

Electrochemistry of Magnesium in Mixed Electrolytes Consisting of Organic Solvents and Ammonium-Based Ionic Liquids

Yuu KANG^{a*}, Atsushi KITADA^{ac*}, Yoshiharu UCHIMOTO^{bc*}, and Kuniaki MURASE^{ac*}

^a Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

^b Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

^c JST-CREST, Kawaguchi, Saitama 332-0012, Japan

Magnesium (Mg) is an attractive candidate for anode materials for post lithium-ion secondary batteries because of its high energy density, high negative reduction potential and natural abundance. However, upon exposure to oxygen, humidity and polar organic solvents, Mg develops blocking layer that inhibits any electrochemical reactions with Mg. Therefore it is challenging to find electrolytes which do not develop surface films on Mg electrodes. Conner's group reported Mg deposition in ethereal solutions where MgBr₂ was dissolved [1]. Liebenow showed the reversibility of Mg deposition and dissolution in ethereal solutions of alkylmagnesium halide (R-MgX, where R = alkyl, aryl groups; X = Cl, Br) [2]. Yoshimoto's group demonstrated reversible deposition and dissolution process of Mg with high current density in the mixed electrolyte of Grignard reagent and an ionic liquid (IL) (*N,N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)-ammonium bis[(trifluoromethyl)sulfonyl]amide) (DEME-TFSA) [3]. Current density obtained for this mixed electrolyte shows ten times higher than that for the pure Grignard reagent. In addition, mixing with non-volatile IL would give safer electrolyte than other ethereous ones. However, such mixed electrolytes have been reported only a few. Thus, other combination of various organic solvents and ammonium-based ILs should be investigated. In this study, we used the mixture of EtMgBr / THF (Grignard reagent) and trimethyl-*N*-hexylammonium bis[(trifluoromethyl)sulfonyl]amide (*i.e.* TMHA-TFSA).

Potential difference was measured between two Mg rod electrodes, Mg in mixed electrolyte and Mg in a pure Grignard reagent (0.95 M EtMgBr / THF). For cyclic voltammetry, a Cu sheet was used as working electrode and Mg rod was used as counter electrode. The water contents of electrolytes were 200~300 ppm. All the experiments were conducted in an Ar-filled glove box (H₂O, O₂ < 1 ppm).

Figure 1 shows the open circuit potentials of Mg electrodes immersed in the mixed electrolytes consisting of 0, 25, 50, and 75 vol% TMHA-TFSA with EtMgBr / THF. The potential became more positive as the IL ratio increased, probably because Mg²⁺ was coordinated by TFSA anion.

Figure 2 shows the cyclic voltammogram (CV) for Cu electrode in the mixed electrolyte with the scan rate of 20 mV s⁻¹. Since Mg electrode potential depends on the mix ratio of IL, we used Mg / EtMgBr in THF reference electrode as potential standard. Similar to the case of DEME-TFSA, the mixed electrolyte of the Grignard reagent and TMHA-TFSA also exhibited reversible deposition/dissolution with approximately ten times as much current density as that obtained for pure EtMgBr / THF. Such very large increase in current density indicates that the IL works as a supporting electrolyte. The largest current density of three electrolytes was obtained in 25 vol% mixed electrolyte (the molar ratio of EtMgBr and TMHA-TFSA is 1 : 1). We suggest that the increased

viscosity by mixing IL made it difficult for Mg²⁺ ions to move in the electrolyte. The overpotential estimated at 10th cycle was 68 mV for TMHA-TFSA 0 vol%, 94 mV for 25 vol% (1 : 1 by mol), 170 mV for 50 vol% (1 : 3 by mol) and 180 mV for 75 vol% (1 : 9 by mol), respectively. Here, overpotentials of Mg electrodeposition increased with the IL ratio, which may depend on their viscosities.

[1] J. H. Conner, W. E. G. Reid, and B. Wood, *J. Electrochem. Soc.*, **104**, 38 (1957).

[2] C. Liebenow, *J. Appl. Electrochem.*, **27**, 221 (1997).

[3] N. Yoshimoto, M. Matsumoto, M. Egashira, and M. Morita, *J. Power Sources*, **195**, 2096 (2010).

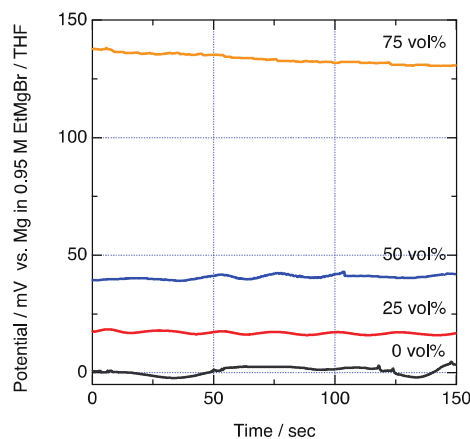


Figure 1. Open circuit potentials of Mg electrode immersed in the mixed electrolyte (consisting of 0, 25, 50, 75 vol% TMHA-TFSA in EtMgBr / THF) vs. Mg in 0.95 M EtMgBr / THF.

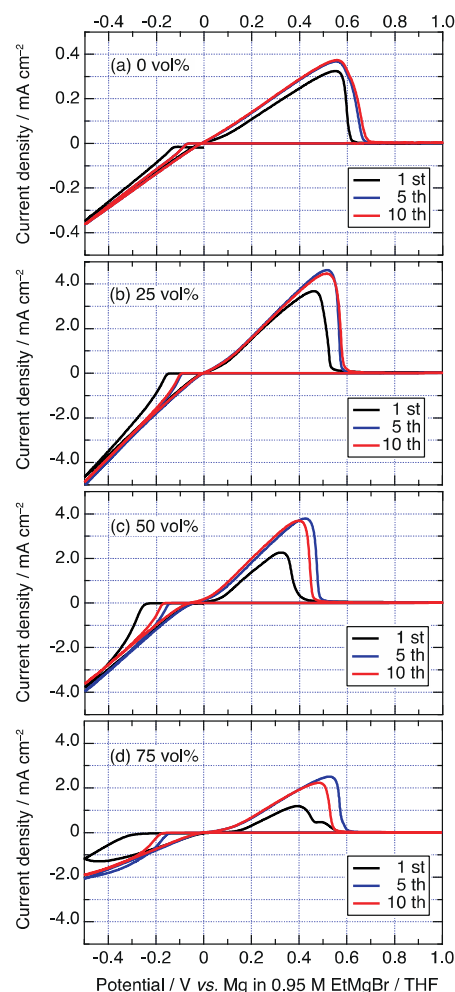


Figure 2. CV for Cu electrode measured in (a) a pure Grignard reagent (0.95 M EtMgBr / THF), (b) a mixture with 25 vol% TMHA-TFSA, (c) 50 vol% and (d) 75 vol%.