**Boron Clusters as Highly Stable Magnesium-Battery Electrolytes**

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**Abstract:** Boron clusters are proposed as a new concept for the design of magnesium-battery electrolytes that are magnesium-battery-compatible, highly stable, and noncorrosive. A novel carborane-based electrolyte incorporating an unprecedented magnesium-centered complex anion is reported and shown to perform well as a magnesium-battery electrolyte. This finding opens a new approach towards the design of electrolytes whose likelihood of meeting the challenging design targets for magnesium-battery electrolytes is very high.

The possibility of developing a rechargeable magnesium battery has been a topic of great interest for several decades. Magnesium batteries are particularly attractive owing to their high theoretical capacity (3832 mAh cm$^{-3}$) as well as the low cost and high abundance of Mg metal as compared to Li. Additionally, Mg possesses an important safety advantage over Li in that Mg metal is not prone to dendrite formation. However, before Mg batteries can see practical application, several challenges must be overcome, including the identification of a suitable solvent/electrolyte combination. It has proven particularly challenging to identify such a system for magnesium-based batteries owing to the tendency of many common electrolytes to form nonconductive ion-blocking layers at the electrode surface. Thus, any solvent/electrolyte combination used in a Mg battery must be stable across the entire potential window at which the battery operates.

This requirement is particularly problematic for the design of high-voltage battery systems, for which an electrolyte candidate must be stable to both Mg metal ($-2.37$ V versus the normal hydrogen electrode, NHE) and the cathode-active material selected, which should ideally operate near $+1$ V (vs. NHE). Furthermore, previous research has suggested that Mg metal is reactive toward many common solvents and electrolyte anions. In fact, most of the previously reported electrolyte systems have been limited to highly inert ethereal solvents, such as tetrahydrofuran (THF). This limitation makes the design of electrolyte materials quite difficult, as a successful candidate must be highly soluble in these nonpolar solvents in addition to being electrochemically robust. As a result, only a handful of potential electrolytes are known to be compatible with Mg anodes.

Recent studies at the Toyota Research Institute of North America have demonstrated Mg(BH$_4$)$_2$ to be a highly competent electrolyte for magnesium-battery applications. This electrolyte was the first non-organomagnesium electrolyte compatible with Mg metal and provided excellent electrochemical performance in glyme. In tandem with further research into this system, we sought to pursue potential routes to materials with enhanced oxidative stability as compared to the observed oxidation onset potential of 1.7 V (vs. Mg on Pt) for Mg(BH$_4$)$_2$.

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improve the oxidative robustness of boron-based electrolytes while retaining their other attractive properties is therefore required. Along these lines, we sought to explore other boron-hydride compounds with unique electronic/geometric structures in an effort to optimize electrolyte stability while maintaining compatibility with magnesium-metal anodes.

In implementing this strategy, we initially drew inspiration from reports of the thermal decomposition of Mg(BH$_4$)$_2$, which was studied as a hydrogen-storage material. The closo-borane magnesium dodecahydrododecarborate (MgB$_{12}$H$_{12}$) has often been implicated as an undesirable, highly stable, by-product in this process that is detrimental for reversible H$_2$ storage.[10] Although, the unique stability of this cluster has proven problematic for hydrogen-storage applications, MgB$_3$H$_2$ may be an intriguing candidate for use as a highly robust electrolyte anion. Indeed, previous studies on various salts of B$_{12}$H$_{12}^-_{}$ demonstrated oxidative stability to above 4 V (vs. Mg), and, to our knowledge, there have been no reports of its electrochemical reduction.[11] Furthermore, our calculations predict that B$_{12}$H$_{12}^-_{}$ should offer comparable reductive stability to BH$_4^-_{}$ (see the Supporting Information).

We therefore opted to study closo-boranes as a new class of electrolytes for Mg batteries. Although MgB$_3$H$_2$ seemed to be an ideal candidate in terms of its high reported stability, we were disappointed to find that MgB$_3$H$_2$ (I) was virtually insoluble in ethers,[12] which are the only solvents known to be compatible with Mg metal. We hypothesized that one of the key factors contributing to the poor solubility of these salts was the high charge associated with both the anion and the cation. Following this logic, we elected to study Mg salts of deprotonated carborane clusters, as they are isoelectronic and isostructural analogues of B$_{12}$H$_{12}^-_{}$ and thus should exhibit similar electrochemical stability, but should also offer greatly enhanced solubility owing to the covalent nature of the Mg–C bond. In fact, comprehensive data on the electrochemical properties of carboranes as well as mercucarborane derivatives were also available, and the $m$ and $p$ isomers of the dicarborane clusters were demonstrated to possess comparable electrochemical inertness to that of the B$_{12}$H$_{12}^-_{}$ anion.[13] Furthermore, previous reports of the use of carboranyl magnesium compounds as synthetic intermediates suggested compounds of this type would be highly soluble in organic solvents, including THF and toluene.[14] Therefore, we hypothesized that carboranyl magnesium compounds would serve as ideal candidates for investigating boron clusters as magnesium-battery electrolytes.

