

Spectro-electrochemical Studies of Europium and Uranium Ions in LiCl-KCl Eutectic

Sang-Eun Bae, Yong Joon Park, Young Hwan Cho, and Kyuseok Song*

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 150-1 Dukjin-dong, Yuseong-gu,
Daejeon, 305-353, Korea

*Corresponding author: sk@kaeri.re.kr

1. Introduction

Pyrochemical processing of nuclear fuels using a molten salt as a solvent is regarded as one of the promising options for future spent nuclear fuel management [1-3]. Molten salts are known as suitable media for electrorefining and electrowinning of metal in the Pyrochemical process[1-3]. There are complicated chemical and electrochemical reactions in the molten salt of the Pyrochemical process. In order to reach a better understanding and control of these metal deposition processes, accurate knowledge of the reaction mechanism is essential.

Spectroscopic methods, such as fluorescence and UV-VIS spectroscopy, are considered to be one of powerful tools to investigate the chemical elements and its oxidation state. In this work, the spectroscopic studies have been performed under the electrochemical control to investigate the reaction mechanisms in the molten salt at high temperature during the electrochemical reactions.

2. Methods and Results

2.1 Experimental

Lithium chloride (LiCl) /potassium chloride (KCl) eutectic salts (anhydrous beads) and europium chloride (EuCl_2) were obtained from Aldrich Co. Ltd. (purity $\geq 99.99\%$). Silver chloride (AgCl) was purchased from Alfa Aesar (purity $\geq 99.998\%$). All the chemicals were used without further purification.

Electrochemical reaction vessel was made from a quartz tube (350 mm in length, 20 mm outer diameter and 2 mm in wall thickness) using a conventional glass blowing technique. Tungsten wire was used as a working electrode and also as a counter electrode. The electrodes were encased in quartz tubes to prevent electrical contact with other electrodes. The surface of the electrodes was polished thoroughly with sand paper prior to every use. The $\text{Ag}|\text{Ag}^+$ reference electrode contains 1.00 wt% of AgCl in the LiCl-KCl eutectic melt. A silver wire was then inserted into the reference electrode, immersing the Ag wire into the molten salts. All the potential values reported hereafter will be with respect to the $\text{Ag}|\text{Ag}^+$ reference electrode unless otherwise specified. More details can be found in our previous paper.[4]

Spectrometric measurement system is interfaced with an integrated glove box-furnace system. A rectangular quartz cell (path length: 1 cm) attached to a 350-mm-

long quartz tube (o.d.: 10 mm) is placed at the center of the electric furnace. The light beam (Ocean Optics Inc.) was guided into the sample chamber by using a quartz optical fiber. A suitable quartz lens and iris was used to collimate the beam path and maximize the intensity. The concentrations of uranium species were determined by ICP-AES after each experiment.

2.2 Results

Fig. 1 shows cyclic voltammograms (CV) obtained from W in LiCl-KCl melt containing (a) UCl_3 and (b) EuCl_2 . In curve (a) of Fig. 1, large cathodic and anodic peaks were found around -1.5 V, which are associated with U deposition and dissolution reactions and a featureless double layer region was observed between -1.2 V and -0.5 V. At -0.4 V, the anodic current started to increase and show a maximum at -0.25 V while the cathodic current of a negative sweep showed a peak at -0.4 V. These peaks are attributed to the $\text{U}^{3+/4+}$ electrochemical redox reactions, consistent with the voltammogram obtained previously with a W wire.[5] The electrochemical current of Eu^{2+} began to increase at +0.2 V in curve (b) of Fig. 1. The anodic and cathodic currents exhibit peaks at +0.5 V and +0.3 V, respectively. From these results, the stable oxidation states of uranium and europium at each potential range can be deduced. For example, uranium tends to exist as a U metal at the potential than less -1.45 V while U^{3+} is stable between -0.5 and -1.45 V. U^{3+} is additionally oxidized to U^{4+} at the more positive potential than -0.3 V. In the europium case, Eu^{2+} mostly stable in this potential window is oxidized to Eu^{3+} over +0.5 V.

