

A Study on the Melting and Vaporization of a LiCl-Li₂O Salt

Jin-Mok Hur, Sung-Bin Park, Chung-Seok Seo, Ki-Jung Jung, Seong-Won Park
Korea Atomic Energy Research Institute, 150 Deokjin, Yuseong, Daejeon, Korea
jmhur@kaeri.re.kr

1. Introduction

The electrochemical reduction of pressurized water reactor (PWR) spent fuel in a LiCl-Li₂O molten salt recently has drawn much attention in the nuclear field. The heat, volume, and radioactivity of the spent fuel can be decreased by this pyrochemical method's functionality of an oxide reduction and a selective separation of high heat-load fission products [1, 2]. This technology has been developed to replace the conventional Li reduction process based on a molten LiCl-Li system because handling chemically active Li causes severe process limitations and stringent system requirements. After the electrochemical reduction of spent fuel, the product obtained mostly consists of a uranium metal and a residual LiCl-Li₂O salt. The salt occluded in the uranium metal should be removed before proceeding to the electrorefining or smelting of the reduced metal. However, unlike the molten LiCl-Li system, the data on a LiCl-Li₂O salt is scarce and thus in the present work, the melting and vaporization of a LiCl-Li₂O salt was studied by especially considering the metal/salt separation.

2. Methods and Results

The inactive test of the electrochemical reduction process was carried out in a LiCl-3wt% Li₂O molten salt by using fresh U₃O₈ powder as a feed material. The recovered product from the cathode of the electrochemical reduction cell after the operation was analyzed by X-ray diffraction (XRD). Only uranium metal, LiCl and Li₂O were observed (Fig. 1). The residual salt occluded in the uranium metal amounted to ~30 wt% and the concentration of Li₂O in LiCl was analyzed as ~20 wt% depending on the operation condition of the electrochemical reduction.

Vaporization in high temperatures was adopted as the method for the separation of the salt from the metal. Therefore, the vapor pressure variation of U and LiCl was calculated by using thermodynamic data [3]. Fig. 2 depicts the results. In the case of LiCl, a drastic increase of the vapor pressure starts above 900 °C. When compared to LiCl, the uranium metal has a very low vapor pressure showing the validity of using the vaporization method for the metal/salt separation. The vapor pressure data for Li₂O is not available to the best of our knowledge. The melting points of uranium metal, LiCl and Li₂O are 1,132 °C, 613 °C, and 1,570 °C, respectively. Consequently, at least, the relative stability of Li₂O can be inferred as such.

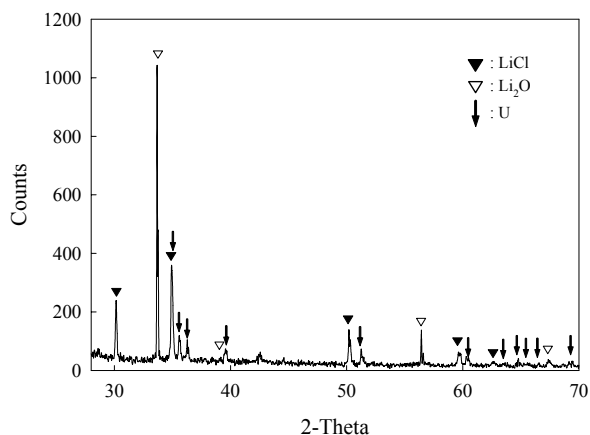


Fig. 1. XRD spectrum of the recovered product after the electrolytic reduction of U₃O₈ in a LiCl-Li₂O molten salt.

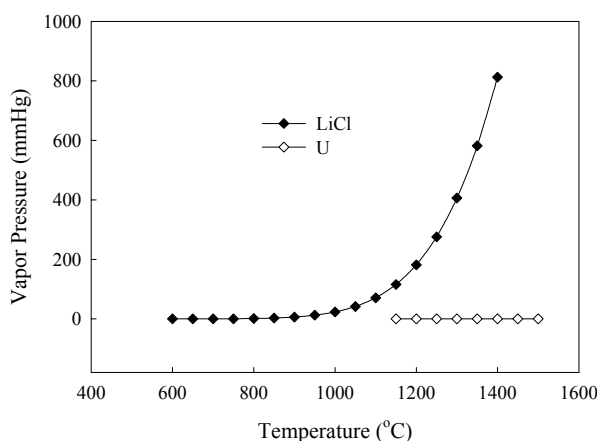


Fig. 2. Vapor pressure change of LiCl and U with temperature.

