Electrochemical analysis of diffusion behavior and nucleation mechanism
for neodymium complex in potassium bis(trifluoromethylsulfonyl)amide melts

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ABSTRACT

The electrochemical behavior of Nd(III) in potassium bis(trifluoromethyl-sulfonyl) amide (KTFSa) melts was investigated in this study. It is speculated that the first reduction peak around +2.3 V likely corresponds to the formation of Nd(II). The electrochemical analysis revealed that the reduction peak of Nd(III) around +1.0 V would be based on the following reactions; $[\text{Nd(III)} + 3\text{e}^- \rightarrow \text{Nd(0)}]$. The diffusion coefficient of Nd(III) in KTFSa melts was measured at 483 K and estimated to be $4.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 483 K by the semi-differential analysis. Moreover, the nucleation and the growth process of Nd(0) were evaluated from chronoamperometry at 473 K. The result indicated that the nucleation mechanism of Nd nuclei altered from instantaneous to progressive nucleation when the induced overpotential became more negative than the peak potential of Nd(0) electrodeposition estimated from the voltammogram.

Keywords: Bis(trifluoromethyl-sulfonyl)amide, Diffusion coefficient, Neodymium complex, Nucleation

1. Introduction

Nd-Fe-B magnets are utilized in a variety of high-tech industries, *e.g.*, voice coil motors (VCMs) for hard disk drives, driving motors for hybrid-type electric vehicles, and so on [1]. The demand for Nd-Fe-B magnets has gradually increased because these magnets play an increasingly important role in applications that require energy saving and efficiency. Hence, the recovery of Nd and Dy from spent Nd-Fe-B magnets is necessary to secure a stable supply of these resources. As one prospective means of recovering Nd metals, the electrodeposition using low-temperature molten salts is attractive from the viewpoint of total saving energy. In particular, the low-temperature molten salts [3-6] containing bis(trifluoromethyl-sulfonyl)amide anion, [TFSA]⁻, have several distinctive properties, such as high conductivity. Recently, we demonstrated the electrochemical and nucleation behaviors for Nd [7-10] and Dy [11,12] in triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide, [P₂₂₂₅][TFSA] and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethyl-sulfonyl)amide [DEME][TFSA]. However, there were no reports concerning the diffusion and nucleation behaviors of neodymium complex in KTFSA melts, which was selected as the electrolyte based on its wide electrochemical window of about 5.0 V [4-6]. Therefore, in this report, the reduction behavior of Nd(III) in KTFSA melts was investigated by cyclic voltammetry (CV). Then, the diffusion coefficient of Nd(III) in KTFSA melts was also evaluated by semi-integral (SI) and semi-differential (SD) analyses. Moreover, chronoamperometry (CA) was also applied for the nucleation mechanism analysis in order to reveal the electrodeposition mechanism at the initial state.

2. Experimental

KTFSA (Kanto Chemical Co., Inc., >99.5%), used as an electrolyte, was dried under vacuum (<1.0×10⁻⁶ atm) at 373 K for 24 h before measurement. A purity of KTFSA was confirmed by a differential scanning calorimetry (Rigaku DSC8230) and thermogravimetry differential thermal analysis (Rigaku, TG8120) at a heating rate of 5.0 K min⁻¹. The measured melting point and the electrochemical window for KTFSA in this study were 461.5±0.5 K and 5.0 V, which was

consistent with the other reports [3-6]. $\text{Nd}(\text{TFSA})_3$ was prepared by reacting Nd_2O_3 (Wako Pure Chemical Industries, Ltd., >99.9%) with 1,1,1-trifluoro-*N*-[(trifluoromethyl) sulfonyl]methanesulfone-amide (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. $\text{Nd}(\text{TFSA})_3$ was obtained as a purplish fine powder and dried at 373 K in a vacuum chamber ($<1.0 \times 10^{-6}$ atm) for 24 h. The yield of the synthesized $\text{Nd}(\text{TFSA})_3$ was >97.2 %. A purity of the synthesized $\text{Nd}(\text{TFSA})_3$ was confirmed by DSC (Rigaku DSC8230) and TG/DTA (Rigaku TG8120). The Nd(III) in KTFSA melts ($x_{\text{Nd}}=0.10$) were used as the electrolyte for the electrochemical experiment and this solution was dried at 373 K in a vacuum chamber ($<1.0 \times 10^{-6}$ atm) for 24 h. The water content of the electrolyte was <50 ppm, as measured by a Karl-Fischer coulometric titrator (MKC-610-DT, Kyoto Electronics Manufacturing Co., Ltd.). The CV at 483 ± 1.0 K was carried out using a cylindrical cell constituted from three-electrode system with an electrochemical analyzer (BAS Inc., ALS760E) under Ar flow. The Pt electrode (surface area: $6.91 \times 10^{-5} \text{ m}^2$) was selected as a working electrode that was mirror polished using alumina paste ($d = 0.05 \text{ }\mu\text{m}$). Platinum wires ($\phi = 0.5 \text{ mm}$) were used as a counter electrode and a quasi-reference electrode (Q.R.E) because the potential obtained using a Pt Q.R.E was stable and exhibited a good reproducibility at medium temperatures. All the potentials reported herein were compensated for the redox reaction of K/K^+ couple. The CA of KTFSA melts including 0.01 M $\text{Nd}(\text{TFSA})_3$ was performed at different overpotentials (+1.1 V, +1.0V, +0.9V vs. K/K^+) at 473 K.

