

Improving Magnesium Electrochemistry in Ionic Liquids Through Enhanced Solvation

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Magnesium anode batteries

A magnesium anode battery would be composed of a Mg metal anode, electrolyte with Mg^{2+} ions and Mg^{2+} intercalation material. Scientists and engineers are in pursuit of advanced battery systems capable of providing higher energy densities than Li-ion technologies while being comprised of safer and cheaper materials. Mg batteries have potential to meet such demands.

To realize a working Mg battery more compatible electrolyte media are necessary. Investigating such potential electrolytes is the primary focus of this work.

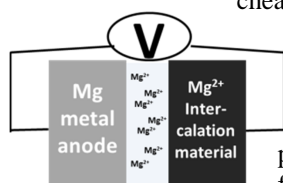


Figure 1: Basic Schematic of idealized Mg secondary battery

Battery electrochemistry in Ionic Liquids

Previously, ionic liquids have been pursued for use in battery systems due to their advantageous properties such as nonvolatility, high intrinsic conductivity, and wide electrochemical windows. Butyl-methylpyrrolidinium bis(trifluoromethylsulfoni)imide (BMPTFSI) was used in this study. The TFSI anion has been the focus of several studies for Li and Li-ion systems as well as a few Mg electrochemical studies giving this report a good means of comparison.^{1,2} The primary interest here is making correlations between electrochemical and solvation properties.

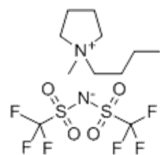
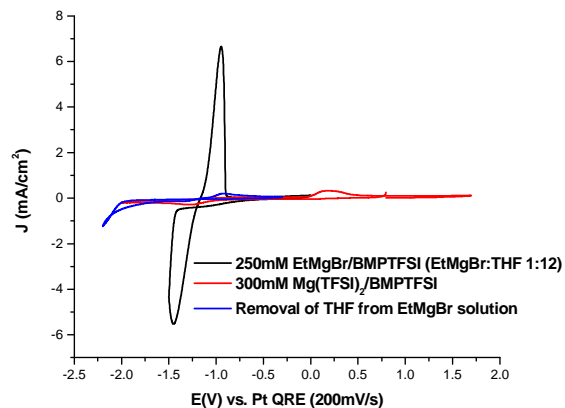


Figure 2: Butyl-methylpyrrolidinium structure

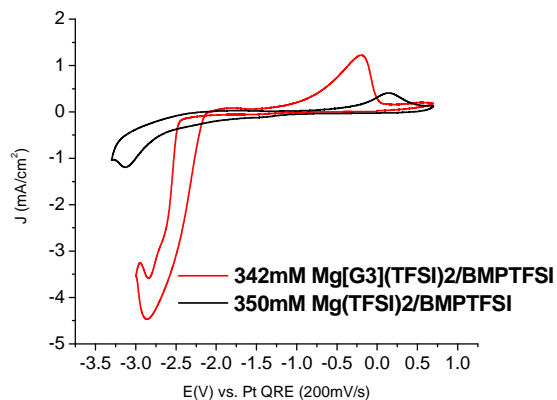
Cyclic Voltammetry (CV) of Mg^{2+} salts: Optimizing the solvation environment.

Reversible electrochemistry of organometallic Mg compounds like Grignard reagents ($RMgX$, $X=Cl, Br, I$) in ethereal solvents like THF has been demonstrated on several occasions before.^{2,3} Unfortunately, these solutions have too narrow an electrochemical window. Why they behave so reversibly is still not fully understood. Figure 3a compares CVs of $EtMgBr/(THF+IL)$ to $Mg(TFSI)_2/IL$. Removal of THF from $EtMgBr$ drastically inhibited reversible deposition and dissolution of Mg. This prompted a more thorough investigation into the solvation environment. Clearly THF provides a more favorable complexation environment for $RMgX$ salts and perhaps aids access to the interface by thinning the crowded cationic build up at negative potentials modeled by Kornyshev et al.⁴ It is thus suggested that the

coordination sphere around the metal center can be improved using appropriate ligand exchange. Oligoether glyme agents have previously been used by Watanabe et al. to improve Li^+ complexation in TFSI ILs.⁵ Glymes were here applied in a similar manner. Figure 3b demonstrates the improvement via substantially increased current responses and lowered overpotential for both Mg deposition and dissolution.



a



b

Figure 3: CVs of a) $EtMgBr$ in THF & BMPTFSI ($EtMgBr:THF$ 1:12) –black, $Mg(TFSI)_2/BMPTFSI$ –red, $EtMgBr/BMPTFSI$ –blue b) $Mg[G3](TFSI)_2/BMPTFSI$ compared against $Mg(TFSI)_2/BMPTFSI$ (G3=Triglyme)

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