

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

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1. Introduction

The Pyro process is a process for recovering reusable uranium and TRU metals that are useful resources in spent nuclear fuel. The pyro process is actively carried out in many countries that have nuclear technology [1]. The waste molten salt generated in the pyro process contains residual actinides. Lanthanide and actinide elements coexist as various compounds in molten salt waste produced. Various process methods have been proposed for recovering and recycling them [2]. PyroRedSox process has been proposed to separate lanthanides from used salt include trans-uranium element using liquid bismuth and bismuth chloride. Pyroredsox processes consist of electrowinning and selective oxidation [3].

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

2. 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 $TmCl_3$ (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 Versastate potentiostat with Versastudio software. Temperature of the salt was measured with Chromel-Alumel thermocouple.

3. Results and Discussion

Results of Cyclic voltammograms of LiCl-KCl- $TmCl_3$ at 773K are shown in Fig. 1.

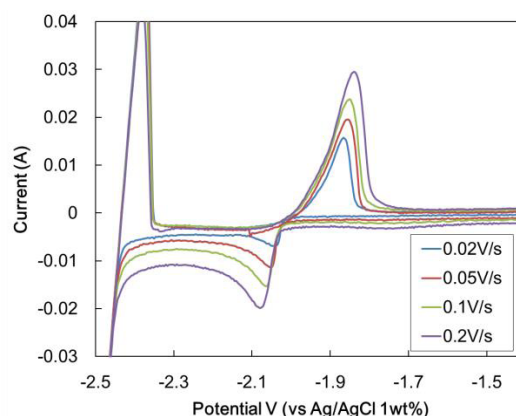


Fig. 1. Cyclic voltammogram obtained for Tm^{3+} in LiCl-KCl melt using the tungsten electrode ($A=0.664\text{ cm}^2$) at 773K, 1wt%, scan rate: 20, 50, 100, 200 mV/s.

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	$Tm \rightarrow Tm^{3+} + 3e^-$	0.016
	$Tm^{3+} + 3e^- \rightarrow Tm$	-0.0066
50mV/s	$Tm \rightarrow Tm^{3+} + 3e^-$	0.019
	$Tm^{3+} + 3e^- \rightarrow Tm$	-0.0118
100mV/s	$Tm \rightarrow Tm^{3+} + 3e^-$	0.0234
	$Tm^{3+} + 3e^- \rightarrow Tm$	-0.0158
200mV/s	$Tm \rightarrow Tm^{3+} + 3e^-$	0.029
	$Tm^{3+} + 3e^- \rightarrow Tm$	-0.0193

We gradually added $BiCl_3$ in LiCl-KCl- $TmCl_3$ to investigate the effect of Bi ion on the Tm ion. The results of the measured CV are shown in Fig. 2.

Comparison of the cyclic voltammograms obtained in LiCl-KCl- $TmCl_3$ and after the addition $BiCl_3$ (0.2~2 wt%) is shown in Fig. 2. The results are consistence with those obtained Tm peak, correspond to the formation of a Tm^{3+}/Tm in the first time. And Cathodic/anodic peak around 0.1~0.6V should be

ascribed to the deposition/dissolution of Bi Metal, respectively. Many anodic and cathodic peaks Tm-Bi alloys observed, so expected to the formation of Tm-Bi intermetallic compounds.

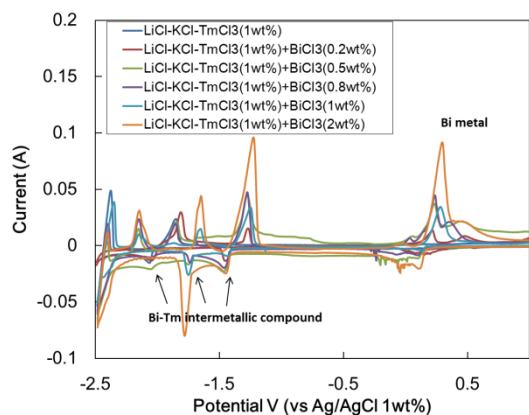


Fig. 2. Cyclic voltammograms of $\text{LiCl-KCl-TmCl}_3(2\text{wt}\%)$ at with $\text{BiCl}_3(0.2\text{--}2\text{wt}\%)$ using tungsten electrode and scan rate 100mV/s .

In order to consider the reduction of intermetallic compound, potential was applied in the positive to negative direction. As a result of Fig. 3, various reduction peaks current appeared. It is estimated the reduction of Bi-Tm intermetallic compound. Also, as Bi ion more increased, the reduction peak of Tm, which appeared at $0.2\text{wt}\%$, disappeared.

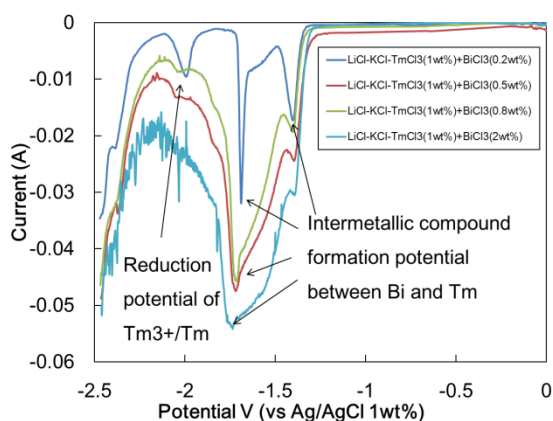


Fig. 3. Square Wave Voltammogram for the reduction (from 1 to -2.5V) of Tm ion with Bi ion (Tm-Bi alloy) in the LiCl-KCl on the tungsten electrode ($A=0.664\text{cm}^2$) at 773K .

4. Summary

This study, electrolytic behavior of Thulium and Tm-Bi ion system was studied. The electrochemical behavior of Tm was studied in LiCl-KCl-TmCl_3 molten salts using electrochemical techniques Cyclic Voltammetry on tungsten electrodes at 773K . During

the process of CV and SWV, intermetallic compound were observed Bi-Tm.

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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