

## Semi-Continuous Electrowinning of Li in a LiCl-Li<sub>2</sub>O Molten Salt

### LiCl--Li<sub>2</sub>O 용융염에서의 리튬의 반연속적 전기정련

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#### Abstract

A Li recovery technology has been developed and related experimental verification efforts were carried out to improve the economical viability and environmental friendliness of the 'Advanced Spent Fuel Conditioning Process' being developed at KAERI. This technology is characterized by the combination of 1) the electrolysis of Li<sub>2</sub>O in a molten salt by using a porous non-conducting magnesia container at the cathode, 2) the separation of the Li in the container from the molten salt by elevating the container above the level of a molten salt, 3) the transport of the Li in the container by using a vacuum siphon to a separated reservoir. Li was semi-continuously recovered from a LiCl-Li<sub>2</sub>O molten salt with a more than 95% yield by using the developed technology.

**Key Words** : Li Recovery, Electrowinning, LiCl, Li<sub>2</sub>O, Molten Salt

#### 요약

한국원자력연구소에서 추진하고 있는 사용후핵연료 관리.이용 기술개발의 경제성과 환경친화성을 증진시키기 위해서 리튬회수 기술을 개발하고 관련 검증실험을 수행하였다. 본 기술은 1) 환원전극과 결합된 비전도성 다공성 마그네시아 용기를 이용한 용융염상에서의 산화리튬 전해, 2) 마그네시아 용기를 용융염 액위 이상으로 상승시켜, 용기 내에 회수된 리튬의 용융염으로부터의 분리, 3) 회수된 리튬의 진공 사이펀을 사용한 별도 저장조로의 이송이라는 3단계의 결합으로 특징지어 진다. 개발된 기술에 의하여 염화리튬-산화리튬 용융염으로부터 95% 이상의 수율로 리튬을 반연속적으로 회수할 수 있었다.

**중심단어** : 리튬회수, 전기정련, 염화리튬, 산화리튬, 용융염

## I. Introduction

Spent nuclear fuel (SNF) is a highly radioactive waste, if it is directly disposed of. However, the disposal burden of spent nuclear fuel can be alleviated, if it is properly treated. Hence, the development of methods for the effective management of the rapidly accumulating SNF is an important and desirable task. In Korea, the Advanced Spent Fuel Conditioning Process (ACP) has been under the development at KAERI since 1997 [1]. The concept is to convert spent oxide fuel into a metallic form and to remove the high heat-load fission products such as Cs and Sr from the SNF. Consequently, it is expected that the heat load, volume, and radioactivity of the SNF can be decreased by a factor of four via this process. Through the experimental verification of unit processes, a reference process was conceptually established. This process consists of 1) the air voloxidation of the oxide fuel pellets, 2) the reduction of oxide fuel powder into a metallic form in a LiCl-Li<sub>2</sub>O molten salt, and 3) the smelting of the metallic product to an ingot. The economical viability of the ACP can be improved by the recycle of the molten salt through Li recovery as a part of the step 2) above..

The present study for the Li recovery has been concentrated on the electrowinning of Li from the molten salt. Electrochemical data on the Li recovery from a molten salt are scarce [2-4]. In addition, there is the salt separation and transfer problem in the conventional Li recovery from a molten salt making a continuous operation impossible. Therefore, in this study, a semi-continuous Li recovery technology was developed and the experimental verification efforts were made in order to examine its viability in improving the economic feasibility and environmental friendliness of the ACP.

## II. Experimental

The reaction system consisted of a resistive heater, K-type thermocouples, a reactor made of stainless steel 304, a cathode, an anode, a quasi reference electrode, Ar gas flow lines and the reactants supplying system. The cathodic part of the electrolysis cell consisted of a stainless steel 304 conductor and a non-conductive porous magnesia membrane as a container for a product, Li. The anode and the quasi reference electrode were made of Pt tube (outer diameter 8mm) and Pt rod (diameter 3mm, Pt | PtO | O<sup>2-</sup>), respectively. Reactivity test for the Li recovery was performed in a LiCl-Li<sub>2</sub>O molten salt system at 650°C. An inert atmosphere in the reactor was maintained by Ar gas flow. LiCl (Alpha, 99%, 200g) was introduced into the reactor at room temperature. Li<sub>2</sub>O (Cerac, 99.5%) was fed into the reactor at 650°C.

