

Electrochemical Behavior for a Reduction of Uranium Oxide in a LiCl-Li₂O Molten Salt with an Integrated Cathode assembly

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SUMMARY

Electrolytic reduction of uranium oxide to uranium metal was studied in a LiCl-Li₂O molten salt system. The reduction mechanism of the uranium oxide to a uranium metal has been studied by means of a cyclic voltammetry. Effects of the layer thickness of the uranium oxide and the thickness of the MgO on the overpotential of the cathode and the anode were investigated by means of a chronopotentiometry. From the cyclic voltamograms, the decomposition potentials of the metal oxides are the determining factors for the mechanism of the reduction of the uranium oxide in a LiCl-3 wt% Li₂O molten salt and the two mechanisms of the electrolytic reduction were considered with regards to the applied cathode potential. In the chronopotentiograms, the exchange current and the transfer coefficient based on the Tafel behavior were obtained with regard to the layer thickness of the uranium oxide which is loaded into the porous MgO membrane and the thickness of the porous MgO membrane. The maximum allowable currents for the changes of the layer thickness of the uranium oxide and the thickness of

the MgO membrane were also obtained from the limiting potential which is the decomposition potential of LiCl.

INTRODUCTION

Spent fuel oxides were reduced to their metals i.e. uranium, plutonium and all the fission products except for the high heat-generating elements such as alkali and alkali-earth metals with the electrolytic reduction process in a molten LiCl-Li salt system. Especially alkali and alkali-earth metals and a part of the rare-earth metal oxides could be selectively separated from the reduced metal products since they could be reduced to chlorides or acid chlorides in the molten LiCl-Li salt system[1-3]. The electrolytic reduction of spent fuel oxides in a LiCl molten salt system and the selective separation of high heat-generating elements have an advantage in the reduction of the decay heat, the volume and the radioactivity of the spent fuel by a factor of a quarter. Interest in the electrolytic reduction of uranium oxide is increasing in the treatment of spent fuel oxides [4,5]. 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 proposed recently in metallurgy [6,7]. 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. [7] proposed the direct electrochemical reduction of titanium dioxide to titanium in a molten calcium chloride.

The lithium reduction process which has been developed in the Argonne National Laboratory (ANL) is a representative technology for a metallization with a molten LiCl-Li salt system at 650°C [8,9]. In this process, uranium, plutonium and noble elements in

the spent fuel oxides were obtained as metal forms from the reduction of the lithium metal. The lithium reduction process is a representative pretreatment process where a recycling, quenching treatment or effective disposal of the oxide fuels are closely connected to a successive electrorefining process for the metal nuclear fuel cycle. In the lithium reduction process, Li_2O which is produced from an electrolytic reduction reaction drop off the conversion rate of the uranium oxide and the TRU oxides, creates a complex oxide or acid chloride by reacting with the rare earth oxides [10,11]. In order to promote the conversion rate of the reduction and restrain the side reactions, the Li_2O concentration in the LiCl molten salt is kept at less than 5.1 wt%.

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_2 reduction runs. Gourishankar et al. [4] classified the mechanisms of the electrolytic reduction of the metal oxides in a $\text{LiCl-Li}_2\text{O}$ molten salt system into two types; the simultaneous reduction and the direct electrochemical reduction. The uranium oxide in $\text{LiCl-Li}_2\text{O}$ 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 the ACP, the electrolytic reduction process (ER process) is the electrochemical reduction process of uranium oxide to uranium metal in a 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 [12].

In this work, cyclic voltammograms for a $\text{LiCl-3 wt\% Li}_2\text{O}$ system and an $\text{U}_3\text{O}_8\text{-LiCl-3}$

wt% Li_2O 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 according to the thickness of the uranium oxide loaded into the cathode assembly. From the potential data, the exchange current densities and the maximum allowable current densities according to the thickness of the uranium oxide were obtained.

