Electrodeposition of Zinc from Lewis Basic 1-Ethyl-3-Methylimidazolium Bromide – Zinc Bromide Molten Salt

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INTRODUCTION

The electrodeposition of zinc from Lewis acidic melts like EMIC-$AlCl_3$ (40:60 mol%)-$ZnCl_2$ and EMIC-$ZnCl_2$ (50:50 mol%) have been studied. It is said that the zinc ion species in the basic melt (melt containing less than 33.3 mol% $ZnCl_2$) such as $ZnCl_4^{2-}$ is not reduced to zinc metal because of the reduction of EMI^+ cation. However we succeeded to obtain the zinc metal from Lewis basic 1-ethyl-3-methylimidazolium bromide (abbreviated EMIB) - zinc bromide molten salt. The addition of ethylene glycol (abbreviated EG) and glycerin (abbreviated G) improved the smoothness and color of the deposits and also increased the cathodic current efficiency at high current density. In this paper, the electrochemical behavior of zinc from Lewis basic EMIB-$ZnBr_2$ melt and the effect of the addition of EG and G are reported.

EXPERIMENT

The melts used in this study were prepared from EMIB, $ZnBr_2$, ethylene glycol, and glycerin. Before use, EMIB was dried at 353 K under vacuum using a rotary oil pump for 259.2 ks, and $ZnBr_2$ was dried for 18 ks at 453 K in air. EG and G were dehydrated by molecular sieve. EMIB and $ZnBr_2$ were weighed and heated up to 393 K and furthermore dehydrated under vacuum for 86.4 ks. Zinc was electrodeposited from EMIB-$ZnBr_2$ with and without EG and G using copper cathode and zinc anode with constant current density (50 - 300 Am^{-2}) at 393 K. The charge passed was 2.5×10^5 Cm^{-2} of the cathode substrate. The cathodic current efficiency was calculated from the mass gain of the cathode. The electrochemical behavior of zinc ion was studied by cyclic voltammetry.

RESULTS

Figure 1 shows the cyclic voltammograms on the copper substrate in the EMIB-$ZnBr_2$ (80:20 mol%) and the EMIB-$ZnBr_2$-EG (45:10:45 mol%) at 393 K. The cyclic voltammogram in the EMIB-$ZnBr_2$ shows that the reduction of Zn(II) to zinc metal occurs at the potential of -0.15 V. A current loop suggesting an overpotential-driven nucleation process is observed after reversal of the forward scan. Chronoamperometry experiments were carried out to investigate the zinc nucleation / growth process. The results showed the electrodeposition of zinc on copper in EMIB-$ZnBr_2$ involves a three-dimensional progressive nucleation / growth process. On the other hand, the cyclic voltammogram of the EG-added melt shows no current loop. Furthermore, the reduction of Zn(II) to Zn occurs at the potential of near 0 V and reduction current is increased. Therefore, it was found that the addition of EG enables the electrolysis at high current density.

The cathodic current efficiencies of the electrodeposition of zinc from the EMIB-$ZnBr_2$ (80:20 mol%) were 98% and 63% at the current densities of 50 and 250 Am^{-2}, respectively. In EG-added melts such as EMIB-$ZnBr_2$-EG (19:5:76 mol%), the cathodic current efficiency was 100% even at 300 Am^{-2} and metallic-colored deposits were obtained. In the case of the addition of G, the same effect on the current efficiency was found.

The surface morphology of the specimens electrodeposited from EG- or G-added melts was superior to those of the deposits from non-added melt.

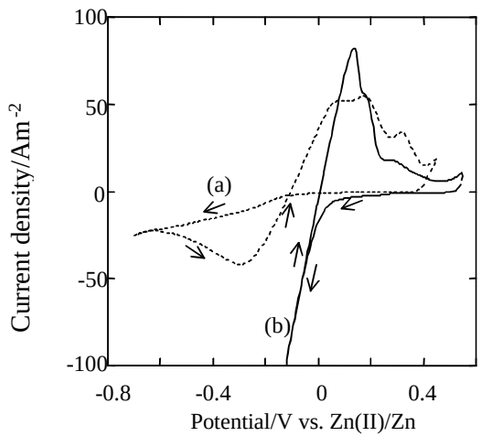

Fig. 1 Cyclic voltammpgrams on the Cu substrate in (a) EMIB-$ZnBr_2$ (80:20 mol%) and in (b) EMIB-$ZnBr_2$-EG (45:10:45 mol%) at 393K. Scan rate was 0.05 Vs^{-1}.