

Study of the Electrolytic Reduction of Uranium Oxide in LiCl-Li₂O Molten Salts with an Integrated Cathode Assembly

LiCl-Li₂O 용융염에서 일체형 음극전극을 사용한 우라늄산화물의 전해환원에 대한 연구

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Abstract

The electrolytic reduction of uranium oxide in a LiCl-Li₂O molten salt system has been studied in a 10 g U₃O₈/batch-scale experimental apparatus with an integrated cathode assembly at 650 °C. The integrated cathode assembly consists of an electric conductor, the uranium oxide to be reduced and the membrane for loading the uranium oxide. From the cyclic voltammograms for the LiCl-3 wt% Li₂O system and the U₃O₈-LiCl-3 wt% Li₂O system according to the materials of the membrane in the cathode assembly, the mechanisms of the predominant reduction reactions in the electrolytic reactor cell were to be understood; direct and indirect electrolytic reduction of uranium oxide. Direct and indirect electrolytic reductions have been performed with the integrated cathode assembly. Using the 325-mesh stainless steel screen the uranium oxide failed to be reduced to uranium metal by a direct and indirect electrolytic reduction because of a low current efficiency and with the porous magnesia membrane the uranium oxide was reduced successfully to uranium metal by an indirect electrolytic reduction because of a high current efficiency.

Key words : integrated cathode assembly, electrolytic reduction, cyclic voltammogram, uranium oxide, molten salt

요약

650 °C 의 LiCl-Li₂O 용융염계에서 10 g U₃O₈/batch 규모의 장치를 이용해서 우라늄산화물의 전

해환원 특성에 대한 평가를 수행하였다. 일체형 음극은 고체전극, 우라늄산화물과 우라늄산화물을 담아주는 다공성 용기(멤브레인)로 구성된다. 멤브레인 재료로는 325-mesh 스테인레스강막과 다공성 마그네시아 도가니를 사용하였다. 일체형 음극의 재질에 따른 LiCl-3 wt% Li₂O계와 U₃O₈-LiCl-3 wt% Li₂O계의 순환 전압측정법 결과로부터 전해환원 반응 메커니즘을 규명하였다. 일체형 음극의 재질에 따른 우라늄산화물의 직접 및 간접 전해환원에 대한 실험을 수행하였다. 그 결과, 325-mesh 스테인레스강막을 사용하여 직접 및 간접 전해환원으로 금속전환을 수행하였을 때 낮은 전류효율로 인해 우라늄산화물을 금속우라늄으로 환원시키지 못했으며, 마그네시아 다공성 도가니를 사용하여 간접 전해환원으로 금속전환을 수행하였을 때는 높은 전류효율로 인해 우라늄산화물을 금속우라늄으로 환원시킬 수 있었다.

중심단어 : 일체형 음극전극, 전해환원, 순환 전압측정법, 우라늄산화물, 용융염

I. Introduction

Interest in the electrolytic reduction of uranium oxide is increasing for the treatment of spent fuel oxides [1,2,3]. 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 [4,5]. 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. [5] proposed the direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride.

Argonne National Laboratory (ANL) has reported the experimental results of an electrochemical reduction of 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 UO₂ reduction runs [2,6]. Gourishankar et al. [1] classified the mechanisms of the electrolytic reduction of the metal oxides in a LiCl-Li₂O molten salt system into two types. In the indirect electrolytic reduction, the metal oxides were reduced by a chemical reaction between the metal

oxides and the electrochemically generated lithium. In the direct electrolytic reduction, the metal oxides were reduced directly with electrons and required no lithium metal as in the indirect electrolytic reduction. The uranium oxide in LiCl-Li₂O molten salt was converted to uranium metal according to two mechanisms. Li et al. [3] reported the experimental results of the electrochemical reduction of UO₂ fuel in a bench-scale apparatus using a cathode basket, which had a 325-mesh stainless screen as the outer wall.

In this study, cyclic voltammograms for a LiCl-3 wt% Li₂O system and an U₃O₈-LiCl-3 wt% Li₂O system using a 325-mesh stainless steel screen in a cathode assembly as used in ANL have been obtained and compared with the results of the cyclic voltammograms using a porous magnesia membrane. Direct and indirect electrolytic reductions of uranium oxide in LiCl-3 wt% Li₂O molten salt have been conducted according to the material of the integrated cathode assembly.

