

Preparation and melting of uranium from U_3O_8

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Abstract

In this paper, we report on the preparation and melting of uranium in association with a spent nuclear fuel conditioning process. U_3O_8 powder was electrochemically reduced in a mixture of molten $LiCl-Li_2O$ (~3 wt.% of Li_2O in $LiCl$) at 650 °C resulting in the formation of uranium and Li_2O with a yield of >99%. When the powder of uranium with a residual $LiCl-Li_2O$ salt was heated in order to melt the metal, the uranium oxidation to UO_2 due to the reaction with Li_2O was observed. We were able to synthesize FeU_6 by using a Fe based cathode during the U_3O_8 reduction procedure. FeU_6 could be melted to below the temperatures where the oxidation of uranium by Li_2O occurred. The idea of compound formation and melting is applicable to the melting and casting of a spent nuclear fuel which contains oxidative residual salts due to its conditioning in a molten salt.

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1. Introduction

Pyrochemical processes have been developed for the treatment of spent nuclear fuels [1,2]. The pyroprocess of the Korea Atomic Energy Research Institute, the Advanced Spent Fuel Conditioning Process (ACP), focuses on the conditioning of Pressurized Water Reactor (PWR) spent oxide nuclear fuel [3]. The ACP consists of an air volume oxidation of the oxide fuel pellets, a reduction of the oxide fuel powder into a metallic form in a mixture of molten $LiCl-Li_2O$, and a smelting of the metallic powder. The ACP's functionality for the oxide reduction enables a spent oxide fuel to be applicable to a metal fuel cycle. Also, high heat load fission products such as Cs and Sr can be chlorinated and then separated from a metallized spent nuclear fuel during an oxide reduction in a molten salt.

About 95% of the PWR spent oxide fuel consists of UO_2 , which in the ACP volume oxidation step at 500 °C is oxidized to U_3O_8 . In the reduction process, the electrolysis of Li_2O to form Li and the reduction of the U_3O_8 powder accomplished by a chemical reaction with Li takes place simultaneously at the cathode basket of the electrolysis cell where the electrolyte is a mixture of molten $LiCl-Li_2O$ [4]. After the electrochemical

reduction, the uranium metal powder with ~30 wt.% residual $LiCl-Li_2O$ is heated to separate the residual salts by vaporization and to consolidate the uranium metal powders by melting. In this study, we investigate the reduction of U_3O_8 and a melting of uranium metal powder by considering the effects of the $LiCl-Li_2O$ salt.

2. Experimental

The electrochemical reduction of U_3O_8 was carried out by using a WPG100 potentiostat/galvanostat of Won-A-Tech. Pt was used as anode and pseudo-reference electrode. The cathode part of the electrolysis cell consisted of a cathode metal (Ni or Fe), U_3O_8 powder, and a porous MgO basket as a container for the U_3O_8 powders. The electrochemical reactions were performed in a mixture of molten $LiCl-Li_2O$ at 650 °C. The inert atmosphere inside the electrolysis cell was maintained by a flow of Ar gas. U_3O_8 powder (2.0 kg) and $LiCl$ (Alpha, 99%, 36.5 kg) were introduced into the cell at room temperature. Li_2O (Cerac, 99.5%, 1.1 kg) was fed into the cell at 650 °C. The conversion of U_3O_8 powder to U metal was determined by a thermogravimetric analysis (Seiko Instruments, TG/DTA 6300). All the reaction products were also identified by a MiniFlex, Rigaku/Bench-top X-ray Diffractometer.

3. Results and discussion

When a volume oxidized uranium oxide, U_3O_8 , was introduced into the liquid $LiCl-Li_2O$ mixture at 650 °C its spontaneous change to UO_2 was observed (Fig. 1). After 5 h U_3O_8 was partly reduced to $UO_{2.25}$ and then after 15 and

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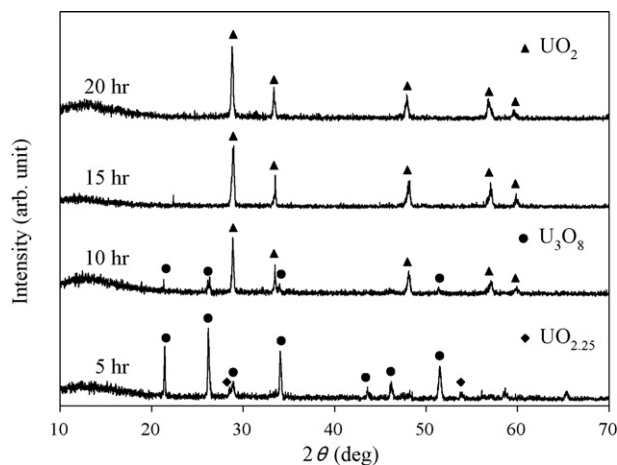


Fig. 1. XRD patterns for the phase change of U_3O_8 as a function of the time in a mixture of molten $\text{LiCl-Li}_2\text{O}$ at 650°C .