3. Results and Discussion

The voltammetric analysis of Nd(III) in KTFSA melts ($x_{\text{Nd}}=0.10$) at 483 K with various scan rates is shown in **Fig. 1**. There was a small anodic peak at +1.3V corresponding to an oxidation of Nd(0) in voltammogram. This result suggested that the reduction of Nd(III) was an irreversible process. Lodermeier et al. [13] also observed that no oxidation peak of Dy(0) in DMF and DMPT.

The report concluded that the reduction process of Dy(III) was an irreversible system by electrochemical quartz crystal microbalance (EQCM) analysis. As seen from Fig.1, there were two reduction peaks around +1.0 V and +2.3 V in voltammogram. It is speculated that the first reduction feature around +2.3 V likely corresponds to the formation of Nd(II) based upon preliminary results. The reduction peak (B) around +1.0 V would be based on the following reactions.

Regarding each peak based on the cathodic reactions (1) and (2), it was confirmed that the plot of the cathodic peak of the current density; j_p vs. the square root of the scan rate; $v^{1/2}$ showed a good linear relations. This result indicated that both of two reduction reactions were controlled by the diffusion process; the mass transport under semi-infinite linear diffusion conditions. Elucidation of the diffusion behavior of Nd(III) in KTFSA melts as well as the reduction behavior is necessary in order to perform the electrodeposition of Nd metal; thus, we evaluated the diffusion coefficient of Nd(III) in KTFSA melts. The diffusion coefficient was analyzed by both SI and SD methods. Initially, the SI curve (solid line) was obtained from convolutional voltammogram for Nd(III) in KTFSA melts as shown in **Fig. 2**. The diffusion coefficients were calculated from the limiting current, m^* according to the following equation [14]:

$$m^* = nFAD_0^{1/2}C_0^* \quad (3)$$

where n is the number of electrons involved in the charge transfer reaction, F is the Faraday constant, A is the electrode surface area, and C^* is the bulk concentration of the electroactive species. As seen from Fig. 2, SD curve (chain line) was also obtained from the voltammogram by SD method.

The value of W_p ; the width of a derivative neopolarographic peak at half its height, and e_p ; the current semi-derivative at the peak of the derivative neopolarogram, were determined from the SD curve. The diffusion coefficients were calculated using the following equations [15] that were established in the case of the irreversible reaction:

$$W_p = 2.94RT/\alpha nF \quad (4)$$

$$e_p = \alpha n^2 F^2 A \nu C_O^* D_O^{1/2} / 3.367 RT \quad (5)$$

The obtained diffusion coefficient by SD analysis was $4.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 483 K and this value was relatively close to the value derived from SI analysis. This congruence suggests high reliability of the calculated diffusion coefficient of Nd(III) in KTFSA melts derived from SI and SD analyses.

The chronoamperogram of 0.01 M Nd(III) with different overpotentials is shown in **Fig. 3**. The CA curves showed that the Faradaic current increased due to the nucleation and growth of Nd nuclei and eventually this increasing current reached a current maximum j_m at time t_m , which was attributed to the three-dimensional growth of a Nd metal over the nuclei resulting in the increase of surface area. Finally, this current decayed due to the increase in the thickness of the diffusion layer after reaching a maximum and reached to a limiting current. The nucleation and the crystal growth of Nd electrodeposition were analyzed by Scharifker-Hills model [16]. According to this model, the nucleation process was described with instantaneous and progressive nucleation mechanisms. In the case of the instantaneous nucleation, the ad-atoms were electrodeposited on the electrode surface and grew at a constant rate which was dependent on the overpotential. In this nucleation process, the j - t curves can be described by the following equation.

$$\left(\frac{j}{j_m}\right)^2 = \frac{1.9542}{t/t_m} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m} \right) \right] \right\}^2 \quad (6)$$

