

## **ELECTROCHEMICAL REDUCTION OF URANIUM OXIDES IN $\text{Li}_2\text{O}$ - $\text{LiCl}$ MOLTEN-SALT**

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### **Abstract**

A concept of electrochemical reduction of spent oxide fuel in  $\text{Li}_2\text{O}$ - $\text{LiCl}$  molten-salt was proposed and several cold tests using fresh uranium oxides have been carried out at KAERI. In this new electrochemical reduction process, electrolysis of  $\text{Li}_2\text{O}$  and reduction of uranium oxide are taking place simultaneously at the cathode part of electrolysis cell. Li produced via  $\text{Li}_2\text{O}$  electrolysis reacts with uranium oxide resulting in the formation of  $\text{Li}_2\text{O}$  of which oxygen ion originates from uranium oxide. The resultant  $\text{Li}_2\text{O}$  is electrolysed and regenerated Li is used for further reduction of the uranium oxide. The cathode part consisted of uranium oxide, stainless steel conductor, and a non-conductive porous magnesia filter. The conversion of uranium oxide to uranium metal reached more than 99% and closed recycle of  $\text{Li}_2\text{O}$  was elucidated by the observation of its concentration variation in molten-salt.

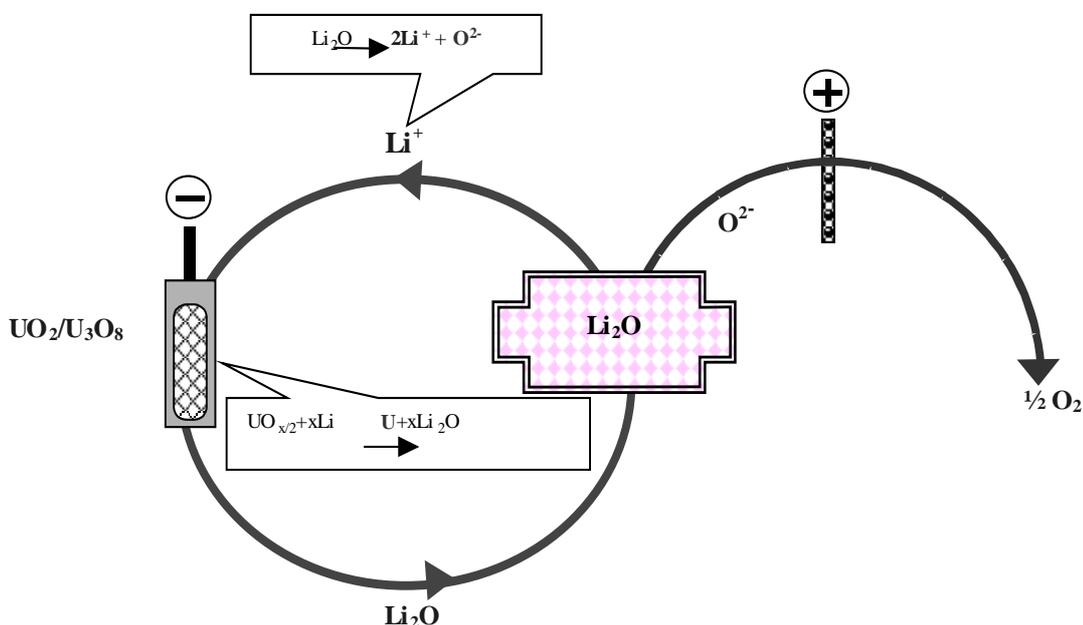
## Introduction

Spent fuel is the natural by-product from electricity generation by nuclear energy systems and is highly radioactive. As the cumulative amount of spent fuel increases around the world, the effective disposition of spent fuel is becoming important. The world-wide trend for the management of spent fuel is to develop advanced nuclear fuel cycles and spent fuel conditioning technologies that enhance environmental friendliness, cost viability, proliferation resistance, and have the potential to maximise the use of natural resources. A globally recognised approach that meet these criteria is the “Dirty Fuel and Clean Waste” concept, which involves the effective management of spent fuel through the development and application of innovative nuclear technologies for electricity generation and the subsequent destruction of long-lived nuclides of the transuranic elements by transmutation. A prominent variation on this concept involves adopting the dry processing technology for conditioning spent fuel and immobilising the radioactive constituents for eventual deep geological disposal. [1-3]