20 h it was reduced to UO_2 . After 10 h the amount of $\text{UO}_{2.25}$ was thought to be too small to be detected by XRD. For a complete dissolution of the Li_2O in molten LiCl , we held the temperature of the salt phase for 16 h at 650°C before starting the chronopotentiometry. Fig. 2 is the chronopotentiogram of the $\text{UO}_2\text{-LiCl-Li}_2\text{O}$ system. The standard reduction potentials of pure Li_2O and UO_2 at 650°C are -2.47 and -2.40 V, respectively. After the initial stage, the cell voltage of the electrolytic reaction was ~ -3.0 V and thus a reduction of both Li_2O and UO_2 was thermodynamically possible. The variation of the Li_2O concentration in the molten salt was measured by a titration method using phenolphthalein indicator and HCl as indicator. Fig. 3 shows that the decrease of the Li_2O concentration was in accordance with Faraday's law of an electrolysis. As we reported [4], this means that the electrochemical reduction reaction of our system proceeds via the electrolysis of Li_2O followed by a chemical reaction between Li and the uranium oxides. With the progress of the reaction, the rate of the O^{2-} formation from the chemical reaction became similar to that of the O^{2-} depletion at the anode showing a steady Li_2O concentration at a later stage after 50 h. The lowering of the Li_2O concentration in the

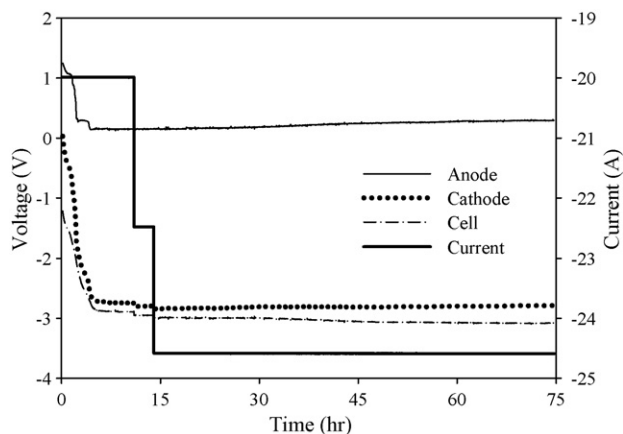


Fig. 2. Variations of the anode, cathode and cell voltage during a chronopotentiometry experiment in a $\text{UO}_2\text{-LiCl-Li}_2\text{O}$ system.

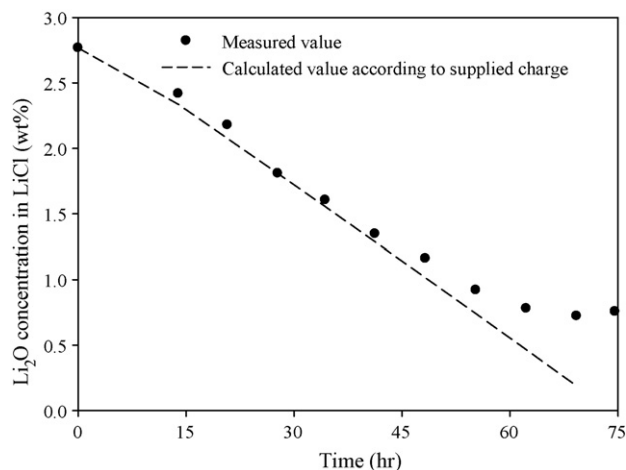


Fig. 3. Variations of the Li_2O concentrations with the reaction time in a $\text{UO}_2\text{-LiCl-Li}_2\text{O}$ system.

molten salt to below 0.5 wt.% caused a decomposition of LiCl and a subsequent dissolution of the Pt anode. Fig. 3 explains the reason why we set the initial Li_2O content in the LiCl as ~ 3 wt.%.

After the electrochemical reduction experiment, the amount of residual $\text{LiCl-Li}_2\text{O}$ in the cathode product ($\text{U-LiCl-Li}_2\text{O}$) was measured as 31.3 wt.%. Li_2O in $\text{LiCl-Li}_2\text{O}$ was 21.4 wt.% and the reason for this much higher Li_2O concentration when compared to the initial value of ~ 3 wt.% could be reasonably attributed to a slow Li_2O diffusion out of the porous magnesia basket and a subsequent accumulation of Li_2O which was mainly formed by a reaction between Li and UO_2 in the basket. We washed the cathode product by using distilled water to remove the residual salts. The obtained uranium metal powder was subjected to a thermogravimetric analysis to measure the mass change owing to the phase change from U to U_3O_8 . The analysis showed that the reduction yield of U_3O_8 in this electrochemical reduction reaction was more than 99%. The XRD pattern of the salt-free sample is that of a uranium metal phase (Fig. 4) and the inserted image in Fig. 4 shows the uranium metal ingot prepared by a melting of the metal powders (weight 18.5 g) by using an arc furnace. The density of the metal ingot was measured as 15.9 g/cm^3 . The reason for this low value can be ascribed to the existence of dross and the method itself which is a powder melting without a pressing step.

