

Covalent Bond Formation of Uranium Ions in a LiCl-KCl Eutectic Melt at 450 °C : Spectroscopic Evidence from Their UV-VIS Spectra

Young-Hwan Cho*, Sang-Eun Bae, Seung-Yong Oh, Jong-Yun Kim, Kyuseok Song, Jei-Won Yeon
Korea Atomic Energy Research Institute, Yuseong P.O Box 105, Daejeon, Rep. of Korea
*E-mail: yhcho@kaeri.re.kr

1. Introduction

Molten salt based electrochemical processes, so called pyroprocessing, have been proposed as a new option for the advanced spent nuclear fuel cycle. One of the important steps in the pyroprocessing of the spent nuclear fuel is the electrorefining of uranium in molten LiCl based media. The knowledge on the electronic states of uranium ions in molten salt media is essential for understanding their optical, electrochemical properties. Electronic absorption spectra may provide detailed information on the chemical state of the ions. Several studies have been reported for the past decades on the electronic absorption spectra of uranium ion species in high temperature molten salt media[1,2]. However, no attempts have been made to interpret the spectra with respect to the electronic state and chemical bonding point of view. Here, report the results of *in-situ* measurement and interpretation of the electronic spectra of the U(III) and U(IV) ion species in a LiCl-KCl eutectic melt at in terms of chemical bonding.

2. Experimental

All the experiments were carried out in the glove box system. The inert atmosphere was maintained by purging with purified Ar gas to avoid exposure to oxygen and water. The O₂ and H₂O level were maintained to be less than 1 ppm. The electrochemical/spectroscopic integrated measurement units interfaced with a glove box-furnace system was designed and set up for spectro and electrochemical measurements simultaneously in high temperature molten salt media. The experimental details of the electrochemical cell design and electrode system are described in our recent paper [1-3].

3. Results

Figure 1 shows the electronic absorption spectrum of U(III) species in LiCl-KCl at 450 °C. It consists of two main peaks in the wavelength range of 400 – 600 nm which are mainly attributable to the interconfigurational $5f^3 - 5f^2 6d^1$ ($5f-6d$) transitions of U(III) ion with $5f^3$ electronic configuration. The $5f-6d$ transitions are easily distinguished from the intraconfigurational $5f-5f$ transitions because they are parity allowed and then

give rise to very intense features in the UV-VIS region of the spectra. And the absorption peaks of U(III) ions due to $5f-5f$ transitions were observed in the range of 700~ 900 nm with appreciable intensity.

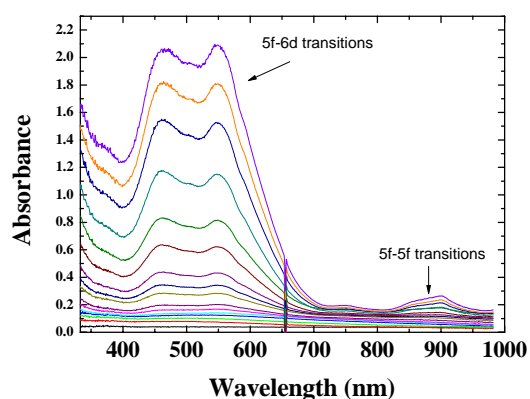


Fig. 1. UV-VIS spectra of U(III) in a LiCl-KCl eutectic melt at 450 °C

From the optical spectroscopy point of view, lanthanides (4f electrons) and actinides (5f electrons) behave differently from the other elements. Actinide ions have greater tendency toward covalent complex formation than that for lanthanides, including complex formation with π -bonding ligands. Especially, early actinides like uranium may provide more electrons for covalent bonding with ligands. The UV-VIS spectra reflects the formation of covalent bonding. As an ion participates to chemical bonding, it loses its pure electronic state. And as a result, the selection rule for electronic transitions is broken by the orbital mixing depending on the strength of bonding formation. Figure 1 accounts for the covalent bonding formation of U(III) with surrounding chloride ligands. The intensity of allowed $5f-6d$ lines was significantly decreased and on the other hand, the intensity from the forbidden $5f-5f$ transitions contributed significantly to the spectrum. Simply, the intensity ratio of $5f-6d/5f-5f$ may be regarded as an indirect measure of covalent bond formation.

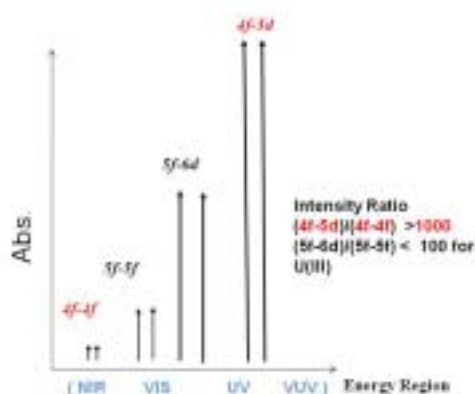


Fig.2. Schematic Diagram of f-d and f-f transition patterns for lanthanides and uranium ions measured in a LiCl-KCl eutectic melt at 450 .

Figure 2 schematically shows the covalent bonding effect on the UV-VIS spectral pattern in lanthanide and actinide ions. The smaller the value of f-d/f-f intensity ratio, the greater tendency of covalent bond formation. The spectral analysis of U(IV) indicates the much weaker covalent bond formation than U(III) species. This means that U(III) species is more stable than U(IV) by forming stronger covalent bond with chloride ligand ions. The reduction rate of U(IV) was faster than that of oxidation of U(III), indicating that U(III) is more stable than U(IV) species.

The UV-VIS spectral analysis method will also be effective to investigate the covalent bonding properties of neptunium and plutonium ions in the molten salt media.

4. Conclusions

Electronic absorption spectra were measured for uranium ions in a LiCl-KCl eutectic melt at 450 . UV-VIS spectra of uranium ions provided not only information on the electronic state of 5f electrons, but also on the covalent bonding properties with ligands. U(III) ion exhibited stronger covalent bonding character than that of U(IV). Lanthanide ions showed no measurable covalent bonding at the same conditions.

REFERENCES

[1] Y.H.Cho, T.J. Kim, S.E. Bae, Y.J. Park, H.J. Ahn, Kyuseok Song, Electron absorption spectra of U(III) ion in a LiCl-KCl eutectic melt at 450 , Microchem. J. 96, 344,2010. and references therein.

[2] Y.H.Cho, S.E. Bae, Y.J. Park, S.Y. Oh, J.Y. Kim, Kyuseok Song, Electronic Structure of U(III) and U(IV) ions in a LiCl-KCl eutectic melt at 450 , Microchem. J. 102, 18,2012.

[3] S.E. Bae, Y.H. Cho, Y. J. Park, H.J. Ahn, and K. Song, Oxidation state shift of uranium during U(III) synthesis with Cd(II) and Bi(III) in LiCl-KCl melt, Electrochem. Solid-State Lett., 13(10),F25,2010