Electrochemistry of Magnesium Electrolytes in Ionic Liquids for Secondary Batteries

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Supporting Information

ABSTRACT: The electrochemistry of Mg salts in room-temperature ionic liquids (ILs) was studied using plating/stripping voltammetry to assess the viability of IL solvents for applications in secondary Mg batteries. Borohydride (BH₄⁻), trifluoromethanesulfonate (TfO⁻), and bis(trifluoromethanesulfonyl)imide (Tf₂N⁻) salts of Mg were investigated. Three ILs were considered: l-n-butyl-3-methylimidazolium (BMIM)-Tf₂N, N-methyl-N-propylpiperidinium (PP13)-Tf₂N, and N,N-diethyl-N-methyl(2-methoxyethyl)ammonium (DEME⁺) tetrafluoroborate (BF₄⁻). Salts and ILs were combined to produce binary solutions in which the anions were structurally similar or identical, if possible. Contrary to some prior reports, no salt/IL combination appeared to facilitate reversible Mg plating. In solutions containing BMIM⁺, oxidative activity near 0.8 V vs Mg/Mg²⁺ is likely associated with the BMIM cation, rather than Mg stripping. The absence of voltammetric signatures of Mg plating from ILs with Tf₂N⁻ and BF₄⁻ suggests that strong Mg/anion Coulombic attraction inhibits electrodeposition. Cosolvent additions to Mg(Tf₂N)₂/PP13-Tf₂N were explored but did not result in enhanced plating/stripping activity. The results highlight the need for IL solvents or cosolvent systems that promote Mg²⁺ dissociation.

KEYWORDS: rechargeable Mg battery, deposition and dissolution of simple Mg salts, Mg deposition from ionic-liquid solvents, magnesium electrolytes

1. INTRODUCTION

Magnesium batteries are recognized as promising next-generation energy-storage devices because of their high theoretical capacities and low raw-materials costs.¹,² Monolithic Mg negative electrodes also appear to have a smaller propensity for dendrite formation than metallic Li, making Mg a potentially safer alternative for long-lived secondary batteries.³

A major barrier to viable secondary Mg cells is the absence of Mg-conducting electrolytes that allow reversible, charge-efficient plating and stripping of metallic Mg.⁴ In a seminal paper, Gregory et al. showed that one can electrodeposit Mg reversibly from solutions of Grignard reagents and suggested that the low partial charge on Mg in the Grignard molecule facilitates desolvation of Mg at the interface where plating occurs.⁵ Moreover, it was postulated that simple salts in which the Mg ion has a high charge density [e.g., highly ionic compounds such as MgCl₂ or Mg(ClO₄)₂] are less likely to promote Mg plating due to the strong Coulombic attraction between ions in the formula unit, which prevents dissociation in solution to produce solvated mobile Mg²⁺.⁶

Addition of Al-based Lewis acids to Grignard reagents has resulted in improved oxidative stability, while highly reversible Mg plating is maintained.⁷–⁸ Addition of Lewis acids promotes the formation of ionic Mg-containing Grignard complexes that dissociate readily, increasing ionic conductivity while a low partial charge on Mg is maintained in the complex cation.⁹,¹⁰ In the past few years there has been considerable effort to develop simple Mg-electrolyte syntheses that use simpler, more-cost-effective precursors.¹⁰–¹¹

Recently, solutions of simple Mg salts combined with Al-based Lewis acids were shown to reversibly deposit and dissolve Mg¹⁰,¹¹ Strong Lewis acids enable Mg dissociation when added

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to Mg salt solutions due to their strong electron-withdrawing nature, which presumably overcomes the Coulomb force that prevents the dissociation of anions from Mg$^{2+}$. Boron-based electrolytes that are halogen-free and Grignard-free have also been studied. In addition, there are conflicting reports of reversible plating from magnesium bis-(trifluoromethanesulfonyl)imide$^{11}$ [Mg(Tf$_2$N)$_2$, also called magnesium TFSI] in organic solvents. In all of these studies, solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME) were used. These ethereal solvents exhibit high vapor pressure and high flammability, making them less desirable from a safety standpoint.

