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Effects of coumarin and saccharin on electrodeposition of Ni from a hydrophobic ionic liquid

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ABSTRACT

The effects of additives, coumarin and saccharin, on electrodeposition of nickel were investigated in a hydrophobic room-temperature ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) containing $Ni(TFSA)_2$. Although the UV-vis spectra showed that the coordination environment of Ni(II) was not affected by addition of coumarin or saccharin, the overpotentials for the Ni(II)/Ni reduction increased and the current density decreased. The diffusion coefficients of the Ni(II) species in the presence of both additives were estimated to be close to that in the base electrolyte from the chronoamperometric results. The nucleation/growth model of Ni was changed from the instantaneous type to the progressive one after addition of coumarin or saccharin. The effects of these two additives on the morphology of the Ni deposits in $Ni(TFSA)_2$/BMPTFSA were also characterized.

1. Introduction

Morphology of metallic materials is strongly influences their physical and chemical properties. It has to be taken into account and mastered as well [1]. Electrodeposition has received considerable attention, since it is a powerful method for fabricating metallic materials with controlled morphology and feasible economically [2,3]. Currently widely used electrolytes are the aqueous and organic solutions. A common problem in aqueous solution is the cathode hydrogen evolution reaction, resulting in low current efficiency and defective structure in the deposit [4]. Due to the poor thermal stability and toxicity, organic electrolyte is considered to be unfriendly to the environment.

Room-temperature aprotic ionic liquids provide a possible alternative in many commercial applications since they have wider electrochemical potential window, higher thermal stability and negligibly low vapor pressure compared with the aqueous or organic solutions [5,6]. Moreover, the ionic liquids consisting of bis(trifluoromethylsulfonyl)amide ($TFSA^-$) and 1-butyl-1-methylpyrrolidinium (BMP^+) are expected to be favorable for practical use due to the hydrophobicity of the anion, low melting point and high cathodic stability of the cation [7]. Electrodeposition of several metals from BMPTFSA has been reported [8–14].

It has been demonstrated that additives, even at a small concentration, have more of an influence on deposit properties than any other plating variables [15]. When they are used under control, organic additives can change the morphology and chemical-physical properties of the deposits [16]. Much interest in the electrodeposition of Ni and its alloys is due to their commercial applications in decorative, functional, and electroforming industries [17]. There are a few papers which have addressed the effects of additives on the electrodeposied Ni in the ionic liquids. Abbott and his co-workers [18] have reported that the morphology of Ni deposits can be changed after addition ethylenediamine (en) or acetylacetonate (acac) into either a urea or ethylene glycol/choline chloride based ionic liquids. Yang [19] also found the Ni coatings can be tailored by addition of nicotinic acid (NA) into ChCl/urea mixture probably due to complexation and adsorption of the additive. Addition of acetonitrile [20] and acetone [21] into $Ni(TFSA)_2$/BMPTFSA resulted in a decrease in the overpotential for the electron transfer of Ni(II)/Ni, and the morphology of the Ni deposit was improved.

It is well-known that coumarin [22–27] and saccharin [2,3,15,16,28–31] are commonly used in the Ni aqueous plating bath to improve the morphology of deposits. It is usually assumed that these two additives act as inhibitors during the electrodeposited process [15,31]. However, few papers have addressed the effects of these two additives on electrodeposition of metals in the ionic liquids. Fukui et. al [32] reported that addition of coumarin made the deposition potential of Co shift to the positive side, which is in contrast with that in the aqueous solution, and resulted in a change in the surface morphology although the coordination

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environment of Co(II) was not affected. In the present study, the effects of the additives, coumarin and saccharin, on the electrochemical behavior of Ni electrodeposition have been investigated in BMPTFSA.

2. Experimental

BMPTFSA and $Ni(TFSA)_2$ were prepared as described in the literature [33]. Saccharin (Tokyo Chemical Industry) and coumarin (Tokyo Chemical Industry) were dried under vaccum at 120 °C for 12 h before use. A certain amount of the additive, saccharin or coumarin, was dissolved into the prepared $Ni(TFSA)_2$/BMPTFSA. The mixture was stirred in the glove box overnight, and the electrolyte was obtained. The water content in $Ni(TFSA)_2$/BMPTFSA with and without the additives was below 10 ppm, which was determined by Karl Fischer titration (Metrohm, 831 KF Coulometer). The conductivities of BMPTFSA and $Ni(TFSA)_2$/BMPTFSA at 25 °C were about 2.0 and 1.6 mS cm^{-1}, respectively. Addition of saccharin or coumarin has little effect on the conductivities of the electrolyte.

All the electrochemical experiments were conducted using a standard three-electrode cell with a potentio/galvanostat (Hokuto Denko, HABF-501) combined with a digital recorder. A platinum disk (7.85×10^{-3} cm^2, Kojima Kagaku) or a copper disk (7.06×10^{-2} cm^2, Nilaco, 99.9%) was employed as a working electrode after mirror polishing by 0.05 μm alumina (Baikowski), electrolytic degreasing in an alkaline solution for 1 min, washing with 10 vol% H_2SO_4 and distilled water, and dried in the air. Platinum (Tokuyama kagaku, 99.9%) or Ni (Nilaco) wire was used as a counter electrode. The reference electrode consisted of a silver wire (Sanwa, >99.5%) immersed in 0.1 M $AgCF_3SO_3$ (Aldrich, >99.0%)/BMPTFSA separated from the main electrolyte by porous glass (Vycor), and was freshly prepared for each electrochemical experiment to guarantee the stability of the reference electrode. All the potentials in this paper were referred to this Ag/Ag(I) electrode. The potential of ferrocenium/ferrocene (Fc^+/Fc) was -0.428 V versus this reference electrode [34]. The measurement errors were within 5 mV.