In Korea, the Advanced Spent Fuel Conditioning Process (ACP) has been under development at KAERI since 1997. [4] The concept is to convert spent oxide fuel into metallic form and to remove high heat-load fission products such as Cs and Sr from the spent fuel. Through the experimental verification of unit processes, a reference process was established. This process consists of 1) the air voloxidation of oxide fuel pellets, 2) the reduction of oxide fuel powder into metallic form in Li-LiCl molten-salt, and 3) the recovery of Li from waste salt by electrowinning. The heat power, volume, and radioactivity of spent fuel can be decreased by a factor of a quarter via this process. However, the conventional Li reduction process for the reduction of oxide fuel powder demands a highly pure inert gas atmosphere inside hot cells to prevent unwanted Li oxidation and explosion. Such a handling problem of chemically active Li in hot cell environments makes the reduction process complicated and expensive. Actually, various issues have been identified from handling and recovery of metallic Li during the mock-up tests of the ACP.

A concept of electrochemical reduction of spent oxide fuel in  $\text{Li}_2\text{O}$ -LiCl molten-salt was proposed to solve the problems attributed to the handling of active Li. [5] The electrochemical reduction technology is based on the integration of a Li reduction process and subsequent electrowinning of  $\text{Li}_2\text{O}$  into one electrolytic reduction step where electrolysis of  $\text{Li}_2\text{O}$  and reduction of spent oxide fuel are taking place simultaneously at the cathode part of electrolysis cell. So,  $\text{Li}_2\text{O}$  instead of Li is a feeding material in this concept. Figure 1 is the schematic diagram of that concept. Experiments to test the viability of this electrochemical reduction technology have been performed using fresh uranium oxides in this study.

Figure 1. Reaction mechanism of electrolytic reduction of uranium oxides in  $\text{Li}_2\text{O-LiCl}$  molten-salt



## Experimental

A reaction system was constructed for the elucidation of the metallisation characteristics of uranium oxides. It consisted of resistive heater, k-type thermocouple, dual type reactor, cathode, anode, a reference electrode, Ar gas, reactants supplying system, and oxygen detector. Alumina crucible was used to insulate the inner reactor from the outer reactor. The structural material for inner reactor was SUS 304 that is relatively corrosion resistive in  $\text{LiCl}$  molten-salt. A cooling jacket was installed at the upper part of the reactor to prevent discharge of molten-salt vapour. The cathode part of electrolysis cell consisted of a SUS conductor, uranium oxide, and non conductive porous magnesia filter (pore size  $3 \mu\text{m}$ ) as a container for uranium oxide. Uranium oxide was filled between the SUS conductor and the magnesia filter and its tap density was  $2.8\text{--}2.9 \text{ g/cm}^3$ . Platinum tube (outer diameter 8 mm) and a SUS conductor were used as an anode. Graphite anode was also used for the comparative experiment. Platinum anode (outer diameter 3 mm) and a SUS conductor were used as a reference electrode.

