Electrochemical cell design for emf measurements of liquid Nd-Bi alloys via coulombic titration in LiCl-KCl-$NdCl_3$ electrolyte

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ABSTRACT:

Using an electrochemical cell containing a two-phase Nd-Sn alloy (x_{Nd} = 0.10) in LiCl-KCl-$NdCl_3$ (1 mol%) as a reference electrode, coulometric titration emf measurements at various cathodic current densities (10–100 mA cm^{-2}) were performed to evaluate the stability of the Nd-Sn electrode and corroborate emf values for Nd (in Bi) at T = 873 K. The potential difference between two identical Nd-Sn reference electrodes was measured before/after the electrochemical evaluation for 45 days, and the stability of the cell for the long-term operation was verified. The emf values of Nd (in liquid Bi) titrated at various current densities were consistent at each Nd concentration, demonstrating the reliability of the cell.

1. Introduction

Electrochemical recovery processes for rare-earth elements are necessary for facilitating the removal of fission products accumulated during the treatment of spent nuclear fuel as well as in developing improved recycling cycles for clean energy technologies [1,2]. Liquid metal electrodes (e.g., Bi and Sn) have been considered for improving the recovery efficiency of alkali, alkaline-earth, and rare-earth metals based on their strong chemical interactions [3,4]. However, determination of reliable thermodynamic properties for rare-earth elements can be difficult due to their high reactivity with certain electrolytes. Electromotive force (emf) measurement is an effective tool for determining the thermodynamic properties of alloys in alkali/alkaline-earth metal chloride, but the high reactivity of Nd in molten chlorides limits electrochemical cell stability and lifetime. For example, the presence of a disproportionation reaction: $Nd + 2NdCl_3 \rightarrow 3NdCl_2$ between pure Nd and the electrolyte results in loss of Nd metal to the electrolyte [5,6].

In a previous study, we determined the thermodynamic properties of the Nd-Bi system through coulometric titration emf measurements using a less reactive two-phase Nd-Sn alloy as a reference electrode [7]. Coulometric titration emf measurement was able to determine thermodynamic properties of the Nd-Bi system including the Bi-rich liquid phase region by fine composition control of the liquid Nd-Bi alloy, and the accuracy of the technique has been verified in relevant studies using liquid metal in molten salts [7–10]. This study describes a cell configuration including a highly stable reference electrode for coulometric titration emf measurement using liquid metals in molten chloride and validates the reliability of the described cell design.

To verify the reliability of the cell, the coulometric titration was repeated with various current densities at 873 K and then the measured open circuit potential (OCP) values following each titration step were compared. In addition, the stability of the developed RE in our previous study was confirmed by comparing the potential difference between two identical REs before/after the electrochemical evaluation. The measured OCP value was determined as the emf value by correcting the established cell potential between the Nd-Sn alloy ($x_{Nd} = 0.10$) versus pure Nd(s) developed in the previous study.

2. Experimental

$LiCl$-KCl-$NdCl_3$ electrolyte (eutectic LiCl-KCl + 1 mol% $NdCl_3$) was prepared from appropriate weights of LiCl (Ultra dry, 99.9%, Alfa Aesar), KCl (Ultra dry, 99.95%, Alfa Aesar), and $NdCl_3$ (anhydrous, 99.5%, Alfa Aesar) powders. The powder mixture was loaded into a quartz crucible (Technical Glass Products) for pre-melting in a stainless-steel vacuum chamber. The chamber was loaded into a crucible furnace (Mellen, CC-12), evacuated to less than 10 mtorr, and heated under vacuum at 373 K for 12 h and at 543 K for 12 h to remove residual moisture and oxygen. The chamber was then purged with ultra-high purity Ar three times and heated to 923 K for 3 h under a flowing (50 mL min^{-1}) argon atmosphere. After cooling, the dry and homogeneous electrolyte was ground into a fine powder using a mortar and pestle for use in the electrochemical cell assembly.

