



## Electrochemical and spectrophotometric study on neodymium ions in molten alkali chloride mixtures

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### ABSTRACT

The thermodynamic stability of Nd(III) complex in various molten alkali chlorides at 923 K was studied by electrochemical analysis. The standard Gibbs free energy change of the Nd<sup>3+</sup> formation,  $\Delta G_{3/0}^\circ$ , decreased by adding MCl (M = Na, K, Rb, or Cs) into LiCl. The Nd(III) complex was more stable in an alkali chloride mixture with larger averaged cationic radius. This means that the stability is controlled by the polarizing power of solvent cations. The electronic absorption spectrum of the hypersensitive *f–f* transition of Nd<sup>3+</sup> was investigated to know the change in its coordination environments. The oscillator strength of the <sup>4</sup>G<sub>5/2</sub>, <sup>2</sup>G<sub>7/2</sub> ← <sup>4</sup>I<sub>9/2</sub> transition and the degree of the energy splitting in electronic energy levels were estimated. The results suggested that the octahedral symmetry of the NdCl<sub>6</sub><sup>3–</sup> complex was more distorted in the melt with higher LiCl content, and the distortion was depressed by decreasing the polarizing power of solvent cations. The local structure around Nd<sup>3+</sup> was significantly correlated with the thermodynamic stability of the Nd(III) complex in molten alkali chlorides.

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### 1. Introduction

The successful management of spent nuclear fuels is a key concern for the future stable utilization of nuclear power. Separation and transmutation of minor actinides (MA) such as Np, Am and Cm, are examined to minimize the amount of nuclear wastes as well as their long-lived radiotoxicities. Pyrochemical reprocessing using molten salts as a solvating medium has been proposed [1–7] due to some advantages for treating MAs, e.g., high radiation and proliferation resistances of the process. In a typical pyrochemical reprocessing, spent nuclear fuels are dissolved in a molten salt and fuel materials are separated from fission products (FP) by electrodeposition or reductive extraction. To optimize the separation process, thermochemical properties of FPs and actinides in molten salt media are essential to be well understood.

Neodymium is one of major FP elements having larger neutron capture cross sections, and hence its removal in the pyrochemical reprocessing is desired. However, the reports for the electrochemical behavior of Nd in molten chlorides have been limited for LiCl–KCl [8–10], NaCl–CaCl<sub>2</sub> [9] and LiCl–CaCl<sub>2</sub> [10] eutectic melts. In order to assess the refining performance of Nd, systematic data

for the chemical stability of Nd(III) complex in various alkali chlorides is necessary. Information on the coordination circumstance of solute ions is also important since it should be correlated with the stability. The predominant Nd(III) complex in molten alkali chlorides with low Nd<sup>3+</sup> concentration has been confirmed to be NdCl<sub>6</sub><sup>3–</sup> with octahedral symmetry (*O<sub>h</sub>*) by Raman spectrometry [11] and molecular dynamic simulation [12], respectively. The degree of the octahedral symmetry has been investigated for LiCl–CsCl mixtures employing absorption spectrum analysis, and the results reported that the NdCl<sub>6</sub><sup>3–</sup> complex was more distorted in the melts with lower CsCl content [13].

In the present study, the chemical stability and the coordination circumstances of the Nd(III) complex for various molten alkali chloride mixtures were investigated by electrochemical and absorption spectrum measurements, respectively. Their dependence on the melt compositions and the correlation between these macroscopic and microscopic properties were discussed.

