



Formation of Nd-Cd Intermetallic Compounds in LiCl-KCl

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The redox reactions of the Nd(III)/Nd(0) couple at W and Mo electrode in the presence of chloride form of Cd (*i.e.*, CdCl₂) in LiCl-KCl eutectic melt were studied by cyclic voltammetry and square wave voltammetry (SWV) at 500 °C. Various anodic and cathodic peaks representing the formation and the decomposition of Nd-Cd intermetallic compounds were observed during the electrochemical measurement. The composition of Nd_xCd_y was analyzed by comparing the accumulated coulomb numbers of the anodic peaks attributed to the decomposition of Nd_xCd_y, since the amount of Cd deposited on the electrode can be evaluated. Molar absorptivity of Nd(III) ions in the LiCl-KCl eutectic melt containing CdCl₂ was determined as $11.16 \pm 0.39 \text{ M}^{-1} \text{ cm}^{-1}$ from the absorption spectra, which was consistent with previous reports. In addition, no effect of Cd(II) on the absorbance of Nd(III) for the quantification analysis was found.

Key Words: Nd-Cd intermetallic compounds, LiCl-KCl eutectic, Voltammetry, UV-visible spectrometry.

INTRODUCTION

Pyroprocessing using molten salts as solvent media has received attention as a future separation technique of group actinides and fission products in spent nuclear fuels by employing electrochemical methods¹⁻³. Among the several distinct processes of pyroprocessing, electrowinning is a key step to recover uranium (U) and transuranic elements (TRUs) simultaneously by using a liquid cadmium cathode (LCC), accompanying a nuclear non-proliferation. The separation of lanthanide nuclides from spent nuclear fuels is required to use the recovered actinides practically as a fuel for sodium-cooled fast reactor (SFR), because lanthanides have large neutron capture cross sections which spoil the neutron economy of the reactor core. This becomes very practical problem in case of transuranic elements are used as a metal fuel for SFR. It is of importance the knowledge of the electrochemical behaviour of actinides and lanthanides on various electrode substrates with and without alloy formation which determines the recovery efficiency since the operation conditions significantly influences the feasibility of pyroprocessing. Therefore, it is necessary to understand the electrochemical behaviour of lanthanides in molten salt to avoid the co-deposition of lanthanides on the liquid cadmium cathode in an alloyed form. Also, a study on the chemical constitution and electronic structure of *f*-elements in molten salt by spectrometric analysis such as UV-visible absorption spectrometry needs to be conducted to improve the efficiency of electrowinning process and for technical applications.

Some researchers have reported the redox reactions of the Np(III)/Np(0) and Pu(III)/Pu(0) couples at the liquid Cd electrode in LiCl-KCl eutectic melt by considering the formation of various intermetallic compounds^{4,5}. Shirai *et al.*⁶ studied the redox reaction of the Ln(III)/Ln(0) couple and the formation energy of various La-Cd alloys and their composition at the Cd-coated W electrode in LiCl-KCl eutectic melt by the use of electrochemical measurement methods. Besides this, Fujii *et al.*⁷ determined the molar absorptivity of Nd(III) over wide range of mole fractions in LiCl-KCl eutectic melt by a sequential addition of neodymium trichloride into the reaction cell.

In this study, the electrode reaction of the Nd(III)/Nd(0) couple at W and Mo electrode in the presence of chloride form of Cd in LiCl-KCl eutectic melt was investigated. The formation and decomposition of Nd_xCd_y intermetallic compounds were examined by the measurement of cyclic voltammetry (CV) and square wave voltammetry (SWV). In addition, molar absorptivity of Nd(III) in the LiCl-KCl eutectic melt containing chloride form of cadmium was determined from the UV-visible spectra in order to examine the influence of cadmium ions on the quantification of neodymium ions.