The Nd-Bi and Nd-Sn alloys for reference electrodes (RE) and counter electrodes (CE) were fabricated using a laboratory arc-melter (MAM-1, Edmund Bühler GmbH) under an inert argon atmosphere from pure Nd (99.1%, Alfa Aesar, Stock No. 00214), Sn (99.9999%, Alfa Aesar, Stock No. 45481), and Bi (99.999%, Sigma-Aldrich, Stock No. 556130). The arc-melted Nd-Sn alloy ($x_{\mathrm{Nd}} = 0.10$) was re-melted inside a boron nitride (BN, Advalue Technology) crucible (35 mm height, 12 mm outer diameter, 8 mm inner diameter, and 30 mm depth) using an induction heater custom-installed inside a glovebox ($O_2 < 0.5$ ppm). Two 1 mm diameter capillary holes were drilled at 7 mm above from the bottom of the crucible. During induction heating, a tungsten wire was inserted into the RE in liquid state to establish electrical contact. A liquid Nd-Bi ($x_{\mathrm{Nd}} = 0.03$) electrode served as the CE. The CE in each cell was contained in a BN crucible (15 mm height, 25 mm outer diameter, 22 mm inner diameter, and 11 mm depth) with a tungsten wire (1 mm diameter) serving as the electrical lead. The alloy was fabricated by melting Bi using an induction heater and gradually adding Nd pieces into liquid metals until the target composition was achieved. The working electrode (WE) was fabricated by induction melting 2.76 g of pure Bi in a BN crucible (12 mm outer diameter, 8 mm inner diameter, 15 mm height, and 10 mm depth). The nominal surface area of WE was estimated to be 0.5 cm^2. The three-electrode electrochemical cell configuration is shown in **Fig. 1**.

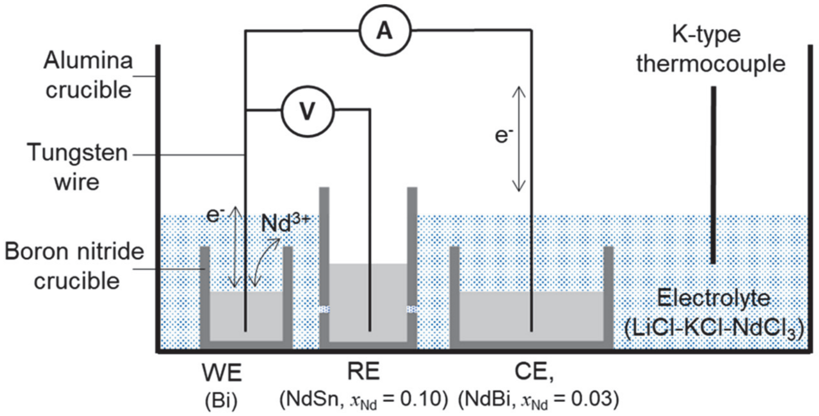


Fig. 1 Three-electrode electrochemical cell configuration used for emf measurement of the Nd-Bi alloys via coulometric titration.

Final assembly of the electrochemical cell was conducted in an Ar-filled glovebox (O_2 concentration < 0.5 ppm). The electrodes were placed in an alumina crucible (Advalue Technology) and electrolyte was poured over the electrodes. The three-electrode cell assembly was loaded in a stainless-steel test chamber. The test chamber was then sealed, removed from the glovebox, loaded into a crucible furnace, and evacuated to ~1 Pa. The chamber was heated to 373 K for 12 h then 543 K for 12 h under vacuum, was purged three times with ultra-high purity Ar and then heated under flowing argon (~10 mL min^{-1}) to 873 K. The cell temperature was measured using a thermocouple (ASTM type-K) located at the center of the electrolyte, and thermocouple data acquisition system (NI 9211, National Instruments).

