

Electrochemical Behavior of La on Liquid Bi electrode in LiCl-KCl molten salt

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1. Introduction

Pyroprocess is currently being developed around the world, Korea is actively studied of the many countries. It has been known that the Pyroprocess has advantage of radioactive, toxic and volume reduction. [1-2] Pyroprocessing technology aims to achieve a grouped and efficiently separation of all actinide for recycling with a sufficient decontamination of fission products generating the minimum. [3] The main steps of the pyroprocess is electrowinning process, where the remaining elements in a molten salt after electrorifinning process. That process is U, MAs are concurrently recovered at the liquid metal. [4-6] Recently, a study of the liquid metal and molten salt using an electrochemical is carried out in a variety of fields.[7-11] However, there is deficient information about the electrode reaction of lanthanide and actinide on the liquid bismuth metal electrodes.

In this paper, the electrochemical behavior of La(III), with liquid bismuth was investigated by the electrochemical method. The aim of this study is to investigate the electrochemical behavior of lanthanum or neodymium among lanthanides in molten LiCl-KCl salt at liquid metal bismuth electrode 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 eute ctic salt (Sigma-Aldrich, 99.99%) containing 1 wt% high purity LaCl₃ (Sigma-Aldrich, 99.99%) and 1 wt% high purity PrCl₃ (Alfa aesar, 99.99%) was placed. And Liquid metal such as Bi (Sigma-Adrich, 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. A W wire (Alfa-Aesar, 99%, OD: 1mm) was used as a working 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 a Solatron 1470E Cell Test System where techniques of cyclic voltammetry (CV) have been employed. Temperature of the salt was measured with Chromel-Alumel thermocouple.

3. Results and Discussion

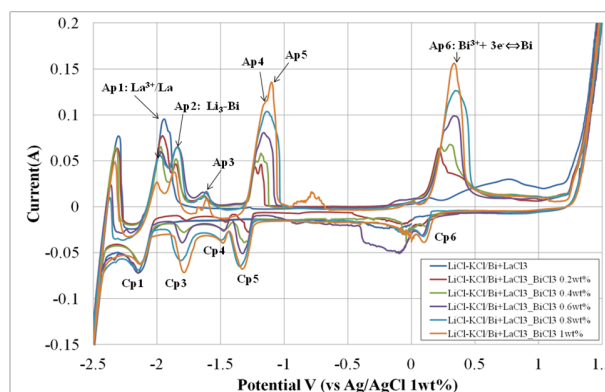


Fig. 1. Cyclic voltammograms of LiCl-KCl-LaCl₃(1wt%) at liquid Bi electrode with BiCl₃(0.2~1wt%)

Results of Cyclic voltammograms of LiCl-KCl-LaCl₃ at 773K are shown in Fig. 1. According to La-Bi Diagram, there are five La-Bi intermetallic compounds. [12] Comparison of the cyclic voltammograms obtained in LiCl-KCl-LaCl₃ and after the addition BiCl₃ (0.2~1 wt %) is shown in Fig 1.

In the LiCl-KCl-LaCl₃, corresponding to the anodic/cathodic of La, two pairs of Ap1/Cp1 are observed. After the addition of BiCl₃ (by 0.2 wt %), the voltammogram is more values then that obtained. The results are consistence with those obtained p2, correspond to the formation of a Li-Bi intermetallic by under-potential deposition of Li on the pre-deposition Bi. Cathodic/anodic peak Ap6/Cp6 around 0.1~0.4V should be ascribed to the deposition/dissolution of Bi metal, respectively.

Between the p2 and p6, peaks of redox couples are ascribed to the formation/dissolution of different intermetallic compounds. Two to four anodic peaks Ap3, Ap4, Ap5 observed correspond to the formation of La-Bi intermetallic compounds, respectively. Reduction peak potentials are very close, we have been difficult to distinguish the peak. However, La/La³⁺ peak were clearly observed at about -1.94V. Peak current value of La/La³⁺ was decreased and p3, p4, p5, p6 was increased due to BiCl₃. For La/La³⁺, can be used to estimate the diffusion coefficient from the following Randles-Sevick formula:

$$i_p = 0.61nFAC \left(\frac{nFvD}{RT} \right)^{1/2} \quad (1)$$

Where I_p is the peak cathodic current (A), A is the electrode surface area (cm^2), C is the bulk concentration of La(III) ions (mol cm^{-3}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), v is the potential scan rate (V s^{-1}). The obtained diffusion coefficient values ($D_{\text{La}^{3+}/\text{La}}$: $8.18 \times 10^{-5} \text{cm}^2/\text{s}$) were derived from the molten salt without BiCl_3 . The La/La^{3+} peak current were changed by the addition of BiCl_3 .

We derive the concentration by using a peak current corresponding to the La/La^{3+} , the diffusion coefficient was assumed a fixed value. Accordingly, the diffusion coefficient formula was modified.

$$\frac{i_p}{0.61nFA \left(\frac{nFvD}{RT} \right)^{1/2}} = C \quad (2)$$

Through the above formula the obtained concentrations at fixed diffusion coefficient value is listed in Table 1.

Table II: Problem Description

Add BiCl_3	Concentration of LaCl_3 [mol/cm ³]	Wight Percent (%)
	6.78×10^{-5}	1
0.2wt%	5.10324×10^{-5}	0.759617453
0.4wt%	4.42867×10^{-5}	0.659207273
0.6wt%	3.99037×10^{-5}	0.593966141
0.8wt%	3.66992×10^{-5}	0.546267058
1wt%	1.50404×10^{-5}	0.223875625

4. Conclusions

The electrochemical behavior of La was studied in LiCl-KCl-LaCl_3 molten salts using electrochemical techniques Cyclic Voltammetry on liquid Bi electrodes at 773K. During the process of cyclic voltammetry electrolysis, intermetallic compound were observed of La, $\text{La}_x\text{-Bi}_y$, Li-Bi. The diffusion coefficient of La was measured by cyclic voltammetry and was found to be $8.18 \times 10^{-5} \text{cm}^2/\text{s}$.

Further study, in order to determine clarity of diffusion coefficient in this experiment, we will compare result of electrochemistry method CP, SWV. Also, we will perform concentration analysis using the ICP-MS.

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