EXPERIMENTAL

The electrolytic reduction experiments were carried out in a 10 g U_3O_8 /batch scale electrochemical reactor. The electrochemical reactor cell was composed of a resistance furnace, K-type thermocouple, alumina and magnesia crucible, anode, cathode, reference electrode and an Ar gas feeder etc. For cooling down the upper part of the reactor and preventing the molten salt from a volatilization and an emission, a water jacket was installed around the flange of the reactor. Electrolytic reactor of the cell was a high-density magnesia crucible fitted with an alumina crucible liner. The inside diameter of the magnesia crucible was 7.1 cm. The cathode was an assembly of a stainless steel conductor which was connected to the current lead and a porous magnesia crucible loaded with uranium oxide. The material of the anode used in this study was platinum. It is difficult to select an anode material which endures severe conditions – a corrosion in the $\text{LiCl-Li}_2\text{O}$ molten salt system at 650°C and an oxidation at the surface of the anode. Platinum is a satisfactory material for an anode. It shows a good corrosion resistance to the $\text{LiCl-Li}_2\text{O}$ molten salt and an endurance to the oxidation of the oxygen ions. The anode of 6 mm in diameter was a platinum tube with a 1 mm thickness. Three

anodes were placed at an equal distance to the cathode. Reference electrode is needed to measure the changes of the potentials of the cathode and the anode due to the changes of the resistance and the surface area of the electrode and a change of the Li_2O concentration. An Ag/AgCl electrode was proposed as a reference electrode in a LiCl molten salt system, but it is limited in its use because of the limited number of usages and a difficult fabrication of the magnesia membrane. A platinum rod of 3 mm in diameter was used as a quasi-reference electrode in this study because platinum is a comparatively stable metal in a LiCl molten salt system. The WMPG 1000 Multichannel Potentiostat/Galvonostat from WonA-Tech Co. was used for the electrochemical experiments. The WMPG 1000 Ver.3.00 software was also used for the electrochemical control and data acquisitions.

The electrolytes used were anhydrous 20-mesh of a 99.6 % purity LiCl and a 99.5 % purity Li_2O powder from Alfa AESAR Co. The uranium oxide used was U_3O_8 powder of which the average size was $30\ \mu\text{m}$. The tap density of the uranium oxide was 2.0~2.1 g/cm^3 . The porosity and average pore size of the porous MgO membrane were 22~25 % and $8\ \mu\text{m}$, respectively. A high-purity dry Ar gas was fed into the reactor at a constant flow rate, an electrolytic reactor cell was operated under an Ar atmosphere. The LiCl was added into the reactor cell and then the reactor cell was heated gradually by a resistance furnace up to 650°C . At room temperature, 300°C and 650°C , the reactor cell was filled with Ar gas and then the Ar gas was released from the reactor cell 20 times over. With about a 20 times repetition of the former method, the LiCl was dehydrated completely under an atmospheric pressure. A given amount of Li_2O was added to the melted lithium chloride, and solvated into the molten salt and it formed a LiCl- Li_2O mixed molten salt at 650°C . In the phase of the electrochemical reaction, a certain current was applied to the electrolytic cell system. As the electrochemical reaction made

progress, the concentration of Li₂O in the LiCl molten salt was measured at regular intervals. To analyze the Li₂O concentration, a 1.0~1.5 g mixed molten salt sample was taken with a quartz tube and then it was titrated with a 0.1 N HCl solution and a phenolphthalein indicator.

RESULTS AND DISCUSSION

The cyclic voltammetry was applied to the electrolytic reduction cell to measure the reduction potentials of the Li₂O and U₃O₈, respectively. The Li₂O and U₃O₈ were reduced to metals at the cathode, and the oxygen ions were reduced to oxygen gas at the anode. Fig.1 shows the cyclic voltammogram of the LiCl-3wt%Li₂O molten salt system at 650 °C. The reduction potential of Li₂O was -1.80 V at the cathode (peak A), where the Li ion started to be reduced to lithium metal. And the lithium metal was oxidized at -1.52 V (peak B). Fig.2 shows the cyclic voltammogram of the U₃O₈-LiCl-3wt% Li₂O system. As shown in Fig.2, the reduction potentials of the U₃O₈ and Li₂O were -1.40 V and -1.88 V (peak A and B), respectively. The reduction potential of Li₂O is similar to the results of the LiCl-3wt%Li₂O system in Fig.1. The uranium and lithium metal was oxidized at -1.32 V and -1.92 V, respectively (peak A'and B'). The potential of peak B'' is considered as the desorption of the oxidized Li₂O from the cathode. From the results of the cyclic voltammetry of the U₃O₈-LiCl-3wt%Li₂O system, the U₃O₈ is chemically reduced by the electrolytic reduced lithium metal at less than a -1.88 V cathode potential as the mechanism shown below.