On the other hand, in the case of the progressive nucleation, the electrodeposited nuclei proceeded at various rates dependent on the electrodeposition time. The resultant j - t curves are described as follows.

$$\left(\frac{j}{j_m}\right)^2 = \frac{1.2254}{t/t_m} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m}\right)^2 \right] \right\}^2 \quad (7)$$

The relationship between the squared dimensionless current density $(j/j_m)^2$ and the dimensionless time (t/t_m) for Nd(III) reduction is shown in **Fig. 4** with the theoretical curves. The curves presented in this study showed a good correlation with the theoretical curves. As seen from Fig. 5, when the overpotential was +1.1 V, the nucleation behavior was obeyed on the instantaneous nucleation model. On the other hand, the nucleation curve at +0.9 V was mostly followed by the progressive nucleation model. This result indicated that the nucleation mechanism of Nd changed depending on the overpotential. The nucleation number density, N_0 was estimated from the maximum current density, j_m and time, t_m of the j - t curve based on the following equation [17].

$$N_0 = 0.065(8\pi C_0^* M / \rho)^{-1/2} (nFC_0^* / j_m t_m)^2 \quad (8)$$

where M and ρ are the atomic mass and the density of the deposited metal, respectively. The calculated nucleation number density with different overpotentials is listed in **Table 1**. The number density of Nd nuclei decreased as the overpotential increased. These nucleation behaviors were observed for the platinum adlayers [18] and the tendencies would be related with the alternation from instantaneous to progressive nucleation. In our previous study, this alternation of the nucleation behaviors under different overpotentials was demonstrated for Nd electrodeposition in [DEME][TFSA] [7]. After all, the nucleation behavior would be controlled by the overpotentials and independent of the metallic species. This difference of the nucleation mechanism would also greatly be influenced on the formation of electrodeposits in the initial stage of the electrodeposition.

Therefore, by inducing the overpotential based on this nucleation mechanism, the surface morphology and the quality of electrodeposits would be improved under the electrowinning process.

4. Conclusion

As for a firstly findings, the diffusion behavior of Nd(III) complex in KTFSA melts was investigated by CV. It is speculated that the first reduction peak around +2.3 V likely corresponds to the formation of Nd(II). The resultant voltammogram expressed that the reduction process of Nd(III) around +1.0 V would be based on the following reaction; $[\text{Nd(III)} + 3\text{e}^- \rightarrow \text{Nd(0)}]$ in KTFSA melts. The semi-differential analysis was applied for the estimation of the diffusion coefficients of Nd(III). This diffusion coefficient of Nd(III) was calculated to be $4.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 483 K. Moreover, the nucleation process of Nd nuclei was evaluated by CA. The relation between the squared dimensionless current density $(j/j_m)^2$ and the dimensionless time (t/t_m) revealed that the nucleation mechanism of Nd nuclei altered depending on the induced overpotential. When the overpotential close to the onset potential for Nd electrodeposition at +1.1 V, the nucleation process was instantaneous nucleation model, however as the overpotential induced more negative, the behavior changed to progressive nucleation model. This result suggested that the quality of Nd electrodeposits could be improved under the electrowinning process by means of applying appropriate overpotential.

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Captions of Figures

Fig.1 Cyclic voltammogram of Nd(III) in KTFSA melts ($x_{\text{Nd}}=0.10$) at 483 K using Pt electrode with different scan rates, 0.02 V s⁻¹ (chain line), 0.05 V s⁻¹ (dotted line) and 0.10 V s⁻¹ (solid line).

Fig.2 Semi-integral (solid line) and semi-differential (chain line) curves obtained from the voltammogram of Nd(III) in KTFSA melts ($x_{\text{Nd}}=0.10$) at 483 K using Pt electrode with scan rate: 0.10 V s⁻¹.

Fig.3 Chronoamperogram on a Pt electrode for 0.01 M Nd(III) in KTFSA melts at 473 K with different overpotentials. ●: +1.1 V, ○: +1.0 V, Δ: +0.9 V

Fig.4 $(j/j_m)^2-t/t_m$ plots for 0.01 M Nd(III) in KTFSA melts evaluated from CA.

Fig.1

Fig.2

Fig.3

Fig.4

Table 1 The nucleation number density of Nd nuclei calculated from j - t curves at each applied overpotential in KTFSA melts including 0.01 M Nd(III).

Applied overpotential / V vs. (K/K ⁺)	+1.1	+1.0	+0.9
Nucleation number density ($10^{11}N_0$) / cm ⁻²	2.0	1.7	1.6