

Electrochemical Behavior of Ce ion and Bi ion in LiCl-KCl Molten Salt

Beom-Kyu Kim*, Hwa-Jeong Han, Ji-Hye Park, Won-Ki Kim, and Byung Gi Park,
Soonchunhyang University, Soonchunhyangro 22, Asan, Chungnam 336-745, Republic of Korea

*qu@sch.ac.kr

1. Introduction

Pyro process is currently being studied worldwide, the Republic of Korea has been conducting the most active research to prepare solutions for spent fuel. The pyro-process is the main purpose of efficiently separating actinides through a sufficient recovery process of fission products [1]. 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 [2-3]. Lanthanide and actinide elements coexist as various compounds in molten salt waste produced from pyrochemical-process. PyroRedSox process has been proposed to separate lanthanides from used salt include trans-uranium elements using cathodic liquid bismuth and bismuth chloride. That processes consist of electrowinning and selective oxidation [4]. Lately studies on the intermetallic compounds of liquid metals and lanthanides have been carried out in various fields. Therefore, the electrochemical reaction of cerium present in the LiCl-KCl molten salt was confirmed by using electrochemical method, and the characteristics study of the existence of Bi ion was carried out.

2. Experimental

Experiments were carried out in a glove box under an argon atmosphere in which oxygen and moisture were kept at 1 ppm or less. And were performed to experiment at an elevated temperature using an electric furnace at the bottom of the glove box. LiCl-KCl and CeCl₃, BiCl₃, and Bismuth as a liquid electrode were all purchased from Alfa aesar and electrochemical measurements were performed in Quartz Cell. Working Electrode (WE) and Counter Electrode (CE) were Tungsten wire (1 mm diameter), the Pyrex guide tube was used to prevent contact between electrodes. 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. The temperature was always 773K.

3. Results and Discussion

Results of Cyclic voltammograms of LiCl-KCl-CeCl₃ at 773K are shown in Fig. 1.

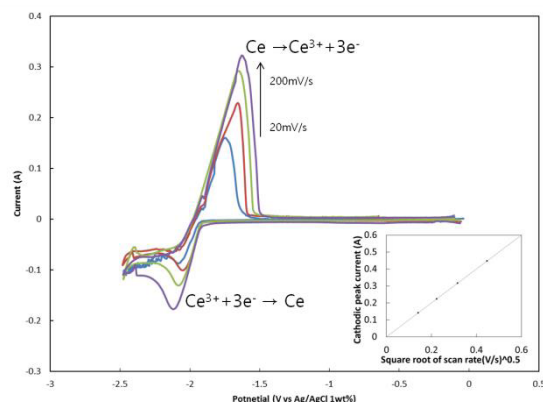


Fig. 1. Cyclic voltammogram obtained for Ce³⁺ in LiCl-KCl melt using the tungsten electrode (A=0.664 cm²) at 773K, 1wt%, scan rate: 20, 50, 100, 200mV/s.

The values of the red-ox currents are shown in Table 1.

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

| | | Current(A) |
|---------|---------------------------------------|------------|
| 20mV/s | Ce→Ce ³⁺ +3e ⁻ | 0.1585 |
| | Ce ³⁺ +3e ⁻ →Ce | -0.0335 |
| 50mV/s | Ce→Ce ³⁺ +3e ⁻ | 0.2243 |
| | Ce ³⁺ +3e ⁻ →Ce | -0.04655 |
| 100mV/s | Ce→Ce ³⁺ +3e ⁻ | 0.2934 |
| | Ce ³⁺ +3e ⁻ →Ce | -0.0818 |
| 200mV/s | Ce→Ce ³⁺ +3e ⁻ | 0.3202 |
| | Ce ³⁺ +3e ⁻ →Ce | -0.10904 |

We gradually added BiCl₃ in LiCl-KCl-CeCl₃ to investigate the effect of Bi ion on the Ce ion. The results of the measured CV are shown in Fig. 2.

