Electrochemical behavior of the Lanthanide at Cd, Bi electrodes in LiCl-KCl molten salt

Beom-Kyu Kim, Ae-Ri Lee, Yong-Il Kim, and Byung Gi Park*
Department of Energy & Environmental Engineering, Soonchunhyang University, Soonchunghyangro 22, Asan,
Chungnam 336-745, Republic of Korea
Corresponding author:

1. Introduction

Pyroprocess based on molten salt electrolysis has been developed in order to reduce a radiotoxicity and a volume of the used nuclear fuels generated from nuclear power plants. [1] Liquid metal cathode is used to recover actinides from molten salt in an electrowinning among the pyroprocess. Reductive or oxidative extraction between molten salt and liquid metal has been also considered for group partitioning of lanthanide and actinide.[2] Cadmium or bismuth as liquid metal has been extensively studied to investigate the effects of liquid metals on the process. However, there is sparse information about the electrode reaction of lanthanide and actinide at the liquid metal electrodes. The purpose of the present study is to investigate the electrochemical behavior of praseodymium and neodymium among lanthanides(Ln) in molten LiCl-KCl salt at liquid metal electrode such as cadmium and bismuth using cyclic voltammetry and derive the thermochemical properties.

2. Experimental

An electrochemical cell was prepared with a one-end closed quartz tube (OD: 13 mm, ID: 10 mm), in which high purity LiCl-KCl eutectic salt (Sigma-Aldrich, 99.99%) containing 1 wt% high purity $PrCl_3$ (Sigma-Aldrich, 99.99%) or 1 wt% high purity $NdCl_3$ (Sigma-Aldrich, 99.99%) was placed. Liquid metal electrode such as high purity Bi (Sigma-Adrich, 99%) or Cd (Sigma-Aldrich, 99%) was placed in the bottom of the quartz tube and was electrically connected with a W wire (Alfa-Aesar, 99%, OD: 1 mm) that was shielded with Pyrex tube. An Ag-AgCl electrode served as a reference electrode. The reference electrode was consisted of an one-end closed Pyrex tube, in which LiCl-KCl eutectic salt containing 1wt% AgCl was placed and a silver wire (Alfa-Aesar, 99%, OD: 1 mm) was immersed in the salt. A W wire (Alfa-Aesar, 99%, OD: 1mm) was used as a counter electrode. The atmosphere of the electrochemical cell was controlled with glove box (H_2O < 1 ppm, O_2 < 1pp). Temperature of the salt was measured with Chromel-Alumel thermocouple. Cyclic voltammogram was obtained with Solatron 1470E Cell Test System

3. Results and Discussion

The phase diagrams of Pr-Cd and Pr-Bi [3,4] show the presence of seven intermetallic compounds for Pr-Cd ($PrCd_{11}$, $PrCd_6$, $Pr_{13}Cd_{58}$, $Pr_{11}Cd_{45}$, $PrCd_3$, $PrCd_2$ and $PrCd$) and five intermetallic compounds for Pr-Bi ($PrBi_2$, $PrBi$, Pr_4Bi_3, Pr_5Bi_3 and Pr_2Bi). The alloying process of Pr-Cd was studied with an electrochemical transient technique.

Cyclic voltamograms of LiCl-KCl-$PrCl_3$ at liquid Bi and Cd metals are shown in Fig. 1. They consist of a number of cathodic and anodic peaks corresponding to the formation-dissolution of different intermetallic compounds. The anodic peak of P_{Pr} corresponds to the dissolution of Pr as Pr^{3+} and P_{Cd} corresponds to the dissolution of Cd. The anodic peaks, P_1, P_2, P_3, P_4, and P_5 are attributed to the dissolution of Pr as Pr^{3+} with the decomposition of Pr-Cd intermetallic compounds.

