

## Study for electrochemical behavior of uranium oxide in a molten LiCl-Li<sub>2</sub>O system

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### 1. Introduction

Interest in the electrolytic reduction of uranium oxide is increasing in the treatment of spent fuel oxides [1,2]. With complicated and expensive procedures many reactive metals can be prepared in a pure metal form, the electrochemical reduction of a metal oxide has been recently proposed in metallurgy [3,4]. The electrochemical reduction process is simple and rapid when compared to the conventional processes. The process can reduce the production costs and be applicable to a wide range of metal oxides. Chen et al. [4] proposed the direct electrochemical reduction of titanium dioxide to titanium in a molten calcium chloride.

Argonne National Laboratory (ANL) has reported the experimental results of an electrochemical reduction of the uranium oxide fuel in a bench-scale apparatus with a cyclic voltammetry, and has designed high-capacity reduction (HCR) cells and conducted three kg-scale UO<sub>2</sub> reduction runs. Gourishankar et al. [1] classified the mechanisms of the electrolytic reduction of the metal oxides in a LiCl-Li<sub>2</sub>O molten salt system into two types; the simultaneous reduction and the direct electrochemical reduction. The uranium oxide in LiCl-Li<sub>2</sub>O molten salt was converted to uranium metal according to two mechanisms.

Korea Atomic Energy Research Institute (KAERI) has developed the Advanced Spent Fuel Conditioning Process (ACP) to be an innovative technology in handling the PWR spent fuel. As part of ACP, the electrolytic reduction process (ER process) is the electrochemical reduction process of uranium oxide to uranium metal in molten salt. The ER process has advantages in a technical stability, an economic potential and a good proliferation resistance. KAERI has reported on the good experimental results of an electrochemical reduction of the uranium oxide in a 20 kg HM/batch lab-scale [5].

In this work, cyclic voltammograms for a LiCl-3 wt% Li<sub>2</sub>O system and an U<sub>3</sub>O<sub>8</sub>-LiCl-3 wt% Li<sub>2</sub>O system with the integrated cathode assembly have been obtained. From the cyclic voltammograms, the mechanisms of the predominant reduction reactions in the electrolytic reactor cell were understood. The potentials of the cathode and anode were measured with respect to the thickness of the uranium oxide loaded into the cathode assembly and the thickness of the magnesia membrane. From the potential

data, the exchange current densities and the maximum allowable current densities were obtained.

### 2. Experimental

The electrolytic reduction experiments were carried out in a 10 g U<sub>3</sub>O<sub>8</sub>/batch scale electrochemical reactor, which was composed of the resistance furnace, K-type thermocouple, alumina and magnesia crucible, anode, cathode, reference electrode and an Ar gas feeder etc. Electrolytic reactor cell was a magnesia crucible fitted with an alumina crucible liner. The cathode was an assembly of a stainless steel conductor and a porous magnesia crucible loaded with uranium oxide. The porosity of the magnesia membrane was 22~25 %. The anode of 6 mm diameter was a platinum tube of 1 mm thick. Three platinum anodes were used. A platinum rod of 3 mm diameter was used as a quasi-reference electrode for measuring the cathode and anode potentials. The WMPG 1000 Multichannel Potentiostat/Galvanostat from WonA-Tech Co. was used for the electrochemical experiments. The WMPG 1000 Ver.3.00 software was also used for electrochemical control and data acquisitions.

### 3. Results and Discussions

The cyclic voltammetry was applied to the electrolytic reduction cell to measure the reduction potentials of the Li<sub>2</sub>O and U<sub>3</sub>O<sub>8</sub>.

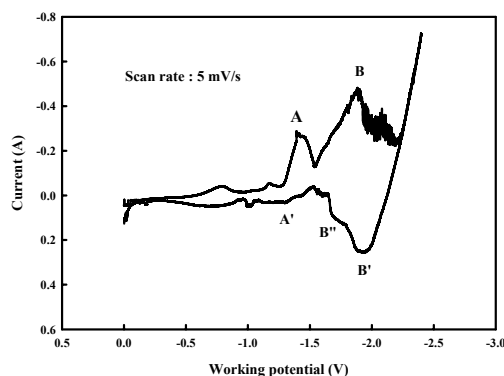


Fig. 1. Cyclic voltammogram of LiCl-3 wt% Li<sub>2</sub>O-U<sub>3</sub>O<sub>8</sub> system at 650°C.