II. Experimental

1. Experimental Apparatus

The electrolytic reduction experiments were

carried out in a 10g U₃O₈/batch scale electrochemical reactor as shown in Fig.1, which was composed of a resistance furnace, a K-type thermocouple, alumina and magnesia crucibles, an anode, a cathode, a reference electrode and an Ar gas feeder etc. For cooling down the upper parts of the reactor and preventing the molten salts from a volatilization and an emission, a water jacket was installed around the reactor flange. The electrolytic reactor was a magnesia crucible fitted with an alumina crucible. The inside diameter of the magnesia crucible was 7.1 cm. The cathode was an assembly of a stainless steel conductor and a steel basket loaded with the uranium oxide. The basket was shielded five-fold with 325-mesh stainless steel screen. The anode of 6 mm in diameter was a platinum tube of 1 mm thick. Three anodes were used. A platinum rod of 3 mm in diameter was used as a quasi-reference electrode for measuring the cathode and anode potentials. A WMPG 1000 Multichannel Potentiostat/Galvanostat from WonATech Co. was used for the electrochemical

experiments. A WMPG 1000 ver.3.00 software was also used for the electrochemical control and data acquisitions.

2. Materials

The electrolytes used here were an anhydrous 20-mesh 99.6 % purity LiCl and 99.5 % purity Li₂O powder from Alfa AESAR Co. The LiCl-3 wt% Li₂O molten salt system was used for the electrolytic reduction, and the operating temperature was 650°C. The uranium oxide used was U₃O₈. The membrane materials for loading the U₃O₈ into the cathode assembly were the 325-mesh stainless steel screen with a stainless steel basket and a porous magnesia of which the porosity was 22~25 %.

III. Results and Discussion

The cyclic voltammetry was applied to the electrolytic reduction cell to measure the reduction potentials of Li₂O and U₃O₈, respectively. The Li₂O and U₃O₈ were reduced at the cathode, and the oxygen ions were oxidized to oxygen gas. Fig.2 shows the cyclic voltammogram of the LiCl-3 wt% Li₂O molten salt system with a stainless steel conductor at 650 °C. The reduction peak potential

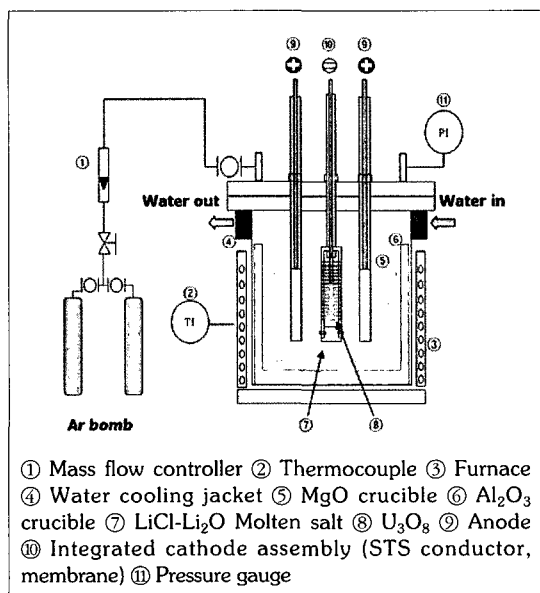


Fig. 1. Experimental apparatus for the electrolytic reduction.

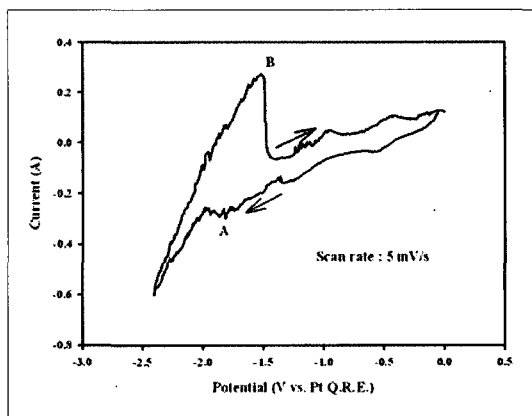
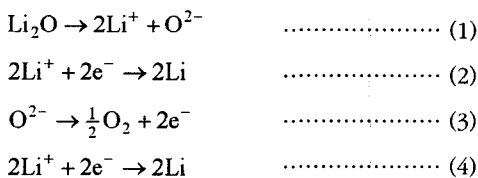


Fig. 2. Cyclic voltammogram of stainless steel conductor with a stainless basket in LiCl-3 wt%Li₂O molten salt at 650 °C.

