

Electrochemical Quartz Crystal Microbalance  
Measurements of Lithium-Aluminum Alloy in  
a Glyme-Lithium Salt Molten Complex

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## INTRODUCTION

The equimolar mixtures of lithium salt and glyme ( $\text{CH}_3\text{-O-(CH}_2\text{-CH}_2\text{-O)}_n\text{-CH}_3$ ) exist in the liquid state at ambient temperature.<sup>1,2</sup> They show such ionic liquid-like characteristics as low vapor pressure and wide electrochemical stability and are classified as solvate ionic liquids.<sup>1-5</sup> Owing to their high oxidation resistance and low solubility of  $\text{Li}_2\text{S}_x$ , it is possible to use the glyme-lithium salt molten complexes as the electrolytes of lithium secondary batteries with a sulfur positive electrode in addition to various transition metal oxide positive electrodes.<sup>5-7</sup>

The electrochemical quartz crystal microbalance (EQCM) is often used for the *in-situ* monitoring of the electrode mass. Moreover the change in the viscosity ( $\eta$ ) and density ( $\rho$ ) of the electrolyte near the electrode can be estimated using an impedance technique EQCM (passive, EQCM-A).<sup>8,9</sup> We have already reported that the drastic changes in the viscosity of the equimolar mixture of lithium bis(trifluoromethylsulfonyl)amide (LiTFSA) and triglyme (G3,  $n=3$ ) were observed during deposition and dissolution of lithium metal using an EQCM-A.<sup>10</sup> However, the quantitative analysis was difficult probably due to the dendritic growth of lithium and/or the formation of some surface film. In this study, EQCM measurements were attempted for a lithium-aluminum alloy electrode, which is expected to work without the dendritic deposition of Li metal.

## EXPERIMENTAL

G3 and LiTFSA were mixed in the equimolar ratio and stirred to give homogeneous liquid. EQCM measurements were conducted using an impedance technique EQCM system (QCA922, SEIKO EG&G Co., Ltd.) with a potentiogalvanostat (HZ-3000, Hokuto Denko Co., Ltd.). An AT-cut quartz crystal coated with Al (9.12 MHz,  $0.196\text{ cm}^2$ ) was used as a working electrode. Li foil was used as a reference and counter electrode. The measurements were conducted in a thermostatic chamber at 298 K with an original air-tight cell.

## RESULTS AND DISCUSSION

Figure 1a shows the potential curves during dope and undope of Li into/from an Al coated quartz crystal electrode. After the large potential drop observed in the initial stage of doping, the electrode potential showed a plateau approximately at 0.22 V vs. Li/Li(I), which is attributable to the two-phase coexisting region of  $\alpha+\beta$  Li-

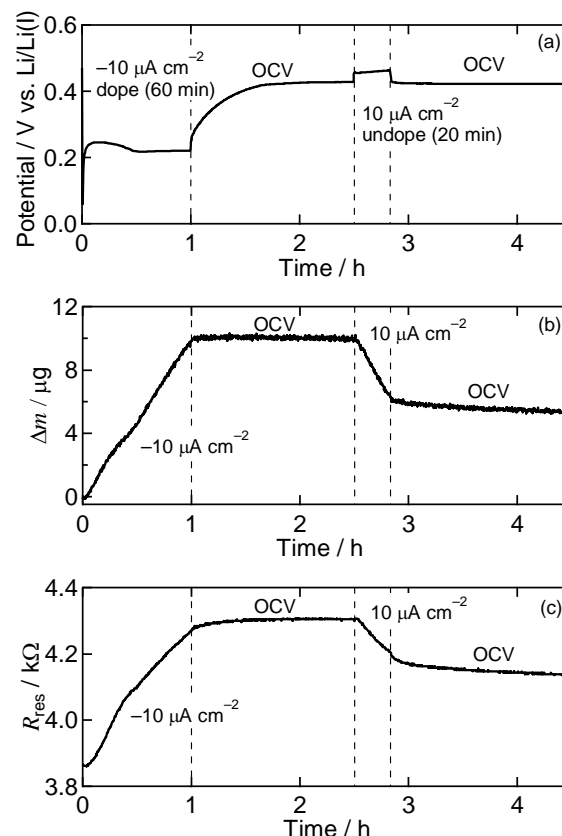
Al alloy. The electrode mass increased and decreased with reductive and oxidative currents (Fig. 1b). However, the observed mass changes were larger than those estimated from the electric charges. The resonance resistance,  $R_{\text{res}}$ , which relates to the product of the viscosity and density of the electrolyte, changed with the dope and undope processes (Fig. 1c). However, the changes in the resonance resistance were inconsistent with the expected changes in the concentration of lithium salt, suggesting the resonance resistance is affected not only by the viscosity and density of the electrolyte near the electrode but also by the physical properties of the anode material on the quartz crystal.

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**Figure 1** (a) Potential curve, (b) the mass change of an Al electrode, and (c) the change in  $R_{\text{res}}$  during the galvanostatic dope and undope of Li in the equimolar mixture of LiTFSA and G3 at 298 K.