EXPERIMENTAL

The mixture of LiCl-KCl (99.99 % purity) with the eutectic composition (59:41 mol %), neodymium trichloride (NdCl₃) and cadmium dichloride (CdCl₂) was purchased from Sigma-Aldrich (USA). A three-electrode cell was used for all

the measurements. The working electrode was a W and Mo wire (dia. = 0.8 mm, dipping height = 13 mm, apparent surface area = 0.3316 cm², Nilaco, Japan). A 3 mm diameter glassy carbon rod (Alfa Aesar, USA) served as a counter electrode and a Ag/AgCl couple was used as a reference electrode. The Ag/AgCl electrode consisted of a Pyrex tube with a very thin bottom in which the LiCl-KCl eutectic mixture containing 1 mol % AgCl was placed and an Ag wire (dia. = 1 mm, Nilaco) was immersed in the salt. Electrochemical reaction vessel was made from quartz tube. All the experiments and sample preparations were carried out in a glove box with a high purity Ar atmosphere where moisture and O₂ concentrations were maintained less than 1 ppm. Temperature of the molten salt was measured with ± 1.0 °C using a calibrated K type Chromel-Alumel thermocouple.

Electrochemical measurements such as cyclic voltammetry and square wave voltammetry were performed using an AutoLAB PGSTAT 302N (The Netherlands). The frequency and amplitude used in the pulse voltammetry (square wave voltammetry) were 8 Hz and 1 mV, respectively. Electronic absorption spectra of Nd in LiCl-KCl eutectic melt at 773 K in the wavelength range from 400-900 nm at 1 nm intervals were measured by using a spectrophotometer, JASCO V-570 (JASCO Co., Japan). A quartz cell having a 1 cm light path welded to a quartz tube (350 mm in length and 13 mm in inner diameter) was used as the sample cell.

RESULTS AND DISCUSSION

Redox reaction of the Nd(III)/Nd(0) couple at W and Mo electrode in the presence of CdCl₂ in LiCl-KCl: Fig. 1 shows cyclic voltammograms obtained at W and Mo electrode in LiCl-KCl eutectic salt containing NdCl₃ (2.504×10^{-5} mol/cm³) and CdCl₂ (0.450×10^{-5} mol/cm³). Large cathodic and anodic peaks were found around -2.1 V, which are associated with deposition and dissolution reactions of Nd ($P_{a,Nd}$ and $P_{c,Nd}$). A small peak of the reduction current was shown before the peak of Nd(III) \rightarrow Nd(0), which is assigned to the one-electron reduction of Nd(III) \rightarrow Nd(II). The anodic and cathodic peaks ($P_{a,Cd}$ and $P_{c,Cd}$), representing the dissolution and deposition of Cd, respectively, were observed around -0.5 V. Besides this, there were a number of cathodic and anodic peaks corresponding to the formation-oxidation of Nd_xCd_y intermetallic compounds. It is mainly due to the different energies of formation of these phases rendering different formation-oxidation potentials⁸. The dissolution of Nd with the decomposition of the Nd_xCd_y into the LiCl-KCl melt was clearly observed in both of the electrodes (*i.e.*, W and Mo) even though some of them were very small, while the formation of various intermetallic compounds was not found well.

The composition of Nd_xCd_y intermetallic compounds were estimated by comparing the accumulated coulomb number of P_1 , P_2 , P_3 , P_4 , P_5 and P_6 with that of $P_{a,Cd}$. The Nd/Cd ratios can be evaluated by the correction of the accumulated amount of Cd metal at each peak since Cd metal is always deposited in the potential region more negative than -0.5 V⁶. The ratios of Nd released at peak potentials to Cd existed on the working electrode were estimated to be 0.451, 0.647, 0.736, 0.819, 0.921 and 0.943, respectively. There are 6 types of Nd_xCd_y

