

Measurement of UV-VIS Spectra of Neptunium Ions in a LiCl-KCl Eutectic Melt at 450 °C

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1. Introduction

Molten salt based electrochemical processes, so called pyroprocessing, have been proposed as a new technology for the development of advanced spent nuclear fuel cycle.

Neptunium is an anthropogenic transuranic element produced in the uranium nuclear fuel in the reactor. In the pyrochemical process of spent nuclear fuel, neptunium may exist as minor actinides together with Pu, Am, Cm, etc. and the Np(IV) and Np(III) ion may be present as dominant neptunium species in electrorefining and electrowinning steps. During the course of these electrochemical processes, information on the chemical behavior of neptunium ions is of great importance. The knowledge on the electronic states of neptunium ions in molten salt media is essential for understanding their optical, electrochemical properties.

The present study is focused on measuring UV-VIS spectra of neptunium ions in an effort to obtain a better understanding of their spectrochemical behavior in a LiCl-KCl eutectic melt in the context of pyroprocessing of spent nuclear fuel. Here, we report the UV-VIS spectra of Np(III) and Np(IV) ion species in a LiCl-KCl eutectic melt at 450 °C

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. A quartz cell containing 4.5 g of LiCl-KCl eutectic mixture containing small amount (up to ~ 3 mg) of NpCl₄ was placed into electric furnace and heated to ~ 450 °C. After the salt is completely melted, spectrum was recorded. The Np(III) species was prepared by the electrochemical reduction of Np(IV) ion. The experimental details of the spectro-electrochemical cell design and electrode system are presented in Figure 1 and described in our recent papers [1-2].

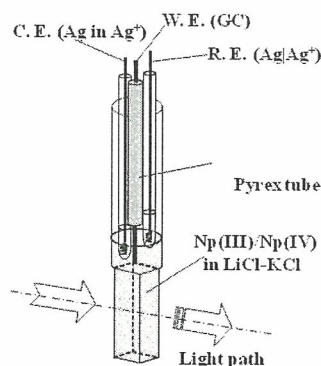


Fig. 1. Electrochemical cell and electrode system for spectroelectrochemical measurements.

3. Results

Figure 2 shows the electronic absorption spectra of Np(III) and Np(IV) species obtained in a LiCl-KCl at 450 °C. It consists of main peaks in the

UV range at around ~ 300 nm which are mainly attributable to the inter-configurational $5f^n \rightarrow 5f^{n-1}6d^1$ transitions of Np(IV) and Np(III) ions with $5f^3$ and $5f^4$ electronic configurations, respectively. The spectral features agree well with that of recently reported in similar conditions [3].

The $5f-6d$ transitions are easily distinguished from the intra-configurational $5f-5f$ transitions because they are parity allowed and then give rise to very intense features in the UV-VIS absorption spectra. And the minor absorption peaks of Np(IV) and Np(III) ions due to $5f-5f$ transitions were observed in the range of 400~ 900 nm with very low intensity compared with the main peaks in ~ 300 nm range.

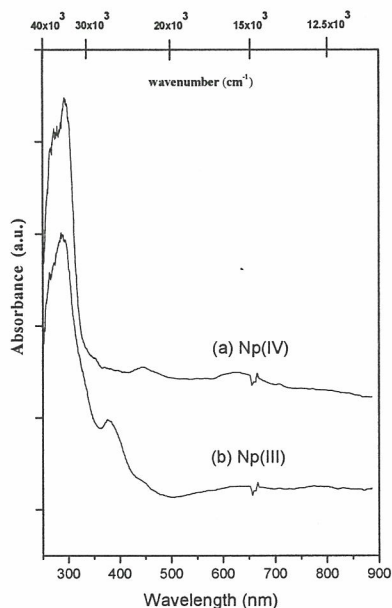


Fig. 2. Electronic absorption spectra of Np^{4+} (a) and Np^{3+} (b) ions in a LiCl-KCl eutectic melt at 450°C .

4. Conclusions

We have measured the electronic absorption spectra of the Np(III), Np(IV) ions in a LiCl-KCl eutectic melt at 450°C . For both of Np(III) and Np(IV) ions the $5f-6d$ inter-configurational transitions were observed at around ~ 300 nm range. The $5f-5f$

intra-configurational transitions occurred in a visible and longer wavelength ranges.

5. Acknowledgements

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6. References

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