

The effect of cyclic ethers on Mg plating/stripping reaction in ionic liquid electrolytes

Fumihiro Sagane^a, Kenta Ogi^a, Akinori Konno^a, Kiyoshi Kanamura^b

^a Department of Electronics and Materials Science, Graduate School of Engineering, Shizuoka University, 3-5-1, Johoku, Naka-ku, Hamamatsu, Shizuoka, 432-8011, Japan

^b Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1, Minamiosawa, Hachioji, Tokyo, 192-0397, Japan

E-mail: sagane.fumihiro@shizuoka.ac.jp

Magnesium metal batteries are expected as the post lithium-ion batteries, due to Mg metal's high capacity and relatively low electrode potential. In order to commercialize the Mg secondary batteries, the smooth Mg plating/stripping reaction must be achieved. Although the reversible Mg plating/stripping reactions have been reported in glyme based electrolytes containing $\text{Mg}(\text{N}(\text{CF}_3\text{O}_2)_2)_2$ ($\text{Mg}(\text{TFSA})_2$)[1], the coulombic efficiency was less than 10 % and the large overpotential was needed, especially for Mg stripping. The large overpotential was also needed for positive electrode materials. In order to decrease the overpotential, high temperature operation is favorable. Although ionic liquid solutions are major candidates for high temperature operation because of their non-combustibility and large electrochemical window, Mg plating in ionic liquid is difficult. So far, the authors succeeded the reversible Mg plating/stripping reaction in $\text{Mg}(\text{TFSA})_2/\text{THF}$ containing crown ether[2]. In the presentation, the effect of crown ether additives on the ionic liquid solution is discussed.

Figure 1 shows the cyclic voltammogram of Pt electrode in $\text{Mg}(\text{TFSA})_2:\text{PP}_{13}\text{TFSA} = 1:5$ with/without 18-crown-6 (18C6) equimolar to Mg^{2+} at 353 K. In 18C6-free solution, any clear reduction or oxidation current did not appear. On the other hand, ionic liquids with 18C6 showed the reduction current from -0.5 V (vs. Mg^{2+}/Mg) and the corresponding oxidation current, indicating that the Mg plating/stripping reaction took place by 18C6 addition. In addition, the overpotential for Mg stripping was hardly seen due to the high temperature operation. Moreover, the disappearance of the ion pair formation between Mg^{2+} and TFSA^- was confirmed from Raman spectra. From the results, it was indicated the coordination between Mg^{2+} and 18C6 was maintained in ionic liquid solutions and realized the electrochemical Mg plating.

The thermogravimetric analysis was also investigated. Although 18C6 thermally decomposed around at 433 K, the 18C6 contained ionic liquid was stable up to 623 K. The result means that the coordination with Mg^{2+} stabilized the 18C6. In other words, the complex behaves like "solvating ionic liquid", reported in glyme based concentrated solutions. From the results, it is concluded that the crown ether contained ionic liquid will be the attractive candidate as the electrolyte solutions for Mg batteries with high voltage and low overvoltage.

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References:

- [1] T.Fukutsuka et.al., *Chem.Lett.*, **43** (2014) 1788
- [2] F.Sagane et.al., *Electrochemistry* **84** (2016) 76

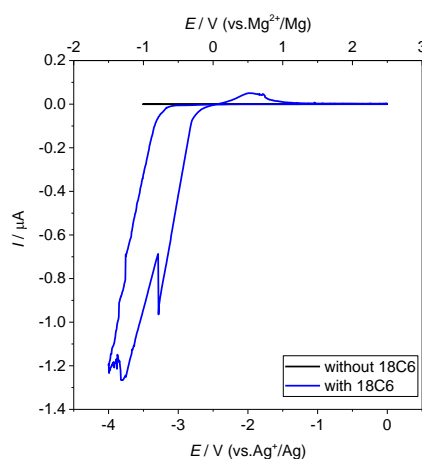


Fig.1 Cyclic voltammograms of Pt in ionic liquid with/without 18C6.