A Thesis for the Degree of Ph.D. in Engineering

Electrodeposition of Cadmium and Selenium in 1-Butyl-1-methylpyrroolidinium Bis(trifluoromethylsulfonyl)amide Ionic Liquid

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Thesis Abstract

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Aprotic room-temperature ionic liquids (RTILs) have gained significant attention as a medium for electrodeposition of metals and alloys due to their several attractive properties. Among aprotic RTILs, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) is one of the promising RTILs for electrodeposition of a wide variety of metals. However, the mechanism of electrodeposition of metals in BMPTFSA has not been revealed in depth. In this study, electrodeposition of cadmium (Cd) and selenium (Se) has been investigated in BMPTFSA with and without the presence of excess chloride.

In chapter 1, the backgrounds of electrodeposition, ionic liquids and electrodeposition of metals and alloys in ionic liquids are introduced briefly.

Chapter 2 explains the general experimental techniques of the present work.

Chapter 3 deals with electrodeposition of cadmium in BMPTFSA. The divalent Cd(II) in BMPTFSA was found to be coordinated by three TFSA⁻ and probably exist as [Cd(TFSA)₃]⁻. Electrochemical reaction of Cd(II)/Cd on a GC electrode was an electrochemically irreversible process, probably involving 2 one-electron transfer steps. The nucleation process and morphology of the electrodeposits were found to be affected by the applied potential under diffusion-controlled region, suggesting the influence of the potential on the electric double layer structure due to the difference in accumulation of cations led to the change in surface processes.

Chapter 4 describes the electrochemical behavior of Se(IV) species in BMPTFSA in the absence and presence of excess chloride. The electrodeposition of metallic Se was possible in BMPTFSA in both absence and presence of excess chloride. SeCl₄ was found to be dissolved in the RTIL with excess Cl⁻ by forming [SeCl₆]²⁻. Morphology and crystal structure of Se deposits were found to be related with the temperature. Reduction of Se to Se(–II) was confirmed at the potential more negative than the reduction of [SeCl₆]²⁻. However, proportionation reaction of Se(–II) and [SeCl₆]²⁻ led to deposition of Se.

Chapter 5 is concerned with electrochemical behavior of Cd(II) species in BMPTFSA in the presence of excess chloride. Cyclic voltammograms of [CdCl₄]²⁻ showed an unusual electrochemical behavior, regardless of electrode materials and ionic liquids, probably related to the adsorption of BMP⁺ on the electrode surface. The possibility of electrodeposition of CdSe alloy was also examined in BMPTFSA containing both [CdCl₄]²⁻ and [SeCl₆]²⁻.

Chapter 6 summarizes the results obtained in this study and describes the perspectives of electrodeposition of metals and alloys using BMPTFSA.