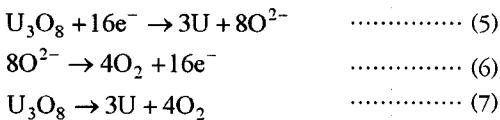
of Li_2O was measured at ~ -1.80 V (peak A), where the Li ion starts to be reduced to lithium metal. And the peak potential of the lithium metal oxidation was at ~ -1.52 V (peak B).

Fig.3 shows the cyclic voltammogram of the 325-mesh stainless steel screen with the U_3O_8 -LiCl-3 wt% Li_2O system. As shown in Fig.3, the reduction peak potentials of U_3O_8 and Li_2O were ~ -1.40 and ~ -1.88 V (peak A and B), respectively. The reduction peak potential of Li_2O is similar to the result of the LiCl-3 wt% Li_2O system in Fig.2. Uranium and lithium metal were oxidized at ~ -1.32 and ~ -1.91 V, respectively (peak A' and B'). The potential of peak B'' is considered as the desorption of the oxidized Li_2O from the cathode.

From the results of the cyclic voltammetry of the U_3O_8 -LiCl-3 wt% Li_2O system, the mechanism of the electrolytic reduction of the uranium oxide is divided into a direct electrolytic reduction process



and an indirect simultaneous electrolytic reduction [1]. At a cathode potential of less than a -1.88V cathode potential, the U_3O_8 can be chemically reduced by the electrochemically reduced lithium



metal as shown below (indirect reduction):

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

Fig.4 shows a comparison of the cyclic voltammograms for the electrolytic reduction of the U_3O_8 -LiCl-3 wt% Li_2O system according to the cathode membrane materials. Park et al. [7] used a porous magnesia membrane in the cathode assembly for loading the U_3O_8 but we used a 325-mesh stainless steel screen. The reduction peak potentials of U_3O_8 and Li_2O showed similar values for the two membranes. But the oxidation potentials of uranium and lithium and the desorption potential of Li_2O were different between the two membranes. Because the current value of the oxidation peak was dependent on the end

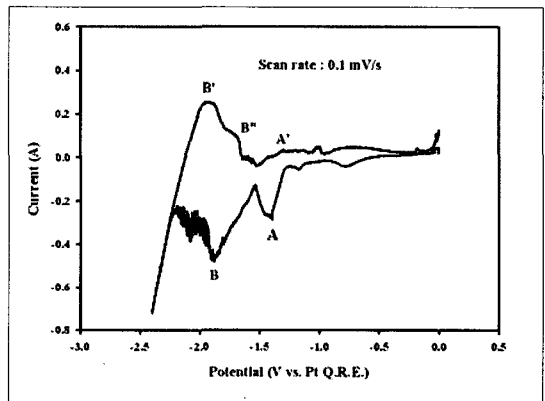


Fig. 3. Cyclic voltammogram for a 325-mesh steel screen loaded with a U_3O_8 in LiCl-3 wt% Li_2O molten salt at 650°C .

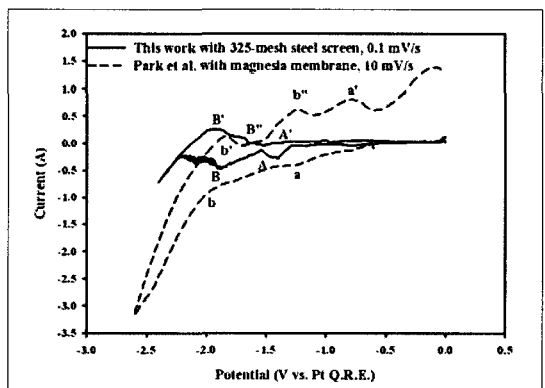


Fig. 4. Comparison of the cyclic voltammograms for a 325-mesh stainless steel screen and a porous magnesia membrane loaded with U_3O_8 in LiCl-3 wt% Li_2O molten salt at 650°C .

voltage of the positive-going scan [3], the differences of the oxidation potential of the reduced metals may be accepted.

