

Electrochemical Behavior of Fission Products in a LiCl Molten Salt

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1. Introduction

The pyrochemical reduction process of spent oxide fuel is one of the options to handle spent PWR fuels in Korea.[1-3] During the reduction of metal oxides in a spent oxide fuel by Li metal produced electrochemically, chemical behaviors of some of the fission products are different from uranium and noble metals.

Electrolytic reduction of uranium oxide performed by KAERI gave more than a 99% conversion yield with a high current efficiency.[4] However, the effect of fission products on the electrolytic reduction process is not fully understood. Lanthanide elements as well as Pu and Am remained as oxide forms at a relatively high Li_2O concentration in the LiCl molten salt.[5,6]

Fission products such as I, Br, and Se are believed to have remained to some extent even after the voloxidation process at 500°C . [7] Li metal produced at the cathode during the electrolytic reduction of a spent fuel can react with these elements to give LiBr, LiI, and Li_2Se , respectively. In this paper the electrochemical behaviors of LiBr, LiI, and Li_2Se were investigated in a LiCl molten salt at 650°C .

2. Experimental and Results

Electrolytic reduction process of uranium oxide in a lithium chloride molten salt at 650°C produces lithium metal, which reacts with the uranium oxides in the spent oxide fuel to give a uranium metal. This process is able to eliminate the limitation of a Li_2O concentration from which the Li metal reduction process has suffered.

However, the electrochemical behaviors of all the elements in the spent oxide fuel were not fully investigated under the electrolytic reduction condition. Even though the electrochemical behaviors of lanthanide elements as well as actinide elements including uranium are relatively well understood, other fission products such as Br, I, and Se have not been studied extensively.

Thus, LiBr, LiI, and Li_2Se were studied to elucidate the electrochemical behaviors in LiCl molten salt by a cyclic voltammetry and each compound was electrolyzed at a constant current to obtain the anodic product as well as Li metal.

Figure 1 shows the cathodic cyclic voltammogram of 3wt% of LiBr in LiCl at 650°C . For the cathodic scan, Li metal was produced below -2.0V and re-oxidized during the reverse scan. It indicates that the Li metal produced at the cathode was stable for the cyclic voltammetric time scale. Fig. 2 shows the anodic cyclic voltammogram of LiBr. Even though Br_2 is known to be volatile at a high temperature, it gave a reversible cyclic voltammogram at the anode. It indicates that most of those produced at the anode remained at the anode surface.

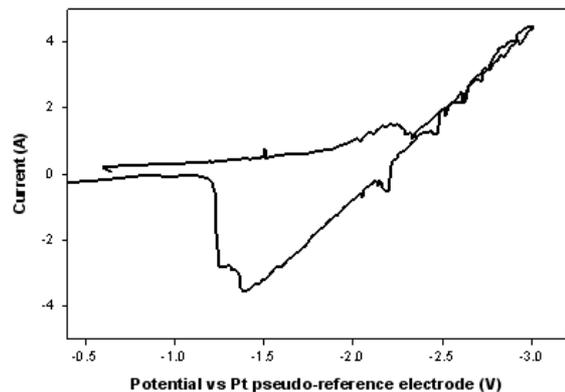


Fig. 1. Cathodic cyclic voltammogram of 3wt% LiBr in LiCl molten salt at 650°C (scan rate = $50\text{mV}/\text{sec}$).

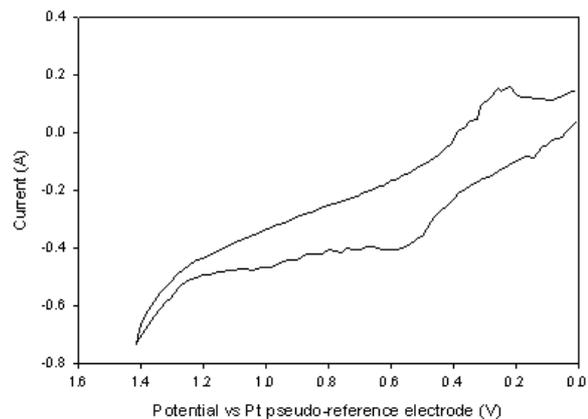


Fig. 2. Anodic cyclic voltammogram of 3wt% LiBr in LiCl molten salt at 650°C (scan rate = $50\text{mV}/\text{sec}$).

After an electrolysis with 100mA for one hour, the reaction mixture was cooled to room temperature. LiCl salt was covered with Br₂ which was easily removed by distilled water.

For the LiI in the LiCl molten salt, at the anode I₂ was produced and it was irreversible. After the electrolysis of LiI for one hour, I₂ was found in the upper part of the anode. Even though the cathode reaction of LiI produced Li metal below -2.0V, a re-oxidation current curve was not found for the reverse scan. It indicates that the Li metal produced during the forward scan disappeared rapidly.

For the Li₂Se in the LiCl molten salt, the final product of an electrolysis for one hour was a bulky black precipitate. Precipitates were washed with distilled water and dried under air for the XRD measurement. Fig. 3 shows the XRD pattern of the black precipitates. The precipitate gave a very pure Pt₂Se XRD pattern without other patterns.

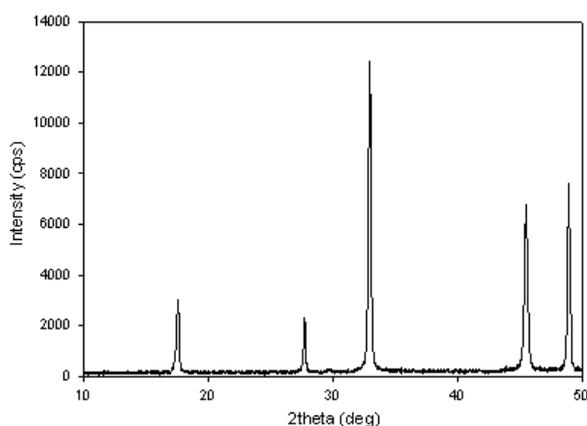


Fig. 3. X-ray diffraction pattern of the black precipitates after the electrolysis of Li₂Se with a 400mA constant current for one hour.

It was assumed that the Se²⁻ anion in LiCl attacked the Pt anode during the electrolysis and the electrode was severely damaged.

The effects of these elements on the current efficiency of a uranium reduction will be studied further.

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