At a cathode potential between -1.40 V and -1.88 V, the U_3O_8 can be reduced to uranium metal without a lithium metal formation as follows,

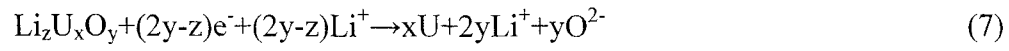
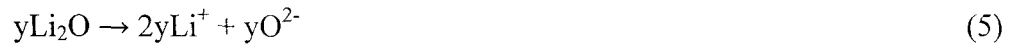


Fig.3 shows the plot for the potential of the cathode and the anode according to the thickness of the uranium oxide loaded into the cathode assembly at the applied currents. If the mass transfer has no effects on the current because of a good stirring or low currents, the Butler-Volmer equation can describe the relationship between the current and the overpotential. For large values of the overpotential, the Butler-Volmer equation becomes Tafel forms as shown below.

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i \quad (9)$$

From the Tafel plot, the exchange current densities and transfer coefficients were readily obtained. As shown in Table 1, the maximum allowable current densities were obtained according to the thickness of the uranium oxide.

Fig.4 shows the plot for the potentials of the cathode and the anode with regards to the

thickness of the MgO membrane. From the Tafel behavior, the exchange current densities and transfer coefficients with regards to the thickness of the MgO membrane were obtained and listed in Table 2. Table 2 also shows the maximum allowable current densities with regards to the thickness of the magnesia membrane.

CONCLUSION

The electrochemical behavior of an electrolytic reduction of uranium oxide was studied with a cyclic voltammetry, and a chronopotentiometry. From the results, it is concluded that the deposition potentials of the metal oxides are the determining factors for the uranium oxide in a LiCl-3 wt% Li₂O molten salt system. According to the applied current to the LiCl-Li₂O-U₃O₈ system, the reduction mechanisms of the uranium oxide were discussed with regards to the cell and anode potentials. From the results of the changes of the overpotential according to the layer thickness of the uranium oxide and the thickness of the MgO membrane at the applied currents, the exchange currents, transfer coefficients and maximum allowable currents for the LiCl-Li₂O-U₃O₈ system were obtained.

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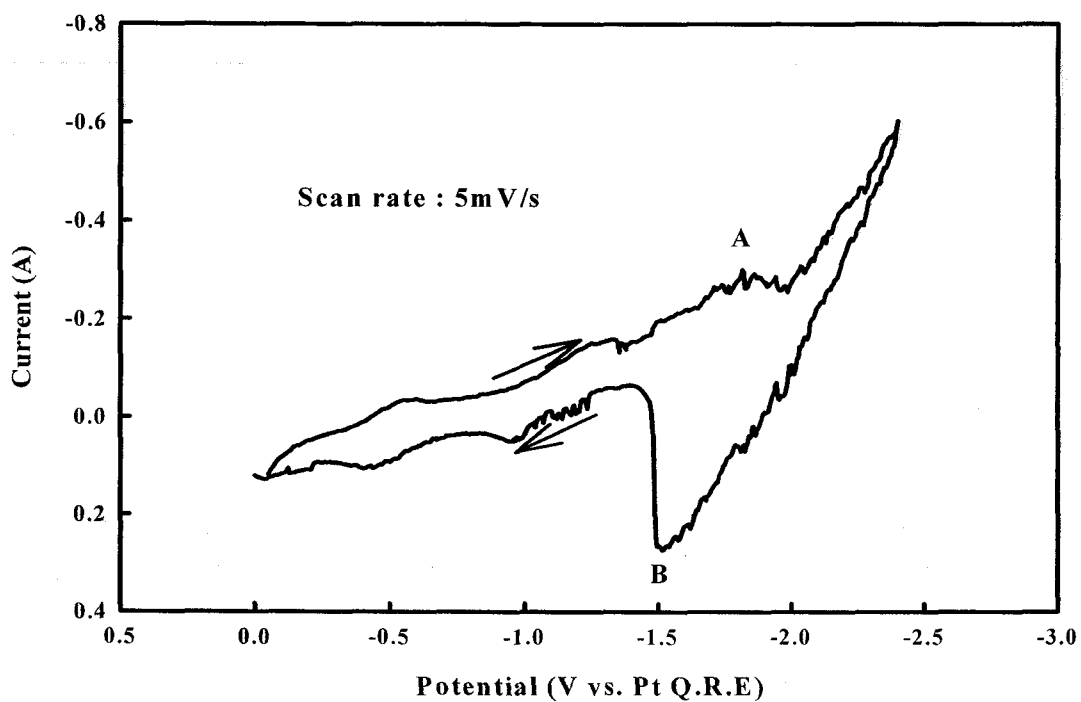


Fig. 1. Cyclic voltammogram of LiCl-3 wt% Li₂O molten salt system at 650°C.

