Measurements of electronic spectra of uranium(III) and neodymium(III) in LiCl-KCl eutectic melt

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1. Introduction

Recently, ionic melts have become attractive reaction media in many fields.[1] Molten salt based electrochemical processes have been proposed as a promising method for future nuclear programs and more specifically for spent fuel processing.[2] Molten alkaline chloride based melts are considered as a promising reaction media. For this, it is interesting to understand the chemical nature of the actinides and lanthanides in high temperature melt. Electronic absorption spectroscopy provides an effective way for studying the electronic nature of some f-block elements, enabling quantification and speciation of corresponding elements. However, the related studies are rare. Here, report the electronic spectra of uranium(III) and neodymium(III) in LiCl-KCl eutectic melt.

2. Experimental

All the experiments were carried out in a glove box system. The inert atmosphere was maintained by purging with purified Ar gas. The oxygen contents and H2O are minimized to be less than 2 ppm. All the electronic spectra were measured with home-built UV-VIS spectrometer combined with optical fiber technology. The details of the design of the reaction cell and spectrometer are introduced elsewhere.[3] The temperature of the melt was maintained to be 450 ^{o}C. The LiCl-KCl eutectic (41.5 mole percent KCl) was prepared from A.R. grade reagent. U(III) were generated by reacting uranium metal with cadmium chloride in the melt and the spectra were recorded in-situ.

3. Results and Discussion

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We obtained electronic spectra of U(III) and Nd(III) by methods described in earlier section. (Figure 1 and 2)

Figure 1 presents the generation of U(III) species by the reaction of U metal with cadmium chloride in the melt (450 ^{o}C). The U(III) spectra matched well with those of Prof. Yamana's group (Kyoto University, by private communications). [4] The information on the nature of U(III) in molten salt media is still very rare. Figure 1 contains the detailed information on the nature of U(III) and the reaction. At this stage, a complementary interpretation of the spectra may not be achievable. However, relevant results from other methods may support to reach full understanding. [5] Figures 1and 2 shows that this method may effectively applied to elucidate the mechanism and kinetics of the reaction in molten salt media and other types high temperature melts.

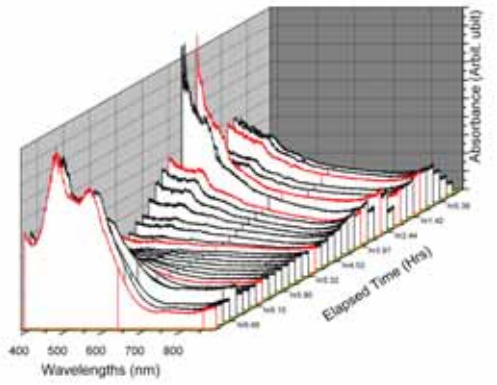

Figure 1. *In-situ* measurements of electronic spectra of U(III) in LiCl-KCl melt (450 ^{o}C)

Figure 2 presents the Nd(III) species (wavelength~ 700 – 900 nm region). This spectra were obtained by *in-situ* monitoring of the reaction of U(III) with Nd_2O_3. It shows the changes in U(III) and Nd(III) simultaneously.

The intensity of U(III) peak decreases as the reaction proceeded, and consequently the intensity of Nd(III) peak increased. In general, molar extinction coefficient of lanthanides are much lower than U(III).

The Nd(III) spectra showed the same features as reported in recent journal.[4,6,7] The characteristic peak patterns of Nd(III), which are attributed to the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transitions, are clearly seen. The spectral pattern of Nd(III) differs slightly depending on the composition and conditions of measurements.

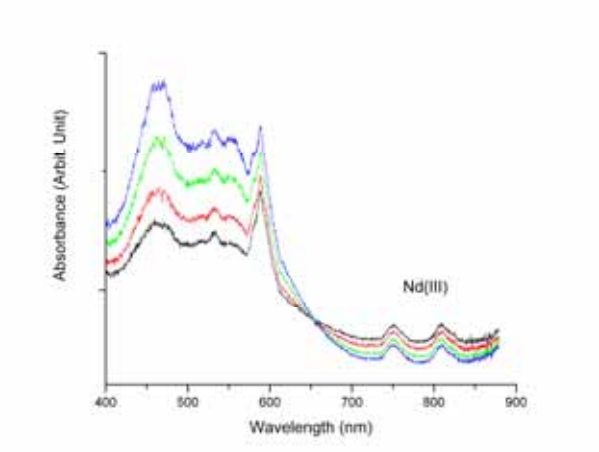

Figure 2. On-line monitoring of the reaction of U(III) with Nd_2O_3 in molten salt.

4. Conclusions

In-situ measurements of U(III) and Nd(III) were successfully achieved. On-line monitoring of the U(III), Nd(III) species involved reactions were possible in high temperature molten salt.

UV-VIS spectroscopy combined with fiber optics technology provided an efficient tool for the on-line quantification and speciation of f-block elements in molten salt media.

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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] T.J. Kim, Y.H. Cho, I.K. Choi and K.Y. Jie, "On-line measurements of UV-VIS spectra in high-temperature molten salt media*", in Conference Proceedings of 2005 KNS Spring Meeting*, Jeju, 2005

[4] 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.

[5] A. I. Bhatt, E. de Kerdaniel, H. Kinoshita, F. R. Livens, I. May, I. B. Polovov,C. A. Sharrad, V. A. Volkovich,J.M. Charnock and R. G. Lewin, “Uranium Oligomerization in Chloride-Based High Temperature Melts: In Situ XAS Studies”, *Inorg. Chem.* 44, 2-4, 2005.

[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