Reversible Mg plating has been reported using ether-free mixtures of Grignard reagents and ionic liquids (ILs), although at significantly elevated temperatures. Grignard reagents dissolved in ethereal solvent/IL mixtures (cosolvents) have also been reported to support reversible Mg plating. However, Grignard reagents are highly reactive when exposed to water and pose a number of other safety concerns. Therefore, a Mg electrolyte that does not include Grignard reagents would also be advantageous.

ILs have wide electrochemical stability windows, low vapor pressures, and low flammabilities, making them attractive as replacements for organic solvents like THF and DME. Nevertheless, results from prior studies of the electrochemistry of Mg salts in ILs have not been reproduced consistently. For example, NuLi et al. reported the electrodeposition of Mg from solutions of magnesium trifluoromethanesulfonate [Mg(TfO)$_2$], also called magnesium triflate, in imidazolium-based ILs, but other research groups have had difficulty replicating this finding. Wang et al. reported both Mg plating and stripping from Mg(TfO)$_2$ dissolved in N-methyl-N-propylpiperidinium (PP13)-Tf$_2$N. On the other hand, Cheek et al. reported that Mg could not be plated out of a mixture of Mg(TfO)$_2$ and 1-ethyl-3-methylimidazolium (EMIM$^+$) tetrafluoroborate (BF$_4^-$). Similarly, no Mg plating was observed when Mg(Tf$_2$N)$_2$ was dissolved in the quaternary ammonium IL N,N-diethyl-N-methyl(2-methoxyethyl)ammonium (DEME)-Tf$_2$N. Furthermore, a report on Mg(Tf$_2$N)$_2$ in an N-butyl-N-methylpyrrolidinium-(Tf$_2$N) IL found that while intercalation reactions are possible with a magnesiated V$_2$O$_5$ cathode, it is unclear whether a Mg anode is compatible with this electrolyte. Taken together, these sometimes contradictory observations suggest a need for additional study of the electrochemistry of Mg salts dissolved in ILs.

This paper presents a systematic investigation of how the types of IL anions and cations in IL-solvated solutions (or IL/organic cosolvent solutions) affect the electrochemistry of several Mg salts. The salt/solvent combinations were selected to cover a broad range of chemically distinct IL-based solutions, with some specific compositions included for comparison to previous reports. Commercially available ILs were selected on the basis of their reported ranges of electrochemical stability, those not stable across the desired 0–3 V window vs Mg/Mg$^{2+}$ were excluded. Mg salts were dissolved in the candidate ILs and the electrochemical responses of the resulting solutions were measured at room temperature by cyclic voltammetry. The experimental design was intended to isolate the effect of each IL anion and cation.

Contrary to some previous studies, reversible Mg plating was not observed for any of the electrolytes considered. This observation supports a hypothesis that the high charge densities on Mg$^{2+}$ and anions such as Tf$_2$N$^-$ and BF$_4^-$ lead to strong Coulombic attraction within the Mg salt; this attraction outweighs the energetic benefit provided by solvation of these highly charge-dense ions, limiting the availability of mobile Mg$^{2+}$ and inhibiting electrodeposition. Following a suggestion from a previous study that the addition of polar cosolvents could lower solvation energy, thereby aiding dissociation of Mg$^{2+}$ from Mg salts, experiments were performed in which DME and acetonitrile (ACN) were added to the Mg(Tf$_2$N)$_2$/PP13-Tf$_2$N system. Cyclic voltammetry did not show evidence of reversible Mg plating from either cosolvent mixture. In BMIM-containing electrolytes, redox activity is observed around 0.8 V vs Mg/Mg$^{2+}$, but this appears to arise mostly from redox events correlated with the presence of BMIM$^+$, rather than Mg stripping.

On the basis of the present study, ILs with anions that associate strongly with Mg$^{2+}$ (including Tf$_2$N$^-$ and BF$_4^-$) are likely unsuitable for use in secondary Mg batteries. Development of new IL structures or cosolvent systems that promote dissociation of Mg-containing ions is needed to foster applications of ILs in Mg batteries.

