Electrochemical behavior on Lu and Bi ion in LiCl-KCl Eutectic Salt Using W Electrode

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1. Introduction

Pyroprocesses that have been developed to improve the sustainability of nuclear energy is under research in many countries. [1] To reduce radioactive toxicity, pyroprocesses recover most uranium and transuranic compounds from LiCl-KCl to liquid metal or transition metals. However, molten salts still contain traces of actinides and are likely to be considered high-level wastes (HLW). The PyroRedSox concept uses liquid Bi for additional recovery of the residual actinides. The PyroRedSox process of PyroGreen is a two-step process: electrolytic reduction using liquid metal Bi to recover both actinides and lanthanides, followed by selective oxidation using an oxidizing agent (Bi ions or $BiCl_3$) to separate and extract lanthanides from liquid Bi to salt. Lanthanides and residual actinides were reduced to their respective liquid metals and intermetallic compounds via electrochemical reductive extraction. In particular, it is necessary to study the effect of liquid metal ions on the reduction of lanthanide and residual actinide ions in an electrochemical reductive extraction process, in which the liquid metal is oxidized and is present in the molten salt as an ion. This phenomenon is also presumed to occur in the electrochemical reductive extraction in the PyroRedSox process [2]. In order to investigate this phenomenon, Lutetium was selected from the lanthanide group and its electrochemical reduction was studied in the presence of Bi ion. In this study, electrochemical behavior of the Nd-Bi alloys by co-reduction at 773K in the molten LiCl-KCl mixture was investigated via a series of cyclic voltammetry (CV) experiments.

2. Experimental

Electrochemical tests were conducted in a glove box saturated with Ar, oxygen and moisture contents being less than 1 ppm. The electrochemical cell was set up inside a steel furnace connected under the glove box. The cell was fabricated to accommodate both working electrodes, counter electrode, reference electrode, and thermocouple. All the electrodes and chlorides were contained in a quartz cell.

The quartz cell was heated using a melting furnace, and the molten salt temperature was monitored to be ~773K using a K-type thermocouple inserted in a closed-end Pyrex tube. A LiCl-KCl eutectic mixture (Alfa Aesar, 99.99%), used as the electrolyte and $LuCl_3$ (Sigma Aldrich, 99.99%) and $BiCl_3$ (Sigma Aldrich, 99.99%) were put in a quartz. Tungsten wire (Alfa Aesar, 99.99%) with a diameter of 1 mm was used as both working and counter electrodes and the guide tube was made with a quartz tube (ID: 1 mm, OD: 3 mm). The reference electrode consisted of a Ag wire (Alfa Aesar, purity 99.999%, 1 mm in diameter) dipped into a silver chloride solution (1 wt%) in LiCl–KCl eutectic mixture, contained in a Pyrex tube (it is clogged at one end and can be heat-treated to a low thickness to act as a membrane).

The electrochemical measuring instrument was Versa Stat3 from Princeton Applied Research Inc. and the software used was Versa studio. The electrochemical methods involved were cyclic voltammetry, square wave voltammetry, and open circuit chrono-potentiometry.

3. Results of Discussion

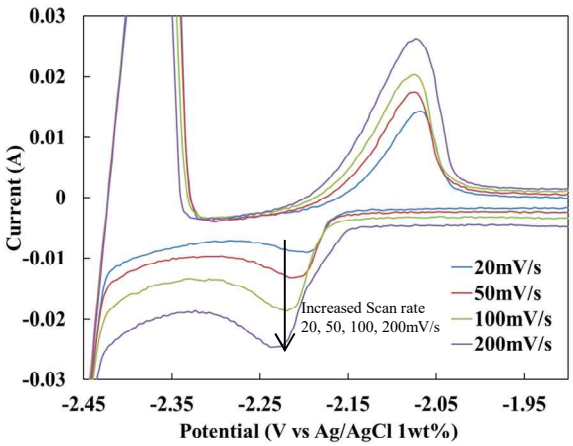

Fig. 1 Cyclic voltammogram obtained for Lu^{3+} in LiCl-KCl melt using the tungsten electrode (A=0.332 cm^2) at 773K, 1wt%, scan rate: 20, 50, 100, 200mV/s.

As a first result, the behavior of Lu was confirmed by electrochemical measurement of Cyclic Voltammetry. At a temperature of 773K, the standard potential of Lu is about -2.1V. The results confirm the current and potential through various scan rates.The Value of the potential and Current are shown in Table. 1.

We gradually added $BiCl_3$ in LiCl-KCl-LuCl3 to investigate the effect of Bi ion on the Lu ion. The results of the measured CV are shown in Fig. 2.

