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Electrochemical analyses of diffusion behaviors and nucleation mechanisms for neodymium complexes in [DEME][TFSA] ionic liquid

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ABSTRACT

The electrochemical and nucleation behavior of Nd(III) in the ammonium-based ionic liquid (IL), *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethyl-sulfonyl) amide, [DEME][TFSA], were investigated in this study. The cathodic reaction of Nd(III) [$Nd(III) + 3e^- \rightarrow Nd(0)$] was observed at −3.30 V vs. Ag/Ag(I) using cyclic voltammetry at 353 K. The diffusion coefficient of Nd(III) was estimated to be $1.35 \pm 0.10 \times 10^{-13}\ m^2\ s^{-1}$ at 353 K using semi-integral and semi-differential analyses. The initial process of Nd electrodeposition was also evaluated by chronoamperometry, indicating that the initial nucleation and growth of Nd on the Pt electrode occurred via instantaneous nucleation at −3.40 V. As the applied potential became more negative, the mechanism changed from instantaneous to progressive nucleation. The number density of Nd nuclei in the initial stage of nucleation decreased as the overpotential increased. Furthermore, the electrodeposition of Nd was carried out under the conditions of −3.40 V and −3.60 V at 353 K. SEM observations of the electrodeposits were consistent with the series of results obtained by chronoamperometry. The electrodeposits consisted mainly of Nd metal and oxide mixtures, whereas bonding with the light elements (C, F, and S) of the IL was suppressed, as demonstrated by EDX and XPS. The results suggested that sufficient dehydration and control of the water content of the electrolyte are important factors for obtaining metallic Nd with high purity.

1. Introduction

Rare earth (RE) elements have become essential for high-tech industry, where they have been applied in many technical fields such as optical materials [1,2], laser materials [3], and magnetic materials [4] by exploitation of their unique properties. The RE element Nd has been incorporated into Nd–Fe–B permanent magnets and Dy has also found similar application. Nd–Fe–B magnets are utilized in a variety of high technology products, *e.g.*, voice coil motors (VCMs) for hard disk drives, magnetic field sources for magnetic resonance imaging (MRI), driving motors for hybrid-type electric vehicles, and so on [5]. The demand for Nd–Fe–B magnets has continued to grow because these magnets play an increasingly important role in applications that require energy saving and efficiency. However, the supply of Nd and Dy is occasionally unstable in certain parts of the world, including Japan, where it is currently difficult to supply such elements locally, and thus Japan has been largely dependent on other countries for RE supply. Furthermore, the prices of such elements are subject to annual fluctuation. Hence, the recovery of Nd and Dy from discarded Nd–Fe–B magnets is necessary to secure a stable supply of these resources. Although processes for the recovery of Nd and Dy from spent Nd–Fe–B magnets have been actively studied [6–8], a practical recovery system has not been established to date. As one prospective means of recovering Nd and Dy metals, electrodeposition using ionic liquids (ILs) is attractive from the viewpoint of environmental harmonization. ILs have several distinctive properties, such as negligibly low vapor pressure, high conductivity, and a wide electrochemical window [9,10]. In particular, the ILs containing bis(trifluoromethyl-sulfonyl) amide, [$TFSA^-$], are hydrophobic, and are thus readily dehydrated compared with other ILs that are miscible with water. Electrodeposition of RE metals in TFSA-based ILs has been reported, *e.g.*, the electrodeposition of La in 1-octyl-1-methyl-pyrrolidinium bis(trifluoromethyl-sulfonyl) amide, [OMP][TFSA] [11].

Recently, we presented the systems comprising Nd [12–14] and Dy [15,16] in triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl) amide, [P_{2225}][TFSA], and 2-hydroxy ethyl-trimethyl-ammonium bis(trifluoromethyl-sulfonyl) amide, [N_{1112OH}][TFSA]. However, there are no reports concerning the mechanism of electrodeposition of Nd in ILs. Therefore, in this report, we investigate the nucleation behavior for Nd electrodeposition in an

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IL. The low viscosity quaternary ammonium RTIL, [DEME][TFSA] was selected as the electrolyte based on its wide electrochemical window of about 5.7 V at 298 K [17]. It is anticipated that [DEME][TFSA] will eventually become available at lower cost given that this IL has been recognized as an electrolyte for power storage devices such as electric double layer capacitors [17] and lithium batteries [18]. Herein, the reduction behavior of Nd(III) in [DEME][TFSA] is investigated by cyclic voltammetry (CV). The diffusion coefficient of Nd(III) in [DEME][TFSA] is also evaluated by semi-integral (SI) and semi-differential (SD) analyses. In addition, the initial nucleation and growth mechanisms of the Nd nuclei are analyzed using chronoamperometry (CA). Furthermore, electrodeposition analyses of Nd using [DEME][TFSA] are performed, and the obtained electrodeposits are characterized via scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation

[DEME][TFSA], used as an electrolyte, was purchased from Nisshinbo Holdings Inc. This IL was dried at 373 K in a vacuum chamber (<−0.1 MPa) for more than 24 h. $Nd(TFSA)_3$ was prepared by reacting Nd_2O_3 (Wako Pure Chemical Industries, Ltd. >99.9%) with 1,1,1-trifluoro-*N*-[(trifluoromethyl) sulfonyl]methanesulfoneamide (HTFSA, Kanto Chemical Co., Inc. >99.0%) at 373 K under agitation. The suspension was clearly transformed to the transparent purple solution after the reaction between the metallic Nd components and the amide acid. The solution was evaporated at 423 K in order to remove the unreacted acid components. $Nd(TFSA)_3$ was obtained as a purplish fine powder and dried at 373 K in a vacuum chamber (<−0.1 MPa) for more than 24 h; the yield of the synthesized $Nd(TFSA)_3$ was >92.0%. A solution of $Nd(TFSA)_3$ in [DEME][TFSA] was used as the electrolyte for the ensuing experiment, and was prepared by adding an appropriate amount of $Nd(TFSA)_3$ to [DEME][TFSA] inside a glovebox (MIWA MFG Co., Ltd. DBO-1KP-YUMO1) filled with Ar (water content <1.00 ppm). This solution was dried at 373 K in a vacuum chamber (<−0.1 MPa) for more than 72 h.

