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

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1. Introduction

The first nuclear power plant Kori in Korea is due to permanently suspended in June 2017. According to the Korea Hydro & Nuclear Power, Kori follows the demolition process at the same time as permanent suspension, and sees the demolition in earnest in 2022.[1]

In dismantling nuclear power plants, it is necessary to ensure safe management and nuclear diffusion resistance in order to process and dispose of spent nuclear fuel. It is imperative that basic research because it is a step that needs to be developed for current processing and disposal. In the PYRO process, the generation of secondary radioactive waste is less than in the PUREX process, and nuclear diffusion resistance is guaranteed by applying the group separation.

The electrolytic reduction process of the pyro process, transfers some unrecovered TRUs to salt waste, resulting in high-level waste. Liquid-liquid extraction processes have been important to co-extract minor actinide for minimizing high level waste. While both liquid metals support the co-extraction capability, it is reported to the CRIEPI, that liquid bismuth is better than liquid cadmium in terms of lanthanide to actinide separation factor.

Pyroredsox process has been proposed to separate lanthanides (La, Sm, etc.) from used salt include trans-uranium element using liquid bismuth and bismuth chloride. Pyroredsox processes consist of electrowinning and selective oxidation.

In this paper, the electrochemical behavior of Samarium ion with bismuth ion was investigated by the electrochemical method. Also, investigated how Bi ions affect La ions.

2. Methods and Results

2.1 Experimental

Electrochemical test were conducted in Glove Box. Its atmospheric environment is filled with argon gas and the concentration of oxygen and water is less than about 1 ppm.

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 (alfa-aesar, 99.99%) containing 1 wt% high purity $SmCl_3$ (Sigma-Aldrich, 99.99%) was placed.

A W wire (Alfa-Aesar, 99%, OD: 1mm) was used as a working & counter 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.

All electrochemical measurements were performed using PAR Versastat3 potentiostat with Versastudio software. Temperature of the salt was measured with Chromel-Alumel thermocouple.

2.2 Results

Results of Cyclic voltamograms of LiCl-KCl-$SmCl_3$ at 773K are shown in Fig. 1

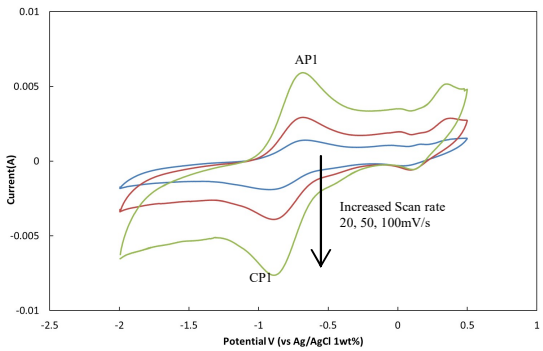

Fig. 1 Cyclic voltammogram obtained for Sm3+ in LiCl-KCl melt using the tungsten electrode (A=0.332 cm^2) at 773K, 1wt%, scan rate: 20, 50, 100mV·s. The Value of the potential and Current are shown in Table 1.

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

		Potential(V)	Current(A)
20mV/s	cathode	-0.87355	-0.002
	anode	-0.69242	0.002187
50mV/s	cathode	-0.87533	-0.004086
	anode	-0.70542	0.00449
100mV/s	cathode	-0.870432	-0.00809
	anode	-0.6986	0.00848

Since the samarium ion in the molten salt is in a soluble-soluble state, the standard potential can be expressed by the following equation.

$$Sm3+ + e- \leftrightarrow Sm2+$$

$$\text{Standard Potential} = (AP1+CP1)/2$$

At a temperature of 773K, the standard potential of Sm is about -0.78V. As already known from other literature [1], Sm exists as a Sm3+/Sm2+ (AP1/CP1) couple in the molten salt at high temperature.

We gradually added BiCl3 in LiCl-KCl-SmCl3 to investigate the effect of Bi ion on the sm ion. The results of the measured CV are shown in Fig.2.

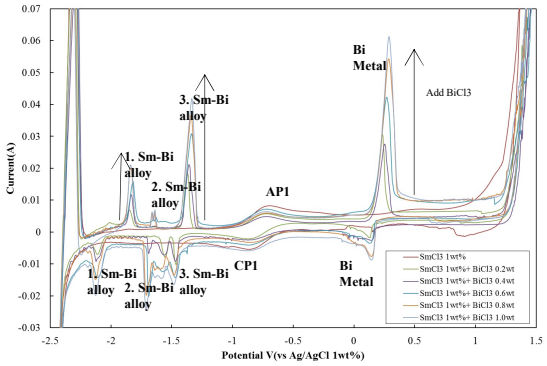

Fig. 2 Cyclic voltammograms of LiCl-KCl-$SmCl_3$(1wt%) at with $BiCl_3$(0.2~1wt%) using tungsten electrode

. Comparison of the cyclic voltemmograms obtained in LiCl-KCl-$SmCl_3$ and after the addition $BiCl_3$ (0.2~1 wt %) is shown in Fig 2.

The results are consistence with those obtained AP1 and CP1, correspond to the formation of a Sm/Sm in the first time. 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 No.1,2 and No.3 Sm-Bi alloys observed, so expected to the formation of Sm-Bi intermetallic compounds.

We measured the SWV to observe the dissimilar metal alloys formed in various ways.

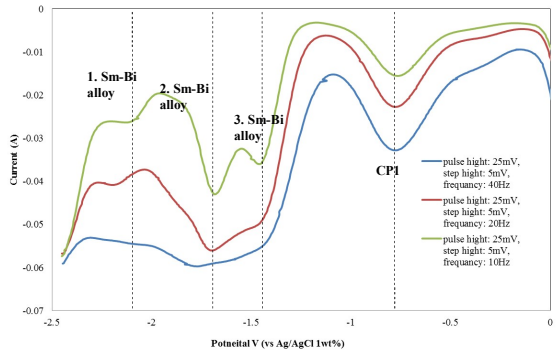

Fig. 3 Square wave voltammogram for the reduction of Sm ion with Bi ion (Sm-Bi alloy) in the LiCl-KCl on the tungsten electrode at 773 K, Pulse hight 25mV, step hight 5mV, Frequency 10, 20, 40Hz

As a result of Square Wave Voltammogram, various curves appeared. In order to consider the reduction of intermetallic compound, potential was applied in the positive to negative direction. CP1 is a reduction of the samarium ion. And a sequential curve, which is a potential curve corresponding to the reduction of the dissimilar metal alloy.

3. Conclusions

The electrochemical behavior of La was studied in LiCl-KCl-$SmCl_3$ molten salts using electrochemical techniques Cyclic Voltammetry and Square Wave Voltammetry on tungsten electrodes at 773K. The standard potential measured by CV was about -0.7 V, when Bi was added, standard potential was also the same.

During the process of CV and SWV electrolysis, intermetallic compound were observed of Sm, Smx-Biy. 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

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[2] T. Iida, T. Nohira, Y. Ito “Electrochemical formation of Sm-Co alloys by codeposition of Sm and Co in a molten LiCl-KCl-SmCl3-CoCl2 system” Electrochimica Acta, 48 (2003), p. 2517