Electrochemical Properties of Uranium and UxBiy IMC in the LiCl-KCl Eutectic

Beom-Kyu Kim[1], Byung-Gi Park[1,*], Sang-Eun Bae[2], and Tae-Hong Park[2]
[1] Soonchunhyang University, 22, Soonchunghyang-ro, Asan-si, Chungcheongnam-do, Republic of Korea
[2] Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea
*qu@sch.ac.kr

1. Introduction

Uranium is the major element in most nuclear fuel cycles, thus the assessment of accurate thermochemical data for this element in molten salts is of high importance. In recent years, various studies have been conducted to develop a behavior of lanthanide and transition metal to form the intermetallic compound(IMC), and to reduce lanthanide and other metals. Many studies have been conducted on the electrochemical reaction and behavior of U^{4+}/U^{3+}, U^{3+}/U in molten chloride salts by Cyclic voltammetry, square wave voltammetry and various voltammetry [1-4]. If Liquid Bismuth is used as a liquid metal electrode in an electrolytic reduction-electrolytic and refining process, Bismuth is likely to be present with the ionic state in the electrolyte. In this case, we need to study the behavior of mixed bismuth and uranium ions in the LiCl-KCl electrolyte. Therefore, the electrochemical reaction of cerium present in the LiCl-KCl molten salt was confirmed by using electrochemical method, and the characteristics study of the existence of Bi ion was carried out.

2. Experimental

Experiments were carried out in a glove box under an argon atmosphere in which oxygen and moisture were kept at 1 ppm or less. And were performed to experiment at an elevated temperature using an electric furnace at the bottom of the glove box. LiCl-KCl and $BiCl_3$ were all purchased from Sigma Aldrich.

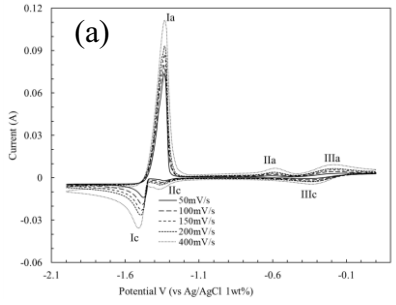
Electrochemical measurements were performed in Quartz Cell. Working Electrode (WE) were Tungsten wire (1 mm diameter) and glassy carbon (GC) were used Counter Electrode (CE). The Pyrex guide tube was used to prevent contact between electrodes.

The reference electrode was consisted of an one-end closed Pyrex tube, in which LiCl-KCl eutectic salt containing 1wt% AgCl was placed and a silver wire (Alfa-Aesar, 99%, OD: 1 mm) was immersed in the salt. The Electrochemical measurements were performed using a Gamry Reference 3000. Temperature of the salt was measured with Chromel-Alumel thermocouple.

3. Result and Discussion

Figure 1 shows the cyclic voltammogram of UCl_3 in the molten salt LiCl-KCl. The applied potential was reduced from 0 V (vs Ag / AgCl 1wt%) to -2 V and oxide 0 V again. Typically, two oxidation / reduction peaks (Ia/Ic, IIIa/IIIc) were produced. The oxidation/ reduction peak potentials of U^{4+}/U^{3+} and U^{3+}/U were confirmed to be the same as those of most of the researchers, and IIa/IIc generated between them was caused by deposition after adsorption on working electrode.

Figure 2 shows CV results measured with $BiCl_3$ (0.5wt%) added. As a result of CV, an oxidation / reduction peak of Bi was generated near 0.2 V, and a Li_3Bi oxidation/reduction peak was generated near -1.8 V. [5] And the dislocation of Bi-U's intermetallic compound was observed between U and Bi (A to E). Both of the Bi and U intermetallic compounds evaluated by KALPHAD show three reactions. [6]



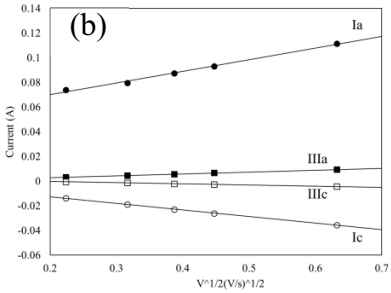


Fig. 1. (a) Cyclic voltammogram obtained for UCl_3 in LiCl-KCl melt, Scan rate: 0.05, 0.1, 0.15, 0.2, 0.4 V/s. (b) Dependence of Redox peaks current on square root of scan rate. working electrode: W wire, concentration of UCl_3: 1.00wt%, temperature: 773 K.

