Solubility Measurement of Li$_2$O in LiCl Molten Salt for Electro-Reduction Process†

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The change of Li$_2$O solubility with the concentration of high heat-generating elements such as Cs and Sr was measured in a LiCl melt, which is generally used as an electrolyte medium in an electrolytic reduction step of pyrochemical processing. The change in Li$_2$O solubility is one of the important parameters in the electrolytic reduction. High temperature filtration using a porous tube and acid-base titration were employed to measure the solubility of Li$_2$O. The solubility of Li$_2$O was found to be 8.8 wt. % in pure LiCl molten salt at 650 ºC. The solubility slightly increased when SrCl$_2$ (alkaline earth metal) was added to LiCl. In contrast, the addition of CsCl (alkali metal) significantly decreased the solubility.

Key Words: Pyroprocessing, Electro-reduction, Molten salt, Lithium chloride, Lithium oxide.

INTRODUCTION

Pyrochemical processing of nuclear fuels consisting of an electrolytic reduction, refining and winning stages has been emerging as one of the most promising options for future spent nuclear fuel management[1-3]. The electrolytic reduction process converts uranium oxide within spent nuclear fuel into a uranium metal ingot in a molten salt electrolyte[4,5]. For a reduction of UO$_2$ and UO$_2$-Pu$_2$O mixed oxide, LiCl is generally used as a molten salt medium[6-10].

Fig. 1 illustrates the scheme of the electrolytic reduction reaction. U$_3$O$_8$ powder and a platinum cathode electrode are placed in a stainless steel vessel, whereas the other platinum anode is located at the outer of the cathode basket in the molten salt.

Reactions of equations 1-4 occur in the electrolytic bath reactor of Fig. 1. At the cathode, Li$^+$ reduces to Li metal (eqn. 1), which reacts with U$_3$O$_8$, leading to U metal and Li$_2$O (eqn. 2). At the same time, Li$_2$O dissociates into Li$^+$ and O^{2-} (eqn. 3) in the molten salt, which diffuses to the anode for the reaction of eqn. 4. Therefore, a small amount of Li$_2$O (3 wt.%) in the molten salt is required at the beginning of the electrolytic reduction process of uranium oxide to initiate the oxidation reaction of O^{2-} at the anode[11-13]. During the reduction process, it is necessary to keep the Li$_2$O concentration in the molten salt at a certain range because the excessive amount of Li$_2$O over the solubility in LiCl for example 11.9 mol % at 650 ºC
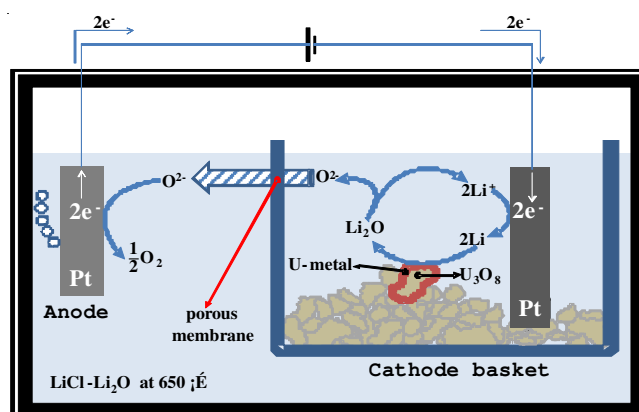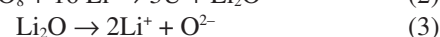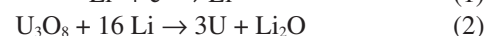

Fig. 1.   Scheme of an electrolytic reduction process of uranium oxide in a LiCl-Li$_2$O molten salt medium

and 16.1 mol % at 750 ºC[14,15] can precipitate with U metal, leading to a reoxidation of U metal[16].