2. EXPERIMENTAL SECTION

2.1. Electrolytes. Structures of the ILs and Mg salts investigated and their relevant physical properties are provided in Tables 1 and 2.

| Table 1. Formulae and Structures of the Ionic Liquids and Mg Salts Tested |
|-----------------|-----------------|
| Ionic Liquids   | Mg salts        |
| BMIM-Tf$_2$N   | Mg(Tf$_2$N)$_2$ |
| PP13-Tf$_2$N   | Mg(TIO)$_2$     |
| DEME-BF$_4$    | Mg(BH$_4$)$_2$  |

| Table 2. Relevant Physical Properties of ILs and Organic Solvents Used |
|-----------------|------------------|-----------------|-----------------|-----------------|
| IL or solvent   | melting point (K) | density (g/cm$^3$) | viscosity (mPa s) | conductivity (mS cm$^{-1}$) |
| BMIM-Tf$_2$N   | 289$^{16}$      | 1.42$^{15}$     | 45$^{15}$       | 3.9$^{13}$       |
| PP13-Tf$_2$N   | 281$^{16}$      | 1.43$^{16}$     | 129$^{16}$      | 1.5$^{15}$       |
| DEME-BF$_4$    | 318$^{18}$      | 1.18$^{18}$     | 1200$^{18}$     | 4.8$^{18}$       |
| DME            | 229$^{19}$      | 0.86$^{19}$     | 0.455$^{19}$    | ~0               |
| ACN            | 254$^{19}$      | 0.79$^{19}$     | 0.369$^{19}$    | ~0               |
Three Mg salts were considered: magnesium borohydride [Mg(BH4)2, 95%, Sigma-Aldrich], Mg(TF2N)2 (98%, Strem Chemicals), and Mg(TiO)2 (97%, Strem Chemicals). These salts were dissolved in the various ILs by stirring with a PTFE-coated magnetic stir bar for 1 h at room temperature. Solvents DME (99.5%, Sigma-Aldrich) and ACN (99.5%, Sigma-Aldrich) were stored over molecular sieves (3 Å, Fisher Scientific) for at least 2 days before use. All microelectrodes were air-dried under a stream of ultrapure argon gas. A standard unstirred three-electrode electrochemical cell was used, in which the reference compartment was connected to the working compartment by a Luggin capillary and the counter compartment was separated from the working compartment by a glass frit. Counter and reference electrodes respectively comprised Mg foil (99%, Goodfellow) and Mg wire (99%, Goodfellow). Exterior surfaces of the Mg electrodes were removed mechanically in the glovebox prior to each experiment, by scraping their surfaces with stainless steel scissors to expose shiny subsurfaces.

For all the solutions tested, the voltage window for voltammetry was initially chosen to range from –1 to 1 V vs Mg/Mg2+. The voltage window was increased by 0.25 V increments separately in the negative or positive directions until reductive or oxidative instability was observed. In each case, the voltammetric response of the Mg salt/IL solution was compared to that of the neat IL, to deduce whether observed redox activity could be attributed to the Mg salt.

3. RESULTS AND DISCUSSION

3.1. Electrolytes Containing TFsI. Figure 1 shows cyclic voltammograms (CVs) of neat BMIM-Tf2N and 10 mM Mg(Tf2N)2 in BMIM-Tf2N on Pt. The observed electrochemical stability window of 4.6 V agrees with prior reports.41 For the 10 mM Mg(Tf2N)2 solution, no appreciable cathodic current was observed between 0 and –1 V vs Mg/Mg2+, indicating that Mg plating is inhibited in the Mg/BMIM/Tf2N system. An increase in cathodic current below –1 V vs Mg/Mg2+ is observed in the CV of the neat IL, as well as in that of the Mg salt/IL solution; this voltammetric signature thus appears to arise from solvent reduction, rather than Mg2+ reduction. An oxidation peak near 0.8 V vs Mg/Mg2+ appears in both the presence and absence of the Mg salt, although it shifts to a lower potential when Mg is present. This peak has been attributed to Mg stripping in the past,26,42 but it has also been observed in previous electrochemical studies using BMIM-BF4,25,29 strongly suggesting that the redox signature arises from BMIM+ oxidation or from oxidation of BMIM+ reaction products or impurities. The height and position of this oxidation peak both remain relatively stable with repeated cycling (see the Supporting Information, Figure S1). Also, as the lower limit of the voltage window was decreased from –1 V vs Mg/Mg2+, the peak height was found to increase dramatically, suggesting that the oxidation peak is coupled to a reduction reaction (or reactions) that occurs below –1 V vs Mg/Mg2+ (see the Supporting Information, Figure S2). Whether or not they illustrate Mg stripping, these data suggest that BMIM-containing ILs are not useful for Mg electrolytes because they exhibit appreciable redox activity in the voltage range where Mg stripping is expected to occur.