Emf measurements were conducted using potentiostat-galvanostat (Autolab PGSTAT302N) at 873 K. The composition of the liquid Bi WE controlled by approximately $x_{\mathrm{Nd}} = 0.0025$ per each step through coulometric titration by applying constant cathodic current densities of 10–100 mA cm^{-2} for 180–1730 sec. After each titration, the WE was relaxed under open-circuit condition for 1 hr for equilibration of the electrode and then the stabilized OCP was measured to emf. Assuming a perfect coulombic efficiency, the concentration of Nd in liquid Bi was calculated by Faraday's law:

$$x_{\mathrm{Nd}} = \left(\frac{m_{\mathrm{WE}}}{M_{\mathrm{WE}}} \frac{zF}{It} \right)^{-1}$$

where m_{WE} is the initial mass (2.76 g) of the WE, M is the molecular weight of the pure Bi, and I is the constant current applied during the titration time, t. The emf values (E_{I}) were obtained from the average of steady OCP ($dE/dt = 0.1$ mV/hr, except for the alloying process) for the last 10 min of each step and then converted to the emf (E_{eq}) versus pure Nd. The cell potential (E_{II}) of the two-phase Nd-Sn alloy ($x_{\mathrm{Nd}} = 0.10$) relative to pure Nd(s) was previously established and exhibited linear behavior at 724–1075 K [6]:

$$E_{\mathrm{II}} = 0.590 + 1.52 \times 10^{-4}\, T \ \ [\mathrm{V}]\ \mathrm{vs.\,Nd(s)}$$

In the present work, the cell emf (E_{eq}) of a Nd-Bi alloy relevant to pure Nd(s) was converted by adding the two cell potentials ($E_{\mathrm{eq}} = E_{\mathrm{I}} + E_{\mathrm{II}}$) at a given temperature 873 K.

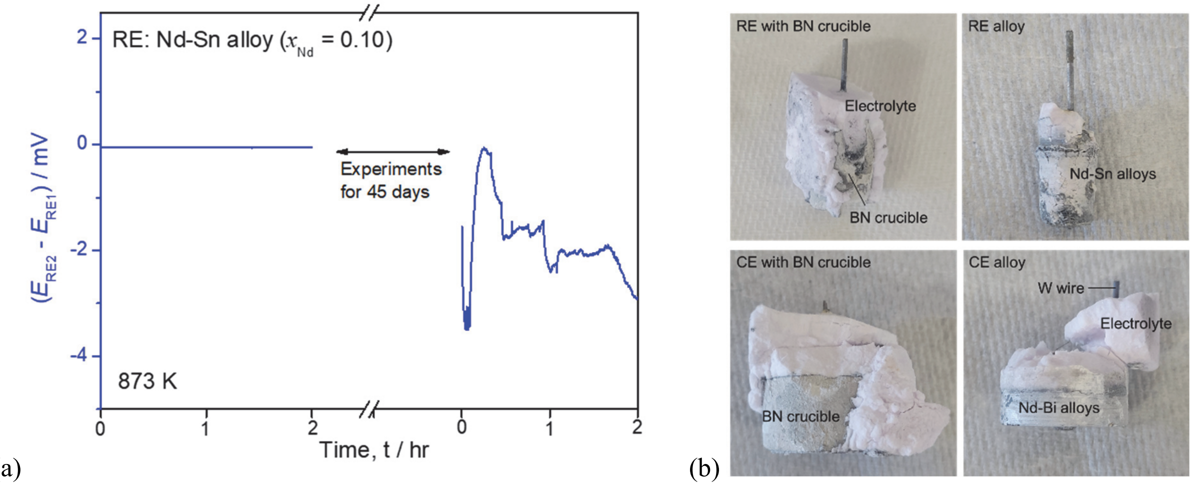
3. Results and discussion

3.1 Reference electrode stability

The potential difference (E_{RE2} **-** E_{RE1}) between the two identical RE (Nd-Sn alloy, $x_{\mathrm{Nd}} = 0.10$) before/after electrochemical evaluations at 773–973 K including coulometric titration emf measurements was observed to monitor the stability of the REs. As shown in **Fig. 2(a)**, the potential difference was less than 0.05 mV during the first 2 h of operating the cell, indicating a highly stable RE. After the 45-day experiment, the potential difference between the REs remained at less than 4 mV. The utilization of alloys with two-phase behavior (e.g., Nd-Bi alloys with $x_{\mathrm{Nd}} = 0.20$ or Nd-Sn alloys with $x_{\mathrm{Nd}} = 0.10$) as REs reduces the reactivity with the electrolyte compared to the reactive pure Nd, leading to greater stability and a significantly longer cell lifetime.