Carboranyl magnesium halides (which are readily prepared by treatment of the appropriate carborane with a commercial Grignard reagent)[15] also offered the advantage of being directly comparable to many previously reported magnesium-battery electrolyte materials that are comprised of Grignard reagents or derivatives thereof. In this way, we hoped to be able to demonstrate the unique properties of closo-boranes as compared to other substituents when incorporated into organomagnesium halide electrolytes. Accordingly, we synthesized 1-(1,7-carboranyl) magnesium chloride 2 by allowing $m$-carborane to react with $i$PrMgCl in THF at reflux (see the Supporting Information for details). Efforts to obtain crystals of 2 by pentane layering of a THF solution produced high-quality single crystals, and we were intrigued to note that the solid-state structure (Figure 1A, bottom) revealed a salt comprised of a chloride-bridged Mg dimer and a unique dicarboranyl magnesium chloride complex anion. The Mg complex anion displays a distorted tetrahedral geometry in which the C25-Mg1-C27 bond angle (117°) is significantly wider than the Cl4-Mg1-O7 angle (102°). The chloride-bridged din magnesium cation is analogical to that observed in single crystals of other magnesium-battery electrolyte systems.[16,17] Mg2 and Mg3 both display octahedral geometry with symmetrical Mg–Cl bond distances (2.480–2.530 Å).

Although Grignard reagents have been known to form complex salts under similar crystallization conditions,[15] this structure is the first example of a Mg complex anion with carborane substituents. Crystalline 2 was also fully characterized by NMR and IR spectroscopy, as well as elemental analysis (see Figures 2, 3, and 5 in the Supporting Information). Although the possibility exists that the composition of the Grignard reagent was altered in the process of crystallization, the fact that the crystalline material displays only subtle differences from the bulk in terms of its $^{11}$B NMR and FTIR spectra (see Figures 3 and 5 in the Supporting Information) suggests that these materials have very similar solution-state compositions.[16] We therefore hypothesized
that 2 was obtained by a perturbation (Figure 1A) of the complex solution chemistry of Grignard reagents,[17] as facilitated by the addition of diethyl ether in the workup procedure.

With this complex in hand, we sought to study its electrochemical properties by determining its oxidation onset potential and compatibility with Mg metal. THF was selected for the electrolyte solution, as it has been demonstrated to be the optimal solvent for the study of simple alkyl Grignard reagents as magnesium-battery electrolytes. Gratifyingly, cyclic voltammetry carried out on a solution of 2 in THF revealed a high oxidation onset potential of 3.2 V (vs. Mg) as well as a reversible redox couple with an onset potential and peak shape consistent with Mg deposition and stripping (Figure 1B). Magnesium deposition was further confirmed by X-ray diffraction analysis of the film obtained following galvanostatic deposition onto a Pt disk (Figure 2A). The deposition and stripping events displayed low overpotentials of 0.5 and 0 V, respectively, and high coulombic efficiency (CE > 98 %; Figure 1B, inset). Additionally, solutions of 2 could be cycled more than 40 times without loss of current density or coulombic efficiency (see Figure 8 in the Supporting Information). The conductivity was measured to be 0.6 mS cm⁻¹, which compares well with that of other high-voltage-stability electrolytes for Mg batteries, as the highest reported conductivity is 2 mS cm⁻¹.[1,6c] These performance traits not only demonstrate the compatibility of closo-borane clusters with Mg metal, but also the possibility of obtaining high oxidative stability from an electrolyte whose crystalline form features a magnesium-centered complex anion. This result is remarkable, as many previously reported high-voltage magnesium-battery electrolytes require the addition of exogenous Lewis acids, such as trivalent aluminum or boron.[6a–c,19] Having confirmed that 2 offered compatibility with magnesium-metal anodes while offering nearly double the oxidative stability (on Pt) of Mg(BH₄)₂, we next investigated its reactivity toward non-noble-metal electrodes, as most known high-voltage magnesium-battery electrolytes are highly corrosive to these materials.[8b] We conducted a series of linear-sweep-voltammetry (LSV) experiments on a variety of working electrodes (Figure 2B). Interestingly, the oxidation onset potential was similar (3.2 V vs. Mg) for Pt, 316-SS, and Al. In previous studies with other halide-containing electrolyte solutions, the oxidation onset was always highly dependent on the electrode material. Furthermore, this result constitutes the highest reported stability on stainless-steel (SS) electrodes for an unmodified Grignard reagent to date, suggesting that the closo-borane scaffold does indeed offer unique stability when incorporated into a magnesium-battery electrolyte material.