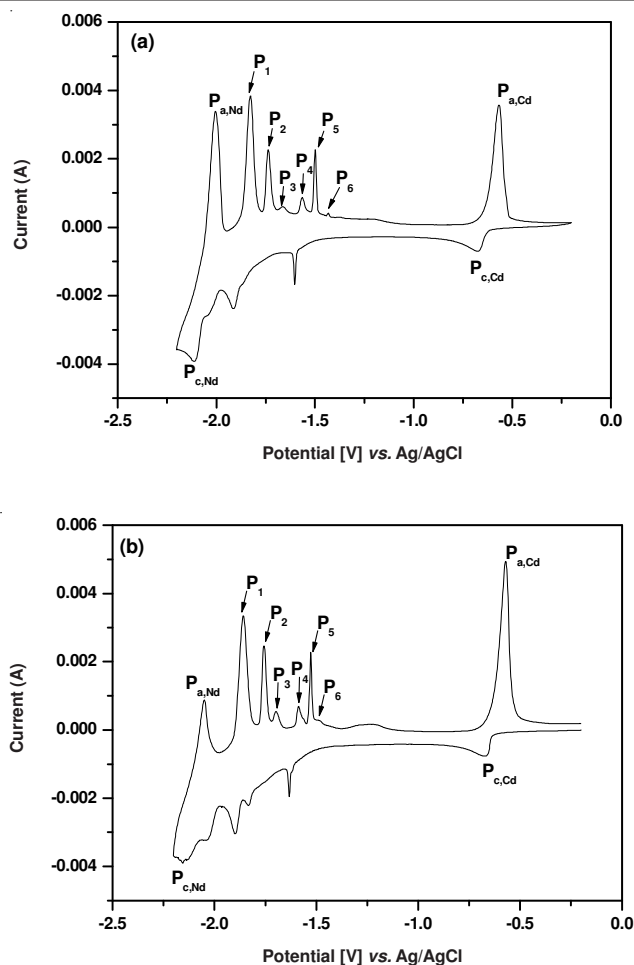


Fig. 1. Cyclic voltammogram for the redox reaction of the Nd(III)/Nd(0) couple in the presence of CdCl₂ at (a) W and (b) Mo electrode (773 K, 100 mV/s)

intermetallic compounds at 500 °C when the weight per cent of Nd is lower than 50 %⁹. Accordingly, the peaks (P_1 , P_2 , P_3 , P_4 , P_5 and P_6) were identified as NdCd₂, NdCd₃, Nd₁₁Cd₄₅, Nd₁₃Cd₅₈, NdCd₆ and NdCd₁₁, respectively.

Square wave voltammetry, one of the pulse voltammetric techniques, was conducted to observe the cathodic peaks indicating the formation of Nd_xCd_y intermetallic compounds. Since it decreases greatly charging current, square wave voltammetry is widely employed in the analysis of electroactive species^{10,11}. As shown in Fig. 2, the reduction reaction of Nd(III)/Nd(II) as well as Nd(III)/Nd(0) were clearly observed at both of the electrodes. Also, more than five peaks which are representing the formation of intermetallic compounds were examined, while they were not clearly found at cyclic voltammetry (Fig. 1).

Spectrophotometry measurement: The absorption spectrum of Nd(III) in LiCl-KCl eutectic melt at 773 K was measured. As shown in Fig. 3(a), clear absorption band was observed at 589 nm which is corresponding to the transitions of $^4G_{5/2} \rightarrow ^4I_{9/2}$ and $^2G_{7/2} \rightarrow ^4I_{9/2}$. These are known as the hypersensitivity transitions^{7,12}. In order to investigate the effect of Cd(II) on the absorption spectrum of Nd(III), various concentrations of CdCl₂ were added to LiCl-KCl-NdCl₃ melt. As shown in Fig. 3(b), no change of absorption spectra was found regardless of the presence of Cd(II).