Figure 2a shows a CV of neat PP13-Tf2N, which, similar to BMIM-Tf2N, has a wide window of electrochemical stability. The use of PP13+ in this case, along with the absence of redox activity, further supports the hypothesis that the anodic peak observed near 0.8 V vs Mg/Mg2+ in the BMIM-Tf2N voltammetry arises from reactions correlated to the presence of BMIM+. As previously described, NuLi et al. reported reversible Mg plating and stripping from PP13-Tf2N with Mg(TiO)2 as the Mg ion source43 over a narrow window of –0.5 to 0.5 V vs Mg/Mg2+. Figure 2b shows CVs on Pt electrodes for three Mg salts dissolved in PP13-Tf2N across a wider potential range (the figure details the –1 to 1 V vs Mg/Mg2+ range from CVs gathered across –2.25 to 4 V vs Mg/Mg2+). The CV for 10 mM Mg(TiO)2 in PP13-Tf2N shows no evidence of Mg plating or stripping. Since the working electrode for the previous report was a Ag plate40 (and not a Pt microelectrode, as used here), the voltammetry experiments for 1 M Mg(TiO)2 in PP13-Tf2N were repeated with a Ag microelectrode and analyzed in the voltage range from –0.5 to 0.5 V vs Mg/Mg2+. No significant
change in the voltammetric response was detected when the Ag microelectrode was substituted for Pt and the voltage window was narrowed. The CV of 10 mM Mg(Tf2N)2 in PP13-Tf2N shows no redox activity corresponding to Mg plating and stripping, similar to the CV for Mg(TfO)2. The CV for 100 mM Mg(BH4)2 in PP13-Tf2N, much like those of the other Mg salts in PP13-Tf2N, also shows no clear evidence of Mg plating or stripping. (In contrast, the previous observation15 that reversible Mg plating and stripping could be obtained from a solution of Mg(BH4)2 in DME was confirmed.)

The absence of significant Mg redox activity in the Mg(BH4)2/PP13-Tf2N system suggests that Tf2N− may play a role in blocking Mg plating. This hypothesis is supported by the observation that neither PP13-Tf2N nor BMIM-Tf2N supports Mg electrochemistry. One possible explanation for the absence of Mg plating/stripping in the presence of Tf2N− could be the formation of a passivating film on the electrode surface by anion adsorption or reaction (chemical or electrochemical).6 Alternatively, plating could be inhibited due to the failure of dissolved Mg(Tf2N)2 to dissociate.

The limited propensity for dissociation of Mg2+ from Tf2N− has been discussed in several prior computational and experimental reports.1,13,43,44 Note, however, that Kakibe et al. and Yoshimoto et al. have observed reversible Mg plating on Au and Ni with solutions of Grignard reagents in ILs containing Tf2N−.20–22 Therefore, Mg can be reversibly deposited in the presence of Tf2N− if Mg is present in the form of a Grignard complex. These results appear to be consistent with Gregory’s hypothesis that the low partial charge on Mg enables the electrochemical removal of Mg from the Grignard molecule.5 It is possible that Grignard reagents chemically remove a passivation layer that naturally exists on the electrode surface, allowing Mg plating. But when viewed in the light of the independence of the electrode material, the lack of plating in the systems studied here more likely results from strong association of Mg2+ and Tf2N− within dissolved Mg(Tf2N)2 formula units, rather than passivation.

3.1.1. Effect of Cosolvent Addition. In a recent study, Kitada et al. reported the effects of adding diglyme to a mixture of Mg(Tf2N)2 and PP13-Tf2N. They found that CVs of cosolvent systems demonstrated anodic peaks at ~1.3 V vs Mg/Mg2+, possibly corresponding to Mg stripping.33 On the basis of these observations, it was hypothesized that the incorporation into ILs of more polar cosolvents, of which ACN is an extreme example, could lower the solvation energies of the Mg2+ and Tf2N− ions, promoting dissociation of the Mg(Tf2N)2 salt.

