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Electronic Absorption Spectra of U(III) and U(IV) in LiCl-KCl at 450 ℃

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1. Introduction

One of the important steps in the pyro-processing of spent nuclear fuel is electro-refining of uranium in molten LiCl-KCl medium. During the course of these electrochemical processes, information on the chemical behavior of uranium ions in high temperature molten salt media is of great importance. The knowledge on the basic chemical properties of several actinide elements in molten salt media is essential for developing suitable processes. In this respect, tools for real time measurement of actinide species are necessary. An electronic absorption spectroscopic method may be used for this purpose. However, few studies have been reported yet on the spectrochemical behavior of uranium ion in high temperature molten salt media[1,2]. The present study is focused on elucidating the chemical nature of U(III), U(IV) ion in an effort to obtain a better understanding of their chemical behavior in LiCl-KCl eutectic melt in the context of pyrochemical processing of spent nuclear fuel.

2. Experimental

All the experiments were carried out in a glove box system. Spectrometric components were interfaced with the glove box-furnace system. A rectangular quartz cell attached to a long quartz tube was placed at the center of the electric furnace. The light beam (Ocean Optics Inc. deuterium-halogen light source) was guided into the inlet and outlet of the sample chamber by using an optical fiber cable. Suitable quartz lens and iris were used to collimate the beam path and adjust the intensity.

3. Result and Discussions

Figure 1 shows the absorption spectrum of U(III) species obtained by the oxidation reaction of U metal with $CdCl_2$ in LiCl-KCl eutectic at 450℃.
The UV-VIS spectra of U(III) consist of two main peaks in the range of 400 ~ 600 nm. The absorption lines in Figure 2 are attributed to the $5f^3$-$5f^26d^1$ transitions, where the 6d is split by the crystal or ligand field. A systematic study of U(III) ions diluted into solid phase supports our spectra originating from the *5f-6d* transitions [3,4]. Until now much less known about is the inter-configurational *5f-6d* transitions. To the best of our knowledge, the spectra presented in figures 1 are the first observed 5*f*-6*d* transitions of actinide ions in high temperature melt. In general, absorption lines originating from 5*f*-5*f* intra-configurational transitions are very weak in intensity compared with 5*f*-6*d* lines because it is quantum mechanically forbidden, in principle. Consequently, *5f-6d* transition lines are much more intense (with molar absorption coefficient > 10^3) than 5*f*-5*f* transitions. Absorption peaks of U(III) ions due to *5f-5f* transition lines were observed in the range of 700 ~ 900 nm with very low intensity compared with the main peaks.

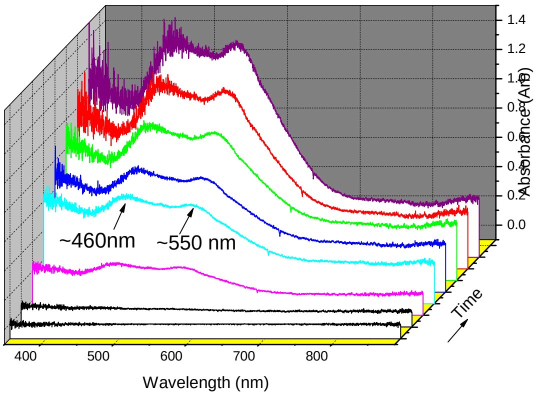

Fig. 1. In Situ monitoring of U(III) formation

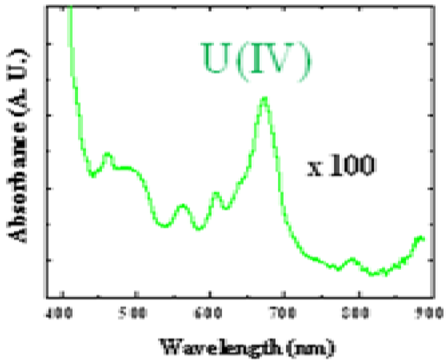

Fig. 2. UV-VIS spectrum of U(VI) species in LiCl-KCl at 450 ℃

Figure 2 shows the absorption spectrum of U(IV) species obtained by the electrochemical oxidation of U(III). Figure 3 shows the color change as seen through the quartz window during oxidation process. The intense red wine color of U(III) becomes pale and turns into pale yellow-green when oxidation process ended. One of the notable feature in the spectrum is the complete disappearance of *5f-6d* transitions as seen in U(III) and the other peak intensity is very low. Until now, very little is known about the *5f-5f* transitions in high temperature molten salt media. A systematic analysis of the spectra along with energy calculation may provide detailed information on the spectro-chemical behavior of U(III) and U(IV) species in pyro process conditions. The *5f-6d* transition lines can be effectively used as an indicator to monitor the electrochemical reaction where U(III) is involved as is the case in an electrorefining process of uranium in high temperature molten salt.

Fig. 3. Color changes before (left) and after (right) the electrochemical oxidation from U(III) to U(IV)

4. Conclusions

Electronic absorption spectra arising from 5*f-6d* and *5f-5f* transitions from U(III) and U(IV) were recorded in an in-situ manner in LiCl-KCl melt at 450℃.

Acknowledgements

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