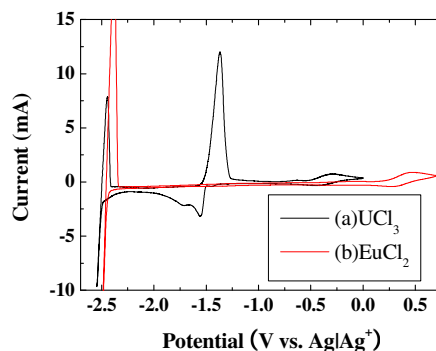


Fig. 1. Cyclic voltammograms of (a) UCl_3 and (b) EuCl_2 in LiCl-KCl eutectic melt

Fig. 2 shows UV-VIS absorption spectra of a LiCl-KCl eutectic melt containing uranium cation. After background spectrum was obtained from LiCl-KCl eutectic, UCl_4 was dissolved into the melt. Initial UV-VIS spectrum shows that the main peak was found at 670 nm and a few small peaks were observed at 455 nm and 605 nm. In this case, the color of the LiCl-KCl melt exhibited bright green, as known the one of U^{4+} . [6] These features are consistent with the spectrum obtained from U^{4+} in molten salt melt. [7] After the measurement of the initial spectrum, -0.6 V was applied to the tungsten working electrode. As time went by, the background of the spectrum gradually increased and bands at 605 nm and 670 nm attributed to U^{4+} slowly disappeared. New features at 480 nm and 570 nm started to increase after one min. It is known that two peaks at 480 nm and 570 nm are attributed to the $5f^3-5f^26d^1$ transition of U^{3+} where the 6d is split by the crystal or ligand field. [7,8] After the measurement of the UV-VIS absorption spectrum, it was shown that the color of the LiCl-KCl melt was changed to dark purple, consistent with reported results. [6,8]

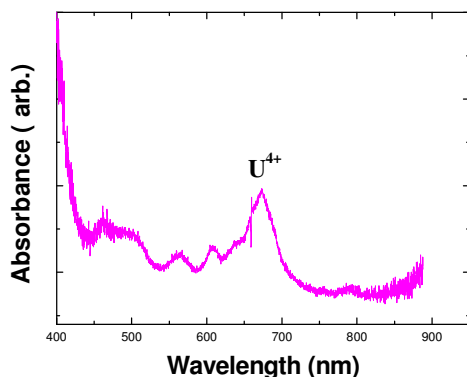


Fig. 2. UV-VIS spectra of U^{4+} obtained during electrochemical control.

3. Conclusions

We performed UV-VIS spectroscopy of UCl_3 and EuCl_2 in LiCl-KCl eutectic melt at 500 °C under electrochemical control. CV results showed that electrochemical reactions of $\text{U}^{0/3+}$ and $\text{U}^{3+/4+}$ take place around -1.5 V and -0.25 vs. Ag/AgCl, respectively. Redox peaks of $\text{Eu}^{2+/3+}$ were found at 0.3 V and 0.5 V. UV-VIS spectroscopic results showed that U^{4+} was converted to U^{3+} at the potential between -0.5 V and -1.45 V. The appearance of purple color of the melt indicated that U^{3+} started to form in the eutectic melt.

REFERENCES

- [1] T. Inoue and L. Koch, Nucl. Development of Pyroprocessing and its future direction, Eng. & Technol., Vol. 40, p 183, 2008.
- [2] J. H. Yoo, C. S. Seo, E. H. Kim and H. S. Lee, A conceptual study of pyroprocessing for recovering actinides from spent oxide fuels, Nucl. Eng. & Technol., Vol. 40, p 581, 2008.
- [3] Y. I. Chang, Nucl. Technol., Vol. 88, p 129, 1989.
- [4] S.-E. Bae, Y. J. Park, S. K. Min, Y. H. Cho and K. Song, Aluminum assisted electrodeposition of europium in LiCl-KCl molten salt, Electrochim. Acta, Vol. 55, p 3022, 2010.
- [5] P. Masset, D. Bottomley, R. Konings, R. Malmbeck, A. Rodrigues, J. Serp and J. P. Glatz, Electrochemistry of uranium in molten LiCl-KCl eutectic, J. Electrochem. Soc., Vol. 152, p A1109, 2005.
- [6] D. M. Gruen and R. L. McBeth, Oxidation States and Complex Ions of Uranium in Fused Chlorides and Nitrates, J. Inorg. & Nucl. Chem., Vol 9, p 290, 1959.
- [7] T. Nagai, A. Uehara, T. Fujii, O. Shirai, N. Sato and H. Yamana, Redox equilibrium of $\text{U}^{4+}/\text{U}^{3+}$ in molten NaCl-2CsCl by UV-Vis spectrophotometry and cyclic voltammetry, J. Nucl. Sci. Technol., Vol. 42, p 1025, 2005.
- [8] T. Nagai, T. Fuji, O. Shirai and H. Yamana, Study on redox equilibrium of $\text{UO}_2^{2+}/\text{UO}^{2+}$ in molten NaCl-2CsCl by UV-Vis spectrophotometry, J. Nuclear Science and Technology, Vol. 41, p 690, 2004.