Neodymium also has six Bi-Nd compounds($NdBi_2$, $NdBi$, $Nd4Bi_3$, Nd_5Bi_3 and Nd_2Bi) and the composition of Cd-Nd is $NdCd_{11}$, $NdCd_6$, $Nd_{13}Cd_{58}$, $Nd_{11}Cd_{45}$, $NdCd_3$, $NdCd_2$, $NdCd$. Cyclic voltamograms of LiCl-KCl-$NdCl_3$ at liquid Bi and Cd metals are shown in Fig. 2. There are various peaks in the Fig2. (a), but the peak of Fig2. (b) Nd-Bi is difficult to figure out.
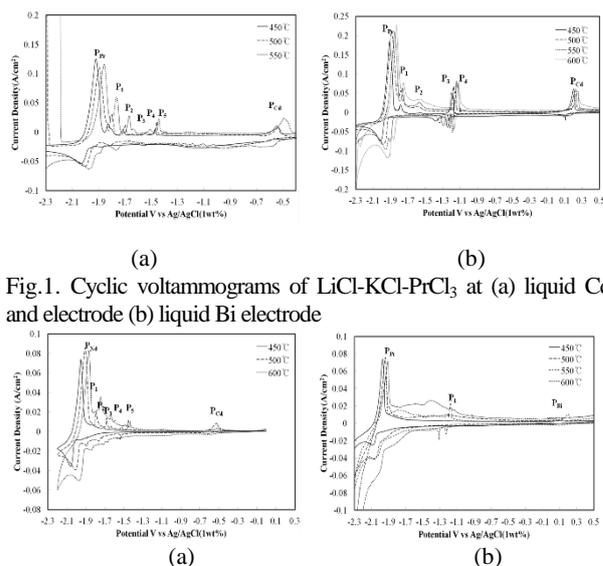

(a)   (b)

Fig.1. Cyclic voltammograms of LiCl-KCl-$PrCl_3$ at (a) liquid Cd and electrode (b) liquid Bi electrode

(a)   (b)

Fig. 2. Cyclic voltammograms of LiCl-KCl-NdCl3 at (a) liquid Cd electrode and (b) liquid Bi electrode

P_n is the anodic peak potential corresponding to the dissolution of the intermetallic compounds. Gibbs free energies of formation of intermetallic compound were determined from by peak potential difference between each peak potential.

$$\Delta E = E_{(Ln)} - E_{(Ln\ in\ Liquid\ metal)} = (RT/3F)ln\alpha_{Ln\ in\ Liquid\ metal}$$

$$\Delta G_{(Ln\ in\ Liquid\ metal)} = -nF\Delta E_{Ln\ in\ Liquid\ metal}$$

Fig. 3. Exhibit a peak potential difference as a function of the temperature. Gibbs energies of formation of intermmetallic compound was determined by equate estimated. There potential differences, $\Delta E_{(Ln-Pn)}$, are transformed into the Gibbs formation energies, $\Delta G_{(Ln-Pn)}$, respectively, as Table. 1.

Table.1. Gibbs free energies of formation of intermetallic compounds with CV method

	Potential difference [V]	Gibbs formation energy[J/mol]
Pr (Cd)	$\Delta E_{(P1-Pr)} = 0.0743 - 0.00004T$	$\Delta G_{(P1-Pr)} = -21506.5 + 11.578T$
	$\Delta E_{(P2-Pr)} = 0.234 - 0.00008\ T$	$\Delta G_{(P2-Pr)} = -67732.4 + 23.156T$
	$\Delta E_{(P3-Pr)} = 0.484 - 0.0005\ T$	$\Delta G_{(P3-Pr)} = -140096 + 144.72T$
	$\Delta E_{(P4-Pr)} = 0.5223 - 0.0003\ T$	$\Delta G_{(P4-Pr)} = -151182 + 86.836\ T$
	$\Delta E_{(P5-Pr)} = 0.601 - 0.0003\ T$	$\Delta G_{(P5-Pr)} = -173962 + 86.836\ T$

	Potential difference [V]	Gibbs formation energy[J/mol]
Pr (Bi)	$\Delta E_{(P1-Pr)} = 0.2636 - 0.0003\ T$	$\Delta G_{(P1-Pr)} = -230087.7 + 28.95\ T$
	$\Delta E_{(P2-Pr)} = 0.587 - 0.0005\ T$	$\Delta G_{(P2-Pr)} = -214601.9 + 17.36\ T$
	$\Delta E_{(P3-Pr)} = 0.741 - 6E\text{-}05\ T$	$\Delta G_{(P3-Pr)} = -169910 + 144.7\ T$
	$\Delta E_{(P4-Pr)} = 0.7949 - 0.0001\ T$	$\Delta G_{(P4-Pr)} = -76300.3 + 86.836\ T$

