Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 10-11, 2007

Study on Chemical Reaction of Lanthanide (III) Elements and Lithium Oxide

Tack Jin Kim, Yong Joon Park, Young Hwan Cho*, In Kyu Choi, Kyuseok Song , Kwang Yong Jee
Korea Atomic Energy Research Institute,150 Dukjin-Dong Yusong-Gu, Daejeon,
305-353 Korea
*corresponding author: yhcho@kaeri.re.kr

1. Introduction

'Molten salts' is the commonly used word for an ionic liquid. In recent years, the ionic liquid has become an attractive reaction media in many fields.[1] Molten salt technology can be applied to a pyrochemical processing technique based on molten salts, which has been proposed as a promising method for future nuclear programs and more specifically for a spent fuel processing.[2] In the electrorefining step of a pyroprocessing, a metal ingot is dissolved into LiCl-KCl eutectic melts from the anode, and the actinides (An) are recovered as a pure metal at the cathode. It has been proposed that uranium is selectively recovered at the solid cathode, since the formation energy of UCl_3 is lower than those of the chlorides of other An. The minor An are then obtained in the LiCl-KCl eutectic melts with fission products such as lanthanides (Ln).[3] Actually, in the electrorefining process, U^{3+} and Ln^{3+} (Ln^{3+} = Eu^{3+}, Nd^{3+}) are dissolved in the LiCl-KCl eutectic melts, and Li_2O may also be introduced into the electrorefiner. In this paper, chemical reaction phenomena were studied by observing spectroscopic results for various reactions between U^{3+}, Ln^{3+} and Li_2O

2. Experimental

The LiCl-KCl eutectic (41.5 mole% KCl) mixture (melting point 634 K) was prepared from LiCl (Aldrich) and KCl (Aldrich). Dried salts were mixed and melted under a purified Ar atmosphere. $EuCl_3$ and $NdCl_3$ were obtained from Alfa Aesar Co. Ltd. (99.99% purity). Li_2O were purchased from Aldrich Co. Ltd. All the chemicals was used without any further purification. All the experiment and sample preparations were carried out in an Ar-atmosphere glove box in which the oxygen content and moisture levels were maintained below 3ppm. The oxygen and H_2O levels were maintained at less than 2 ppm. U^{3+} was prepared by the reaction of a uranium metal chip with cadmium chloride in a LiCl-KCl eutectic mixture. The chemical reactions were in-situ monitored by UV-VIS Spectrometer. The spectrometer component was purchased from Ocean Optics, Inc.(Model USB 2000). Data collection was done by an interfacing with a PC via USB port. The light beam passes through an optical fiber into the sample chamber. Suitable quartz lens and iris were used to collimate the beam path and adjust the intensity. All the reaction products were also identified using a Simens D5000 X-ray Diffractometer and ICP-AES.

3. Results and Discussion

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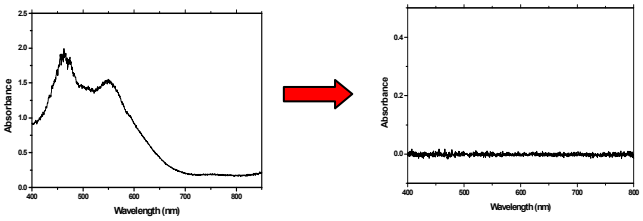
By using the hardware system described in an earlier section, we were able to collect UV-VIS spectra.[4]



(a) (b)

Figure 1. UV-VIS spectrum of U(III) and Li_2O before and after reaction.

Figure 1 (a) presents the generation of the U(III) species by the reaction of U metal with cadmium chloride in the melt (723 K). The U(III) spectra was in good agreement with those of Yamana's group (Kyoto University, by private communications). After Li_2O powder was added into the U(III) molten salt, the absorption spectrum disappeared as shown in Figure 1 (b). The first spectrum in Figure 1 is the typical peak of U(III), where band decreased as a function of the time, and consequently, all the U(III) band disappeared. This result suggests a reaction by the following equation:

$$U(III) + O^{2-} \rightarrow UO_2$$

Figure 3 (a) shows the XRD patterns of the resulting salt containing UO_2 with LiCl and KCl. Both the UV-visible spectra and XRD patterns indicate that Li_2O was reacted with U(III) to produce UO_2.

