Electrochemistry Communications 65 (2016) 23–26

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

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

Atsuki Nishimura [a], Masahiko Matsumiya [a,*], Hisashi Ota [a], Satoshi Kawakami [b]

[a] Graduate School of Environment and Information Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[b] Environmental Protection Laboratory, DOWA ECO-SYSTEM Co., Ltd., 65-1 Omoriyama-shita, Hanaoka, Akita 017-0005, Japan

ARTICLE INFO

Article history:
Received 14 August 2015
Received in revised form 24 December 2015
Accepted 12 January 2016
Available online 28 January 2016

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

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 reaction; [Nd(III) + $3e^- \rightarrow$ Nd(0)]. The diffusion coefficient of Nd(III) in KTFSA melts was estimated to be 4.39×10^{-10} m^2 s^{-1} at 483 K by semi-differential analysis in voltammogram. 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.

© 2016 Published by Elsevier B.V.

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 [2] 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 a 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, $[P_{2225}]$[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 ($<1.0 \times 10^{-6}$ atm) at 373 K for 24 h before measurement. 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]. $Nd(TFSA)_3$ was prepared by reacting Nd_2O_3 (Wako Pure Chemical Industries, Ltd., >99.9%) with 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl] 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. $Nd(TFSA)_3$ 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 $Nd(TFSA)_3$ was >97.2%. Purity of the synthesized $Nd(TFSA)_3$ was confirmed by DSC (Rigaku DSC8230) and TG/DTA (Rigaku TG8120). The Nd(III) in KTFSA melts ($x_{Nd} = 0.10$) were used as the electrolyte for the electrochemical experiment and this solution

* Corresponding author.
E-mail address: mmatsumiya@ynu.ac.jp (M. Matsumiya).

http://dx.doi.org/10.1016/j.elecom.2016.01.005
1388-2481/© 2016 Published by Elsevier B.V.

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: 6.91×10^{-5} m^2) was selected as a working electrode that was mirror polished using alumina paste (d = 0.05 μm). Platinum wires (φ = 0.5 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 $Nd(TFSA)_3$ was performed at different overpotentials (+1.1 V, +1.0 V, +0.9 V vs. K/K^+) at 473 K.

3. Results and discussion

The voltammetric analysis of Nd(III) in KTFSA melts ($x_{Nd} = 0.10$) at 483 K with various scan rates is shown in Fig. 1. There was a small anodic peak at +1.3 V corresponding to an oxidation of Nd(0) in voltammogram. This result suggested that the reduction of Nd(III) was an irreversible process. Lodermeyer 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:

$$Nd(III) + e^- \rightarrow Nd(II) \quad [peak(A)] \tag{1}$$

$$Nd(III) + 3e^- \rightarrow Nd(0) \quad [peak(B)]. \tag{2}$$

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

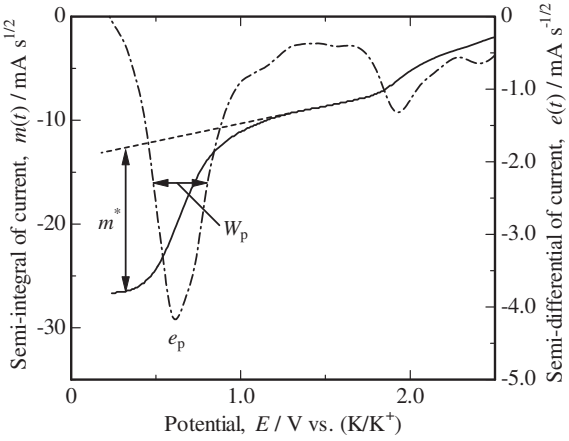

Fig. 2. Semi-integral (solid line) and semi-differential (chain line) curves obtained from the voltammogram of Nd(III) in KTFSA melts ($x_{Nd} = 0.10$) at 483 K using Pt electrode with scan rate: 0.10 V s^{-1}.

(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]:

$$m^* = nFAD^{1/2}C^* \tag{3}$$

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:

$$W_p = 2.94RT/\alpha nF \tag{4}$$

$$e_p = \alpha n^2 F^2 AvC^* D^{1/2}/3.367RT. \tag{5}$$

The obtained diffusion coefficient by SD analysis was 4.39×10^{-10} m^2 s^{-1} at 483 K and this value was relatively close to the value derived from SI analysis. This congruence suggests high

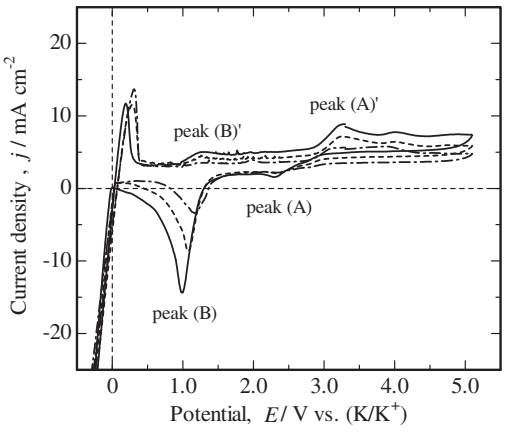

Fig. 1. Cyclic voltammogram of Nd(III) in KTFSA melts ($x_{Nd} = 0.10$) at 483 K using Pt electrode with different scan rates, 0.02 V s^{-1} (chain line), 0.05 V s^{-1} (dotted line) and 0.10 V s^{-1} (solid line).

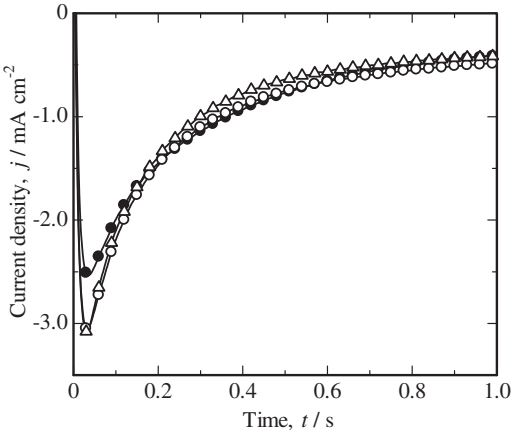

Fig. 3. Chronoamperogram on a Pt electrode for 0.01 M Nd(III) in KTFSA melts at 473 K with different overpotentials, ●: +1.1 V, ○:+1.0 V, △: +0.9 V.

Download English Version:

https://daneshyari.com/en/article/178732

Download Persian Version:

https://daneshyari.com/article/178732

Daneshyari.com