Fig.5 shows the chronoamperogram of the electrolytic reduction of the uranium oxide in the LiCl-3 wt% Li₂O molten salt using the cathode assembly with a 325-mesh stainless steel screen. The direct electrolytic reduction of the uranium oxide was conducted with a -1.8 V applied potential according to the results of the cyclic voltammetry. The reactor cell system was unstable at the initial stage, and at the end the anode potential had increased to 0.58V. The concentration of Li₂O was to be constant during the

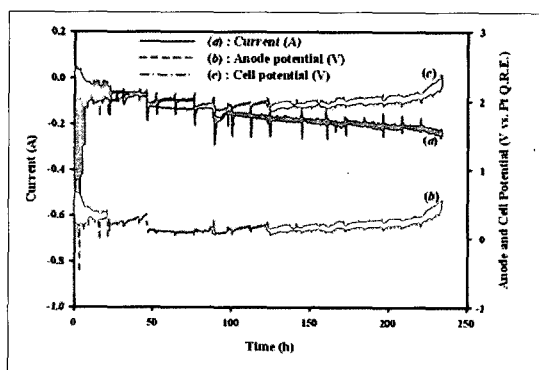


Fig. 5. Chronoamperogram of the direct electrolytic reduction of U₃O₈ in LiCl-3 wt% Li₂O with a 325-mesh stainless steel screen. The applied cathode potential is -1.8V.

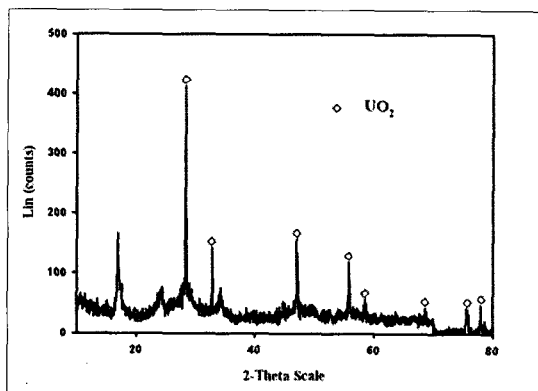


Fig. 6. XRD pattern of the direct electrolytic reduction of uranium oxide using a 325-mesh stainless steel screen in LiCl-3 wt% Li₂O at 650 °C

direct electrolytic reduction, but it was slowly decreased from 2.55 wt% to 1.43 wt% as time elapsed. It was considered that Li metal was formed because the applied potential was close to the reduction potential of Li₂O. The current of the cell increased from 0.06 A to 0.24 A. The reduced product was analyzed with an X-ray diffraction (XRD) method. As shown in Fig.6, the XRD analysis showed that the reduced product was UO₂. From the results, a direct electrolytic reduction of the uranium oxide failed to reduce it to uranium metal because the electrodeposited lithium metal at the cathode lowered the current efficiency of the cell.

The direct electrolytic reduction of the uranium oxide with a porous magnesia membrane as shown in Fig.7 did not show a successful reduction of the uranium oxide. The applied voltage was -1.6 V and the current of the cell was 5~10 mA. In spite of the long reaction time (276 h), the applied current was so small that the current efficiency was low. The concentration of Li₂O decreased slowly from 2.78 wt% to 2.14 wt%. It was considered that the decrease of the concentration of Li₂O was caused not from the Li metal formation but from the formation of the lithium urinate (Li_xU_yO_z) in the

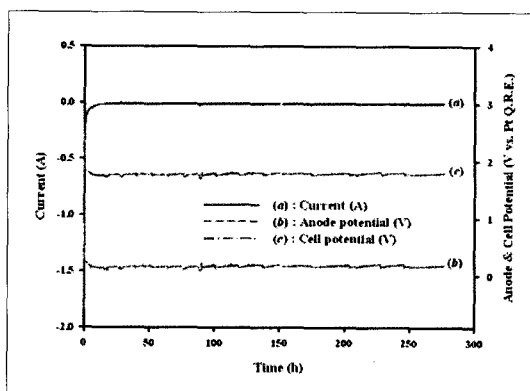


Fig. 7. Chronoamperogram of the direct electrolytic reduction of U₃O₈ in LiCl-3 wt% Li₂O with a porous magnesia membrane. The applied potential is -1.6V.

cathode assembly because the applied potential was below the reduction potential of Li_2O and the ionized oxygen ion caused the local increases in the activity of Li_2O in the cathode assembly [8].