During the reduction reaction, the variation of the Li<sub>2</sub>O concentration in a molten salt was measured by taking samples and conducting titration method using a phenolphthalein indicator and HCl. Chronopotentiometry and linear sweep voltammetry methods were employed to investigate the characteristics of this particular electrowinning process. The recovery yield of the Li was also measured by the above mentioned titration method after the Li contained in the magnesia membrane was separated from the molten salt.

## III. Results and Discussion

During the mock-up test for the recovery of the Li from a multi-component molten salt, the porous metal cathode concept was introduced. A stainless steel screen (325 mesh, wrapped on a stainless steel 304 rod) was employed as a porous metal cathode. However, a Li deposition on the outside

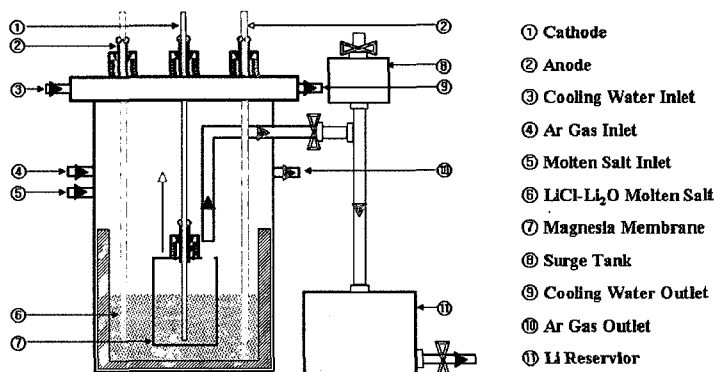


Fig. 1. Sketch of the reaction apparatus used in the Li electrowinning.

of the screen and the difficulty of the separation of the produced Li from the screen make the Li recovery yield low. To solve this problem, a Li recovery method by using a porous non-conducting ceramic container was developed and the experimental verification efforts were conducted in this study. This technology is characterized by the combination of 1) the electrolysis of  $\text{Li}_2\text{O}$  from a molten salt using a porous non-conducting container at the cathode, 2) the separation of the Li from a molten salt by elevating the container above the molten salt, 3) the transport of the Li in the container by using a vacuum siphon to a separate reservoir.

Equation (1) shows the pressure needed for the leakage of the contained Li to the outside of the magnesia container.  $\gamma_{\text{Li}}$  and  $D$  represent the surface tension of the Li and the diameter of the membrane pores, respectively. The variation of the Li surface tension can be expressed as Equation (2) [5].

$$P = 4\gamma_{\text{Li}} / D \dots\dots\dots (1)$$

$$\gamma_{\text{Li}}(\text{N/m}) = 0.398 - 0.147 \times 10^{-3} \times T(\text{K}) \dots\dots(2)$$

If this pressure,  $P$ , is higher than the pressure originating from the liquid head (Equation (3)), the Li could be contained inside the ceramic container. The liquid head is expressed as follows;

$$P = \rho_{\text{Li}}gh \dots\dots\dots (3)$$

$\rho_{\text{Li}}$  (0.47g/cm<sup>3</sup> at 650°C),  $g$ , and  $h$  denote the

density of the Li, acceleration due to gravity, and the height of the Li in the ceramic container, respectively. The surface tension of the Li is 0.262N/m at 650°C and so the Li can be contained to the height of 27.2m if the average pore diameter of the ceramic container is 8356nm. Unlike Li metal,  $\text{Li}^+$  and  $\text{Cl}^-$  of LiCl molten salt can freely migrate through a ceramic container and thus the electrolytic reaction and the separation of the metal and salt can be accomplished.

Magnesia ( $\text{MgO}$ ) is a non-conducting ceramic and was selected as a material for the Li container in this study. Hence, a magnesia container (O.D.40mm, I.D.30mm) was manufactured and then tested. The properties of this magnesia container are shown in Table 1.

