

Boron Clusters as Highly Stable Magnesium-Battery Electrolytes**

Tyler J. Carter, Rana Mohtadi,* Timothy S. Arthur, Fuminori Mizuno, Ruigang Zhang, Soichi Shirai, and Jeff W. Kampf

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.^[1] Magnesium batteries are particularly attractive owing to their high theoretical capacity (3832 mA h cm⁻³) as well as the low cost and high abundance of Mg metal as compared to Li.^[1,2] Additionally, Mg possesses an important safety advantage over Li in that Mg metal is not prone to dendrite formation.^[3] However, before Mg batteries can see practical application, several challenges must be overcome, including the identification of a suitable solvent/electrolyte combination.^[2] 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.^[4] 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 polar solvents and electrolyte anions.^[5] In fact, the majority of previously reported electrolyte systems have been limited to

highly inert ethereal solvents, such as tetrahydrofuran (THF).^[6] 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.^[6]

Recent studies at the Toyota Research Institute of North America have demonstrated Mg(BH₄)₂ to be a highly competent electrolyte for magnesium-battery applications.^[7] 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(BH₄)₂.

High oxidative stability is crucial for the development of Mg batteries for operation with future high-voltage cathodes. Although organomagnesium compounds with oxidative stability above 3 V (vs. Mg) have been reported, most have significantly reduced oxidation onset potentials when deposition and stripping occurs on non-noble-metal surfaces.^[2,6c,8] This reduced stability has been linked to corrosion of the metal by the electrolyte solution^[2,8b] and constitutes a major hurdle to the utilization of current high-voltage electrolytes, as non-noble metals are the most appropriate materials for the construction of battery-casing and current-collector materials.^[9] Notably, Mg(BH₄)₂ displayed enhanced stability on these metals, as corrosion of the electrode material did not occur.^[7] We therefore sought to identify an electrolyte candidate which would retain the attractive properties of Mg(BH₄)₂ but offer enhanced oxidative stability. The identification of such an electrolyte would effectively overcome a major hurdle towards the development of Mg batteries with high energy densities.

A logical method for improving the oxidative stability of the Mg(BH₄)₂ system would be modification of the BH₄[−] anion to incorporate one or more electron-withdrawing groups. However, any gains in oxidative stability achieved in this way would most likely come at the expense of reductive stability and potentially compromise compatibility with magnesium-metal anodes. For example, our ab initio calculations in THF solvent (see the Supporting Information) show that the gain in oxidative stability (evident from the +3.7 V increase in the electrochemical oxidation potential) that is achieved when switching to BF₄[−] occurs at the expense of the reductive stability, as reflected in the +0.44 V change in the reduction potential. This result is consistent with previous experimental evidence of the passivation of magnesium-metal anodes in the presence of BF₄[−].^[4a] An alternative strategy to

[*] Dr. R. Mohtadi, Dr. T. S. Arthur, Dr. F. Mizuno, Dr. R. Zhang
Materials Research Department
Toyota Research Institute of North America
Ann Arbor, MI 48105 (USA)
E-mail: rana.mohtadi@tema.toyota.com

T. J. Carter, Dr. J. W. Kampf
Department of Chemistry, University of Michigan (USA)
Dr. S. Shirai
Toyota Central R&D (Japan)

[**] T.J.C. thanks his graduate advisor Prof. N. Szymczak for his support. T.J.C., R.M., and T.S.A. thank N. Singh for the helpful discussions. Funding was provided by Toyota Motor Engineering and Manufacturing North America Inc. and NSF grant CHE-0840456 for X-ray instrumentation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201310317>.