The effect of cosolvent polarity was investigated by adding DME (dielectric constant 7.2, dipole moment 1.97 D) or ACN (dielectric constant 36.6, dipole moment 3.92 D) to a Mg(Tf2N)2/PP13-Tf2N solution. The volume ratio (DME or ACN):PP13-Tf2N was 4:1 on a neat-liquid basis, and the Mg2+ concentration in the mixed cosolvent was 100 mM, similar to the previous study.33 Parts a and b of Figure 3 show CVs of Mg(Tf2N)2 in PP13-Tf2N/DME and PP13-Tf2N/ACN on a 50 μm diameter Pt electrode. Measurements were performed with a scan rate of 20 mV s−1 at room temperature. Numbering adjacent to curves indicates the cycle number at which they were gathered.

Figure 2. Cyclic voltammograms of (a) neat PP13-Tf2N and (b) Mg salts in PP13-Tf2N (black) compared to neat PP13-Tf2N (gray), using 50 μm diameter Pt electrodes at room temperature; scan rate 100 mV s−1. Similar voltage windows were used in all cases.

Figure 3. Cyclic voltammograms of (a) 100 mM Mg(Tf2N)2 in PP13-Tf2N/DME and (b) 100 mM Mg(Tf2N)2 in PP13-Tf2N/ACN on a 50 μm diameter Pt electrode. Measurements were performed with a scan rate of 20 mV s−1 at room temperature. Numbering adjacent to curves indicates the cycle number at which they were gathered.
but no change in the voltammetric response was detected. In summary, no evidence of reversible Mg plating and stripping was seen in solutions where DME or ACN cosolvents were added to binary solutions of Mg(Tf2N)2 in PP13-Tf2N.

3.2. Electrolytes Containing Tetrafluoroborate. An IL containing BF4\textsuperscript{−}\ was also studied. Due to the unavailability of Mg(BF4)2, Mg(BH4)2 was used as the Mg salt on the basis of prior reports, reversible Mg plating was not observed for any of these salt/IL combinations. In some cases the disagreement with prior observations arises from different interpretations of the voltammograms, as suggested by more robust control experiments in which the identity of the IL cation was varied, as well as by exploration of wider voltage ranges during voltammetry.

The present results indicate that when evaluating a new Mg-containing IL solution, it is imperative also to evaluate the redox activity associated with the neat IL. It was found that the anodic peak observed at ∼0.8 V vs Mg/Mg\textsuperscript{2+} in the voltammetry of Mg(TfO)2 dissolved in BMIM-BF4\textsubscript{4} previously attributed to Mg stripping, likely originates from redox activity correlated to the presence of BMIM\textsuperscript{+}.

Mg(TfO)2 dissolved in PP13-Tf2N has been reported to exhibit reversible Mg plating, but voltammetry of three Mg salts in PP13-Tf2N did not show evidence of reversible Mg plating in the present investigation. The addition of two organic solvents of varying polarity to Mg(Tf2N)2/PP13-Tf2N also did not give rise to signatures of Mg plating or stripping.

Mg(BH4)2 in DEME-BF4 was also considered, but similar to the other systems, no evidence of Mg plating or stripping was observed. A voltammetric signature that looked qualitatively like a plating/stripping voltammogram could be obtained by constraining the voltammetry, but the magnitudes of the cathodic currents during the downward and upward voltage sweeps were inconsistent with a plating process, and the net anodic charge transfer above 0 V vs Mg/Mg\textsuperscript{2+} far outweighed the Mg solution in Figure 4b is far greater than the charge transferred between −1 and 0 V vs Mg/Mg\textsuperscript{2+}. Thus, the observed anodic current must involve an oxidation process other than Mg stripping, since it is not possible to strip more Mg than is plated. Second, the magnitudes of the currents during the downward sweeps and upward sweeps of voltage—indicated by arrows in Figure 4b—appear to be the reverse of what would be expected in the region where Mg plating should occur. In particular, the cathodic current during the return plating sweep (−1 to 0 V vs Mg/Mg\textsuperscript{2+}) is lower in magnitude than the cathodic current observed during the forward plating sweep (0 to −1 V vs Mg/Mg\textsuperscript{2+}), an atypical characteristic for a plating process. Finally, comparison of the CVs with and without Mg in Figure 4b reveals that both show significant cathodic current in the 0 to −1 V vs Mg/Mg\textsuperscript{2+} range, suggesting that the observed cathodic current likely arises from a reduction event associated with the neat IL that is enhanced by the presence of Mg(BH4)2.

