_2$.^[20,21] So far, battery testing using highly Mg compatible electrolytes, of this type of cathodes in coin cells beyond 2.5 V was precluded by corrosion induced by current electrolyte systems. For instance, while the expected discharge capacity of $\alpha\text{-MnO}_2$ cathode is obtained in a representative halogen-based ($2\text{PhMgCl}\text{-AlCl}_3$)/THF (APC) and MMC/G4 electrolytes (Figure 4), charging of the coin cell using APC electrolyte was not possible owing to

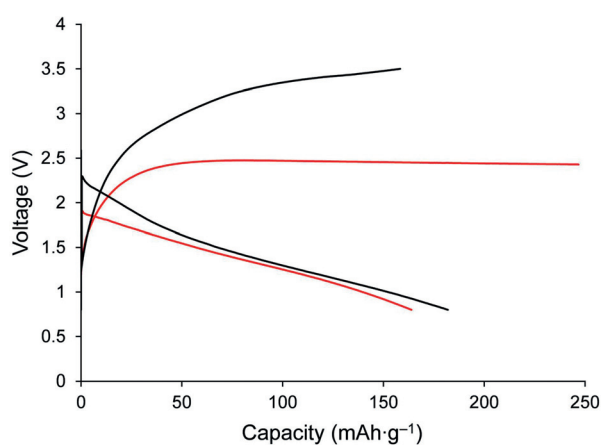


Figure 4. Initial discharge–charge profiles of a rechargeable Mg battery with 0.75 M MMC/G4 (black line) and 0.2 M APC (red line) as the electrolyte, a Mg anode, and a $\alpha\text{-MnO}_2$ cathode under a constant current density of 0.2 mA cm^{-2} .

corrosion occurring at around 2.5 V (Figure 4). In contrast, the non-corrosive MMC/G4 electrolyte allowed cell charging up to 3.5 V (Figure 4), thus marking the first time coin cells employing highly performing electrolytes are used to examine high voltage Mg cathodes (for cycling performance, see the Supporting Information, Figure S46).^[22]

In summary, we have presented the first report of a Mg electrolyte based on a simple-type salt that is compatible with Mg metal ($>99\%$ coulombic efficiency), possesses high anodic stability (3.8 V vs. Mg), and is non-corrosive. These outstanding properties, coupled with an inert and benign character, make MMC-based electrolytes well-suited for future Mg batteries. In the short term, tangible impact of MMC electrolyte on accelerating the research and development of high-voltage cathodes is expected by enabling the examination of a variety of cathodes in coin cells. Finally, as the anodic stability of MMC surpasses that of ethers, discovering new Mg-compatible and oxidatively stable solvents emerges as one of the new avenues for electrolyte

research that can widen the portfolio of accessible high-voltage Mg cathodes.

Experimental Section

General experimental details and characterization data are included in the Supporting Information. CCDC 1038586, 1038587, 1038588, and 1039287 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Keywords: carboranes · electrochemistry · magnesium · non-corrosive electrolytes · rechargeable batteries

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- [21] High-voltage Mg cathodes that are reversible, robust, and have stable cycling, such as those used in Li-ion systems, have not yet been demonstrated. Studies of cathodes showing reversible Mg²⁺ insertion/deinsertion, such as V₂O₅ (nano or thin film), were limited to three-electrode cells that use Mg-passivating electrolytes (that is, Mg(ClO₄)₂/CH₃CN) and do not warrant performance in a battery setup. As our purpose is to demonstrate a coin cell, we used α-MnO₂ despite its capacity fade (ca. 50%) because it was studied and analyzed in a battery configuration (used GC current collectors to mitigate corrosion). Future battery and fundamental interfacial studies of MMC/G4 on cathodes such as V₂O₅ may be fruitful in further understanding this system and enabling these cathodes. For details on Mg cathodes, see Refs. [3a,c,7,20].
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