# Electrochemical Study for Electrolytic Reduction of Uranium Oxide in LiCl-$Li_2O$ Molten Salt with Integrated Cathode Assembly

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## 1. Introduction

Interest of electrolytic reduction of uranium oxide is increasing in treatment of spent metal fuels[1,2,3]. Argonne National Laboratory (ANL) has reported the experimental results of electrochemical reduction of uranium oxide fuel in a bench-scale apparatus with cyclic voltammetry[2,3]. From the cyclic voltammograms, the mechanism of electrolytic reduction of metal oxides is analyzed. The uranium oxide in LiCl-3wt%Li2O is converted to uranium metal according to two mechanisms; direct and indirect electrolytic reduction [1]. In this study, cyclic voltammograms for LiCl-3wt%Li2O system and U3O8-LiCl-3wt%Li2O system using the 325-mesh stainless steel screen have been obtained.

## 2. Experimental apparatus and Materials

### *2.1 Experimental apparatus*

The electrolytic reduction experiments were carried out in 10g$U_3O_8$/batch scale electrochemical reactor, which is composed of resistance furnace, K-type thermocouple, alumina & magnesia crucible, anode, cathode, reference electrode and Ar gas feeder etc. For cooling down the reactor and preventing molten salts from volatilization and emission, water jacket was installed to the upper of the reactor flange. The electrolytic reactor was magnesia crucible fitted with alumina crucible. The inside diameter of the magnesia crucible was 7.1 cm. The cathode was an assembly of the stainless steel conductor and the stainless basket loaded with uranium oxide. The basket was shielded five-fold with 325-mesh stainless steel screen. The anode was 6mm diameter, 1mm thickness platinum tube. The three anodes were used. A 3mm diameter platinum rod was used as reference electrode for measuring the cathode and anode potentials. A WMPG 1000 Multichannel Potentiostat/Galvanostat from WonATech co., was used for electrochemical experiments. And a WMPG 1000 Ver.3.00 software was used for electrochemical control and data acquisitions.

### *2.2 Materials*

The electrolytes used were anhydrous 20-mesh 99.6% purity LiCl and 99.5% purity $Li_2O$ powder from Alfa AESAR. LiCl-3wt% $Li_2O$ molten salt system was used for electrolytic reduction, and the operating temperature was 650□. The uranium oxide used was the $U_3O_8$. The 325-mesh stainless steel screen with stainless steel basket was used for loading the $U_3O_8$ in the assembly cathode.

## 3. Results and Discussions

The cyclic voltammetry was applied to the electrolytic reduction cell to measure reduction potentials of the $Li_2O$ and $U_3O_8$. The $Li_2O$ and $U_3O_8$ were reduced to the metals at the cathode, and oxygen ions were reduced to the oxygen gas. Fig.1 shows the cyclic voltammogram of the LiCl-3wt% $Li_2O$ molten salt system with stainless steel conductor at 650□. The reduction potential of $Li_2O$ was ~-1.80V at the cathode (peak A), where Li ion started to be reduced to lithium metal. And the lithium metal was re-oxidized at ~-1.52V(peak B).

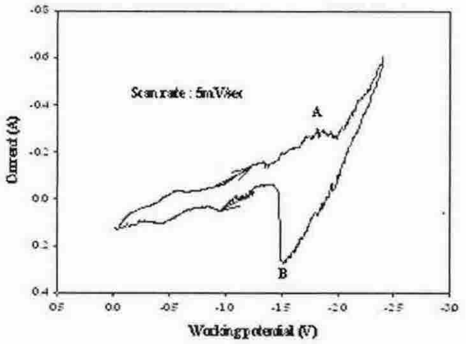

**Fig1. Cyclic voltammogram of stainless steel conductor with stainless basket in LiCl-3wt%$Li_2O$ molten salt at 650°C.**

Fig.2 shows the cyclic voltammogram of the 325-mesh stainless steel screen with the $U_3O_8$-LiCl-3wt%$Li_2O$ system. As shown in Fig.2, reduction potentials of the $U_3O_8$ and $Li_2O$ were ~-1.40V and ~-1.92V (peak A and B), respectively. The reduction potential of $Li_2O$ is similar with the results of LiCl-3wt%Li2O system in Fig.1. And the uranium and lithium metal was re-oxidized at ~-1.32V and ~-1.91V, respectively (peak A' and B'). The potential of Peak B" is considered as the desorption of re-oxidized $Li_2O$ from the cathode.