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 $\text{Mg}(\text{BH}_4)_2$, which was studied as a hydrogen-storage material. The *closo*-borane magnesium dodecahydrododecaborate ($\text{MgB}_{12}\text{H}_{12}$) 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, $\text{MgB}_{12}\text{H}_{12}$ may be an intriguing candidate for use as a highly robust electrolyte anion. Indeed, previous studies on various salts of $\text{B}_{12}\text{H}_{12}^{2-}$ 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 $\text{B}_{12}\text{H}_{12}^{2-}$ 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 $\text{MgB}_{12}\text{H}_{12}$ seemed to be an ideal candidate in terms of its high reported stability, we were disappointed to find that $\text{MgB}_{12}\text{H}_{12}$ (**1**) 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 $\text{B}_{12}\text{H}_{12}^{2-}$ 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 mercurycarborane 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 $\text{B}_{12}\text{H}_{12}^{2-}$ 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)^[14b] 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

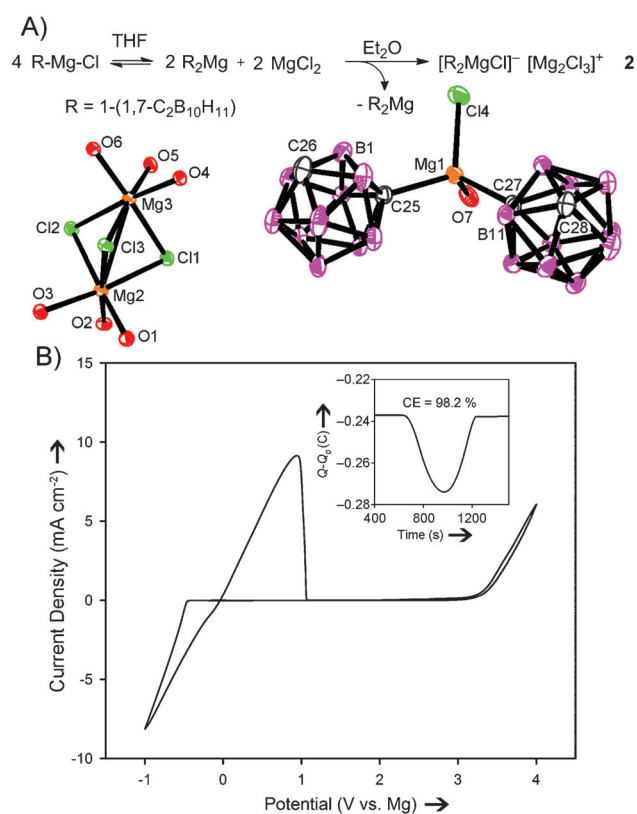


Figure 1. A) Top: Proposed mechanism for the formation of **2**. Bottom: X-ray crystal structure of **2**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and THF carbon atoms are omitted for clarity (i.e. each oxygen atom represents a THF solvent molecule). B) Cyclic voltammogram of a solution of **2** in THF (inset: charge balance of Mg deposition/stripping).

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 dimagnesium cation is analogous to that observed in single crystals of other magnesium-battery electrolyte systems.^[6b,c] 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 ¹¹B 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**^[18] 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 $\text{Mg}(\text{BH}_4)_2$, 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, $\text{PhMgCl}/\text{AlCl}_3$ (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