Table 1. Physical properties of the magnesia membrane used in this study

Average Pore Diameter	8356 nm
Bulk Density at 0.03 atm	2.74 g/ml
Porosity	17.92 %

To study the stability of  $\text{MgO}$  in a LiCl- $\text{Li}_2\text{O}$  molten salt,  $\text{MgO}$  was immersed fully in a quartz reactor containing LiCl-8wt%  $\text{Li}_2\text{O}$  molten salt at 650°C for 6 hrs under an Ar gas atmosphere. After that, the sample was washed with anhydrous isopropanol(Aldrich, 99.5%) and then analyzed by

an X-ray diffractometer to examine the interaction extent of MgO with a LiCl-Li<sub>2</sub>O molten salt (Figure 2). Neither the LiCl nor Li<sub>2</sub>O originating structure was observed in Figure 2. The ionic radius of the Li<sup>+</sup>(0.68Å) is similar to that of Mg<sup>2+</sup> (0.66Å). So, lithium doping of MgO can occur. However, the solubility of Li<sub>2</sub>O in MgO is very low (around 0.7at%) ensuring the structural stability of the MgO in the LiCl-Li<sub>2</sub>O molten salt [6].

The concentration of Li<sub>2</sub>O in LiCl should be kept at 5.1% or below to prevent the reoxidation of metal products of spent fuel [4]. So, Li recovery in this study was conducted in the LiCl-3wt% Li<sub>2</sub>O condition. Figure 3 shows the linear sweep voltammogram of a LiCl-3wt% Li<sub>2</sub>O molten salt to find the dissociation potential of Li<sub>2</sub>O in this system. The dissociation potential of Li<sub>2</sub>O can be changed according to the activity of Li<sub>2</sub>O in a molten salt (Equation (4)). The equilibrium potential calculated from Gibbs free energy is 2.47V when the activity of Li<sub>2</sub>O is 1.

$$E = E(\text{Li}|\text{Li}_2\text{O})^\circ + \frac{RT}{nF} \ln a_{\text{Li}_2\text{O}} \dots\dots\dots(4)$$

As shown in Figure 3, the dissociation of Li<sub>2</sub>O in this system started from ~2.3V which is similar to the theoretically calculated value. This result

suggests that the potential drop due to magnesia membrane is relatively small at least at the initial state of the Li recovery experiment. The current flow before -2V was attributed to the reduction of corroded stainless steel 304 component materials (Fe<sub>2</sub>O<sub>3</sub>, NiO, Cr<sub>2</sub>O<sub>3</sub>).

To confirm the feasibility of the semi-continuous Li recovery by using a magnesia membrane, the recovery yield and potential variation were measured. A LiCl-2.35wt% Li<sub>2</sub>O molten salt was used and the chronopotentiometry (1.0A, 0.088A/cm<sup>2</sup>) method was employed. When the concentration of the Li<sub>2</sub>O in the LiCl molten salt reached 0.23wt%, the magnesia container was elevated above the molten salt level and the Li metal was separated from the molten salt. Figure 4 shows the variation of the potential during the electrolysis. The cell and cathode voltages changed to more negative values while the anode voltage increased in the positive direction as the electrolysis proceeded. The voltage was measured with respect to the Pt rod as the quasi reference electrode. The dissociation potential of Li<sub>2</sub>O is related to the activity of the Li<sub>2</sub>O in a molten salt as shown in Equation (4). Therefore, the voltage variation during electrolysis can be explained by the diminishing activity of the Li<sub>2</sub>O. However the

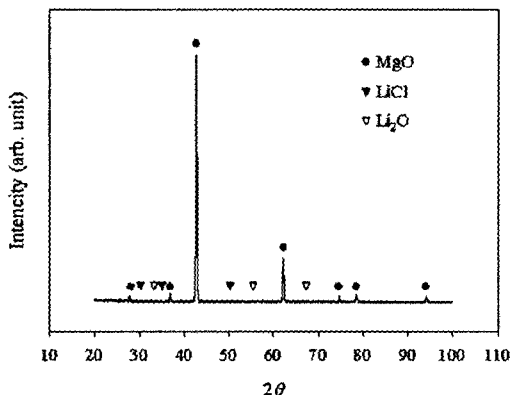


Fig. 2. XRD spectrum of the MgO after immersing it in a LiCl-Li<sub>2</sub>O molten salt at 650°C.

