

## Electrochemical Deposition and Dissolution of Magnesium Metal in Various Ether-based Electrolytes

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### Introduction:

Recently, higher-energy-density rechargeable batteries beyond lithium-ion batteries are required for electric vehicles or energy storage systems of renewable energies. There are some candidates for the rechargeable batteries. Among them, rechargeable magnesium batteries have attracted much attention.

Magnesium metal shows a low standard electrode potential of - 2.37 V (vs. NHE) and large theoretical volumetric capacity as much as 3839 mAh cm<sup>-3</sup>. Therefore, rechargeable magnesium batteries using magnesium metal as a negative electrode have been extensively studied. The charge and discharge reactions of a magnesium negative electrode correspond to the deposition and dissolution of magnesium metal. However, the reversible magnesium metal deposition and dissolution at ambient temperature is not easy, since fresh magnesium metal shows high reactivity with water, oxygen, and most protic/aprotic solvents, resulting in the formation of stable passivation films on its surface [1]. After the formation of passivation films, the deposition of magnesium was suppressed and the dissolution of magnesium metal needs high over potential. So far, Grignard reagent or organic-magnesium compounds based electrolytes have been used to prevent the formation of passivation films [2]. However, these compounds show high reactivity and care should be taken when handling. Therefore, we have focused on the fabrication of new electrolyte systems without organic magnesium compounds and reported that reversible deposition and dissolution of magnesium metal proceeded in the MgBr<sub>2</sub>/2-methyltetrahydrofuran (2-MeTHF) and MgBr<sub>2</sub>/*n*-butyl methyl ether (*n*-BME) [3]. However, these solvents show low boiling point below 80 °C and higher boiling point is preferable for the improvement in safety.

In this study, we focused on the various glymes with higher boiling point and the deposition and dissolution behaviors of magnesium metal in glyme-based solutions were investigated.

### Experimental:

A three-electrode cell was used for electrochemical measurements. Platinum plate was used as a working electrode and magnesium wires were used as a counter and a quasi-reference electrode. Unless otherwise stated, potential is referred to quasi-Mg/Mg<sup>2+</sup>. Solvents used were glyme (bp: 85 °C), diglyme (bp: 162 °C), triethylene glycol dimethyl ether (triglyme, bp: 216 °C), and tetraglyme (bp: 275 °C). MgCl<sub>2</sub> was used as a magnesium salt and AlCl<sub>3</sub> was used as an additive. The concentration of MgCl<sub>2</sub> and AlCl<sub>3</sub> was both 0.5 mol dm<sup>-3</sup>. Cyclic voltammetry was carried out between - 1.0 and 2.0 V at a scan rate of 1.0 mV s<sup>-1</sup>. Potentiostatic measurement was carried out at - 1.5 V for 2 h. X-ray diffraction (XRD)

measurement, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were conducted for the characterization of deposits on the platinum electrode. All operations and electrochemical measurements were carried out in Ar-filled glove box.

### Results and discussion:

Figure 1 shows cyclic voltammograms measured in triglyme-based solution. Reduction and corresponding oxidation currents were observed. Deposits on the Pt electrode after potentiostatic measurement were identified as magnesium metal by XRD and EDX, and SEM image confirmed that they were non-dendritic. Moreover, potential window at positive potential of this solution was over 3 V and higher than that of MgBr<sub>2</sub>-based solutions which we have reported. Thus, we clarified that reversible deposition and dissolution of magnesium metal occurred in this thermally and electrochemically stable solution. We found that other glyme-based solution act as the electrolyte solution for the reversible magnesium deposition and dissolution and the results will be reported at the conference.

### Acknowledgement:

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### Reference:

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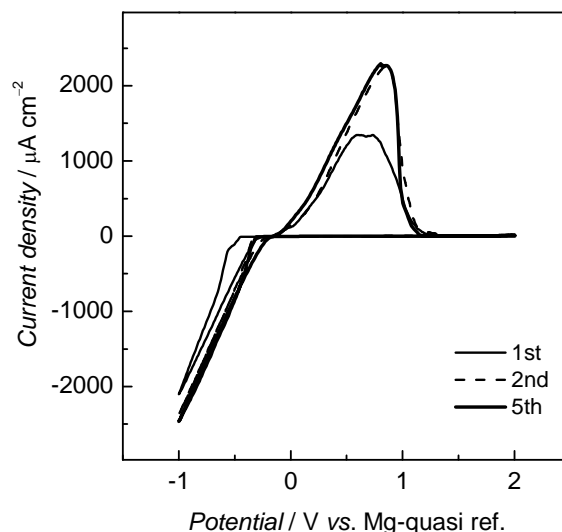


Fig. 1. Cyclic voltammograms of platinum electrode in 0.5 mol dm<sup>-3</sup> MgCl<sub>2</sub> + 0.5 mol dm<sup>-3</sup> AlCl<sub>3</sub>/triglyme. Scan rate: 1.0 mV s<sup>-1</sup>