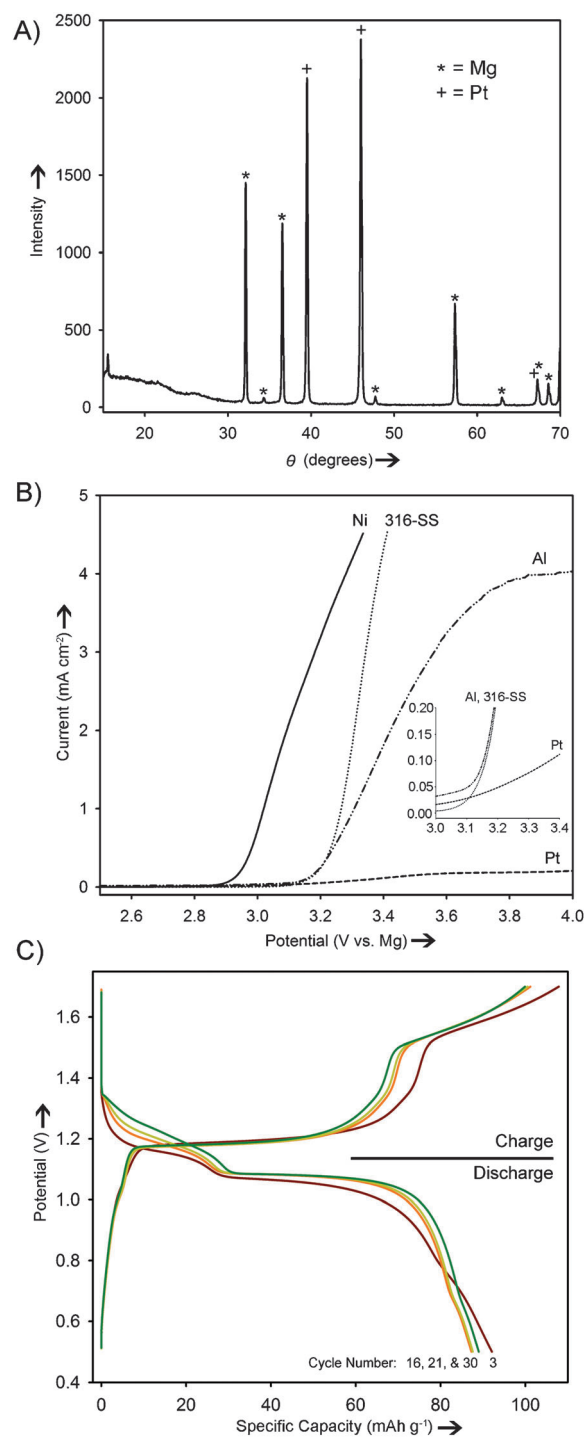


Figure 2. A) XRD plot of a Pt disk following the galvanostatic deposition of Mg from a solution of **2** in THF. B) Linear sweep voltammograms of **2** on Pt, SS, Ni and Al electrodes (inset: expanded view of the oxidation onset). C) Typical charge/discharge profiles for a rechargeable battery with **2** as the electrolyte, a Mg anode, and a Chevrel phase cathode at cycles 3 (dark red), 16 (orange), 21 (light green), and 30 (dark green).

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 (Mo_6S_8) cathode, which is the most widely studied and understood cathode for Mg batteries.^[1] 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^[20] or extremely sluggish kinetics requiring ultrathin film morphologies (ca. 200 nm thick)^[21] make high-voltage cathodes impractical for the study of stable and reversible magnesium-ion insertion in a battery. Therefore, a full battery cell was constructed by the use of a magnesium-metal anode and a Chevrel phase Mo_6S_8 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 mA h 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 mA h g⁻¹ at coulombic efficiencies averaging about 90% were reported).^[6c,d] 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 mA h 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 demagnesiumation of Mo_6S_8 at high cycling rates.^[22] These results demonstrate that **2** can be successfully utilized in a rechargeable Mg battery.

Inspired by our previous studies with $\text{Mg}(\text{BH}_4)_2$, 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.

Received: November 27, 2013

Published online: February 12, 2014

Keywords: carboranes · clusters · electrochemistry · magnesium · rechargeable batteries