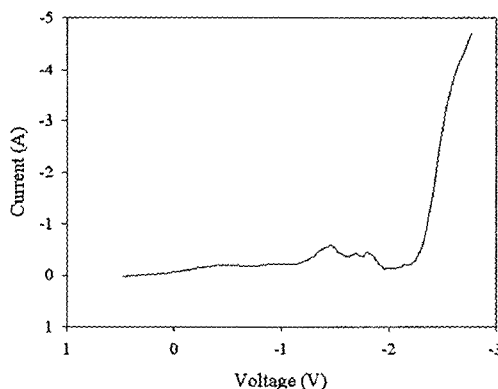


Fig. 3. Linear sweep voltammogram of Li<sub>2</sub>O reduction in a LiCl-Li<sub>2</sub>O molten salt at 650°C.

activity of  $\text{Li}_2\text{O}$  should be below 10-12 to reach 3.6V at 650°C when only considering the activity effect. Therefore, the instability of an anode such as the formation of oxide layer (confirmed as  $\text{Li}_2\text{PtO}_3$  by XRD) should be considered. After completion of the reaction, the amount of Li contained in the magnesia membrane was 2.02g meaning the recovery yield is more than 95%. Chlorine evolution from an anode was not observed during the reaction.

The effect of the current density was investigated as shown in Figures 5 and 6. The surface area of the anode used in this study was 11.4cm<sup>2</sup>. Hence supposing there is no alteration of the anode, the 0.5, 1.0, 1.5 ampere conditions correspond to the current density of 0.044, 0.088, 0.132A/cm<sup>2</sup>, respectively. Li recovery in this study proceeded roughly in proportion to the quantity of the applied charge (Figures 5 and 6). In other words, the recovery rate increased linearly with the current density. When the concentration of the  $\text{Li}_2\text{O}$  becomes lower than 0.5wt%, the cell voltage exceeded the equilibrium dissociation potential of the LiCl, -3.46V. LiCl is a main constituent of a molten salt and hence its activity can be considered to be unity. The process should advance to the next step when the  $\text{Li}_2\text{O}$  in a molten salt diminishes

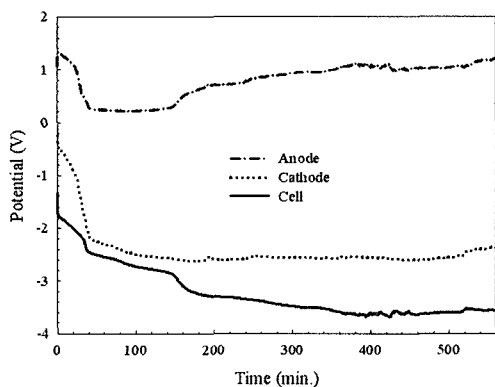


Fig. 4. Variation of the voltages during chronopotentiometry (1.0A) in a LiCl- $\text{Li}_2\text{O}$  molten salt.

below 0.5wt%.

The economical viability of the Li recovery process can be enhanced if the initial concentration of the  $\text{Li}_2\text{O}$  is made as high as it can be. However,  $\text{Li}_2\text{O}$  can be soluble up to 8.7wt% in a LiCl molten salt at 650°C. In addition, the concentration of the  $\text{Li}_2\text{O}$  should be controlled below 5.1wt% when the salt is used for the treatment of spent fuel to prevent the reoxidation of americium. So, the  $\text{Li}_2\text{O}$  concentration effect was investigated in this study by using 2, 3, 5wt%  $\text{Li}_2\text{O}$ -LiCl molten salt, respectively. The chronopotentiometry method was employed using 1.0 ampere and the variation of the  $\text{Li}_2\text{O}$  concentration and potential was observed with time. In all the cases, the reduction yields were

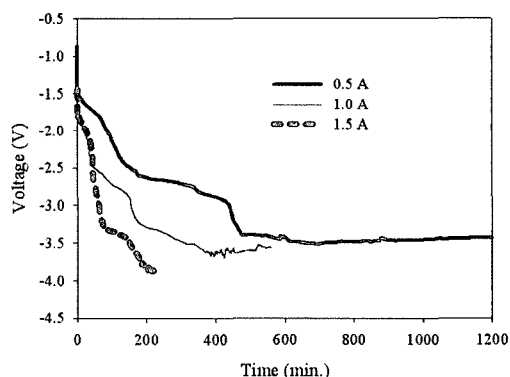


Fig. 5. Changes of the cell voltage during chronopotentiometry (0.5, 1.0, and 1.5A) in a LiCl- $\text{Li}_2\text{O}$  molten salt.