2.2. Electrochemical analysis

CV and CA were carried out using a three electrode cell with an electrochemical analyzer (BAS Inc. ALS1140Bz) under Ar atmosphere (water content <1.0 ppm) in a glovebox. The Pt disk electrode (BAS Inc. ϕ1.6 mm) was selected as a working electrode that was mirror polished using alumina paste (d = 0.05 μm). Ag wire immersed in 0.1 M $AgCF_3SO_3$ (Wako Pure Chemical Industries, Ltd. >97.0%) in [DEME][TFSA] was applied as a reference electrode. All the potentials reported herein were referred to this Ag/Ag(I) couple. A Nd-Fe-B rod (Nilaco Co., >99.5%) immersed in 0.5 M Nd $(TFSA)_3$ in [DEME][TFSA], which was separated from the main electrolyte by Vycor glass, was employed as a counter electrode for CV in order to prevent decomposition of the main electrolyte. Pt wire (BAS Inc. ϕ0.5 mm) was used as a counter electrode for CA. The main electrolyte for the CV and CA measurements was 0.5 M $Nd(TFSA)_3$ in [DEME][TFSA].

2.3. Electrodeposition of Nd metal

The electrodeposition of Nd metal from 0.5 M $Nd(TFSA)_3$ in [DEME][TFSA] was conducted with a three electrode cell in the Ar filled glovebox (water content <1.0 ppm). A Cu substrate was selected as a working electrode; the electrode was polished using waterproof abrasive papers (#400–#1500) and washed with super dehydrated ethanol (Wako Pure Chemical Industries, Ltd. >99.5%, water content: <10 ppm). The counter and reference electrodes for the CV measurement were similar to those described above. The potentiostatic electrodeposition experiments were performed at −3.40 V and −3.60 V at 353 K. Subsequent to electrodeposition, the electrodeposits on the cathodic substrate were rinsed with super dehydrated ethanol in order to thoroughly remove the electrolyte. The surface morphology and the composition of the electrodeposits were evaluated by using SEM/EDX (JEOL Ltd. JSM-6510LA). In addition, these electrodeposits were analyzed via XPS (ULVAC PHI, Inc. Quantera SXM^{TM}) in order to investigate the chemical bonding state and the ratio of each element. The electrodeposit samples were transported to the XPS equipment without exposure to the atmosphere by using a transfer vessel to prevent oxidation of the deposit surface. The detection angle from the sample surface was set to 45°. For all measurements presented herein, a monochromated Al Kα line was used. A survey spectrum was acquired with the pass energy of 280 eV. The electrodeposited sample on the substrate was analyzed with etching in some cases by using an Ar ion beam. The sputtering parameters were as follows: acceleration voltage: 4 keV; sputtered area: $2 \times 2\ mm^2$; incidence angle: 45°. The sputtering rate of Nd was 20 nm/min, as estimated from the data for Si.

3. Results and Discussion

3.1. Electrochemical behavior of Nd(III) in [DEME][TFSA]

The reduction behavior of Nd(III) in [DEME][TFSA] was investigated by CV. The cyclic voltammogram of 0.5 M Nd(III) in [DEME][TFSA] using a Pt electrode at 353 K is shown in Fig. 1. This cyclic voltammogram was scanned cathodically from the initial potential of 0 V. A cathodic peak was observed around −3.30 V. The electrodeposits obtained from Nd(III) in [DEME][TFSA] by potentiostatic electrodeposition at −3.40 V and −3.60 V consisted mainly of Nd metal, indicating that this cathodic peak was ascribed to the reduction reaction of Nd(III) in [DEME][TFSA] according to the following reaction:

$$Nd(III) + 3e^- \rightarrow Nd(0) \quad (1)$$

On the other hand, no anodic peaks corresponding to the oxidation of Nd(0) were apparent in this voltammogram, suggesting that the reduction of Nd(III) is an irreversible reaction. More detailed analysis of this irreversible reaction is presented below.

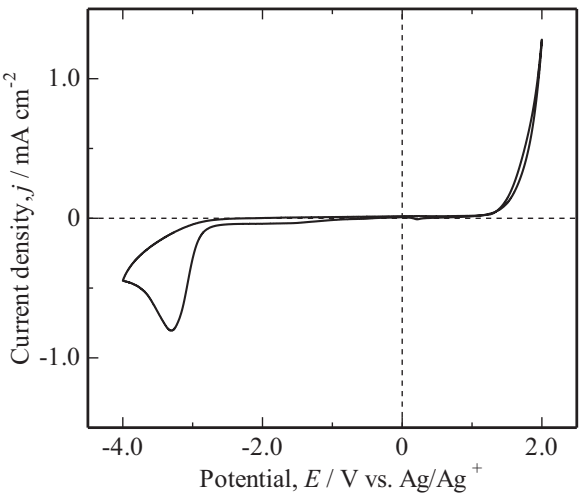

Fig. 1. Cyclic voltammogram of 0.5 M $Nd(TFSA)_3$ in [DEME][TFSA] at 353 K using Pt electrode with scan rate: 0.01 V s^{-1}.