At Cathode
$$Li^+ + e^- \rightarrow Li \qquad (1)$$
$$U_3O_8 + 16\,Li \rightarrow 3U + Li_2O \qquad (2)$$
$$Li_2O \rightarrow 2Li^+ + O^{2-} \qquad (3)$$
At Anode
$$O^{2-} \rightarrow 1/2O + 2e^- \qquad (4)$$

When spent nuclear fuel is employed to the pyrochemical processing, high-heat-generating elements such as Cs, Sr and Ba are significantly dissolved into the molten salt. Addition-

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ally, these elements are accumulated as the reduction process proceeds[17], which would significantly affect the solubility of Li_2O in the system. Herein, we monitor the change of Li_2O concentration in the LiCl molten salt at 650 °C by varying the amount of high heat-generating elements such as Sr and Cs.

EXPERIMENTAL

Anhydrous lithium chloride (LiCl), lithium oxide (Li_2O), cesium chloride (CsCl) and strontium chloride ($SrCl_2$) with a purity of 99.99 % were obtained from Sigma-Aldrich and used without further purification. All the performance and sample preparations were conducted inside a glove box under an inert Ar atmosphere (H_2O < 1ppm, O_2 < 1ppm) as shown in Fig. 2.

The furnace was attached to the floor of the glove box and the measurement of Li_2O solubility was carried out in the furnace at 650 °C. Because the solubility of LiO_2 in LiCl melt strongly depends on the temperature, the reaction vessel system in this study consists of two glassy carbon containers and a tube-shaped magnesia filter[18].
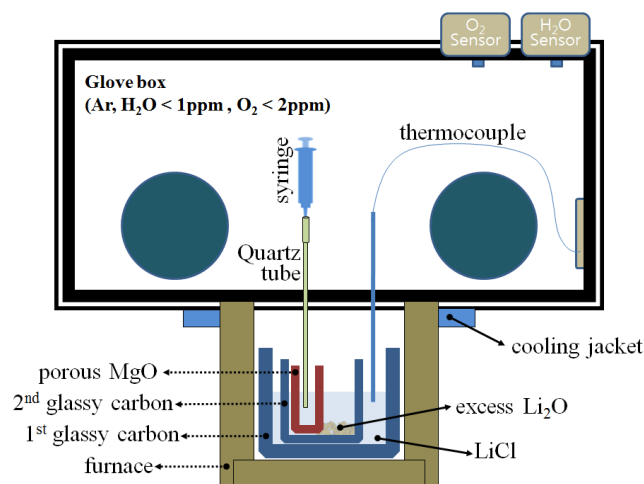

Fig. 2. Schematic drawing of the experimental apparatus for Li_2O solubility measurements

LiCl was melted in an external vessel (GC1) where another container (GC2) containing a mixture of LiCl (40 g) and Li_2O (10 g) was placed. When the salt was completely melted, the magnesia filter was immersed into the GC2. After the system temperature was maintained at 650 °C for 1 h, the first sample was taken from inside of the filter using a glass tube connected to a syringe and the filter was then removed from the vessel. 30 g of CsCl (or $SrCl_2$) was added to the molten salt (GC2) and melted completely. The magnesia filter was immersed again in the salt and samples were taken at 1 h intervals.

The samples (*ca.* 1.0 g) after cooling down to room temperature were dissolved in water and were titrated using 0.3 N HCl and a phenolphthalein indicator to determine the Li_2O solubility. The solubility of Li_2O was calculated by the following;

$$Li_2O \text{ solubility (wt \%)} = \frac{W_{Li_2O}}{W_{Li_2O} + W_{LiCi} + W_{MClx}} \times 100 \quad (5)$$

$$= \frac{\text{Equivalent amount of } Li_2O}{\text{Taken sample}} \times 100 \quad (6)$$

$$= \frac{Li_2O \text{ molar mass} \times 0.3N \times \text{titration volume (mL)} \times 10^{-3}}{\text{Taken sample}} \times 100 \quad (7)$$

where W_{Li_2O} are the weight of LiCl, Li_2O and metal chlorides, respectively.