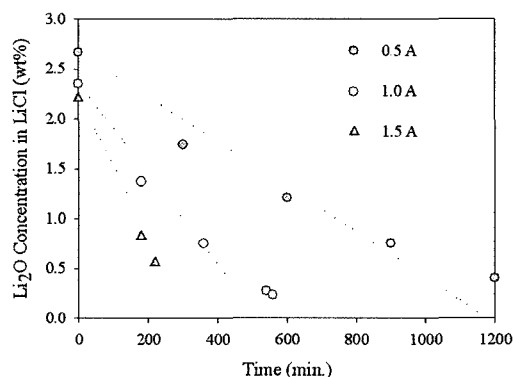


Fig. 6. Changes of the  $\text{Li}_2\text{O}$  concentration during chronopotentiometry (0.5, 1.0, and 1.5A) in a LiCl- $\text{Li}_2\text{O}$  molten salt

proportional to the quantity of the applied charge (Figures 7 and 8). When the initial concentration of the  $\text{Li}_2\text{O}$  was 5wt%, the electrolysis of  $\text{Li}_2\text{O}$  occurred at about -2.7V that was significantly higher than those of the 2 and 3wt% cases after 5 hours. This findings suggest that the cell potential is much more dependent on the concentration of  $\text{O}_2^-$  in a molten salt than expected from Equation (4). As a result, considering the energy consumption, it can be concluded that the economic viability of the process can be improved by maintaining the concentration of  $\text{Li}_2\text{O}$  as high as possible. As shown in Figure 8, there is a difference in the quantity between the supplied and measured concentration of  $\text{Li}_2\text{O}$ . The reason can be attributed to the solubility of  $\text{Li}_2\text{O}$  in the  $\text{MgO}$  structure as mentioned before. Further studies to obtain quantitative data will be carried out.

#### IV. Conclusion

A semi-continuous Li recovery technology was developed by using a porous magnesia container and the experimental verification efforts were made. This technology is characterized by the

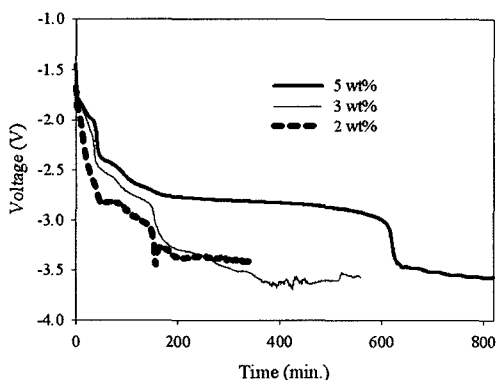


Fig. 7. Changes of the cell voltage during chronopotentiometries (1.0A) when the initial  $\text{Li}_2\text{O}$  concentration in a  $\text{LiCl-Li}_2\text{O}$  molten salt was 5, 3, 2wt%, respectively.

combination of 1) the electrolysis of  $\text{Li}_2\text{O}$  from a  $\text{LiCl-Li}_2\text{O}$  molten salt by using a magnesia container at the cathode part, 2) the separation of the Li contained inside the magnesia from the molten salt by elevating the magnesia container above the molten salt, 3) the transport of the Li by using a vacuum siphon to a separate reservoir.

The physical stability of the  $\text{MgO}$  in the  $\text{LiCl-Li}_2\text{O}$  molten salt at  $650^\circ\text{C}$  was verified by the XRD analysis. During the electrowinning, the cathode voltages changed to more negative values while the anode voltage increased in the positive direction. Oxygen evolution occurred at the anode and chlorine evolution was not observed when the  $\text{Li}_2\text{O}$  concentration in the molten salt was controlled to be higher than 0.5wt%. Li was semi-continuously recovered from the  $\text{LiCl-Li}_2\text{O}$  molten salt with a more than 95% recovery yield via this technology.

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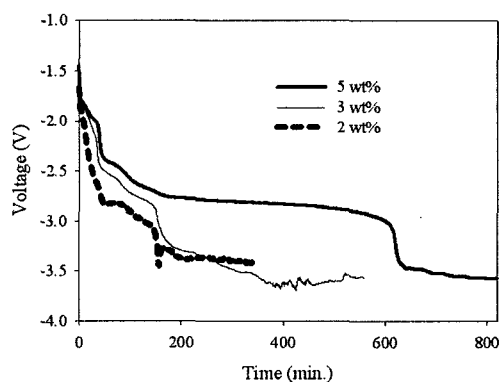


Fig. 8. Changes of the  $\text{Li}_2\text{O}$  concentration during chronopotentiometries (1.0A) when the initial  $\text{Li}_2\text{O}$  concentration in a  $\text{LiCl-Li}_2\text{O}$  molten salt was 5, 3, 2wt%, respectively.

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