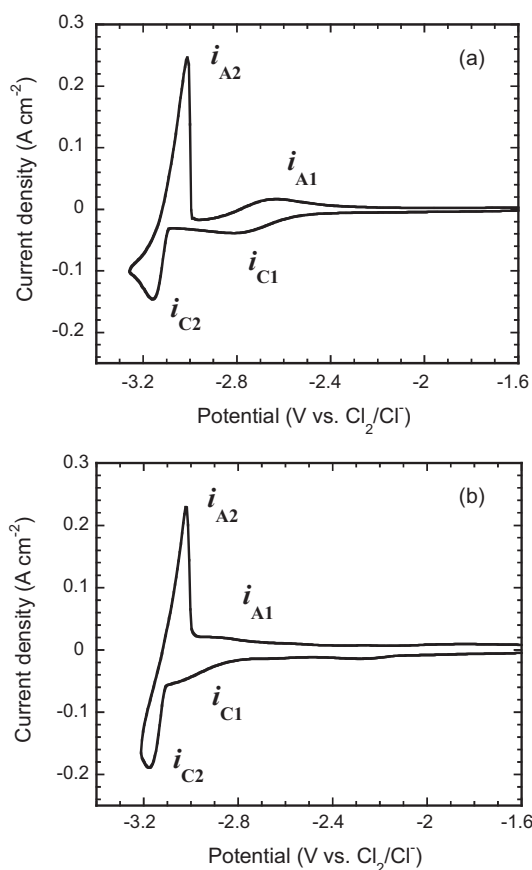
### 2. Experimental

All experiments were carried out under an argon atmosphere, in which humidity and oxygen impurity were continuously kept less than 1 ppm. Anhydrous chlorides (99.99% purity) were purchased from Aldrich–APL LLC and used without further purification. 0.2–0.7 mol% NdCl<sub>3</sub> was dissolved in a quartz tube by various binary mixtures of alkali chlorides, LiCl–KCl, LiCl–NaCl, LiCl–RbCl and LiCl–CsCl.

An electrochemical measurement system Hz-5000 (Hokuto Denko Co.) was used for cyclic voltammetry (CV) and the differential pulse voltammetry (DPV). The sweep rate of CV for extracting peak potentials was 100 mV s<sup>–1</sup>. The pulse height, period,

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**Fig. 1.** Cyclic voltammograms of Nd in alkali chlorides at 923 K. Potential sweep rate of CV was  $100 \text{ mV s}^{-1}$ . (a) LiCl system. Mole fraction of  $\text{NdCl}_3$  in LiCl was 0.60%. (b) LiCl–KCl eutectic system. Concentration of  $\text{NdCl}_3$  in LiCl–KCl was 0.47%.

and width of DPV were 50 mV, 100 ms and 10 ms, respectively. A tungsten wire (99.95%, The Nilaco Co.) of 1 mm diameter, a pyrographite rod (99.99%, Tokai Carbon Co., Ltd.) of 3 mm diameter, and a  $\text{Ag}/\text{Ag}^+$  electrode were used for the working, counter, and reference electrodes, respectively. In each measurement, the potential of chlorine gas evolution ( $\text{Cl}_2/\text{Cl}^-$ ) on the pyrographite electrode [14] was determined to calibrate the  $\text{Ag}/\text{Ag}^+$  electrode.

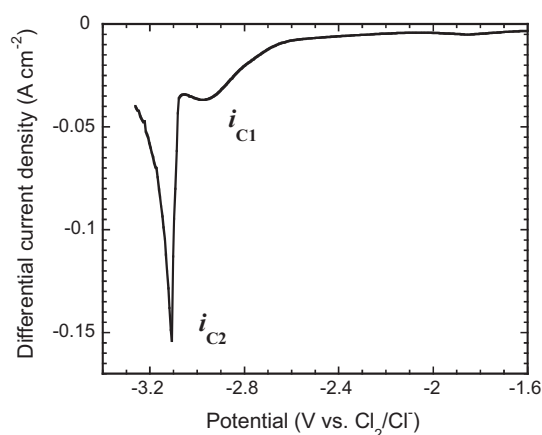
The electronic absorption spectra of Nd(III) in the melts were measured by using an UV/vis/NIR spectrometer (V-570, JASCO). The experimental apparatus was described in [15]. The analytical light from a light source (a tungsten halogen lamp) was guided to the electric furnace with quartz windows by using optical fibers, and the light passed through the sample in a quartz tube with a 10 mm light path inside the furnace. The light which traveled through the furnace was again guided to the spectrophotometer, in which a monochromator was set in front of detectors to decrease the background noise. The light intensity for the molten alkali chloride ( $I_0$ ) and that including Nd(III) ( $I$ ) was measured in the wavelength range of 300–850 nm at 0.5 nm intervals and 700–550 nm at 0.1 nm intervals. The absorbance was determined to be  $-\log(I/I_0)$ .

All the experiments were performed at  $923 \pm 3 \text{ K}$ . In order to compare our results with reported data [9,16], the same experiment at different temperature,  $723 \pm 3 \text{ K}$ , was also performed for a LiCl–KCl eutectic system.