Handling of hygroscopic reagents and all the electrochemical experiments were conducted in the glove box, which was purified with continuous gas apparatus (Miwa MFG, DBO-1KSH). The concentrations of H_2O and O_2 in the gas were kept under 0.8 and 1 ppm, respectively. Each electrochemical measurement was repeated at least three times to make sure the reproducibility of the experimental results.

The electrodeposits washed with acetone and dried in the air were characterized by a scanning electron microscopy (SEM, KEYENCE VE-9800), X-ray photoelectron spectrometer (XPS, JOEL JPS-9000 MC) and energy-dispersive X-ray analysis (EDX, EDAX Phoenix). The absorption spectra of BMPTFSA containing $Ni(TFSA)_2$ with and without additives were measured by using an air-tight quartz cell (light path length 0.1 cm) with the aid of a UV–vis spectrometer (JASCO, V-530).

3. Results and discussion

3.1. Ni(II) coordination environment

The solvation structure of metallic ions highly influences their electrodeposition process in solutions. In our previous study, addition of acetonitrile [20] and acetone [21] resulted in a change in the Ni(II) coordination environment in BMPTFSA and a decrease in the overpotential of reduction of Ni(II), leading to improve the morphology of Ni deposits. Fig. 1 shows the UV-vis spectra of 0.05 mol dm^{-3} $Ni(TFSA)_2$/BMPTFSA without and with 0.01 mol dm^{-3} coumarin or saccharin. Since the UV-vis spectra and the colors of 0.05 mol dm^{-3} $Ni(TFSA)_2$/BMPTFSA with coumarin or saccharin were identical to those of the ionic liquid without these additives, it is inferred that the divalent Ni species is considered to be existed as $[Ni(TFSA)_3]^-$ regardless of the presence of these additives [33]. This is similar to the effects of thiourea on the Ni(II) coordination environment in the same ionic liquid [21].

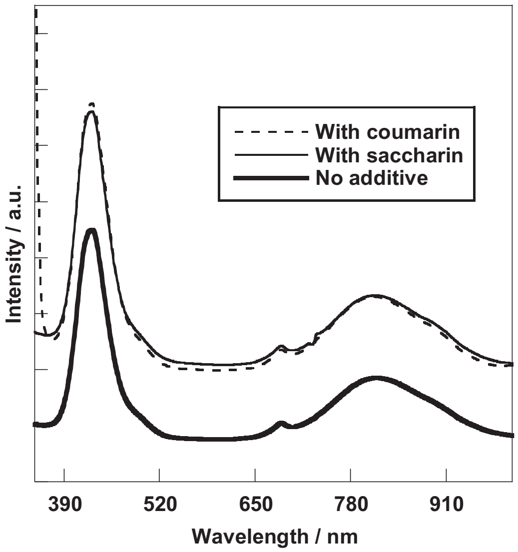

Fig. 1. UV-vis spectra of 0.05 mol dm^{-3} $Ni(TFSA)_2$/BMPTFSA without and with 0.01 mol dm^{-3} coumarin or saccharin.

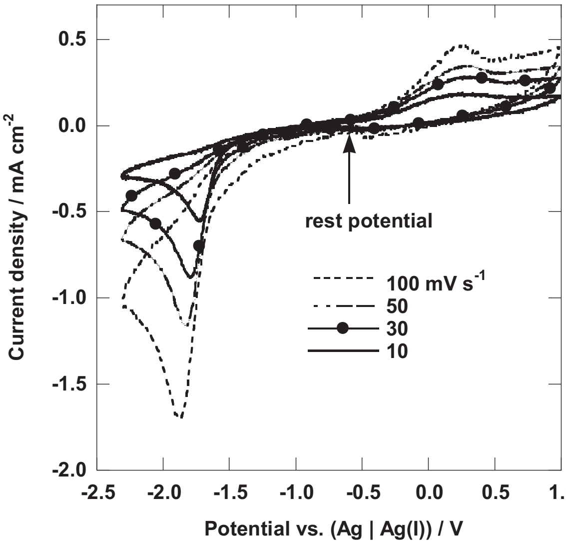

Fig. 2. Cyclic voltammograms of a Pt electrode in 0.05 mol dm^{-3} $Ni(TFSA)_2$/BMPTFSA with 0.01 mol dm^{-3} saccharin at 25 °C with various scan rates.

3.2. Cyclic voltammetry

The cyclic voltammograms of a Pt electrode in BMPTFSA containing 0.05 mol dm^{-3} $Ni(TFSA)_2$ in the presence of 0.01 mol dm^{-3} saccharin with various scan rates are shown in Fig. 2. These cyclic voltammograms were scanned cathodically from the rest potential of about -0.55 V. The cathodic and anodic potential limits of Fig. 2 were set to -2.3 V and +1.0 V, respectively. As shown in Fig. 2, the potential for the electron transfer process on the cathode, which is ascribed to the Ni(II) reduction, was onset at about -1.30 V and reached a maximum of -1.79 V at 30 mV s^{-1}. The anodic current