

## Electrochemical processes of La(III) and Uranium ions in Molten LiCl-KCl

Gao Fanxing, Won Il Ko\*

Korea Atomic Energy Research Institute

P.O. Box 105, Yusong, Taejeon 305-353, Korea

Wang Changshui, Ouyang Yinggen

Department of Radiochemistry, China Institute of Atomic Energy, P.O.Box 275-26, Beijing, 102413, China

\*Corresponding author: nwiko@kaeri.re.kr

### 1. Introduction

Electrolytic technology in the reaction media of molten salts has been considered as an important route to treat raw materials, prepare metals and alloys. Moreover, dry process employing electrolytic technology in molten salts, adopted in spent nuclear fuel cycle, is a promising method to deal with high-burn-up, short-cooled, high-plutonium-concentration spent fuels. The basic data concerning actinides electrolysis is of great importance in developing molten salts electrolytic pyroprocessing such as formal potential, diffusion coefficient, electrode mechanism and so on. There are a few studies reported on the electrochemical process of uranium ion in the molten chlorides [1-6]. However, the data published varies considerably due to the differences in the exact experimental conditions such as salts composition, temperature, and electrode material. The different ways of introducing electroactive ions into the molten salts considerably affect the occurring forms of the studied ions in the melts and the subsequent electrochemical measurements. In the present work, certain amount of anhydrous  $\text{LaCl}_3$  was dissolved into the desiccated LiCl-KCl melt, and LiCl-KCl- $\text{LaCl}_3$  salt was obtained. With two batches of uranium chloride synthesized, LiCl-KCl- $\text{UCl}_3$  and LiCl-KCl- $\text{UCl}_3$ - $\text{UCl}_4$  molten salts were prepared. Cyclic voltammetry and chronopotentiometry measuring techniques were adopted to investigate these three melts respectively.

### 2. Methods

#### 2.1 Preparation of LiCl-KCl- $\text{UCl}_3$ and LiCl-KCl- $\text{UCl}_3$ - $\text{UCl}_4$ salts

The chloride mixture of 59mol%LiCl-41mol%KCl was treated by the following procedures: the mixture was firstly desiccated under a dynamic vacuum(less than 80Pa) through step-by-step increasing the temperatures: 373K (1h)-400K (1h)-573K (1h). Then, the mixture was melted in a purified argon atmosphere. Uranium chloride was prepared by chloridizing  $\text{UH}_3$  by passing HCl in a quartz chamber heated by a set of resistance oven. By controlling the chlorination time, two batches of uranium chlorides were obtained. One was a mixture of  $\text{UCl}_3$  and a little residual  $\text{UH}_3$  powder, and the other was a mixture of  $\text{UCl}_3$  and a certain amount of  $\text{UCl}_4$ . By dissolving uranium chlorides into treated LiCl-KCl melts under Ar atmosphere, the

molten LiCl-KCl- $\text{UCl}_3$  and LiCl-KCl- $\text{UCl}_3$ - $\text{UCl}_4$  were prepared. The total concentration of uranium ions in the melt was determined by ICP-AES method (IRIS-ADVANTAGE).

#### 2.2 Experimental apparatus

A simple-structure, steady-performance Ag-AgCl (5mol %) reference electrode adopting Pyrex glass as ions conducting membrane was fabricated. A 1mm diameter Mo wire (99.95% purity, purchased from Alfa Aesar) was used as the working electrode. The Mo wire was carefully polished and desiccated in vacuum oven before every experiment. The active area of the working electrode was determined by measuring the immersion length of the electrode in the molten salts [3-7]. A 6mm diameter graphite rod served as the auxiliary electrode. Connected with a potentiostat, a three-electrode electrochemical measuring system was set up. Cyclic voltammograms and chronopotentiograms were recorded by PAR 273A potentiostat with an EG&G M273A electrochemical software.

### 3. Results

Cyclic voltammetry and chronopotentiometry were employed to study the electrode process of La(III) and uranium ions at Mo electrode in the molten LiCl-KCl respectively. The electrode processes inferred by these two techniques separately are in good agreement with each other [3,4,7].

#### 3.1 Results obtained by cyclic voltammetry

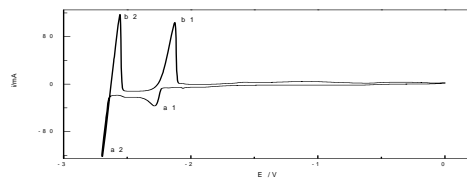


Fig.1. Cyclic voltammogram of LiCl-KCl- $\text{LaCl}_3$ .

