Conditioning – Free Electrolytes for Magnesium Batteries Using Sulfone – Ether Mixtures with Increased Thermal Stability

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Abstract We report an investigation of electrochemical properties and speciation of electrolytes composed of magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂) and magnesium chloride in sulfone-ether mixtures. The inclusion of sulfones dramatically increased the thermal stability of the electrolytes to 80 °C. The addition of ether was necessary to form an electrochemically active species. Electrochemical reversibility was maintained above 90 % for 50 cycles for equivolume mixtures of butyl sulfone and THF. Sulfolane based solutions demonstrated low reversibilities and mass spectrometry measurements showed the preferential formation of an MgCl⁺ cation over the Mg₂Cl₃⁺ cation. Greater amounts of Mg₂Cl₂⁺ compared to MgCl⁺ is linked with higher performing electrolytes. Spectroscopic measurements showed co-solvation of the active magnesium cation with both solvents.

Increasing demands for higher performing and more sustainable batteries have led to research in beyond lithium-ion battery chemistries. Magnesium metal serves as a viable option as a new anode material due to its widespread abundance, about 1000 times more abundant in the earth’s crust compared to lithium, and its high volumetric capacity (3833 mAh/cm³ vs. 2062 mAh/cm³ for lithium metal). The development of the practical magnesium metal battery requires development of electrolytes with several characteristics including non-corrosiveness with common inactive components, sufficiently wide electrochemical stability, sufficient thermal stability, ability to electrodeposit and dissolve magnesium metal with high efficiency, and ability to facilitate reversible electrochemical behavior at a cathode.¹⁻³

Recently, magnesium electrolyte research has focused almost exclusively on ethereal solvent formulations.⁴⁻⁷ In many electrolyte formulations containing higher molecular weight and more thermally stable ethers such as glymes, irreversibility is observed during cycling from electrolyte decomposition.⁸,⁹ This is hypothesized to be due to the chelating effect of longer chain glymes that leads to decomposition prior to desolvation during charge transfer. This effect is reported in works that identify Mg₂Cl₃⁺ and MgCl⁺ as the active species.⁸,⁹ A few recent reports demonstrated magnesium electrolytes based on sulfones.¹⁰,¹¹ Sulfones are attractive due to their high boiling points and low vapor pressures. Prior studies showed low reversibility in early cycles, and very negative potentials (less than -1 V vs. Mg²⁺/Mg⁰) were required to induce magnesium deposition.¹⁰ Improvement in reversibility was achieved only upon conditioning, or repeated cyclic voltammetry until reversible behavior is achieved.

We herein report that Lewis acid-free Mg(HMDS)₂ – MgCl₂ containing electrolytes based on certain sulfone/tetrahydrofuran (THF) mixtures, in contrast, exhibit magnesium deposition at low underpotentials with reversibilities above 90 % on the first cycle, with much higher thermal stability than the pure THF counterpart. The Mg(HMDS)₂ – MgCl₂ formulation is particularly attractive for its facile preparation from already commercialized salts, but to date this system has shown high electrochemical performance only in THF, and little to no solubility in higher boiling point ethers such as glymes, thus limiting practical application.¹² This electrolyte formulation was reported in glyme/THF mixtures, how-
ever significant magnesium deposition/stripping was not observed. We report here on insights into the sulfone/THF electrolyte solution speciation through NMR and mass spectrometry studies and show that the relative population of Mg$_2$Cl$_3^+$ versus MgCl$^+$ cations is a determining factor in reversible anodic electrochemistry.

Electrolytes were prepared in different solvents (THF, di-$n$-butyl sulfone (BS), and/or sulfolane (SL)) with the salt ratios and magnesium concentration kept constant (Mg(HMDS)$_2$ – 4 MgCl$_2$, 1.25 M Mg). The thermal stability of the electrolytes was measured using TGA.

Figure 1 shows the resulting mass loss curves for electrolytes based on BS/THF mixtures as compared to pure THF. The 30 THF/70 BS (v/v) electrolyte and 50 THF/50 BS (v/v) electrolyte demonstrated thermal stability to 100 °C and 80 °C, respectively. The volatile nature of the pure THF electrolyte is demonstrated as the mass fraction is immediately decreasing; it was impossible to get an accurate starting mass of the THF electrolyte as the solvent was evaporating off at room temperature. The 50 THF/50 SL (v/v) electrolyte was similar to the pure THF electrolyte and had an immediate decrease in mass, however the rate of mass loss was much lower.

Both 50 THF/50 BS and 30 THF/70 BS electrolytes facilitated magnesium electrodeposition at fairly low deposition underpotentials (about -200 mV vs. Mg$^{2+}$/Mg$^0$ reference electrode), as depicted in Figure 2. The voltammogram shows high reversibility was observed for equal volume mixtures of THF and BS. Conversely, the electrolyte based on pure butyl sulfone did not facilitate magnesium electrodeposition. In addition, the 50 THF/50 SL electrolyte showed reductive currents only at very low potentials and little reversibility, suggesting electrolyte decomposition.