### 3. Results and discussion

#### 3.1. Determination of the standard potentials of the $\text{Nd}^{3+}$ reduction

Typical cyclic voltammograms of Nd in LiCl and LiCl–KCl eutectic at 923 K are shown in Fig. 1. The electrochemical reduction process of Nd(III) in the eutectic has been identified to be a two-step process via Nd(II) by CV and chronopotentiometry [17],



**Fig. 2.** Differential pulse voltammogram in LiCl–KCl eutectic melt at 923 K. Sweep rate of DPV was  $50 \text{ mV s}^{-1}$ . Concentration of  $\text{NdCl}_3$  was 0.47 mol%.

The cathodic wave  $i_{C1}$  associated with an anodic wave  $i_{A1}$  is attributable to the soluble–soluble  $\text{Nd}^{3+}/\text{Nd}^{2+}$  couple. The cathodic peak  $i_{C2}$  associated with a sharp anodic peak  $i_{A2}$  corresponds to the  $\text{Nd}^{2+}/\text{Nd}^0$  soluble–insoluble system. All peaks were separately observed for the LiCl system, where the cathodic peak currents were proportional to the square root of the potential sweep rate and the potential difference between positive and negative peak pairs were not significant. Hence both reactions were treated as reversible.

In the present study, the overlap of  $i_{C1}$  and  $i_{C2}$  in CV (Fig. 1b) was enhanced by adding MCl (M: Na, K, Rb, or Cs) into LiCl and it could not be resolved. In order to obtain sharp wave  $i_{C1}$ , the reduction reaction of Eq. (1) was analyzed by DPV. The result in the LiCl–KCl eutectic is shown in Fig. 2, in which the first peak was clearly obtained.

The following disproportionation reaction of Nd takes place in molten chlorides [8,9,18],



It has been reported that the reaction is completed within several minutes [8]. This is much slower than the transient time during electrochemical measurement, and hence the interference of reaction 3 in our electrochemical analyses is considered to be insignificant.

The standard redox potential of the  $\text{Nd}^{3+}/\text{Nd}^{2+}$  couple,  $E_{3/2}^\circ$ , was determined by DPV as [19],

$$E_{3/2}^\circ = E_{\text{max}} + \frac{\Delta E}{2} - \frac{RT}{F} \ln \left( \frac{D_{\text{Nd}^{2+}}}{D_{\text{Nd}^{3+}}} \right)^{1/2} - \frac{RT}{F} \ln \frac{\gamma_{\text{Nd}^{3+}}}{\gamma_{\text{Nd}^{2+}}} - E_{\text{ref}} \quad (4)$$

where  $E_{\text{max}}$ ,  $\Delta E$ , and  $E_{\text{ref}}$  are the peak potential of  $i_{C1}$ , the applied potential pulse height, and the potential of the  $\text{Ag}/\text{Ag}^+$  electrode vs.  $\text{Cl}_2/\text{Cl}^-$ , respectively.  $R$  is the gas constant,  $\gamma$  the activity coefficient,  $T$  the absolute temperature, and  $F$  the Faraday constant. The  $E_{3/2}^\circ$  values were constant within the analytical uncertainty of  $\pm 10 \text{ mV}$  in our experimental range from 0.2 mol% to 0.7 mol%. This means that the ratio of activity coefficients  $\gamma_{\text{Nd}^{3+}}/\gamma_{\text{Nd}^{2+}}$  is constant and approximates that of diluted condition. Hence,  $\gamma_{\text{Nd}^{3+}}/\gamma_{\text{Nd}^{2+}}$  set to be unity in the present study.  $D$  represents the diffusion coefficient of suffixed species. Due to the disproportionation reaction (Eq. (3)), it is impossible to measure an accurate diffusion property of  $\text{Nd}^{2+}$  and hence  $D_{\text{Nd}^{2+}}$  is not available. In the present study, the ratio  $D_{\text{Eu}^{2+}}/D_{\text{Eu}^{3+}}$  reported for europium [20] was substituted for  $D_{\text{Nd}^{2+}}/D_{\text{Nd}^{3+}}$ . The uncertainty of this substitution was examined to be small since both  $D_{\text{Ln}^{2+}}$  and  $D_{\text{Ln}^{3+}}$  decrease with the increase of atomic number and the decrease trends in lanthanide

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