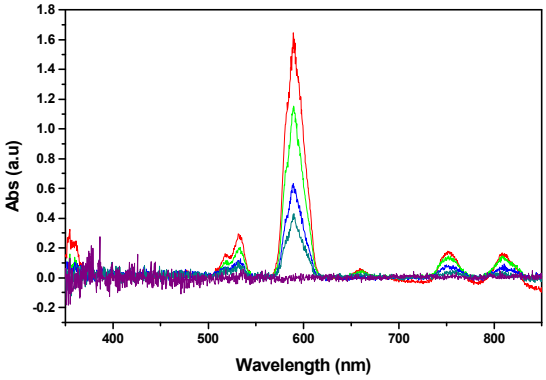
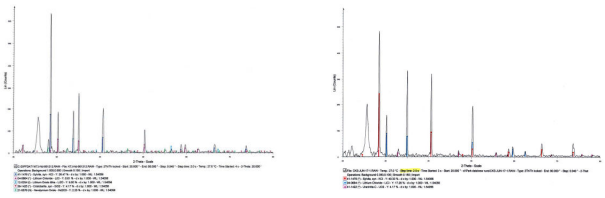


Figure 2. UV-VIS spectrum of reaction between Nd(III) and Li_2O.

The reaction between Nd(III) and Li_2O was also monitored by UV-VIS spectrometer, and its spectrum is shown in Figure 2. The spectral feature of Nd(III) was well matched with that reported in a recent journal. The spectral pattern was a variable depending on the conditions of the measurement.[5.6.7] After the Li_2O powder was added into the Nd(III) molten salt, the absorption spectrum changes as shown in Figure 2. Nd(III) band disappeared as a function of the time similar to the results for U(III). This result suggests a reaction by the following equation:

$$Nd\ (III) + O^{2-} \rightarrow Nd_2O_3$$

And the XRD patterns indicate that Li_2O reacts with Nd(III) to produce Nd_2O_3 (see Figure 3 (b)). Also, in the case of Eu(III), similar results were obtained to those of U(III) and Nd(III).



(a) UO_2 (b) Nd_2O_3

Figure 3. XRD pattern of reaction procuct.

4. Conclusions

Chemical reaction phenomina were studied for the reaction between U(III), Ln(III) and Li_2O in LiCl-KCl eutectic melts at 450℃ by using UV-VIS spectrophotometric and an X-ray Diffraction technique. Consequently, the Li_2O present in the final product from an electrolytic reduction process should be removed before the electrorefining process to improve the efficiency of the said process.

Acknowledgement

This study was supported by the Mid- and Long-Term Atomic Energy R&D Fund of Korean Ministry of Science and Technology.

REFERENCES

[1] Derek. J. Fray, “Emerging molten salt technologies for metals production” *J. of Metallur.* 26-31 (2001)

[2] B.H. Park, J.M. Hur, C.S. Seo, and S.W. Park, “A study on the electrochemical reduction of uranium oxide in a LiCl-Li_2O molten salt”, *Proceedings of Global 2003 Conference*, New Orleans, Louisiana, Nov. 16 - 20 (2003)

[3] O. Shirai, A. Uehara, T. Fujii, H. Yamana, “Thermochemical properties of the intermetallic compounds in the lanthanum-cadmium system” Journal of Nuclear Materials 344 (2005) 142-145

[4] Y.H. Cho, T.J. Kim, I.K. Choi and K.Y. Jie, " Measurements of electronic spectra of uranium(III) and neodymium(III) in LiCl-KCl eutectic melt ", in Conference Proceedings of 2005 KNS Spring Meeting, Jeju, 2005

[5] T. Fujii, T. Nagai, N. Sato, O. Shirai, H. Yamana, "Electronic absorption spectra of lanthanides in a molten chloride II. Absorption characteristics of neodymium (III) in various molten chlorides", J. Alloys and Compounds, in press.

[6] H. Yamana, T. Fujii, and O. Shirai, " UV/Vis Absorption Spectrophotometry of Some f-elements in Chloride Melt" in Proceedings of International Symposium on Ionic Liquids in Honour of Marcelle Gaune-Escard, Carry le Rouet, France, June 27-28, 2003

[7] T. Fujii ,H. Moriyama, H. Yamana, "Electronic absorption spectra of lanthanides in a molten chloride I. Molar absorptivity measurement of neodymium(III) in molten eutectic mixture of LiCl–KCl", J. Alloys and Compounds Vol.351, L6-L9, 2003