![Figure 1: TGA of Mg(HMDS)$_2$ – 4 MgCl$_2$ in THF (light blue), 50 THF/50 BS (blue), and 30 THF/70 BS (green).](image)

![Figure 2: Cyclic voltammograms of Mg(HMDS)$_2$ – 4 MgCl$_2$ at 1.25 M Mg in (a) 50 THF/50 BS, (b) 30 THF/70 BS, (c) BS, (d) 50 THF/50 SL. The voltammogram of (d) was collected at 80 °C as this formulation is solid at room temperature. Data for the first cycle is shown. The working electrode was platinum wire and the reference and counter electrodes were magnesium ribbon. A scan rate of 5 mV/s was used.](image)

Magnesium was electrochemically deposited onto a platinum wire from the three solvent mixtures using a constant potential hold. The SEM/EDS of the deposits (Figure 3) showed that the two butyl sulfone containing electrolytes produced deposits with high magnesium content and low amounts of carbon, sulfur, chlorine, and sili-
con. The magnesium that was deposited from the butyl sulfone containing electrolytes did show some decomposition products, primarily carbon and chlorine. Given the low amounts of sulfur present in the deposit, it is unlikely that the decomposition products are predominantly due to the butyl sulfone species.

The deposit from the sulfolane containing electrolyte had a lower amount of magnesium with higher carbon and chlorine contents along with a spongy morphology as opposed to the dense, spherical morphology of deposits present for the other two electrolytes. This confirms that the lowered reversibility of the sulfolane electrolyte is related to solvent decomposition.

Despite the high reversibility of the 50 THF/50 BS electrolyte, it still has lowered current densities and greater deposition underpotentials as compared to the pure THF electrolyte, as shown in Figure 4a. This is, in part, reflected in the ionic conductivity of the electrolyte, shown in Figure 4b. The addition of butyl sulfone to THF increases the viscosity of the electrolyte and can slow the ion transport in solution. Furthermore, the butyl sulfone has a stronger coordination to the magnesium cation, as discussed later, and therefore may require a stronger driving force for the magnesium ion to shed its solvent shell and electrochemically deposit. It is hypothesized that the greater current density observed in the cyclic voltammogram from the THF-only electrolyte are also attributed to the greater amount of active species, MgCl$^+$. The differences in speciation between the electrolytes are elaborated upon later in the text.

The oxidative stability limit of the 50 THF/50 BS electrolyte we find to be 2.6 V (vs. Mg$^{2+}$/Mg$^0$); this value is nearly identical to the oxidative stability of the electrolyte in pure THF. This value is low but sufficient for cathodes such as sulfur and Mo$_6$S$_8$.

Figure 3: SEM of magnesium deposits from Mg(HMDS)$_2$ - 4 MgCl$_2$ in (a) 50 THF - 50 Butyl Sulfone, (b) 30 THF - 70 Butyl Sulfone, and (c) 50 THF - 50 Butyl Sulfone; and (d) the corresponding EDS data.

Figure 4: Cyclic voltammograms (a) and conductivity measurements (b) of Mg(HMDS)$_2$ - 4 MgCl$_2$ in THF (light blue), 50 THF/50 BS (blue), and 30 THF/70 BS (green). For the voltammetry, the working electrode was platinum wire and the reference and counter electrodes were magnesium ribbon. A scan rate of 5 mV/s was used.

Galvanostatic cycling at 20 and 50 °C of symmetric cells containing the 50 THF/50 BS electrolyte shows that interfacial resistance is fairly stable with repeated deposition and dissolution at either temperature. However, a slight overpotential appears to be necessary for magnesium depo-
position, especially at 50 °C, given the shape of potential profiles. It is hypothesized that this is due to the formation of an adsorbed layer at the magnesium-electrolyte interface.

Galvanostatic cycling of magnesium-copper coin cells was used to more quantitatively measure the reversibility of the electrolyte. Coulombic efficiencies around 92 % were maintained during room temperature cycling (Figure 5b), compared with 95 % measured for the THF only electrolyte. The efficiency for the mixture at 50 °C averaged 2 % less than the efficiency at 20 °C. The exact cause of the non-unity coulombic efficiency is not known, but could be due to trace impurities, trace moisture, and the formation of uneven, high surface area deposits. Trace water can alter the structure of the double layer at the magnesium electrode; this changes the interfacial chemistry and can lead to slow deposition kinetics. Large amounts of magnesium still present on cycled copper electrodes after stripping indicate that these deposits are electronically isolated, thus some of the irreversibility is not correlated with side reactions. The non-uniformity could be related to adsorptive layer formation; this is beyond the scope of this work but is under investigation. We hypothesize that the deposition morphology of the magnesium is the primary cause of the gradual polarization over cycling and related to the non-unity efficiency.