	Potential difference [V]	Gibbs formation energy[J/mol]
Nd (Cd)	$\Delta E_{(P1-Nd)} = 0.0687 - 0.0001\ T$	$\Delta G_{(P1-Nd)} = -19885.55 + 28.95\ T$
	$\Delta E_{(P2-Nd)} = 0.228 - 0.00001\ T$	$\Delta G_{(P2-Nd)} = -65995.7 + 2.895\ T$
	$\Delta E_{(P3-Nd)} = 0.241 - 0.00006\ T$	$\Delta G_{(P3-Nd)} = -69758 + 17.37\ T$
	$\Delta E_{(P4-Nd)} = 0.352 - 0.00006\ T$	$\Delta G_{(P4-Nd)} = -101888 + 17.37\ T$
	$\Delta E_{(P5-Nd)} = 0.0612 - 0.0003\ T$	$\Delta G_{(P5-Nd)} = -17714.6 + 86.84\ T$
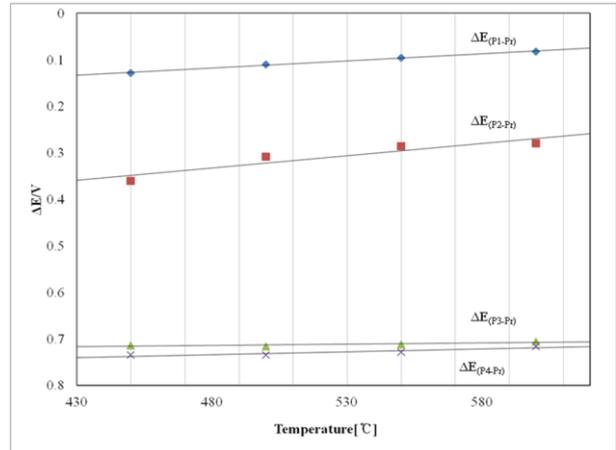
(a) LiCl-KCl +PrCl$_3$/Cd

(b) LiCl-KCl +PrCl$_3$/Bi
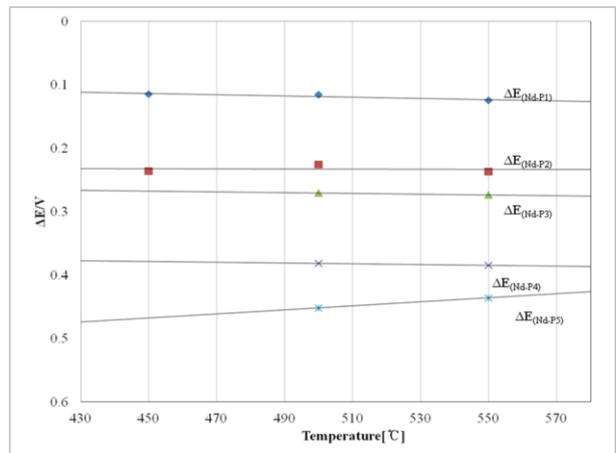

(c) LiCl-KCl +NdCl$_3$/Cd

Fig.3. Plots of potential difference between peaks against temperature.

3. Conclusions

Electochemical behavior of PrCl$_3$ and NdCl$_3$ it the liquid metal electrode studied using cyclic-voltammetry. The electro-reduction of Pr, Nd on electrodes proceeds via the formation of distinct non-homogeneous phases. The measurement for various intermetallic compounds in two-phase coexisting states was carried out in the high temperature. Gibbs free energies of formation Pr-Cd, Pr-Bi, Nd-Cd and Nd-Bi intermetallic compounds was with data of cyclic-voltammetry.

REFERENCES

[1] Lee, H., Park, G., Kang, K., Hur, J., Kim, J., Ahn, D., Cho, Y., Kim, E., 2011, "Pyroprocessing Technology Development at KAERI", Nuclear Science and Technology, 43(4), pp. 317-328.
[2] K.A. Gschneidner, Jr., F.W. Calderwood, 1988. T.B. Massalski (Ed) 1990, Binary alloy phase diagrams, ASM International, Materials Park, OH, p. 776 and 1015, 1990
[3] Y.Castrillejo et al, Jourmal of Electroanalytical Chemistry 579, 343-358, 2005
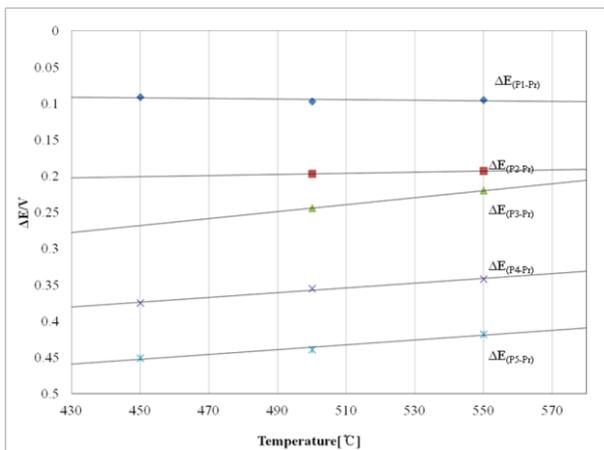
[4] Osamu Shirai, Akihiro Uehara, Toshiyuki Fujii, Hajimu Yamana,
Journal of Nuclear Materials 344, pp 142–145, 2005