

# On-Line Monitoring of Metal Ions in LiCl-KCl Melt

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## 1. Introduction

Recently, the pyrochemical process has attracted much attention in that the electrochemical process recovers the unreacted uranium and reduces the volume of high-level wastes in spent nuclear fuel. Since the uranium and transuranium (TRU) elements are recovered during the pyrochemical process [1,2], it is critical to accurately determine the material flow of actinides and fission products in an electrolyte of molten salt during the process operation. Conventionally, destructive analysis techniques are performed for quantitative and qualitative analyses of uranium and transuranium elements, but they often require tedious chemical separation procedures and radiometric or spectrometric measurements [3]. In contrast, the direct determination of elements in the molten salt may present the real-time monitoring of nuclear materials and the meaningful information on the safeguards if the electrochemical process operates as declared [1]. In this work, we developed an electrochemical technique and optimized the technique for on-line monitoring during the pyrochemical process.

## 2. Experimental

All the experiments were carried out in a glove box under Ar where O<sub>2</sub> and H<sub>2</sub>O level were maintained to be less than 1 ppm. Lithium chloride

(LiCl)/potassium chloride (KCl) eutectic salts (anhydrous beads), and silver chloride (AgCl) were obtained from Sigma Aldrich. Cerium chloride (CeCl<sub>3</sub>), lanthanum chloride (LaCl<sub>3</sub>), and magnesium chloride (MgCl<sub>2</sub>) were purchased from Alfa Aesar (purity ≥ 99.99%). UCl<sub>3</sub> was made from chemical dissolution of U metal by CdCl<sub>2</sub> in LiCl-KCl.

Electrochemical measurements were performed in a quartz tube (20 mm in outer diameter and 2 mm in wall thickness). W wire (Alfa Aesar, dia. 0.2 mm) and glassy carbon (Alfa Aesar, dia. 2 mm) electrodes were used as the working and counter electrodes, respectively. The W wire electrode was mechanically polished with sand paper prior to use. The reference electrode was Ag wire immersed in 1 mol% AgCl-LiCl-KCl melt.

The Electrochemical measurements were performed using a Gamry Reference 3000. The concentrations of uranium and magnesium ions were examined using inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Ultima 2C, Horiba Jobin Yvon).

## 3. Results and Discussion

Fig. 1 shows cyclic voltammograms (CV) obtained from s W electrode immersed in LiCl-KCl containing uranium and some lanthanides. Around -1.5 V and -2.0 V, the redox currents of U<sup>0/3+</sup> and Ce<sup>0/3+</sup> are observed. These results are well consistent in literatures[4]. Fig. 1(b) also shows CV according to

the addition of the some other lanthanides such as La, Nd. The current for U redox reaction was changed little but the currents for the lanthanide redox reactions increased as the lanthanide ions were added. These results mean that there is not the formation reaction of alloy among U and lanthanide ions.

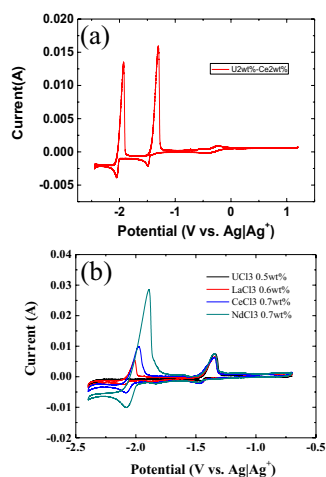


Fig. 1. CA results obtained from W wire in LiCl-KCl melt containing.

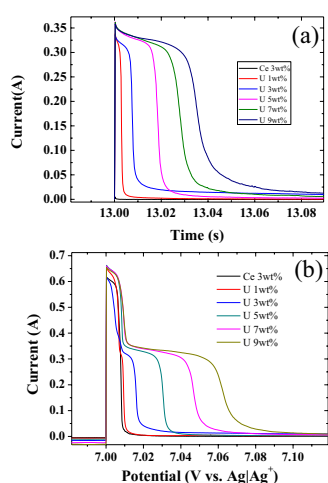


Fig. 2. CA results obtained from W wire in LiCl-KCl melt containing.

Fig. 2 shows chronoamperometry (CA) results obtained from a W electrode immersed in LiCl-KCl containing uranium and cerium cations. The dissolution reactions in Fig. 2(a) were performed for the electrodeposition of U. As the concentration of the U cation increased, the dissolution current response proportionally last more.

Fig. 2(b) shows CA results obtained after the simultaneous electrodeposition of U and Ce. In this case, new sharp peak firstly and then the second current, similar shape of U dissolution, in turn appeared. The first sharp peaks were nearly changed but the second dissolution currents last further with the concentration increment of U cation. The results denote that the passed charge, which can be calculated by the integration of the CA in Fig. 2, can be useful to extract the information for the concentration of the metal ions in LiCl-KCl melt.

#### 4. Conclusion

To develop an on-line monitoring system for use in the pyrochemical process, electrochemical techniques, CV and CA, were employed. The passed charges obtained from the integration of CA results show a good relation with the concentration of the metal ions in LiCl-KCl melt. This means that the CA technique may be one of the promising candidates for an on-line monitoring system during the pyrochemical process.

#### REFERENCES

- [1] D.-H. Kim, S.-E. Bae, T.-H. Park, J.-Y. Kim, C.-W. Lee, and K. Song, *Microchemical Journal*, 114, 261-265 (2014).
- [2] T. Inoue, L. Koch, *Development of Pyroprocessing and its future direction*, *Nucl. Eng. & Technol.*, 40, 183-190 (2008).
- [3] Y.J. Park, S.-E. Bae, Y.H. Cho, J.Y. Kim, K. Song, UV-vis absorption spectroscopic study for on-line monitoring of uranium concentration in LiCl-KCl eutectic salt, *Microchem. Journal*, 99, 170-173 (2011).
- [4] S.-E. Bae, Y.-H. Cho, Y.J. Park, H.J. Ahn, K. Song, Oxidation State Shift of Uranium during  $U^{3+}$  Synthesis with  $Cd^{2+}$  and  $Bi^{3+}$  in LiCl-KCl melt, *Electrochem. Solid State Lett.*, 13, F25-F27 (2010).