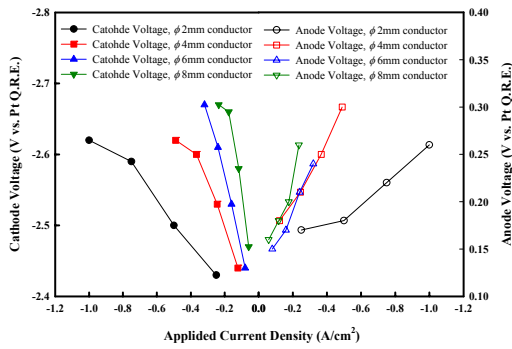


Fig. 2. The plot for the potential of cathode and anode vs. the applied current density with respect to thickness of uranium oxide.

The  $\text{Li}_2\text{O}$  and  $\text{U}_3\text{O}_8$  were reduced to metals at the cathode, and the oxygen ions were reduced to oxygen gas at the anode. In the  $\text{LiCl-3wt\%Li}_2\text{O}$  molten salt system at  $650^\circ\text{C}$ , the reduction potential of  $\text{Li}_2\text{O}$  was  $-1.80\text{ V}$  at the cathode, where  $\text{Li}$  ion started to be reduced to lithium metal, and the lithium metal was oxidized at  $-1.52\text{ V}$  [6]. Fig.1 shows the cyclic voltammogram of the  $\text{U}_3\text{O}_8\text{-LiCl-3wt\% Li}_2\text{O}$  system. As shown in Fig.1, the reduction potentials of the  $\text{U}_3\text{O}_8$  and  $\text{Li}_2\text{O}$  were  $-1.40\text{ V}$  and  $-1.88\text{ V}$  (peak A and B), respectively. The reduction potential of  $\text{Li}_2\text{O}$  is similar to the results of the  $\text{LiCl-3wt\%Li}_2\text{O}$  system in Fig.1. The uranium and lithium metal was oxidized at  $-1.32\text{ V}$  and  $-1.92\text{ V}$ , respectively (peak A' and B'). The potential of peak B'' is considered as the desorption of the oxidized  $\text{Li}_2\text{O}$  from the cathode. From the results of the cyclic voltammetry of the  $\text{U}_3\text{O}_8\text{-LiCl-3wt\%Li}_2\text{O}$  system,  $\text{U}_3\text{O}_8$  is chemically reduced by the electrolytic reduced lithium metal in less than a  $-1.88\text{ V}$  cathode potential. Fig.2 shows the plot for the potential of the cathode and anode according to the thickness of uranium oxide loaded into the cathode assembly.

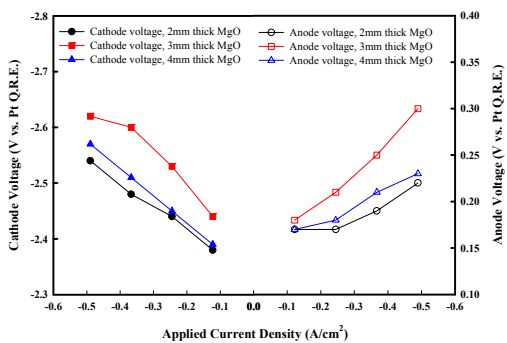


Fig. 3. The plot for the potential of cathode and anode vs. the applied current density with respect to thickness of uranium oxide.

Table 1. The exchange current densities, transfer coefficients and maximum allowable current densities from the relation between the overpotential and the current with respect to thickness of uranium oxide.

Conductor size / Thickness of the uranium oxide (mm)	Exchange current (A)	Transfer coefficient ( $\alpha$ )	Maximum allowable current density ( $\text{A}/\text{cm}^2$ )
2/6.5	0.24	0.57	2.50
4/5.5	0.23	0.55	1.14
6/4.5	0.22	0.56	0.73
8/3.5	0.24	0.46	0.55

Table 2. The exchange current densities, transfer coefficients and maximum allowable current densities from the relation between the overpotential and the current with respect to the thickness of  $\text{MgO}$  membrane.

Thickness of $\text{MgO}$ (mm)	Exchange current (A)	Transfer coefficient ( $\alpha$ )	Maximum allowable current density ( $\text{A}/\text{cm}^2$ )
2	0.27	0.72	1.76
3	0.23	0.55	1.14
4	0.27	0.63	1.50

Fig.3 shows the plot for the potential of the cathode and anode according to the thickness of  $\text{MgO}$  membrane. For large values of the overpotential, the Tafel behavior can be applied. From the Tafel plot, the exchange current densities and transfer coefficients were obtained as shown in Table 1 and Table 2. Table 1 and Table 2 also shows the maximum allowable current densities with respect to the thickness of the uranium oxide and the porosity of the magnesia membrane, respectively.

## REFERENCES

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