

A Study of Integrated Cathode Assembly for Electrolytic Reduction of Uranium Oxide in LiCl–Li₂O Molten Salt

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1. Introduction

Interest of electrolytic reduction of uranium oxide is increasing in treatment of spent metal fuels. Argonne National Laboratory (ANL) has reported the experimental results of electrochemical reduction of uranium oxide fuel in bench-scale apparatus with cyclic voltammetry, and has designed high-capacity reduction (HCR) cells and conducted three kg-scale UO₂ reduction runs. From the cyclic voltammograms, the mechanism of electrolytic reduction of metal oxides is analyzed. The uranium oxide in LiCl–Li₂O is converted to uranium metal according to the two mechanism; direct and indirect electrolytic reduction. In this study, cyclic voltammograms for LiCl–3wt% Li₂O system and U₃O₈–LiCl–3wt% Li₂O system using the 325-mesh stainless steel screen in cathode assembly have been obtained. Direct electrolytic reduction of uranium oxide in LiCl–3wt% Li₂O molten salt has been conducted.

2. Experimental apparatus and Materials

The electrolytic reduction experiments were carried out in 10gU₃O₈/batch scale electrochemical reactor, which is composed of resistance furnace, K-type thermocouple, alumina and 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 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. The electrolytes used were anhydrous 20-mesh 99.6% purity LiCl and 99.5% purity Li₂O powder from Alfa AESAR co. The uranium oxide used was the U₃O₈ powder.

3. Results and Discussions

The cyclic voltammetry was applied to the electrolytic reduction cell to measure reduction potentials of the Li₂O and U₃O₈. The Li₂O and U₃O₈ 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 $\text{LiCl}-3\text{wt}\% \text{Li}_2\text{O}$ molten salt system with stainless steel conductor at 650°C . The reduction potential of Li_2O was $\sim -1.80\text{V}$ at the cathode (peak A), where Li ion started to be reduced to lithium metal. And the lithium metal was oxidized at $\sim -1.52\text{V}$ (peak B). Fig.2 shows the cyclic voltammogram of the $\text{U}_3\text{O}_8-\text{LiCl}-3\text{wt}\%\text{Li}_2\text{O}$ system with 325-mesh stainless steel screen in the cathode assembly. As shown in Fig.2, reduction potentials of the U_3O_8 and Li_2O were $\sim -1.40\text{V}$ and $\sim -1.92\text{V}$ (peak A and B), respectively. The reduction potential of Li_2O is similar with the results of $\text{LiCl}-3\text{wt}\%\text{Li}_2\text{O}$ system as shown Fig.1. And the uranium and lithium metal was oxidized at $\sim -1.32\text{V}$ and $\sim -1.91\text{V}$, respectively (peak A' and B'). The potential of Peak B" is considered as desorption of oxidized Li_2O from the cathode. From the results of cyclic voltammetry of $\text{U}_3\text{O}_8-\text{LiCl}-3\text{wt}\%\text{Li}_2\text{O}$ system, the mechanism of the electrolytic reduction of the uranium oxide is distinguished between direct electrolytic reduction process and indirect simultaneous electrolytic reduction. In the case of $< -1.91\text{V}$ cathode potential, U_3O_8 is chemically reduced by the electrolytic reduced lithium metal. In the case between -1.40V and -1.91V , U_3O_8 is directly reduced without lithium metal formation.

Fig.3 shows the chronoamperogram of electrolytic reduction of uranium oxide in $\text{LiCl}-3\text{wt}\% \text{Li}_2\text{O}$ molten salt. Direct electrolytic reduction of uranium oxide was conducted with -1.8V working potential according to the result of cyclic voltammetry. The concentration of Li_2O was to be constant during the direct electrolytic reduction, but that was decreased from $2.55\text{wt}\%$ to $1.43\text{wt}\%$. The current of the cell increased from 0.06A to 0.24A . The products of reduced uranium oxide were analyzed with thermal gravity (TG) method. The weight percentage increased was $\text{xxx wt}\%$. From the result, the product of electrolytic reduction was considered to be UO_2 . The uranium oxide was to be reduced to uranium metal directly, but U_3O_8 was reduced to UO_2 . As shown in Fig.3, the reactor cell system was unstable at the initial time, and at the last time the anode potential increased to the 0.58V . The concentration of Li_2O decreased slowly as time elapsed, the Li metal was considered to be formed. The direct electrolytic reduction of uranium oxide failed to obtain the uranium metal. So we have to adjust the working potential of cathode for direct electrolytic reduction in the next experiment.

