

Alkoxy-functionalized Ionic Liquid Electrolytes: Understanding Ionic Coordination of Magnesium Ion Speciation for the Development of Rechargeable Magnesium Batteries

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Magnesium-ion batteries have motivated significant efforts due to its high volumetric capacity (3833 mAh•cm⁻³ for Mg vs. 2050 mAh•cm⁻³ for Li) and much higher abundance than lithium. However, the development of competitive Mg-ion batteries has so far stagnated mainly due to the lack of stable electrolyte. The most reported Mg electrolytes allowing reversible Mg deposition/dissolution are based on the combination of Grignard reagents and strong Lewis acid dissolved in ether solvents. Regardless of the unattractive safety concerns arise from Grignard reagents and ether solvents, all these halide containing electrolytes are corrosive toward typical current collecting metals. To eliminate such safety and corrosion concerns in electrolyte applications generally, ionic liquids have recently been explored as electrolytes for Mg battery systems, but so far with only limited success.

We describe here an effort to better understand Mg-ion speciation in TFSI⁻ based ILs through the design of alkoxy-functionalized cation with different alkoxy substituent. Two type alkoxy-functionalized ILs (one with alkoxy-pyrrolidinium cation, and the other with alkoxy-ammonium cation) showed substantial improvement over the widely studied N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (Pyr₁₄TFSI) for Mg electrodeposition/dissolution. Reversible Mg electrodeposition was achieved in N,N-di-(2-methoxyethyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl) imide (N₀₂TFSI) and N,N,N-tri-(2-(2-methoxyethoxy)ethyl)-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl) imide (N₀₇TFSI) electrolytes. Electrolyte solutions of [Mg(BH₄)₂]_{0.3}[N₀₇TFSI]_{0.7} have been shown to allow the reversible cycling of a coin cell containing a Mg metal anode, a V₂O₅ cathode, and Al current collectors with a reversible capacity of 101 mAh/g at first cycle and 92.5 mAh/g after 10 cycles. And for the first time, comparison of Raman spectroscopy and electrochemical results between different IL electrolytes suggested that coordination sphere of Mg⁺ may play key role in Mg reversible deposition/dissolution while previous studies mainly focus on the coordination sphere of Mg²⁺.

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References

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