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 U\(_{3}\)O\(_8\) and UO\(_2\)-PuO\(_2\) 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 UO\(_2\), 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 °C

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ally, these elements are accumulated as the reduction process proceeds\textsuperscript{17}, which would significantly affect the solubility of Li$_2$O in the system. Herein, we monitor the change of Li$_2$O concentration in the LiCl molten salt at 650 ºC by varying the amount of high-heat-generating elements such as Sr and Cs.

EXPERIMENTAL

Anhydrous lithium chloride (LiCl), lithium oxide (Li$_2$O), 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$_2$O < 1 ppm, O$_2$ < 1 ppm) as shown in Fig. 2.

The furnace was attached to the floor of the glove box and the measurement of Li$_2$O solubility was carried out in the furnace at 650 ºC. Because the solubility of Li$_2$O 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\textsuperscript{18}.

Fig. 2. Schematic drawing of the experimental apparatus for Li$_2$O solubility measurements

LiCl was melted in an external vessel (GC1) where another container (GC2) containing a mixture of LiCl (40 g) and Li$_2$O (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 ºC 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$_2$O solubility. The solubility of Li$_2$O was calculated by the following:

\begin{equation}
\text{Li}_2\text{O solubility (wt %)} = \frac{W_{\text{Li}_2\text{O}}}{W_{\text{Li}_2\text{O}} + W_{\text{LiCl}} + W_{\text{MCl}}} \times 100 \quad (5)
\end{equation}

\begin{equation}
= \frac{\text{Equivalent amount of Li}_2\text{O}}{\text{Amount taken sample}} \times 100 \quad (6)
\end{equation}

RESULTS AND DISCUSSION

As an excess amount of Li$_2$O was suspended in the LiCl melt at a constant temperature using the system depicted in Fig. 2, liquefied Li$_2$O 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$_2$O filtrate evaluated the solubility of Li$_2$O in LiCl at 650 ºC. Fig. 3 shows that Li$_2$O 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\textsuperscript{14}.

Fig. 3. Solubility change of Li$_2$O 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 ºC). Thus, these elements will have a direct influence on the solubility of Li$_2$O in the reduction process. Fig. 4 shows the solubility of Li$_2$O in LiCl containing SrCl$_2$ or CsCl at 650 ºC as a function of time. Despite a slight increase
over time, the measurement after 4 h seemed to provide a value close to the solubility at 650 °C. The addition of SrCl₂ (7 wt. %) enhanced the Li₂O 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 Li₂O solubility in LiCl to 8.4 wt. % for 7 wt. % of the additive.

Fig. 5 displays the Li₂O solubility with the concentration of SrCl₂ and CsCl in the LiCl molten salt at 650 °C. As the concentration of SrCl₂ increases in the melt, the solubility of Li₂O in LiCl slightly rises. In contrast, the addition of CsCl drops the Li₂O 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 Li₂O solubility can be explained thermodynamically. A slight difference in the Gibbs free energies of formation of Li₂O (-476 kJ/mol) and SrO (-498 kJ/mol) at 650°C leads to a moderate Li₂O solubility increase in the melt. On the other hand, a much smaller Gibbs free energy of formation of Cs₂O (-227 kJ/mol) at 650°C results in Li₂O precipitation with the addition of CsCl to the LiCl melt saturated with Li₂O. It seems reasonable that the dissolution of CsCl displaces Li⁺ ions surrounding O²⁻ ions with Cs⁺ ions, leading to the formation of Li₂O precipitation more favourably than a Cs₂O solid in the molten salt system.

Conclusion

In this study, we measured the solubility of Li₂O in a LiCl melt largely employed in the electrolytic reduction step of Pyrochemical processing and observed the changes of Li₂O solubility with the concentration of high-heat generating elements such as Cs and Sr. The addition of SrCl₂ results in a slight increase of Li₂O solubility in the melt. In contrast, the addition CsCl to the LiCl-Li₂O molten salt leads to Li₂O 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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REFERENCES