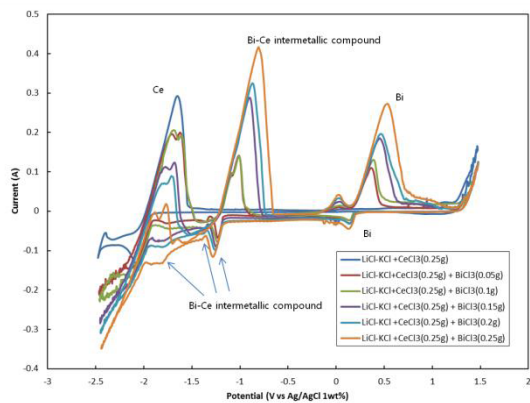


Fig. 2. Cyclic voltammograms of LiCl-KCl-CeCl₃(5wt%) at with BiCl₃(0.9~4.5wt%) using tungsten electrode and scan rate 100mV/s.

Comparison of the cyclic voltammograms obtained in LiCl-KCl-CeCl₃ and after the addition BiCl₃ (0.9~4.5 wt%) is shown in Fig. 2.

The results are consistent with those obtained Ce peak, correspond to the formation of a Ce³⁺/Ce in the first time. And Cathodic/anodic peak around 0.1~0.6 V should be ascribed to the deposition/dissolution of Bi Metal, respectively. Many anodic and cathodic peaks Ce-Bi alloys observed, so expected to the formation of Ce-Bi intermetallic compounds.

And we have derived a Potential-Current Voltammogram summarized from the Cyclic Voltammetry method.

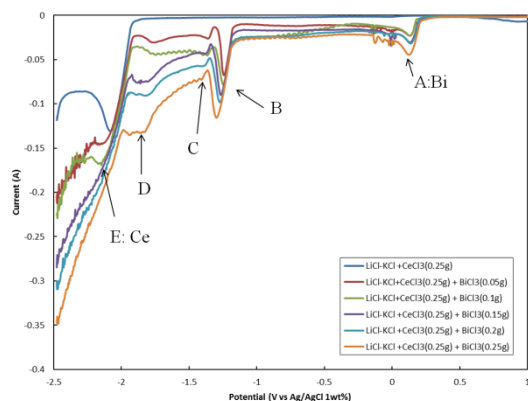


Fig. 3. Potential-Current Voltammogram for the reduction (from 1 to -2.5V) of Ce ion with Bi ion (Ce-Bi alloy) in the LiCl-KCl on the tungsten electrode (A=0.664cm²) at 773 K.

As a result of Fig. 3, various peak current appeared (A, B, C, D, E). In order to consider the reduction of intermetallic compound, potential was applied in the positive to negative direction.

A and E was a reduction of the Bismuth Cerium ion. And a sequential curve, which is a potential curve corresponding to the reduction of the dissimilar metal alloy.

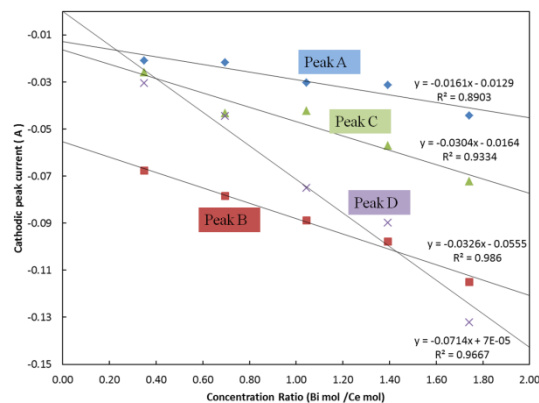


Fig. 4. Peak current according to mole concentration ratio (Bi/Ce).

Fig. 4 shows bismuth and Cerium reduced peak value as the concentration of bismuth ion increases. As a Result, Bi ions affect to the Ce ion.

4. Summary

In this paper, electrolytic behavior of Cerium and Ce-Bi ion system was studied. The electrochemical behavior of Ce was studied in LiCl-KCl-CeCl₃ molten salts using electrochemical techniques Cyclic Voltammetry on tungsten electrodes at 773K. During the process of CV electrolysis, intermetallic compound were observed of Ce, Ce-Bi.

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.

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