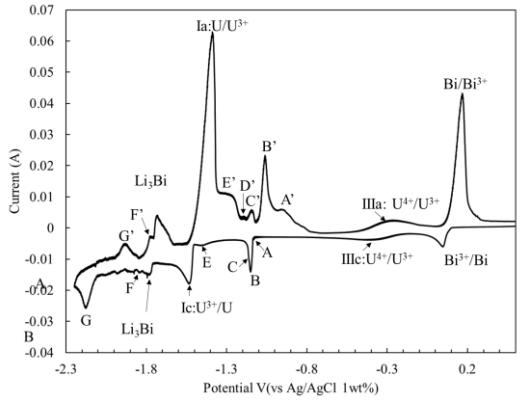


Fig. 2. Cyclic voltammogram obtained for LiCl-KCl with UCl_3(1wt%) and $BiCl_3$(0.5wt%) melt using the tungsten electrode at 773 K, scan rate: 0.1 V/s.

$$I_{c/a}: U^{3+} + 3e^- \leftrightarrow U \quad (1)$$

$$III_{c/a}: U^{4+} + e^- \leftrightarrow U^{3+} \quad (2)$$

$$Bi: Bi^{3+} + 3e^- \leftrightarrow Bi \quad (3)$$

$$Li_3Bi: 3Li \quad + 3e^- \leftrightarrow Li_3Bi \quad (4)$$

$$BiU_{1/2}: Bi + U^{3+} + 3/2e^- \leftrightarrow BiU_{1/2} \quad (5)$$

$$BiU_{3/4}: Bi + U^{3+} + 9/4e^- \leftrightarrow BiU_{3/4} \quad (6)$$

$$BiU \quad : Bi + U^{3+} + 3e^- \leftrightarrow BiU \quad (7)$$

4. Conclusion

We conducted electrochemical measurements to explore the intermetallic compounds of U and U-Bi. Electrochemical test results confirmed the formation potential of UxBiy intermetallic compounds.

ACKNOWLEDGEMENT

This work was financially supported by the National Research Foundation of Korea(NRF) grate funded by the Ministry of Science, ICT and Future Planning, Republic of Korea. (NRF-2016M2B2B1945263).

REFERENCES

[1] B. Prabhakara Reddy, S. Vandarkuzhali, T. Subramanian, P. Venkatesh “Electrochemical studies on the redox mechanism of uranium chloride in molten LiCl–KCl eutectic”, Electrochimica Acta 49, 2471–2478 (2004).

[2] Patrick Masset, David Bottomley, Rudy Konings, Rikard Malmbeck, Alcides Rodrigues, Jérôme Serp, and Jean-Paul Glatz, “Electrochemistry of Uranium in Molten LiCl-KCl Eutectic”, Journal of The Electrochemical Society, 152(6) A1109-A1115 (2005).

[3] Robert O.Hoover, et al., “Electrochemical studies and analysis of 1–10 wt% UCl_3 concentrations in molten LiCl–KCl eutectic”, Journal of Nuclear Materials, Volume 452, 389-396(2014).

[4] Dalsung Yoon and Supathorn Phongikaroon, “Electrochemical and Thermodynamic Properties of UCl_3 in LiCl-KCl Eutectic Salt System and LiCl-KCl-$GdCl_3$ System”, Journal of The Electrochemical Society, 164 (9) E217-E225 (2017).

[5] Pavlyuk, Volodymyr, Sozanskyi, Martyn, Dmytriv, Grygoriy, Indris, Sylvio, Ehrenberg, Helmut, “Amendment of the Li-Bi Phase Diagram Crystal and Electronic Structure of LiBi”, Journal of Phase Equilibria & Diffusion. , 36 (6) p544-553 (2015).

[6] Jian Wang, Kun Wang, Chunhua Ma, Leidong Xie, “Critical evaluation and thermodynamic optimization of the (U + Bi), (U + Si) and (U + Sn) binary systems”, J. Chem. Thermodynamics, 92, 158–167(2016).