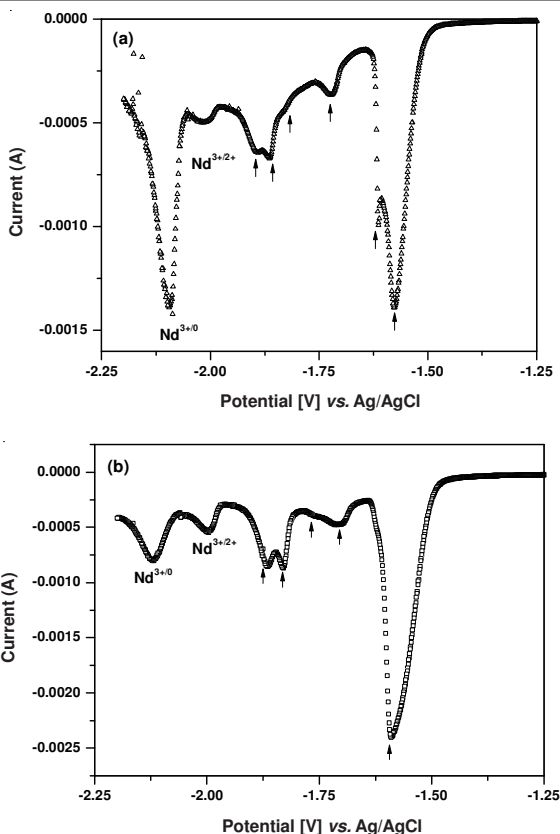


Fig. 2. Square wave voltammogram for the formation of Nd- Cd intermetallic compounds and the reduction of Nd(III) at (a) W and (b) Mo electrode (773 K, 100 mV/s)

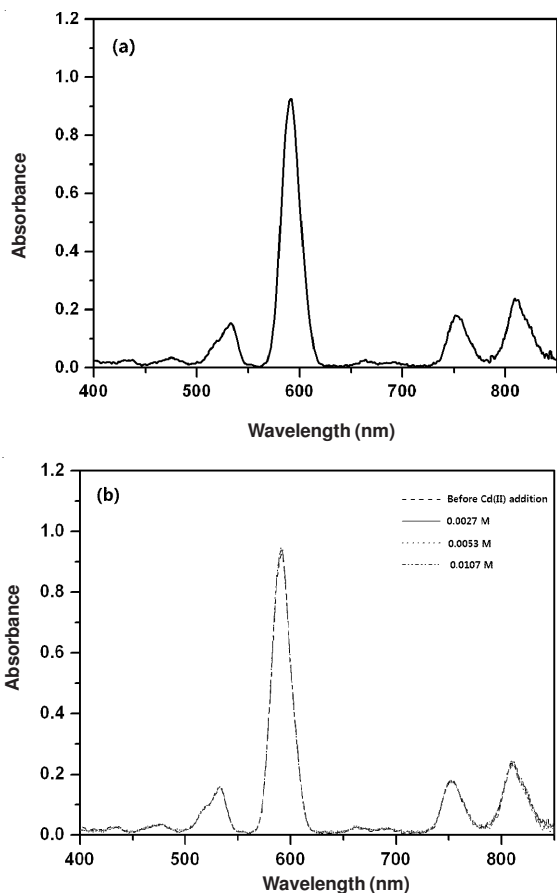


Fig. 3. Absorption spectra of Nd(III) in the LiCl-KCl eutectic melt at 773 K (a) before and (b) after the addition of $CdCl_2$ (0.0027-0.0107 M)

Fig. 4(a) shows the absorption spectra for various concentrations of Nd(III) which are coexisting with Cd(II) in LiCl-KCl eutectic melt at 773 K. From the absorbance and the concentrations of Nd(III), the molar absorptivity at the maximum of absorption peak (*i.e.*, 589 nm), was determined to be $11.16 \pm 0.39 \text{ M}^{-1} \text{ cm}^{-1}$. As shown in Fig. 4(b), a linear line was obtained with a high correlation coefficient ($R^2 = 0.9984$). For comparison, the molar absorptivity values in LiCl-KCl eutectic melt at 673 and 873 K were listed in Table-1. As shown in Table-1, the absorptivity value in this study is reasonable and comparable to those in the previous reports^{7,13}. These results suggest that the effect of Cd(II) which co-exists in the LiCl-KCl eutectic melt on the absorbance measurement of Nd(III) is negligible. The presence of Cd(II) does not affect the quantification of Nd(III) by UV spectrometry.