- [1] H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, *Energy Environ. Sci.* **2013**, *6*, 2265–2279.
- [2] J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Zajicek, Y. Kotani, *Energy Environ. Sci.* **2012**, *5*, 5941–5950.
- [3] M. Matsui, *J. Power Sources* **2011**, *196*, 7048–7055.
- [4] a) T. D. Gregory, R. J. Hoffman, R. C. Winterton, *J. Electrochem. Soc.* **1990**, *137*, 775–780; b) Z. Lu, A. Schechter, M. Moshkovich, D. Aurbach, *J. Electroanal. Chem.* **1999**, *466*, 203–217.
- [5] a) L. P. Lossius, F. Emmenegger, *Electrochim. Acta* **1996**, *41*, 445–447; b) E. Peled, *J. Electrochem. Soc.* **1979**, *126*, 2047–2051.
- [6] a) D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724–727; b) D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer, I. Goldberg, *J. Electrochem. Soc.* **2002**, *149*, A115–A121; c) Y. Guo, F. Zhang, J. Yang, F. Wang, Y. NuLi, S. Hirano, *Energy Environ. Sci.* **2012**, *5*, 9100–9106; d) Z. Zhao-Karger, X. Zhao, O. Fuhr, M. Fichtner, *RSC Adv.* **2013**, *3*, 16330–16335.
- [7] R. Mohtadi, M. Matsui, T. S. Arthur, S.-J. Hwang, *Angew. Chem.* **2012**, *124*, 9918–9921; *Angew. Chem. Int. Ed.* **2012**, *51*, 9780–9783.
- [8] a) Q. S. Zhao, Y. N. NuLi, Y. S. Guo, J. Yang, J. L. Wang, *Electrochim. Acta* **2011**, *56*, 6530–6535; b) J. Muldoon, C. B. Bucur, A. G. Oliver, J. Zajicek, G. D. Allred, W. C. Boggess, *Energy Environ. Sci.* **2013**, *6*, 482–487.
- [9] a) S. Yagi, A. Tanaka, Y. Ichikawa, T. Ichitubo, E. Matsubara, *J. Electrochem. Soc.* **2013**, *160*, C83–C88; b) D. Lv, T. Xu, P. Saha, M. K. Datta, M. L. Gordin, A. Manivannan, P. N. Kumta, D. Wang, *J. Electrochem. Soc.* **2013**, *160*, A351–A355.
- [10] a) H. W. Li, K. Miwa, N. Ohba, T. Fujita, T. Sato, Y. Yan, S. Towata, M. W. Chen, S. Orimo, *Nanotechnology* **2009**, *20*, 204013; b) G. L. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R. C. Bowman, S.-J. Hwang, J.-C. Zhao, *Int. J. Hydrogen Energy* **2009**, *34*, 916–928.
- [11] a) J. H. Morris, H. J. Gysling, D. Reed, *Chem. Rev.* **1985**, *85*, 51–76; b) R. T. Boeré, S. Kacprzak, M. Kessler, C. Knapp, R. Reibau, S. Riedel, T. L. Roemmele, M. Rühle, H. Scherer, S. Weber, *Angew. Chem.* **2011**, *123*, 572–575; *Angew. Chem. Int. Ed.* **2011**, *50*, 549–552.
- [12] Anhydrous $\text{MgB}_{12}\text{H}_{12}$ (**1**) was obtained by treating decaborane ($\text{B}_{10}\text{H}_{14}$) with magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) in diglyme at reflux. $\text{MgB}_{11}\text{H}_{11}$ and $\text{Mg}(\text{B}_{11}\text{H}_{14})_2$ 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.
- [13] L. I. Zakharkin, *Pure Appl. Chem.* **1972**, *29*, 513–526.
- [14] a) W. Clegg, D. A. Brown, S. J. Bryan, K. Wade, *J. Organomet. Chem.* **1987**, *325*, 39–46; b) H. Beall in *Boron Hydride Chemistry* (Ed: E. L. Muetterties), Academic Press, New York, **1975**, pp. 316–317.
- [15] S. Sakamoto, T. Imamoto, K. Yamaguchi, *Org. Lett.* **2001**, *3*, 1793–1795.
- [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.
- [17] a) B. J. Wakefield in *Organomagnesium Methods in Organic Synthesis*, Academic Press, San Diego, **1995**, pp. 4–7; b) K. C.

- Cannon, G. R. Krow in *Handbook of Grignard Reagents* (Eds: G. S. Silverman, P. E. Rakita), Marcel Dekker, New York, **1996**, pp. 271–273.
- [18] All electrochemical experiments were carried out with bulk **2** at a concentration of 100 mg mL⁻¹.
- [19] Y. Guo, F. Zhang, J. Yang, F. Wang, *Electrochem. Commun.* **2012**, *14*, 24–27.
- [20] R. Zhang, X. Yu, K.-W. Nam, C. Ling, T. S. Arthur, W. Song, A. M. Knapp, S. N. Ehrlich, X.-Q. Yang, M. Matsui, *Electrochem. Commun.* **2012**, *14*, 110–113.
- [21] G. Gershinsky, H. D. Yoo, Y. Gofer, D. Aurbach, *Langmuir* **2013**, *29*, 10964–10972.
- [22] D. Aurbach, G. S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, *Adv. Mater.* **2007**, *19*, 4260–4267.
-