The chronopotentiogram of the electrolytic reduction of the uranium oxide in the LiCl -3 wt% Li_2O molten salt using the cathode assembly with a 325-mesh stainless steel screen is shown in Fig.8. The indirect electrolytic reduction was conducted with a 0.3 A applied current of the cathode. The measured potential of the cathode exceeded -1.88 V, therefore lithium metal would be formed in the cathode assembly, and mostly electrodeposited at the 325-mesh screen. The concentration of Li_2O

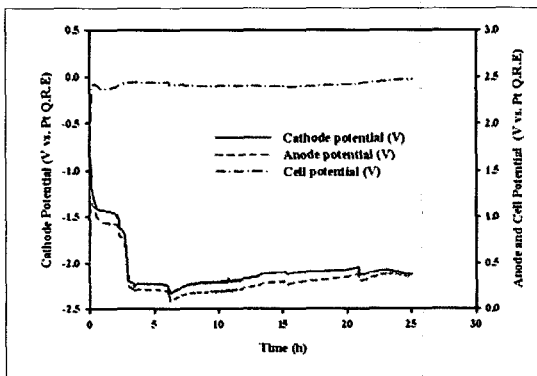


Fig. 8. Chronopotentiogram of the direct electrolytic reduction of U_3O_8 in LiCl -3 wt% Li_2O with a 325-mesh stainless steel screen. The working current is 0.3A.

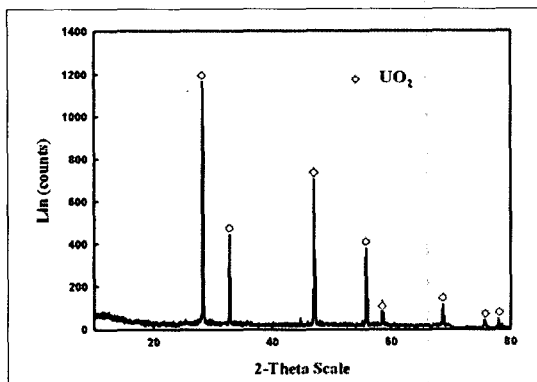


Fig. 9. XRD pattern of the indirect electrolytic reduction of uranium oxide using a 325-stainless steel screen in LiCl -3 wt% Li_2O at 650°C .

was decreased from 2.84 wt% to 2.40 wt% as time elapsed. According to Faraday's law, the concentration of Li_2O must be 1.02 wt% at the end of the experiment if the current efficiency of the system is to be 100%. It is considered that the deposited lithium at the 325-mesh screen lowered the current efficiency of the system. The reduced product was analyzed with the thermogravimetry (TG) and XRD analyses. The weight gain percentage was 4.05 wt%. Most of the U_3O_8 was reduced to UO_2 . XRD analysis in Fig.9 shows that the reduced product was UO_2 . The indirect electrolytic reduction of uranium oxide using the cathode assembly with a 325-mesh stainless steel screen also failed to reduce it to uranium metal.

On the other hand, the indirect electrolytic reduction of uranium oxide using the cathode assembly with a porous magnesia membrane showed a successful reduction of the uranium oxide to uranium metal. As shown in Fig.10, the potential of the anode increased rapidly at the end of the reaction. At that time, the reaction of the reduction was thought to be terminated. The concentration of Li_2O decreased from 3.33 wt% to 1.26 wt%. The XRD analysis of the reduced product showed that the product was uranium metal as shown in Fig.11. The conversion rate of the uranium oxide was

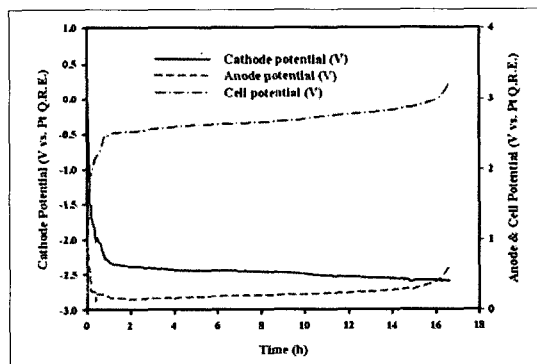


Fig. 10. Chronopotentiogram of the indirect electrolytic reduction of U_3O_8 in LiCl -3 wt% Li_2O with a porous magnesia membrane. The working current is 0.5 A.

obtained from the ratio of the weight gain of an oxidation of the reduced uranium metal and UO₂ to U₃O₈ by the TG analysis, if the reduced products were the uranium metal, UO₂ and U₃O₈. The conversion rate of an indirect reduction with a porous magnesia membrane was about 99.4wt% as shown in Fig.12.