4. Conclusions

Using the 325-mesh stainless steel mesh screen in the cathode assembly, 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 direct electrolytic reduction of uranium oxide has been examined in the $\text{LiCl}-3\text{wt}\%\text{Li}_2\text{O}$ molten salt system. In the future, we will examine the direct electrolytic reduction of uranium oxide with the adjusted working potential and the indirect electrolytic reduction of uranium oxide using the 325-mesh stainless steel mesh screen. And we will also examine the direct and indirect electrolytic reduction using the magnesia membrane in the cathode assembly.

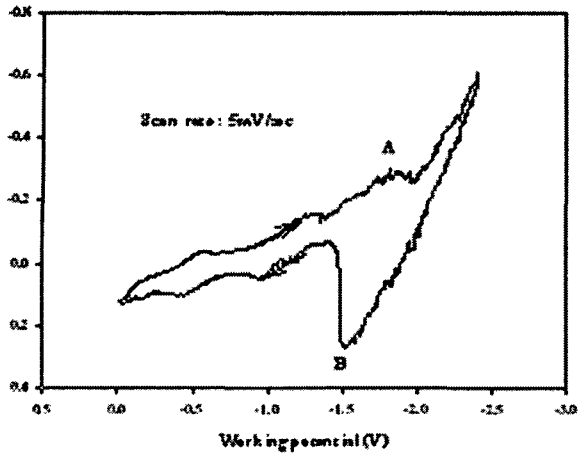


Fig.1. Cyclic voltammogram of stainless steel conductor with stainless basket in LiCl-3wt% Li₂O molten salt at 650° C

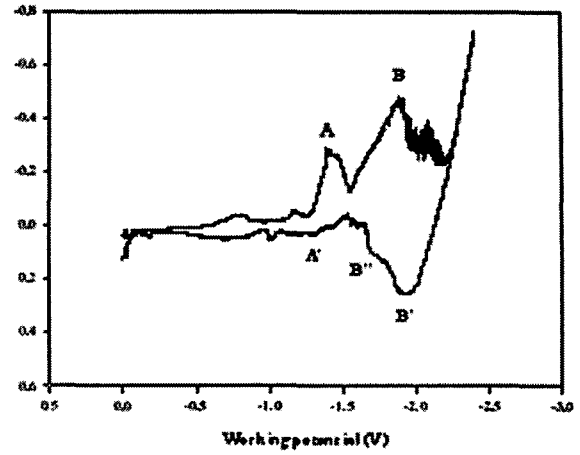


Fig.2. Cyclic voltammogram for 325-mesh steel screen loaded with U₃O₈ in LiCl-3wt% Li₂O molten salt at 650° C

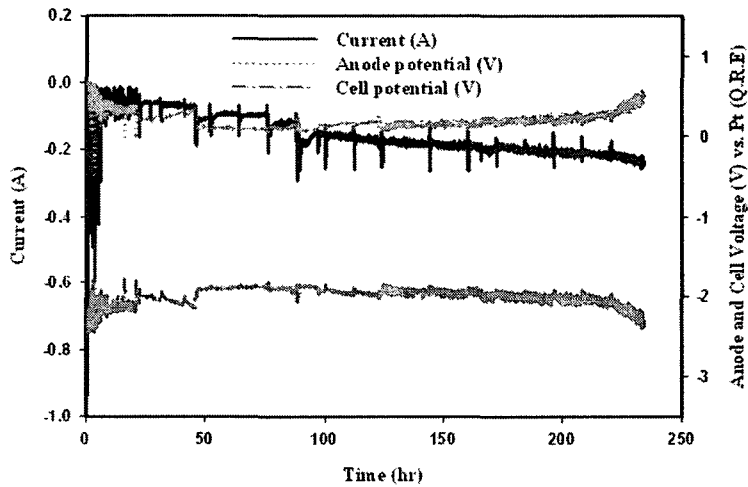


Fig. 3. Chronoamperogram of direct electrolytic reduction of U₃O₈ in LiCl-3wt% Li₂O. The working potential is -1.8V