A pyrochemical treatment of spent fuel is based on a solvent-free process to secure its critical safety. Therefore, in the cathode process at the Argonne National Laboratory, the vaporization at high temperatures has been used as a method to separate the residual LiCl-KCl salts from the electrorefined metal [5,6]. However, our endeavors to melt the cathode product with a $\text{LiCl-Li}_2\text{O}$ residual salt resulted in the formation of U-UO-UO_2 mixed powders instead of a consolidated uranium metal ingot. The reason for the uranium metal reoxidation can be explained by a reaction between Li_2O and U (Fig. 5). According to the calculation based on the published data, the oxidation of uranium by Li_2O is thermodynamically feasible above 945°C [7]. The melting temperature of uranium is 1132°C and thus

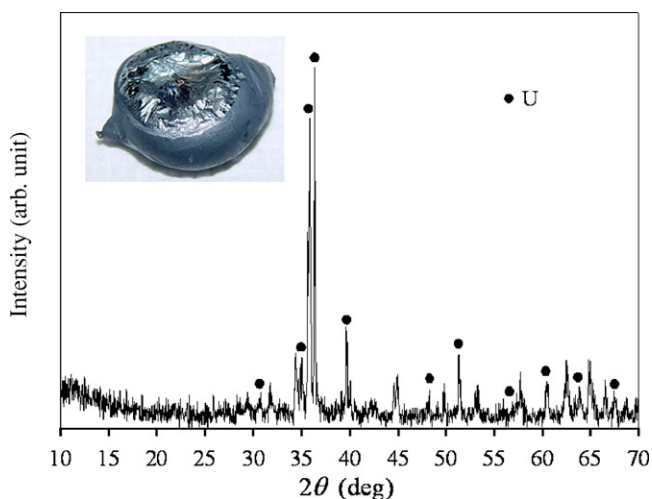


Fig. 4. XRD patterns of the produced uranium metal after an electrochemical reduction of U_3O_8 in a mixture of molten $LiCl-Li_2O$. The insert is a photograph of a uranium metal ingot.

before the heating system reaches that temperature, the oxidation of U by Li_2O occurs.

After heating at $1400\text{ }^\circ\text{C}$ for 3 h by using an induction furnace, the remaining Li content in the product in form of $LiCl$, Li_2O and Li was measured as 6.3 ppm by an atomic absorption spectroscopy. The vapor pressures of the interesting materials were calculated using published data [8]. It is clear from Fig. 6 that Li and $LiCl$ can be separated easily from U metal by vaporization. As mentioned above, the amount of residual $LiCl-Li_2O$ salt in the cathode product and Li_2O in the $LiCl-Li_2O$ were 31.3 and 21.4 wt.%, respectively. Therefore, the Li_2O content in the sample before a melting test was 6.7 wt.%. However, the vapor pressure of Li_2O is even lower than that of uranium metal. Actually, when we investigated the vaporization behavior of pure Li_2O under the same heating condition, the vaporization of solid Li_2O at $1400\text{ }^\circ\text{C}$ was not detectable. Therefore, the decrease of the Li_2O content from the % to the ppm level means the existence of a reaction between U and Li_2O and a subsequent

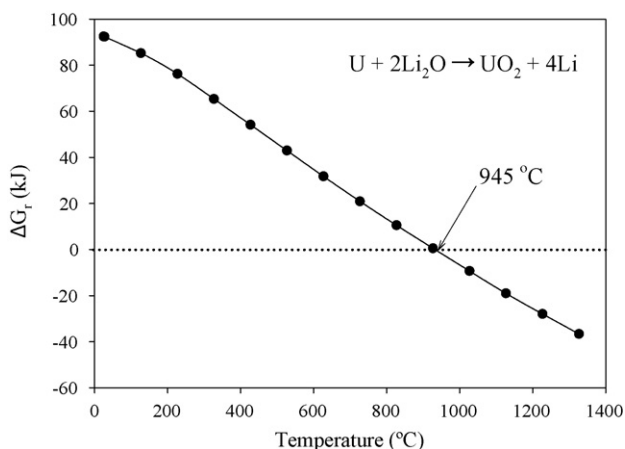


Fig. 5. Calculated Gibbs free energy change for the oxidation of uranium due to Li_2O at various temperatures.