Reactivity test of electrochemical reduction process was performed in  $650^\circ\text{C}$ ,  $\text{Li}_2\text{O-LiCl}$  molten-salt system and Ar gas flow was applied to maintain an inert atmosphere in the reactor. Uranium oxides ( $\text{UO}_2$  or  $\text{U}_3\text{O}_8$  powder) and  $\text{LiCl}$  (Alpa, 99%) were supplied to the inner reactor at room temperature.  $\text{Li}_2\text{O}$  (Cerac, 99.5%) was treated carefully to prevent the formation of  $\text{LiOH}$  and fed to the inner reactor at  $650^\circ\text{C}$ . During the reduction reaction, the variation of  $\text{Li}_2\text{O}$  concentration in molten-salt was measured by titration method using a phenolphthalein indicator and 0.1 N  $\text{HCl}$ . After the electrochemical reduction reaction, the cathode part of electrolysis cell was cooled to room temperature in inert atmosphere to prevent the reoxidation of uranium metal and then separated from the reaction system. The residual  $\text{LiCl-Li}_2\text{O-Li}$  molten-salt in the product was washed away using distilled water and methanol, and then the product was vacuum dried. The conversion of uranium oxide to uranium metal was determined by thermogravimetry analysis.

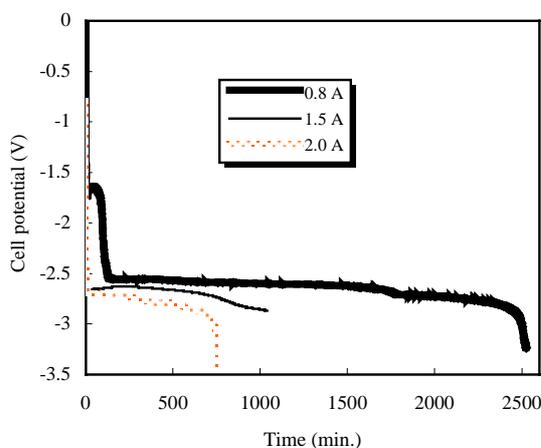
## Results and discussion

In this electrolytic reduction concept, uranium oxide powder to be reduced is a constituent unit of cathode part. A significant issue for designing of a cathode is to find an innovative concept to contain oxide powder effectively. The containment structure should be porous, and stable against thermal and mechanical shocks. Porous Magnesia filter and stainless steel mesh (325 mesh) were tested as uranium oxide container. In the case of stainless steel mesh, Li deposited on the outside of stainless steel mesh showing about less than 10% conversion of uranium oxide to uranium metal. The reason was attributed to the conductive nature of stainless steel mesh. So, a non-conductive porous magnesia filter (pore size 3  $\mu\text{m}$ ) was applied as a container and the conversion of  $\text{U}_3\text{O}_8$  to U metal reached more than 99%.  $\text{Li}^+$  in molten-salt is attracted to cathode through a porous magnesia filter and reduced and deposited on uranium oxide for a chemical reaction with it to form uranium metal.  $\text{O}^{2-}$  comes out through the porous magnesia filter and discharges at the anode as oxygen gas.

Platinum and graphite tube were tested as an anode. The use of graphite anode was advantageous considering the cell potential because oxygen ion discharged as CO and  $\text{CO}_2$  in this case. However, the formation of  $\text{Li}_2\text{O}_3$  was observed by XRD analysis and it made the closed recycle of  $\text{Li}_2\text{O}$  impossible. So, platinum tube was used as an anode. However, in this electrolytic reduction system, oxidation reaction of oxygen ion takes place at the surface of the anode, and thus the anode material is subject to an aggressive attack by oxygen ions. Actually, the formation of oxide layer on the surface of platinum anode was observed and the anode potential increased as the electrolytic reduction reaction proceeded. The study on a thermodynamically or kinetically stable anode will be carried out to solve this problem.

The potential for the reduction of uranium oxide was measured using a linear sweep voltammetry method and the results are shown in Figure 2. Molten-salt was prepared using 200 g LiCl with 3wt%  $\text{Li}_2\text{O}$ . In case of uranium oxide presence, the weight of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  was 30 g, respectively. In all cases, the increase of current increase due to electrolytic reduction was observed when the cell potential reached  $\sim -2.5$  V which is similar to equilibrium electrolysis potential of  $\text{Li}_2\text{O}$ . [6] It means that firstly electrolytic reduction of  $\text{Li}_2\text{O}$  occurs and then the reduced Li chemically reacts with uranium oxide. The current before  $-2.5$  V may be attributed to the corrosion and reduction of SUS 304 which consists of Fe, Ni, Cr, etc.