Fig. 2(a) indicates that the lifetime of the RE was improved in the molten chloride electrolyte in comparison with the potential difference between the REs of ±5.0 mV for about 40 h reported in the previous study using Nd-Bi alloys ($x_{\mathrm{Nd}} = 0.20$) as REs [6]. Furthermore, as the Nd-Bi alloy exhibits the peritectic phase transitions [L + $\mathrm{NdBi_2}$ = $\mathrm{Nd_3Bi_7}$] and [L + NdBi = $\mathrm{NdBi_2}$] at 774 K and 932 K, the emf exhibited discontinuous linearity [6,7]. On the other hand, the Nd-Sn alloys do not experience any phase transitions in the 724–1075 K range and therefore exhibit linear emf behavior. These observations indicate that the Nd-Sn two-phase RE is a more viable option than the Nd-Bi two-phase RE for use in electrochemical cells.

The post-mortem images of each cooled electrode (RE and CE) are shown in **Fig. 2(b)**. The BN crucibles containing electrodes with molten salts electrolyte were structurally intact and the BN surface remained white, unlike in measurements using pure Nd as a RE which were shown to blacken the electrolyte due to loss of pure Nd into the salt. The CE appeared similarly unchanged in structure and color, despite the lengthy measurement time.



(a) (b)

Fig. 2 (a) The potential difference between Nd-Sn alloy ($x_{Nd} = 0.10$) reference electrodes for 2 h at 873 K before/after coulometric titration emf measurement for 45 days. (b) The post-mortem images of the electrodes after electrochemical evaluation for 45 days.

3.2 Coulometric titration emf measurements

Emf of the Nd-Bi alloys in liquid phase was measured via coulometric titration using various constant cathodic current densities (10–100 mA cm^{-2}) at 873 K against the aforementioned Nd-Sn two-phase RE. The coulometric titration emf measurement of the ±25 mA cm^{-2} current density is shown in **Fig. 3**; the electrode potential decreased as Nd was deposited under cathodic constant current and stabilized as the open-circuit potential (OCP) condition was held for 1 h to reach a homogeneous composition of the electrode. As the titration proceeds, the OCP of the Nd-Bi alloy decreases in the and gradually reaches a constant value due to the phase transition, which is described in detail in our previous study [7].

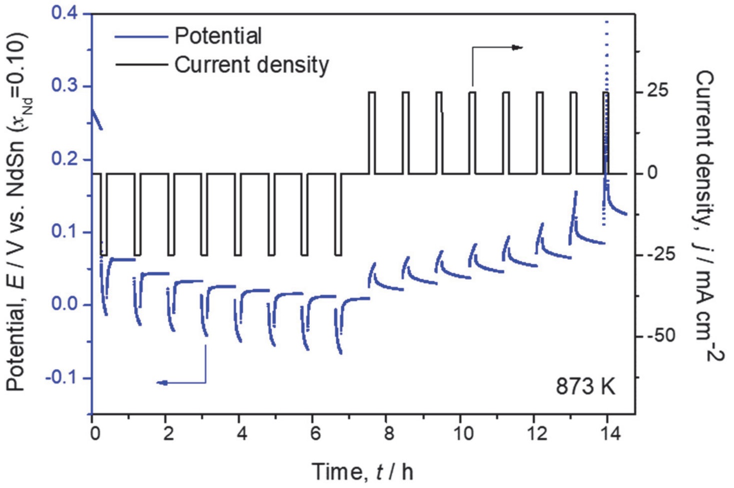


Fig. 3 Representative coulometric titration emf measurement data of liquid Nd-Bi alloy WE ($j = \pm 25$ mA cm^{-2}) as a function of time at $T = 873$ K.