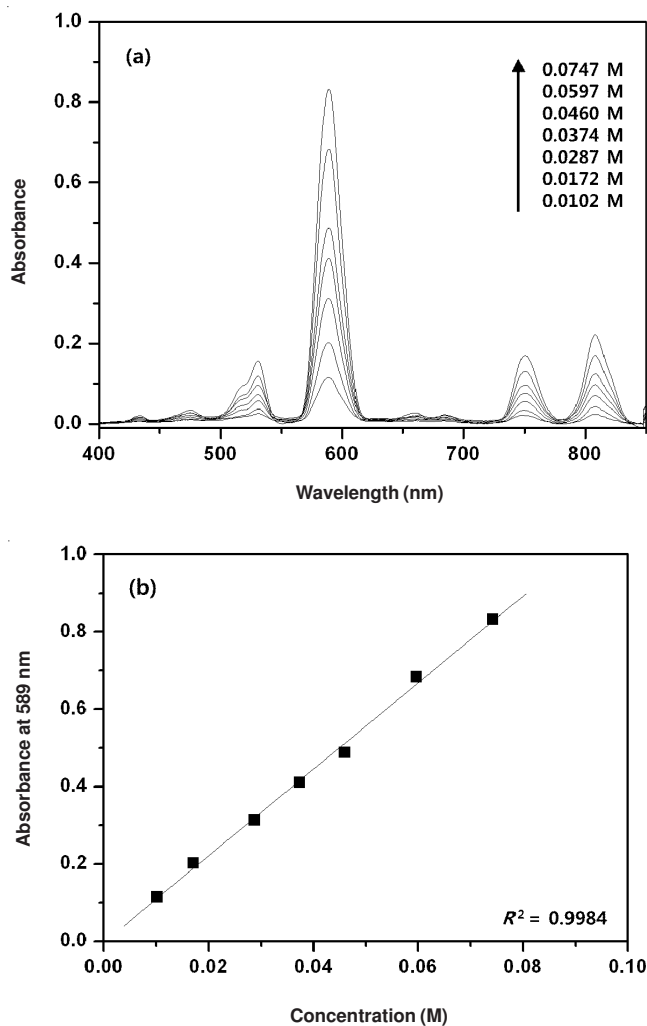


Fig. 4. (a) The absorption spectra and (b) the absorbance values at 589 nm for various concentrations of Nd(III) in LiCl-KCl eutectic melt at 773 K. The values in the Fig. 4(a) are the concentrations of Nd(III)

Temperature (K)	Wavelength (nm)	Molar absorptivity ($\text{M}^{-1} \text{ cm}^{-1}$)	Reference
673	589	11.90	13
773	589	11.16 ± 0.39	This study
873	589	11.67 ± 0.22	7

Conclusion

We examined the redox reaction of Nd(III)/Nd(0) couple at W and Mo electrode in LiCl-KCl eutectic melt containing CdCl₂ by cyclic voltammetry and square wave voltammetry. The formation and decomposition of intermetallic compounds Nd_xCd_y was observed by showing several anodic and cathodic peaks in the voltammograms. Also, the Nd_xCd_y compositions were estimated by accumulated coulomb numbers of anodic peaks in cyclic voltammogram. From the UV-visible spectroscopy, the molar absorptivity of Nd(III) ions in the LiCl-KCl eutectic melt was determined to be $11.16 \pm 0.39 \text{ M}^{-1} \text{ cm}^{-1}$. No influence of Cd(II) on the absorbance of Nd(III) was confirmed.

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