

Investigation on the electrolytes containing Grignard reagents and allyl-functionalized ionic liquids for magnesium batteries

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Recently, the demands for safe and cost-effective batteries have been increasing for applications to medium- and large-scale energy storages such as energy storage systems (ESS) and electric vehicles (EV). In this regard, rechargeable Mg batteries have been considered as one of the most viable candidates, since magnesium is inherently safe and abundant in the earth's crust. Furthermore, Mg metal possesses a high gravimetric (2,205 A h kg⁻¹) and volumetric (3,833 A h L⁻¹) capacities with a low reduction potential (-2.372 V vs. SHE). However, there are still limitations for magnesium to be used as an anode material. One of major issues is the formation of passivation layers on Mg metal surface in most protic solvents. Because these layers are non-permeable for Mg²⁺ ions, it is important to develop Mg metal-compatible electrolytes. Grignard reagents (RMgX, R=alkyl or aryl, X=halides) have been known for the reversible Mg deposition-stripping with the high coulombic efficiency (> 99%) since the 1920s. However, this solution shows too low oxidative stability of less than 1 V (vs. Mg) to be used as practical electrolytes for batteries. Many researchers have attempted to widen the electrochemical stability windows of Grignard reagents (up to ~ 3 V) mostly by adding strong acidic salts such as organohaloaluminates or organoborates.^[1,2] For instance, Aurbach *et al.* developed famous APC solutions with high oxidative stability up to ~ 3 V by adding AlCl₃ (Lewis acid) into PhMgCl (Lewis base) in the molar ratio of 2 : 1 dissolved in THF or DME.^[2] In addition, the substitution of R groups in Grignard reagents with alkoxy or amido groups also enhanced the oxidative stability.^[3,4]

In this study, we applied ionic liquids to enhance the electrolytic properties including electrochemical stability and conductivity of phenylmagnesium chloride (PhMgCl) and ethylmagnesium chloride (EtMgCl). Especially, we utilized allyl or butyl functionalized pyrrolidinium based ionic liquids and characterized the electrolytic properties through various electrochemical tools. Interestingly, remarkable increase in the anodic stability of Grignard reagents were observed in the equimolar solutions of PhMgCl and ionic liquids. This solution was analyzed by ¹H NMR spectra to uncover the reaction mechanism and the charge-transport species. We also successfully applied these electrolytes to rechargeable Mg batteries composed of Mo₆S₈ cathodes and Mg anodes.

References:

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