Figure 2. Linear sweep voltammograms of  $\text{Li}_2\text{O}$ -LiCl,  $\text{UO}_2$ - $\text{Li}_2\text{O}$ -LiCl, and  $\text{U}_3\text{O}_8$ - $\text{Li}_2\text{O}$ -LiCl systems



The electrolytic reduction reactions were performed at 650°C to measure reduction yield and potential variations using chronopotentiometry method. The reactants consisted of 40 g  $U_3O_8$  and 500 g LiCl (with 3wt%  $Li_2O$ ). Figure 3 shows the variations of cathode, anode, and cell potential as a function of time. It was expected that cathode resistance would decrease as non-conductive uranium oxide transformed to conductive uranium metal. However, the metallisation in cathode parts have little effect on potential variation. The anode potential was 0.16 V at the reaction time of 80 min and it increased rapidly after the reaction time of 800 min. The reason was attributed to the formation of oxide layer on platinum anode and decrease of  $Li_2O$  concentration in molten-salt. The variation of cell potential was measured as shown in Figure 4. The operating currents were 0.8, 1.5, and 2.0 A, respectively. Current change showed little effect on the cell potential. The conversion of  $U_3O_8$  to U metal was more than 99% in case of 0.8 and 1.5 A. Relatively low conversion of 94% was observed when 2.0 A current was applied. It means that the metallisation rate of uranium oxide is relatively slower than electrolysis rate of  $Li_2O$ .

Figure 3. Variation of anode, cathode, and cell potential with time in  $U_3O_8$ - $Li_2O$ -LiCl system

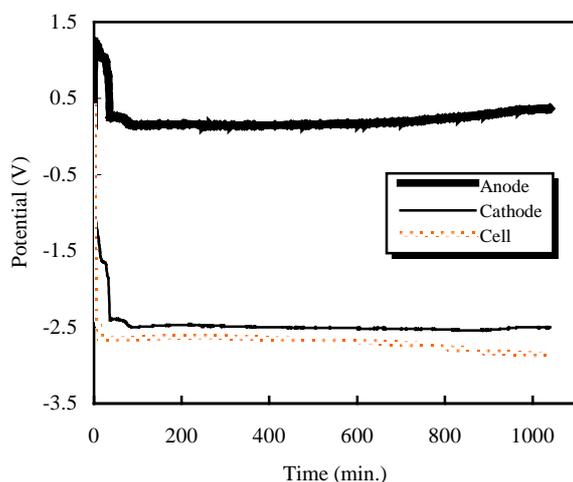
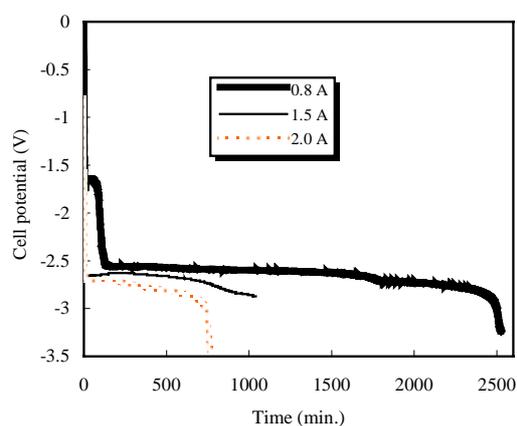
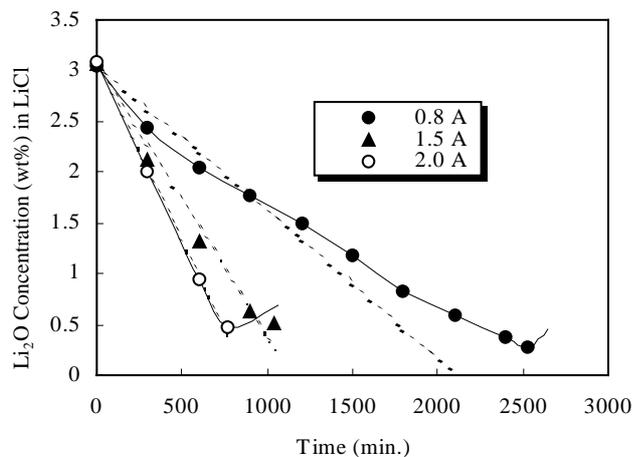