From the results of the indirect electrolytic reduction, the performance of the cathode assembly for the electrolytic reduction was compared according to the materials of the cathode. With a 325-mesh stainless steel screen in the cathode assembly the uranium oxide failed to reduce to uranium metal, while the uranium oxide was reduced to uranium metal successfully with a porous magnesia membrane. The physical properties of the two materials of the cathode assembly are compared in Table 1. The porous magnesia membrane has several advantages: a

good refractoriness, a good corrosion resistance, a high thermal conductivity and a low electric conductivity. But the magnesia membrane is weak against a physical and thermal impact. On the other hand, the stainless steel one has a good mechanical stability. The average pore size of the 325-mesh stainless steel screen is larger than that of the magnesia membrane. The mass transfer of the oxygen ion which was formed in the cathode across the 325-mesh screen is easier than the mass transfer across the magnesia membrane. However, the 325-mesh stainless steel screen has a high electric conductivity, and the lithium metal formed in the cathode might be electrodeposited at the 325-mesh screen. The deposited lithium around the 325-mesh screen could hinder a further reduction by making it more difficult for the oxygen ions in the cathode to diffuse out into the electrolyte. Free lithium droplets can be formed in the electrolyte, and they can have

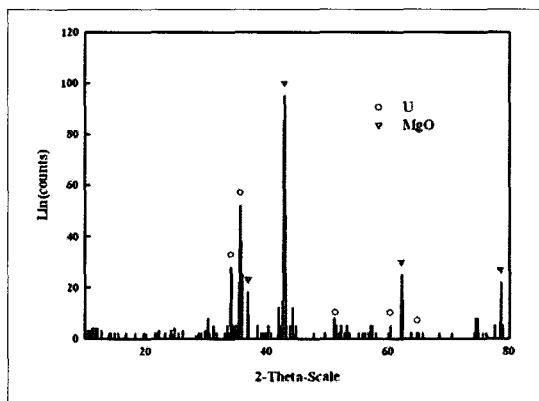


Fig. 11. XRD pattern of the indirect electrolytic reduction of uranium oxide using a porous magnesia membrane in LiCl-3 wt% Li₂O at 650 °C.

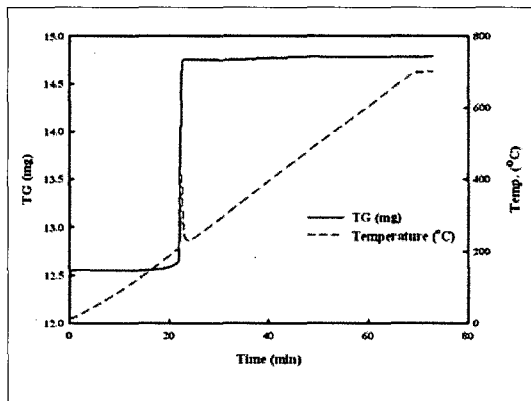


Fig. 12. TG curve for an oxidation of the reduced uranium metal in air. The heating rate, 10 °C/min.

Table 1. Physical properties of the membranes in the integrated cathode assembly

	Density (g/cm ³)	Melting point (°C)	Specific Heat Capacity (J kg ⁻¹ K ⁻¹)	Electric Conductivity (Ω ⁻¹ cm ⁻¹)	Average pore size (μm)
325-mesh stainless steel (STS 304)	8.06	1400	503	8.89 × 10 ³	44
Porous Magnesia	3.58	2800	877	~2.0 × 10 ¹¹	8

serious effects on the cell current efficiency [1]. Direct and indirect electrolytic reductions of the uranium oxide failed to reduce it to uranium metal with a stainless steel screen. The porous magnesia membrane had a low electric conductivity, and the cell current efficiency was high. A successful lithium deposition took place in the cathode assembly and an indirect electrolytic reduction of the uranium oxide succeeded in reducing it to uranium metal.

IV. Conclusions

By using a 325-mesh stainless steel screen and a porous magnesia membrane in the cathode assembly, we have observed the electrolytic reduction of U_3O_8 and Li_2O with a cyclic voltammetry. From the results, it is concluded that the deposition potentials of the metal oxides are the determining factors for the mechanism of the electrolytic reduction of uranium oxide in a LiCl-3 wt% Li_2O molten salt system: direct electrolytic reduction and indirect electrolytic reduction processes. Direct and indirect electrolytic reductions with a 325-mesh stainless steel screen in the cathode assembly fail to reduce the uranium oxide to uranium metal due to a hindrance of the stainless steel membrane, which causes a very low cell current efficiency. On the other hand, an indirect electrolytic reduction with a porous magnesia membrane reduces the uranium oxide to uranium metal due to a lithium metal deposition within the electric nonconductor, which causes a high cell current efficiency.

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