To further explore the stability of 2 on stainless-steel electrodes, we carried out chronoamperometry experiments in which 2 was compared with a previously reported electrolyte, PhMgCl/AlCl₃ (2:1), on 316-SS working electrodes at a variety of potentials (see Figure 9 in the Supporting Information). The current observed in this experiment can be considered a direct measure of electrode corrosion, as no other redox events occur at the selected potentials (2.5 and 2.9 V vs. Mg). We were pleased to note that 2 displayed a significantly lower corrosion current at all potentials studied. This result is consistent with the absence of an obvious corrosion current in the LSV experiments (Figure 2B).
Having established a clear understanding of the electrolyte properties of 2, we sought to demonstrate its potential for reversible magnesium-ion insertion by constructing a rechargeable Mg battery with a Chevrel phase (Mo₆S₈) cathode, which is the most widely studied and understood cathode for Mg batteries. Additionally, the cycling stability of this cathode makes it an ideal choice for examining the potential of new electrolytes in a battery system. Although both the true value of our electrolyte and the high energy density of Mg batteries will ultimately be showcased by the use of high-voltage cathodes, tremendous challenges related to these cathodes remain: Severe capacity loss caused by partial structural collapse or extremely sluggish kinetics requiring ultrathin film morphologies (ca. 200 nm thick) or extremely sluggish kinetics requiring ultrathin film morphologies (ca. 200 nm thick) makes high-voltage cathodes impractical for the study of stable and reversible magnesium-ion insertion in a battery system. Therefore, a full battery cell was constructed by the use of a magnesium-metal anode and a Chevrel phase Mo₆S₈ cathode with 2 as the electrolyte. The battery was cycled 30 times at 6 mA g⁻¹ (0.05 C), and we were pleased to observe a stable reversible specific capacity of about 90 mAh g⁻¹ (Figure 2C). The reversible capacity, the observation of two magnesium-insertion plateaus, and the high coulombic efficiency (90%) are consistent with previous systems using the Chevrel phase cathode under similar conditions (for which capacities ranging from 80 to 90 mAh g⁻¹ at coulombic efficiencies averaging about 90% were reported). The battery was also cycled at a rate of 100 mA g⁻¹ (see Figure 10 in the Supporting Information). The decreased stable capacity (45 mAh g⁻¹) and voltage profiles under these conditions are similar to those reported for other electrolytes and were attributed to the kinetic limitations of the demagamisation of Mo₆S₈ at high cycling rates. These results demonstrate that 2 can be successfully utilized in a rechargeable Mg battery.

Inspired by our previous studies with Mg(BH₄)₂, we have demonstrated, for the first time, that closo-borane compounds can function as high-oxidative-stability magnesium-battery electrolytes while maintaining compatibility with magnesium-metal anodes. This study also led to the discovery of an unprecedented class of high-stability electrolytes based on an anionic Mg center. Furthermore, the key insight obtained with 2 into the behavior of closo-boranes in these systems will prove highly valuable for further optimization of nontraditional electrolyte systems for Mg batteries. We have thus established 2 as a competent electrolyte for rechargeable Mg batteries, and the future development of new, high-voltage, cathodes should provide an opportunity to finally realize the impressive theoretical capacities of Mg batteries.

**Experimental Section**

General experimental details and characterization data are included in the Supporting Information. CCDC 950050 contains 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.

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[12] a) Anhydrous MgB₄H₁₂ (1) was obtained by treating decaborane (B₁₀H₁₄) with magnesium borohydride (Mg(BH₄)₂) in diglyme at reflux. MgB₄H₁₂ and Mg(B₈H₁₄)₂ were also obtained as by-products. All three species were insoluble in THF, diglyme, and tetraglyme, even in the presence of chelating agents, such as crown ethers and TMEDA.
[16] Further study revealed only minor differences in the electrochemical behavior of bulk and crystalline 2 (see Figure 7 in the Supporting Information). The bulk material offers a slightly lower overpotential for Mg deposition as well as an enhanced current density. The cause of this enhancement is currently under investigation.

[18] All electrochemical experiments were carried out with bulk 2 at a concentration of 100 mg mL$^{-1}$.