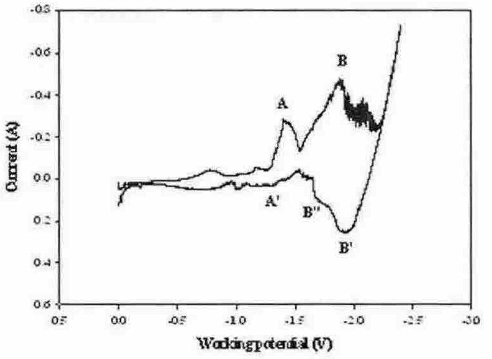

Fig 2. Cyclic voltammogram for 325-mesh steel screen loaded with $U_3O_8$ in LiCl-3wt%$Li_2O$ molten salt at 650°C.

From the results of cyclic voltammetry of $U_3O_8$-LiCl-3wt%$Li_2O$ system, the mechanism of the electrolytic reduction of uranium oxide is distinguished between direct electrolytic reduction process and indirect simultaneous electrolytic reduction [1,3]. In the case of <-1.91V cathode potential, $U_3O_8$ is chemically reduced by the electrolytic reduced lithium metal as shown below.

$$Li_2O \rightarrow 2Li^+ + O^{2-}$$

$$2Li^+ + 2e^- \rightarrow 2Li \qquad \text{(Cathode reaction)}$$

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e^- \qquad \text{(Anode reaction)}$$

$$U_3O_8 + 16Li \rightarrow 3U + 8Li_2O$$

In the case between -1.40V and -1.92V, $U_3O_8$ is directly reduced without lithium metal formation as follows

$$U_3O_8 + 16e^- \rightarrow 3U + 8O^{2-}$$

$$8O^{2-} \rightarrow 4O_2 + 16e^-$$

$$U_3O_8 \rightarrow 3U + 4O_2$$

Fig.3 shows the comparison of cyclic voltammetry for electrolytic reduction of $U_3O_8$-LiCl-3wt%$Li_2O$ system. Park et al.[4] had used the magnesia membrane in the assembly cathode for loading the $U_3O_8$ and we used the 325-mesh stainless steel screen. The redox of $U_3O_8$ and $Li_2O$ showed similar results in the two cases except the re-oxidization of uranium metal. Because the current value of the oxidization peak was dependent on the end voltage of the positive-going scan [3] and many of the reactor cell conditions had effects on the electrochemical reactions, the differences of oxidization potential of redued metals may be ignored.

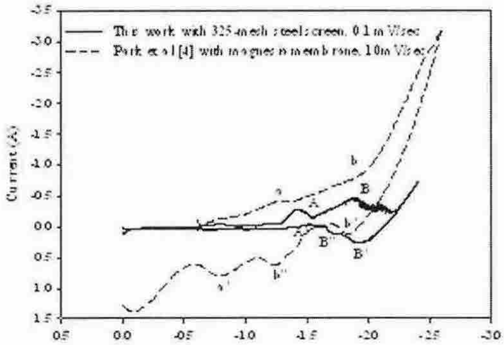

Fig 3. Comparison of Cyclic voltammograms for 325-mesh stainless steel screen and magnesia membrane loaded with $U_3O_8$ in LiCl-3wt%$Li_2O$ molten salt at 650°C.

## 4. Conclusions

Using the 325-mesh stainless steel mesh screen in the assembly cathode, we have observed the electrolytic reduction of $U_3O_8$ and $Li_2O$ with cyclic voltammetry. From the value of reduction potential of $U_3O_8$ and $Li_2O$, the reduction potentials are the determining factor for the mechanism of electrolytic reduction of uranium oxide in LiCl-3wt%$Li_2O$ molten salt system. In the future, we will examine the direct and indirect electrolytic reduction of uranium oxide using the 325-mesh stainless steel mesh screen in addition to magnesia membrane in the assembly cathode.

## REFERENCES

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