RESULTS AND DISCUSSION

As an excess amount of Li_2O was suspended in the LiCl melt at a constant temperature using the system depicted in Fig. 2, liquefied Li_2O and LiCl penetrated through the porous magnesia filter wall and were collected inside the magnesia vessel, in addition the acid-base titration of the aqueous solution prepared from the LiCl-Li_2O filtrate evaluated the solubility of Li_2O in LiCl at 650 °C. Fig. 3 shows that Li_2O solubility increases with time and is saturated at 8.8 wt.% after *ca.* 3 h. This value is very similar to the solubility previously reported[14].
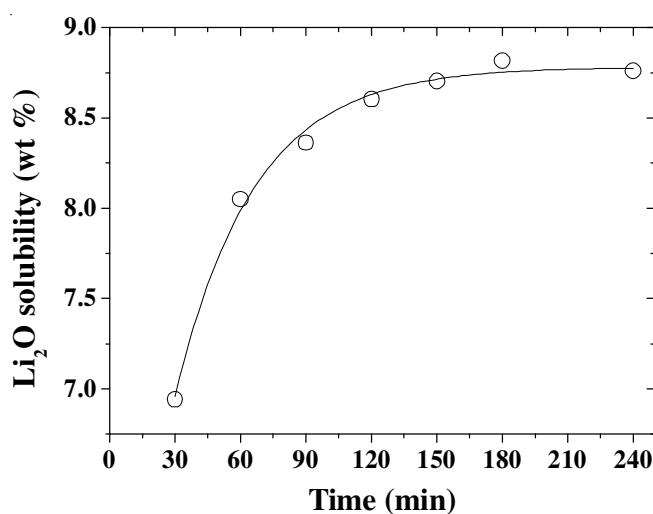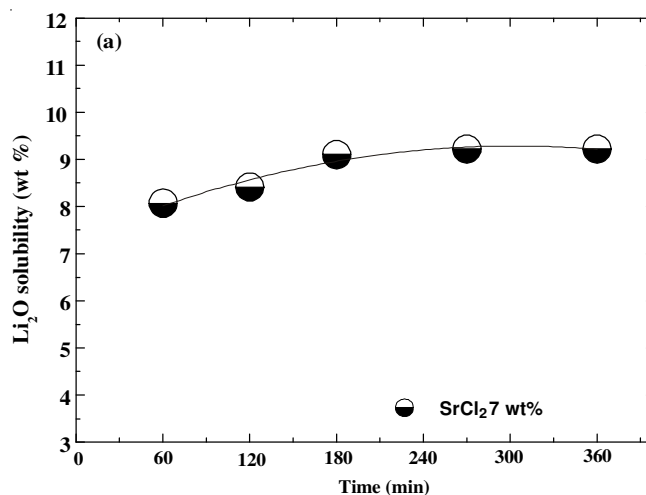

Fig. 3. Solubility change of Li_2O as a function of time in LiCl melt

In the pyroprocessing, a molten salt medium contains many species of elements dissolved from spent nuclear fuel. In particular, among fission products, Cs and Sr possess high solubility in a LiCl melt (47.1 wt. % for CsCl and 37.8 wt.% for $SrCl_2$ at 650 °C). Thus, these elements will have a direct influence on the solubility of Li_2O in the reduction process. Fig. 4 shows the solubility of Li_2O in LiCl containing $SrCl_2$ or CsCl at 650 °C as a function of time. Despite a slight increase
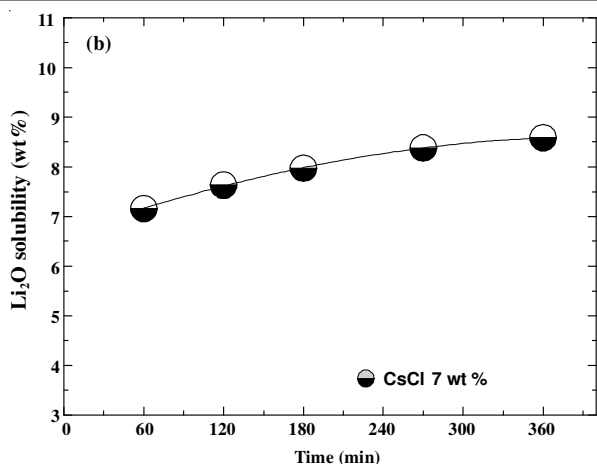
Fig. 4. Solubility changes of Li$_2$O as a function of time in LiCl melt containing (a) 7 wt. % of SrCl$_2$, (b) 7 wt. % of CsCl