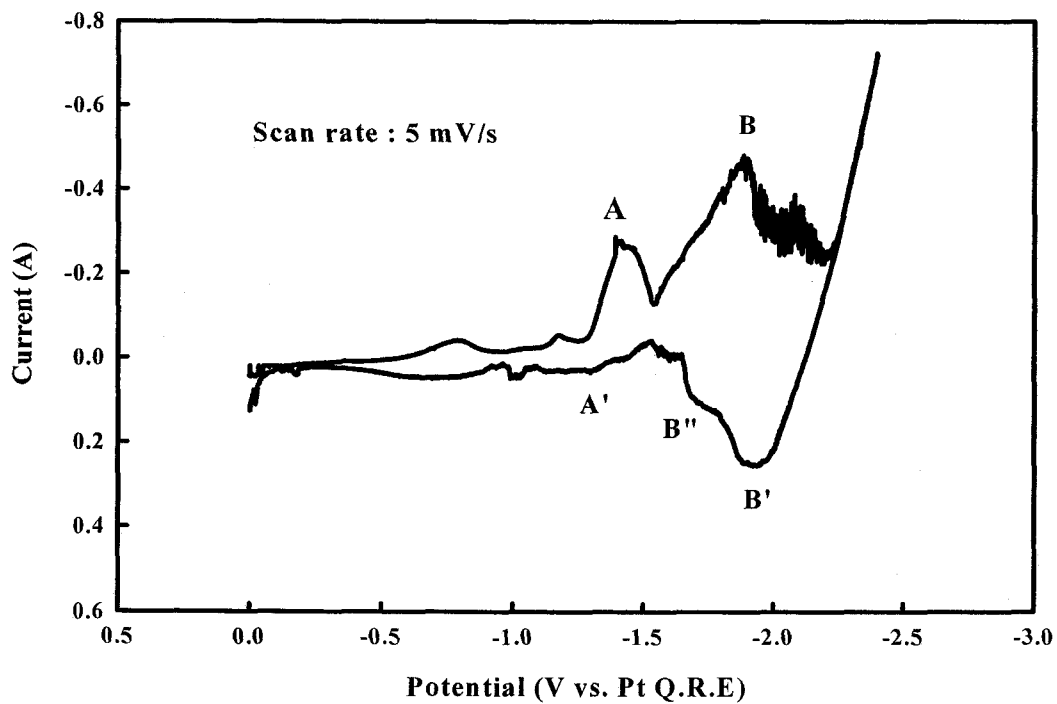


Fig. 2. Cyclic voltammogram of LiCl-3 wt% Li₂O-U₃O₈ system at 650°C.