The reduction peak near 0 V vs Mg/Mg\textsuperscript{2+} observed for neat DEME-BF4 in Figure 4a is absent in Figure 4b. Thus, its appearance can be associated with an oxidation event that takes place above 1 V vs Mg/Mg\textsuperscript{2+}.

Since it was confirmed that Mg(BH4)2 allows reversible Mg plating from ethereal solvents such as DME, the apparent absence of Mg plating/stripping in the DEME-BF4/Mg(BH4)2 system suggests that solvent effects are significant. In the DEME-BF4 solvent case, it appears that the anion of the IL can strongly associate with dissociated Mg\textsuperscript{2+} and hinder reversible Mg plating.

4. CONCLUSIONS

Cyclic voltammetry was used to investigate the electrochemistry of electrolytic solutions consisting of various Mg salts [Mg(TfO)2, Mg(Tf2N)2, Mg(BH4)2], IL solvents (BMIM-Tf2N, PP13-Tf2N, DEME-BF4), and organic cosolvents (DME, ACN) on Pt working electrodes. Contrary to some prior reports, reversible Mg plating was not observed for any of these salt/IL combinations. In some cases the disagreement with prior observations arises from different interpretations of the voltammograms, as suggested by more robust control experiments in which the identity of the IL cation was varied, as well as by exploration of wider voltage ranges during voltammetry.

The present results indicate that when evaluating a new Mg-containing IL solution, it is imperative also to evaluate the redox activity associated with the neat IL. It was found that the anodic peak observed at ∼0.8 V vs Mg/Mg\textsuperscript{2+} in the voltammetry of Mg(TfO)2 dissolved in BMIM-BF4 previously attributed to Mg stripping, likely originates from redox activity correlated to the presence of BMIM\textsuperscript{+}.

Mg(TfO)2 dissolved in PP13-Tf2N has been reported to exhibit reversible Mg plating, but voltammetry of three Mg salts in PP13-Tf2N did not show evidence of reversible Mg plating in the present investigation. The addition of two organic solvents of varying polarity to Mg(Tf2N)2/PP13-Tf2N also did not give rise to signatures of Mg plating or stripping.

Mg(BH4)2 in DEME-BF4 was also considered, but similar to the other systems, no evidence of Mg plating or stripping was observed. A voltammetric signature that looked qualitatively like a plating/stripping voltammogram could be obtained by constraining the voltage window, but the magnitudes of the cathodic currents during the downward and upward voltage sweeps were inconsistent with a plating process, and the net anodic charge transfer above 0 V vs Mg/Mg\textsuperscript{2+} far outweighed...
the net cathodic charge transfer below 0 V vs Mg/Mg\textsuperscript{2+}, suggesting an oxidation reaction besides stripping.

Taken together, these findings suggest that the failure of Mg to plate from electrolytes containing Tf\textsubscript{2}N\textsuperscript{−} and BF\textsubscript{4}\textsuperscript{−} owes to the strong Coulombic attraction between these anions and the extremely charge-dense Mg\textsuperscript{2+} cation. The strong association of Tf\textsubscript{2}N\textsuperscript{−} and Mg\textsuperscript{2+} could not be overcome by attempts to lower the ion solvation energies via the addition of high-polarity cosolvents. It therefore seems unlikely that simple Mg salts can be used as the Mg source in IL-based electrolytes for secondary Mg batteries unless new measures are taken to foster dissociation of the Mg salt or lower ion solvation energies significantly. It can be foreseen that a Mg-containing IL cation with lower charge density than Mg\textsuperscript{2+}, or an anion shared by the salt and IL that is more readily solvated by the IL, could enable Mg plating. It is also possible that addition of strong Lewis bases to IL-based solutions could overcome the attraction between ions in simple Mg salts, favoring dissociation and enabling Mg plating from ILs. These approaches are suggested for future development of IL-based Mg electrolytes.

■ ASSOCIATED CONTENT

Supporting Information
Figure S1, cyclic voltammograms of 10 mM Mg(Tf\textsubscript{2}N\textsubscript{2})\textsubscript{2} in BMIM-Tf\textsubscript{2}N showing stability of the peak at \(~0.8 V vs Mg/Mg\textsuperscript{2+} with cycling; Figure S2, cyclic voltammograms of 10 mM Mg(Tf\textsubscript{2}N\textsubscript{2})\textsubscript{2} in BMIM-Tf\textsubscript{2}N showing the impact of the negative voltage limit of the potential window. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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