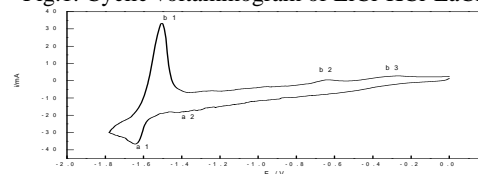


Fig.2. Cyclic voltammogram of LiCl-KCl- $\text{UCl}_3$ .

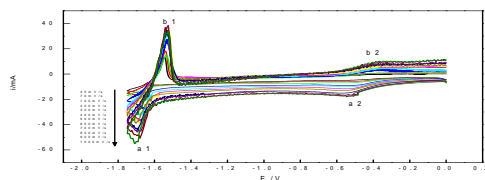


Fig.3. Cyclic voltammograms of LiCl-KCl-UCl<sub>3</sub>-UCl<sub>4</sub>

The reduction of La(III) occurs in a step with a global exchange of three electrons. Cyclic voltammetry studies indicated that at a sweep rate less than 0.2Vs<sup>-1</sup>, the electroreduction of La(III) to lanthanum metal is reversible and controlled by diffusion of La(III). However, the process becomes under a mixed control of both diffusion and electron transfer when sweep rate exceeds 0.2Vs<sup>-1</sup>.

It was determined that the reduction of U(IV) to uranium metal takes two steps. Firstly, U(IV) is reduced to U(III). Then, the reduction of U(III) to uranium metal occurs in a step with a global exchange of three electrons. Cyclic voltammetry studies indicated that at low sweep rates, the reduction of U(III) to uranium is reversible. However, a mixed control of both diffusion and electron-transfer is observed as the sweep rate increases.

### 3.2 Results obtained by chronopotentiometry

An empirical temperature dependence of the diffusion coefficient of La(III) was proposed:  
 $LnD_{La(III)} = 7.742 - 1.441 \times 10^4 / T$ . The relation between the formal potential of La(III)/La versus Ag/AgCl reference electrode and temperature was described in the following equation:  $E^{\theta'} = -1.402 - 4.689 \times 10^2 / T$ .

Some basic electrochemical results concerning uranium ions in the molten LiCl-KCl are listed in Table1 and Table 2[8].

Table 1 Diffusion coefficient of U(III)

LiCl-KCl-UCl <sub>3</sub> , 728 K		LiCl-KCl-UCl <sub>3</sub> -UCl <sub>4</sub> , 723 K	
$C_{UCl_3}: 9.10 \times 10^{-6} \text{ mol cm}^{-3}$		$C_{U_{\text{ions}}}: 6.46 \times 10^{-5} \text{ mol cm}^{-3}$	
	CV	CP	CV
$D, \text{cm}^2 \text{ s}^{-1}$	$(8.1 \pm 0.2) \times 10^{-5}$	$(3.47 \pm 0.01) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-6}$
			$(3.17 \pm 0.01) \times 10^{-5}$

Table 2 Formal potential of U(III)/U

LiCl-KCl-UCl <sub>3</sub> , 728 K		LiCl-KCl-UCl <sub>3</sub> -UCl <sub>4</sub> , 723 K	
$C_{UCl_3}: 9.10 \times 10^{-6} \text{ mol cm}^{-3}$		$C_{U_{\text{ions}}}: 6.46 \times 10^{-5} \text{ mol cm}^{-3}$	
	VvsAg/AgCl	VvsCl <sup>-</sup> /Cl <sub>2</sub>	VvsAg/AgCl
$E^{\theta}, \text{V}$	-1.40±0.02	-2.47±0.02	-1.44±0.01
			-2.51±0.01

### 3. Conclusions

The electrode processes of La(III) and uranium ions at a Mo electrode in the molten LiCl-KCl for temperatures ranging from 683K to 773K was studied by cyclic voltammetry and chronopotentiometry respectively. Several electrochemical results were obtained such as redox process of La(III), U(IV) and U(III), diffusion coefficient of La(III) and U(III), and the formal potential of La(III)/La and U(III)/U versus Ag/AgCl reference electrode in these two salts systems were calculated respectively.

Based on the data of the electrode processes of lanthanum ion and uranium ions, the separation of lanthanum and uranium in LiCl-KCl molten salts could be conducted. Electro-deposition of uranium metal could be carried out.

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