The measured steady OCP value after titration at various cathodic current densities (10−100 mA cm^{-2}) including **Fig. 3** was converted into the emf (E_{eq}) versus pure Nd and plotted as a function of the mole percent of Nd in **Fig. 4**. Compared with the emf trajectory, which was separated into a two-phase region (dotted lines in **Fig. 4**) and the liquid single-phase region (solid line in **Fig. 4**) to determine solubility in the study on thermodynamic properties of the Nd-Bi system [7], emf values measured in this study show a good agreement within ±5 mV at each Nd concentration. The results in **Fig. 4(a)** indicate that the proposed electrochemical cell configuration, including highly stable Nd-Sn alloys as REs, provide reliable emf measurements under various current density conditions and long-term operation at 873 K.

As shown in **Fig. 4(b)**, the measured OCP values during alloying process and de-alloying process under a current density of ± 25 mA cm^{-2} at 873 K were inconsistent. The electrode potential quickly stabilized to equilibrium during the alloying process, but did not reach equilibrium within relaxation time during the de-alloying process. The initial flux boundary condition formed at the interface between the liquid metal and the electrolyte can be different according to the deposition/dissolution of Nd by the applied current direction, which is expected to cause a difference in the chemical diffusivity of Nd in liquid Bi. Based on the report of fast charge-transfer properties in the study of electrochemical recovery of reactive elements such as alkali/alkaline-earth using liquid metal in molten salt [8,10,11], mass transport property is considered as a dominant factor, and it is thought to be related to the difference in the change of electrode potential during titration and back-titration in **Fig. 3**.

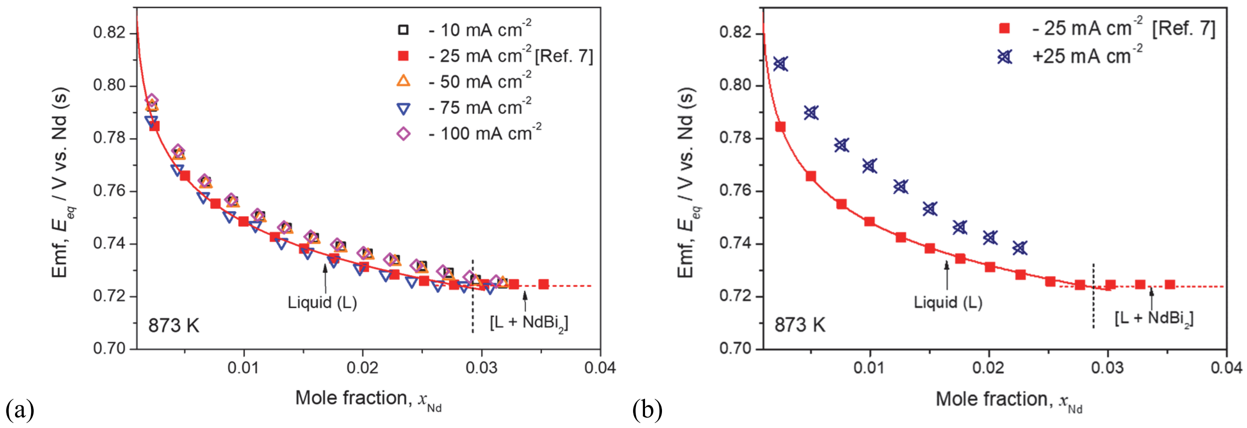


Fig. 4 (a) Emf measured at various cathodic current densities (10–100 mA cm^{-2}) as a function of the mole percent of Nd at 873 K, where solid lines represent logarithmic curve fit in the liquid phase. (b) Comparison of emf values determined during titration (alloying process) and back-titration (de-alloying process) in **Fig. 3**

4. Conclusion

Coulometric titration emf measurements of liquid Nd-Bi alloys were performed under various current densities using the proposed electrochemical cell containing an Nd-Sn alloy ($x_{\mathrm{Nd}} = 0.10$) with two-phase behavior as a stable reference electrode. The reliability of the cell was demonstrated as all emf results measured at various cathodic current densities (10–100 mA cm^{-2}) were consistent within the ±5 mV range compared with the equilibrium potential determined in the previous study [7]. In addition, the long-term stability of the cell was validated as the potential difference between the REs was measured within 3.5 mV before/after the electrochemical evaluation for 45 days.

5. Acknowledgements

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