Figure 4. Chronopotentiograms (0.8, 1.5, and 2.0 A) of in  $U_3O_8$ - $Li_2O$ -LiCl system



The variation of  $Li_2O$  concentration in molten-salt was measured every 5 hours. As shown in Figure 5, the decreased amount of  $Li_2O$  at the initial stage of the reduction reaction in molten-salt exceeded theoretical value calculated according to supplied electricity. However, the decrease rate of  $Li_2O$  reduced after 15 hours. The corrosion of SUS 304, the structural material of inner reactor, resulted in the formation of sesquioxides such as  $Fe_2O_3$ ,  $Ni_2O_3$ , and  $Cr_2O_3$ , and XRD analysis showed the existence of  $LiFe(Ni, Cr)O_2$  which originated from  $Li_2O$  and sesquioxides. So, slow decrease of  $Li_2O$  concentration in initial stage can be explained. In the conventional Li reduction process, the rate determining step is back diffusion of  $Li_2O$  from uranium metal pore, and its mass transfer and dissolution rate is relatively fast. However, in this electrolytic reduction system, the small amount of LiCl inside the magnesia filter limits the amount of soluble  $Li_2O$  and consequently makes the mass transfer of oxygen ions to the anode through porous magnesia difficult. Consequently, the reduction of decrease rate of  $Li_2O$  due to closed recycle of  $Li_2O$  could be observed at the later stage of reaction. These results suggest that the thickness of the uranium oxide layer in magnesia filters should be as thin as possible to facilitate mass transfer of oxygen ions.

Figure 5. Variation of  $\text{Li}_2\text{O}$  concentration with reaction time in  $\text{U}_3\text{O}_8\text{-Li}_2\text{O-LiCl}$  system



## Conclusions

A concept of electrochemical reduction of spent oxide fuel in  $\text{Li}_2\text{O-LiCl}$  molten-salt was experimentally verified using fresh uranium oxides. In this new electrochemical reduction process, electrolysis of  $\text{Li}_2\text{O}$  and reduction of uranium oxide are taking place simultaneously at the cathode part of electrolysis cell. Li produced via  $\text{Li}_2\text{O}$  electrolysis reacts with uranium oxide resulting in the formation of  $\text{Li}_2\text{O}$  of which oxygen ions originate from uranium oxide. The resultant  $\text{Li}_2\text{O}$  is electrolysed and regenerated Li is used for further reduction of uranium oxide. Non-conductive porous magnesia filters could be used to contain the uranium oxide powder at the cathode. In case of platinum anode,  $\text{Li}_2\text{O}$  could be recycled for the electrochemical reduction of uranium oxide. However, when graphite was used as an anode, the closed recycle of  $\text{Li}_2\text{O}$  was not feasible due to the formation of  $\text{Li}_2\text{CO}_3$ . As the reaction proceeded, the anode potential increased due to decrease of  $\text{Li}_2\text{O}$  concentration and the formation of oxide lay on platinum anode. The cell potential of electrolytic reduction reaction was 2.7-2.8 V and the conversion of uranium oxide to uranium metal reached more than 99% in this electrolytic reduction system.

## Acknowledgement

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