X-ray photoelectron spectroscopy (XPS) was completed on magnesium electrodes after cycling in Cu-Mg cells. Due to limitations of the facility instrumentation, ambient air exposure was unable to be avoided. Decomposition products present on the surface included carbon, sulfur, chlorine, and silicon. The sulfur content was very low in comparison to the other elements, thus it is unlikely that the low efficiencies are primarily due to the decomposition of the sulfone.

Figure 5: (a) Galvanostatic cycling data of Mg(HMDS)2 - 4 MgCl2 in 50 THF/50 BS in a Mg - Cu coin cell, (b) zoom in of early cycling profiles, (c) zoom in of later cycling profiles, and (d) corresponding Coulombic efficiencies. A current of 0.25 mA was applied for 1000 seconds, beginning with a negative current to induce magnesium deposition onto the copper electrode. The upper voltage limit was 1.5 V.

To probe the differences between the sulfolane and butyl sulfone containing electrolytes, ESI-MS and NMR spectroscopy were used to investigate speciation. Cation coordination with both THF and the sulfone is confirmed via proton NMR spectroscopy. The ¹H NMR spectra of the 50 THF/50 BS mixture shows that the protons on the α-carbon of THF and of BS both shift down-field in the presence of the salt, 0.070 and 0.072
ppm respectively. Given that timescale of NMR is slow in comparison with the solvation shell exchange kinetics, $^1$H peak shifts are representative of the average environment of the proton.\textsuperscript{14}

Table 1 summarizes the major cation speciation as identified from the ESI-MS. The ESI-MS for both sulfone electrolyte mixtures showed the most intense peak being an MgCl$^+$ cation solvated by one sulfone molecule and one water molecule. The water molecules are assumed to come from residual moisture within the equipment. Both spectra show an MgCl$^+$ species as the most intense peak, yet full spectral analysis of the butyl sulfone-THF electrolyte shows a ratio of MgCl$^+$ to Mg$_2$Cl$_3^+$ of about 1:1. The sulfolane-THF electrolyte, on the other hand, exhibits a ratio of about 4:1 MgCl$^+$ to Mg$_2$Cl$_3^+$ suggesting that the formation of the magnesium cation dimer at adequate concentration must be required for reversible magnesium deposition. Furthermore, the THF-only electrolyte had a ratio of MgCl$^+$ to Mg$_2$Cl$_3^+$ of 1:3.

The mass spectra for both electrolytes show solvation shells with varying numbers of sulfone molecules, ranging from one to three, however no THF molecules are observable. This, as similarly demonstrated by Xu and Greenbaum for lithium-ion electrolytes, is due to the weaker coordination of the ether oxygen as compared to the sulfone oxygen.\textsuperscript{14} THF molecules are likely stripped from the cation as it enters the mass spectrometer. This gives rise to an appearance of an incomplete solvation shell. Thus the mass spectra cannot give a complete picture as to the coordination of the magnesium cation. Magnesium cations are expected to have 4 or 6 coordination sites.\textsuperscript{15} As each sulfone contains two oxygens that may coordinate the cation, steric constraints are expected to be a contributing factor in the average solvent shell population. As mentioned above, NMR spectroscopy does confirm THF incorporation in the cation solvent shell.

We have developed a conditioning-free, reversible electrolyte for magnesium batteries that is thermally stable up to 80 °C and can be facilely prepared by mixing commercially available materials. Sulfone-THF mixtures greatly increase the operating temperature range of the electrolyte. MgHMDS$_2$-4MgCl$_2$ BS-THF electrolytes support magnesium metal cycling with reversibilities above 90% at 20 °C and 50 °C. Similar formulations based on SL-THF do not facilitate reversible magnesium electrodeposition and dissolution. Through mass spectrometry, it is observed that Mg$_2$Cl$_3^+$ and MgCl$^+$ form in the solutions, and that higher performing electrolytes have a higher magnesium dimer content. Evidence from NMR and mass spectrometry shows that both the sulfones and THF are solvating the magnesium cation. This research suggests that solution speciation is critical to electrochemical activity and that non-ethereal solvents can support highly efficient magnesium metal electrodeposition and dissolu-

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<th>Cationic Species</th>
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<tr>
<td>MgCl$^+$•THF</td>
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A magnesium cation occupies a portion when occupying a partial cation solvation shell.

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**ABBREVIATIONS**
BS, butyl sulfone; CE, Coulombic efficiency; NMR, nuclear magnetic resonance; SEM/EDS, scanning electron microscopy/energy dispersive x-ray spectroscopy; SL, sulfolane; TGA, thermal gravimetric analysis, THF, tetrahydrofuran; XPS, x-ray photoelectron spectroscopy.

**REFERENCES**