Table. 1. The Value of the Potential and Current at 773K

Scan Rate	reaction	Potential(V)	Current(A)
20mV/s	$Lu \rightarrow Lu^{3+} + 3e^-$	-2.06	0.015
	$Lu^{3+} + 3e^- \rightarrow Lu$	-2.19	-0.01
50mV/s	$Lu \rightarrow Lu^{3+} + 3e^-$	-2.0718	0.017
	$Lu^{3+} + 3e^- \rightarrow Lu$	-2.21	-0.013
100mV/s	$Lu \rightarrow Lu^{3+} + 3e^-$	-2.068	0.02
	$Lu^{3+} + 3e^- \rightarrow Lu$	-2.21	-0.021
200mV/s	$Lu \rightarrow Lu^{3+} + 3e^-$	-2.069	0.026
	$Lu^{3+} + 3e^- \rightarrow Lu$	-2.23	-0.025

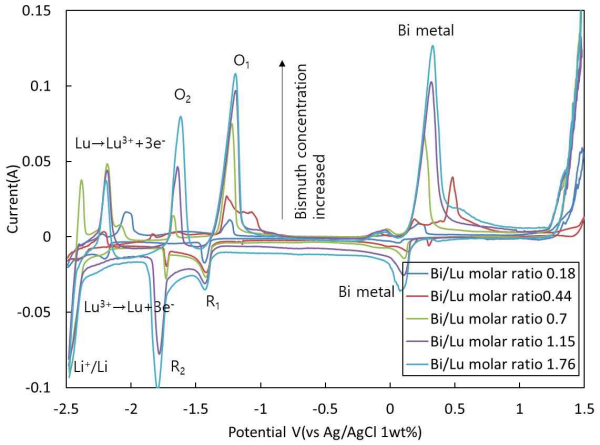

Fig. 2. Cyclic voltammogram obtained for Lu^{3+} in LiCl-KCl melt using the tungsten electrode (A=0.332 cm^2) at 773K, 1wt%, scan rate: 20, 50, 100, 200mV/s.

Comparison of the cyclic voltemmograms obtained in LiCl-KCl-$LuCl_3$ and after the addition $BiCl_3$ (0.2~2 wt %) is shown in Fig. 2.

The results are consistence with those obtained Lu^{3+}/Lu couples, correspond to the formation of a Lu. And Cathodic/anodic peak around 0.1~0.4V should be ascribed to the deposition/dissolution of Bi Metal, respectively. Many anodic and cathodic peaks R1/O1 and R_2/O_2 and Lu-Bi alloys observed, so expected to the formation of Lu-Bi intermetallic compounds. Various Lu-Bi intermetallic compounds were formed in LiCl-KCl and the corresponding potentials were observed using CV. According to the phase diagram, the LuBi and Lu_5Bi_3 phases are clearly shown and the corresponding reduction potentials are R_1 and R_2.

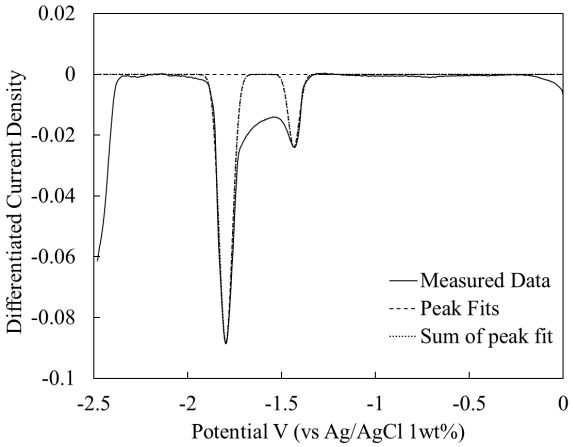

Fig. 3. Fitting of semi-differentiated semi-cyclic voltammogram

3. Conclusions

In this paper, electrolytic behavior of lutetium and Ce-Bi ion system was studied. The electrochemical behavior of Lu was studied in LiCl-KCl-$LuCl_3$ molten salts using electrochemical techniques Cyclic Voltammetry on tungsten electrodes at 773K. During the process of CV electrolysis, intermetallic compound were observed of Lu, LuBi and Lu_5Bi_3.

Further study, in order to determine clarity of diffusion coefficient in this experiment, we will compare result of electrochemistry method and we also need to quantitative research.

REFERENCES

[1] H. Lee, G.-I. Park, K.-H. Kang, J.-M. Hur, J.-G. Kim, D.-H. Ahn, Y.-J. Cho, and E.-H. Kim, "Pyroprocessing Technology Development at KAERI", Nuclear Engineering and Technology, 43 (4), 317-328, 2011.

[2] H. O. Nam, "All the Spent Nuclear Wastes to Low and Intermediate Level Wastes: PyroGreen", Proceedings of Global 2009, Paris, France, September 6-11, 2009