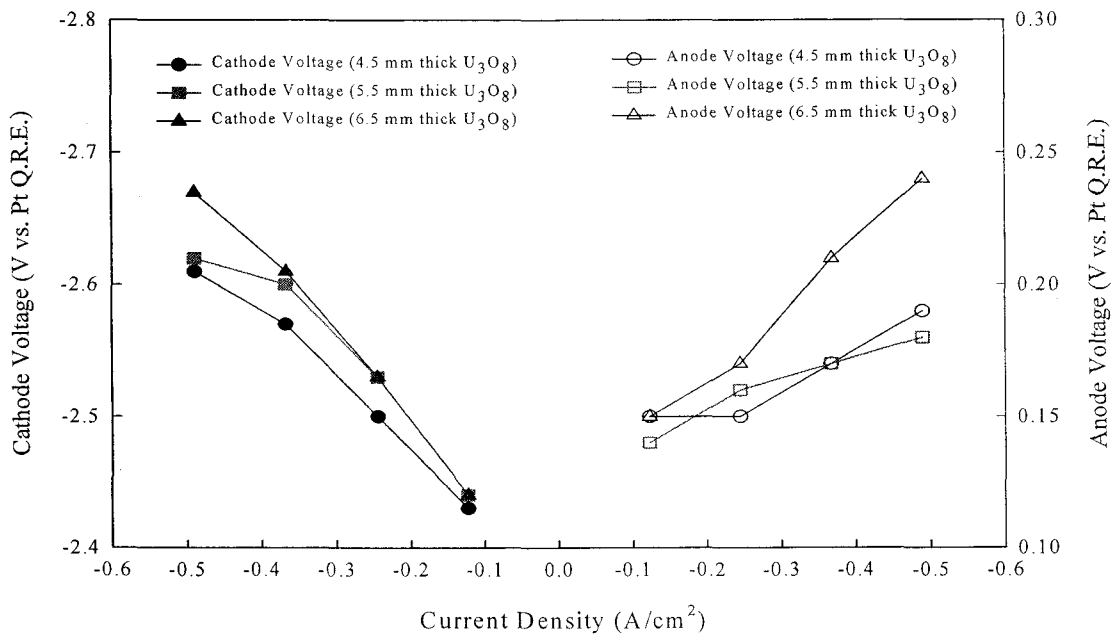


Fig.3. The plot for the potential of the cathode and the anode vs. the applied current density with respect to the thickness of the uranium oxide.

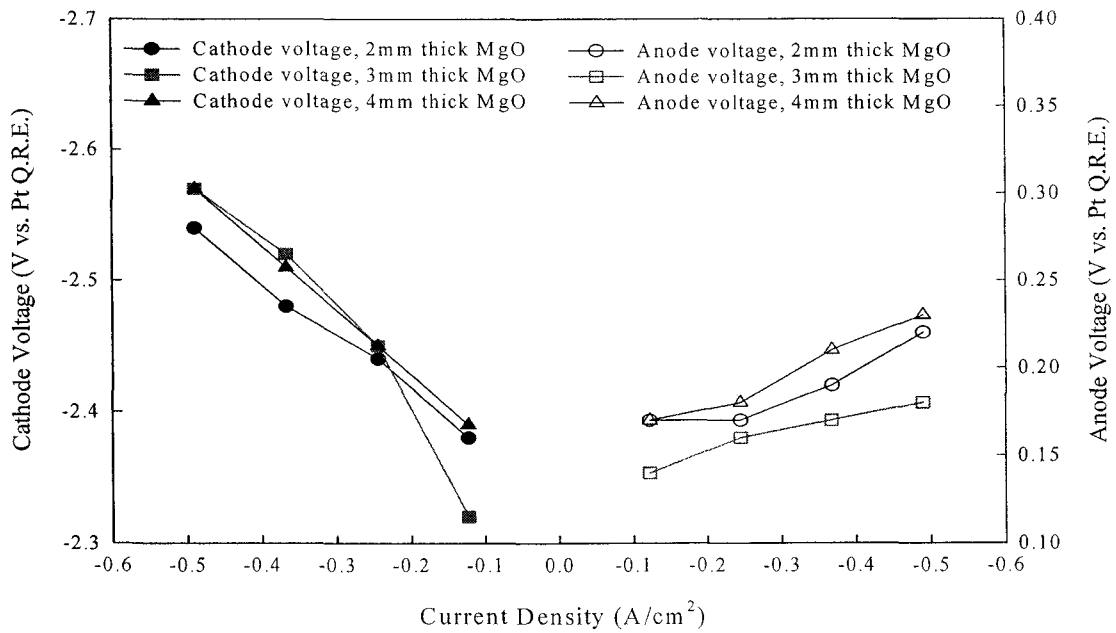


Fig.4. The plot for the potential of the cathode and the anode vs. the applied current density with respect to the thickness of the MgO membrane.

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

<i>Layer thickness of the uranium oxide (mm)</i>	<i>Exchange current (A)</i>	<i>Transfer coefficient (α)</i>	Maximum allowable current density (A/cm²)
4.5	0.28	0.61	1.57
5.5	0.28	0.44	1.51
6.5	0.29	0.56	1.22

Table 2. The exchange current densities, transfer coefficients and maximum allowable current densities from the relationship between the overpotential and the applied current with respect to the thickness of MgO membrane.

<i>Thickness of MgO (mm)</i>	<i>Exchange current (A)</i>	<i>Transfer coefficient (α)</i>	Maximum allowable current density (A/cm²)
2	0.27	0.72	1.76
3	0.23	0.55	1.14
4	0.27	0.63	1.50