over time, the measurement after 4 h seemed to provide a value close to the solubility at 650 °C. The addition of SrCl$_2$ (7 wt. %) enhanced the Li$_2$O solubility (9.1 wt. %) with respect to that in pure LiCl (8.8 wt. %) after 4 h. In contrast, the addition of CsCl reduced the Li$_2$O solubility in LiCl to 8.4 wt. % for 7 wt. % of the additive.

Fig. 5 displays the Li$_2$O solubility with the concentration of SrCl$_2$ and CsCl in the LiCl molten salt at 650 °C. As the concentration of SrCl$_2$ increases in the melt, the solubility of Li$_2$O in LiCl slightly rises. In contrast, the addition of CsCl drops the Li$_2$O solubility from 8.8 wt.% in the LiCl melt to 7 wt. % when 15 wt. % of CsCl is added to the system. Such contrast effect of the additives on Li$_2$O solubility can be explained thermodynamically[19]. A slight difference in the Gibbs free energies of formation of Li$_2$O (-476 kJ/mol) and SrO (-498 kJ/mol) at 650 °C leads to a moderate Li$_2$O solubility increase in the melt. On the other hand, a much smaller Gibbs free energy of formation of Cs$_2$O (-227 kJ/mol) at 650 °C results in Li$_2$O precipitation with the addition of CsCl to the LiCl melt saturated with Li$_2$O. It seems reasonable that the dissolution of CsCl displaces Li$^+$ ions surrounding O^{2-} ions with Cs$^+$ ions, leading to the formation of Li$_2$O precipitation more favourably than a Cs$_2$O solid in the molten salt system[19].
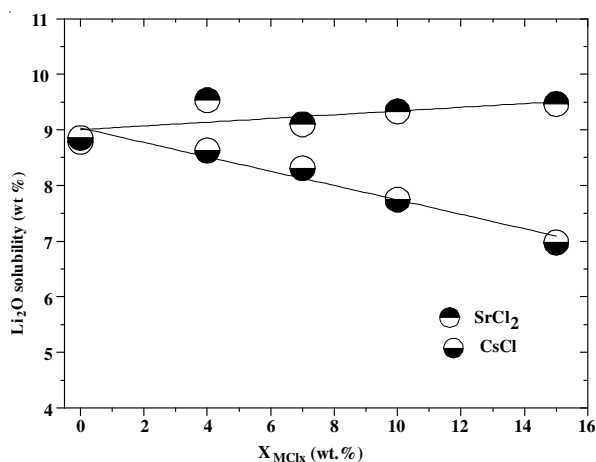

Fig. 5. Li$_2$O solubilities in LiCl at 650 °C as a function of metal chloride content (M = Sr or Cs) in LiCl melt

Conclusion

In this study, we measured the solubility of Li$_2$O in a LiCl melt largely employed in the electrolytic reduction step of Pyrochemical processing and observed the changes of Li$_2$O solubility with the concentration of high-heat generating elements such as Cs and Sr. The addition of SrCl$_2$ results in a slight increase of Li$_2$O solubility in the melt. In contrast, the addition CsCl to the LiCl-Li$_2$O molten salt leads to Li$_2$O precipitation in the melt. The different solubility tendency of Cs and Sr in the LiCl molten salt can be explained by comparing the values of the Gibbs free energy of the metal oxide formation.

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