Thermogravimetry (TG) measurements were carried out under an argon gas flow condition to investigate the vaporization behaviors of the recovered product denoted as U-LiCl-Li₂O in Fig. 3. The separation of the occluded salt was completed below 1,100 °C. Remaining Li content analyzed by the atomic absorption spectroscopy was less than 10 ppm. For a comparison, the vaporization of LiCl (Alpha, 99.95%), Li₂O (Cerac 99.5%) and its mixture, LiCl-8 wt% Li₂O was also performed. The vaporization of single Li₂O was not detected even at 1,400 °C confirming the relative stability of solid Li₂O. However, in the case of LiCl-8 wt% Li₂O, a complete evaporation of Li₂O with LiCl was accomplished below 1,150 °C as shown in Fig. 3. The results suggest an interaction between the salts leading to a co-vaporization of LiCl and Li₂O.

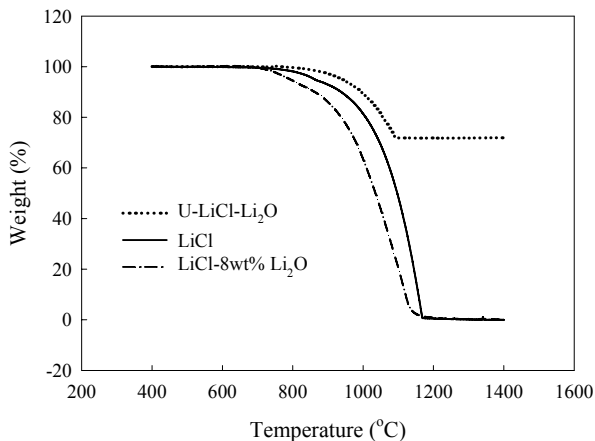


Fig. 3. TG temperature scan (10 °C/min.) curves for U-LiCl-Li₂O, LiCl, LiCl-8wt% Li₂O.

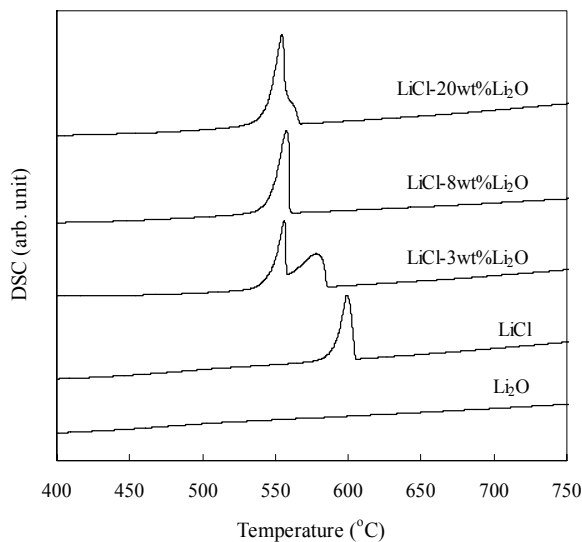


Fig. 4. Cooling (20 °C/min.) curves of DSC for Li₂O, LiCl, LiCl-3wt% Li₂O, LiCl-8wt% Li₂O, LiCl-20wt% Li₂O.

Differential scanning calorimetry (DSC) using a sealed stainless steel pan was applied and the onset points of the peaks on the cooling curves were taken for the temperatures of the phase transitions. Pure LiCl showed a liquid to solid phase transition at 605 °C. Interestingly, LiCl-8 wt% Li₂O and LiCl-20 wt% Li₂O showed a single solidification peak at ~ 560 °C which is much lower than that of LiCl. The lowering of the LiCl melting point means an enhanced stabilization of a LiCl melt by an interaction with Li₂O (or O²⁻). In the case of LiCl-3 wt% Li₂O, two solidification peaks were observed at 560 °C and 586 °C, respectively. The peak at 586 °C may be interpreted as the relatively weak interaction between LiCl and Li₂O. The dissolution of Li₂O in LiCl and the possible formation of a compound may lead to the co-vaporization of a LiCl-Li₂O molten salt. In addition, it should be noted that the operation temperature of the electrochemical reduction can be optimized according to the melting behavior of a LiCl-Li₂O salt. Practically, the electrochemical reduction is

operated in a LiCl-Li₂O salt at 650 °C by considering only the melting point of LiCl. However this study suggests that a lowering of the operation temperature is possible.

3. Conclusion

The interaction between LiCl and Li₂O was identified by thermochemical methods. The dissolution of Li₂O in LiCl and the formation of a compound enables the complete separation of a LiCl-Li₂O salt from the uranium metal. The possibility of lowering the operation temperature of a LiCl molten salt based process by the addition of Li₂O was also proposed.

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