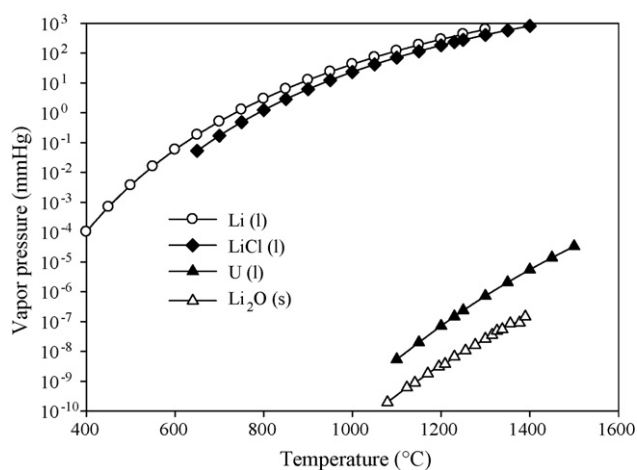


Fig. 6. Vapor pressures of Li, $LiCl$, U and Li_2O as function of temperature.

vaporization of Li, a product of the reaction, from the uranium powder.

For an efficiency of the electrochemical reduction process, the initial Li_2O content was optimized at ~ 3 wt.%, causing a relatively large amount of residual Li_2O in the cathode product. However, as we mentioned, a solvent washing and a vaporization method are not appropriate for the separation of the residual Li_2O . Therefore, we implemented a new approach. The cathode products of the ACP can be further treated in an electrorefining process where the uranium contained in the stainless steel anode basket is oxidized and simultaneously reduced at the cathode while the stainless steel basket is stable [9]. Thus, it is expected that the introduction of a Fe-element into the anode basket of an electrorefiner would have little effect on the overall performance of an electrorefiner. This led us to investigate the possibility of melting uranium together with Fe. To produce a U-Fe compound during an electrochemical reduction of U_3O_8 in a mixture of molten $LiCl-Li_2O$ at $650\text{ }^\circ\text{C}$ we used a Fe-based rod (stainless steel 304) as the cathode metal. The resulting product, which was sampled near the conductor was identified as FeU_6 (Fig. 7a).

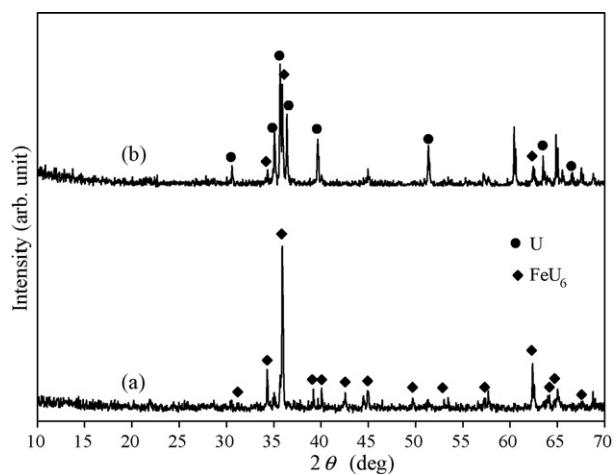


Fig. 7. XRD patterns of (a) inner-part of a cathode product and (b) outer-part of a cathode product after an electrochemical reduction with a stainless steel 304 rod as a cathode.

Its peritectic transformation to liquid and bcc-uranium occurs at 831 °C [10,11] and thus it can be consolidated below the temperatures where the oxidation of uranium by Li_2O prevails. While pure uranium metal was also observed at the outer-part of the cathode product (Fig. 7b), the formation of FeU_6 via the diffusion of Fe from the cathode to the uranium metal phase could progress further with an extension of the reaction time. No other U–Fe compound was observed under our electrochemical reduction conditions.

4. Conclusions

The electrochemical preparation of uranium metal and its melting were studied, regarding the effects of a $\text{LiCl-Li}_2\text{O}$ salt. U_3O_8 powders were successfully reduced to uranium metal powders with more than a 99% yield showing an interesting spontaneous phase change of U_3O_8 to UO_2 in a mixture of molten $\text{LiCl-Li}_2\text{O}$ at 650 °C. When the uranium metal powders were heated for their melting and consolidation, the existence of residual Li_2O in the uranium metal powders caused a reoxidation of the uranium metal. Under the electrochemical reduction conditions, we were able to synthesize FeU_6 , which can be melted and consolidated below the temperatures of oxidation due to Li_2O . It can be hoped that this idea of a compound formation and melting will be applicable to the treatment of a spent nuclear fuel, which contains oxidative residual salts.

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