Absorption spectroscopic observation of interactions between neptunium and oxide ions in molten LiCl-KCl eutectic

Tae-Hong Park* a,b, Dae-Hyeon Kim a, Sang-Eun Bae a,b, Jong-Yun Kim a,b and Young-Hwan Cho a

**Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yusung-gu, Daejeon 34057, Korea; 2Department of Radiochemistry and Nuclear Nonproliferation, University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Korea

Understanding the chemical and electrochemical behavior of oxide ions in the presence of actinide and lanthanide ions in molten chlorides is of key relevance to the pyroprocessing technology. In this work, we examined the reaction between Np⁴⁺ (neptunium cations) and O²⁻ (oxide ions) in LiCl-KCl eutectic using UV-visible-NIR absorption spectroscopy. O²⁻ is known to react with Np⁴⁺, causing precipitation of NpO₂ in the LiCl-KCl melt. However, we observed a new absorption band at ~380 nm upon the addition of Li₂O to the melt containing Np⁴⁺. We assigned this absorption signal to the f-d transition of Np³⁺ and suggested the possible reduction or disproportionation of Np⁴⁺ in its reaction with O²⁻, concomitant with the precipitation of NpO₂ from the melt.

Keywords: pyroprocessing; molten salt; neptunium; oxide; absorption spectroscopy

1. Introduction

The pyrochemical method is a promising back-end fuel cycle option to handle the accumulation of spent nuclear fuel resulted from nuclear electric power generation [1]. This approach enables electrochemical partitioning and recovery of actinides and fission products from spent nuclear fuel based on their thermodynamics. Many studies have been performed to understand the electrochemical behavior of uranium, lanthanide, and transuranium (TRU) species in high-temperature molten salt media. In addition to such understanding of the electrode reactions, comprehensive knowledge of chemical interactions between the elements present in the molten salt is important for pyroprocessing.

Oxide ion (O²⁻) is a common impurity in the electrorefining process, and it is generated by impurities in metal fuel feeding [2] or contamination by traces of oxygen and moisture [3]. Therefore, understanding the interactions between actinide/lanthanide and oxide ions in the melt can improve the electrorefining process. However, studies on TRUs are relatively rare [4] as compared to those on uranium and lanthanides [2].

Absorption spectroscopy is a useful tool for the speciation and quantification of solutes in solutions. In particular, it is suitable for monitoring electrochemical and chemical reactions in corrosive, high-temperature molten salt media [5].

In the present work, we studied the chemical reactions between neptunium and oxide ions in LiCl-KCl eutectic melts using UV-visible-NIR absorption spectroscopy. The oxidation state of neptunium was controlled electrochemically. The results showed that the reaction between Np⁴⁺ and O²⁻ resulted not only in the precipitation of neptunium oxide, as anticipated, but also the formation of a soluble species that exhibited an absorption band around 380 nm.

2. Experimental

All experiments were carried out in a glove box filled with Ar. The oxygen content and moisture level were maintained below 1 ppm. A furnace designed for absorption and electrochemical measurements was equipped in the lower part of the glove box, as described elsewhere [6]. Electrochemical experiments were performed with a Gamry Reference 3000 potentiostat. Figure 1a shows the spectroelectrochemical cell used in this study. A rectangular quartz cell (path length: 1 cm) was attached to a 350-mm-long quartz tube and placed in the middle of the furnace. Three electrodes were carefully immersed into the LiCl-KCl eutectic from the top, to avoid blocking of the light path. The Ag|Ag⁺ reference electrode was prepared by immersing a Ag wire into a LiCl-KCl eutectic melt containing 1.0 wt% AgCl. The counter electrode was prepared by immersing a tungsten wire into the LiCl-KCl eutectic melt. Both the electrodes were cased in pyrex tubes to prevent direct
electrical contact with each other. A glassy carbon rod or a tungsten wire was used as the working electrode. Light beam from a deuterium-halogen lamp was guided by an optical fiber and directed into the sample chamber within the furnace. Then, the light beam was allowed to pass through a spectroelectrochemical cell containing the LiCl-KCl eutectic sample (Figure 1) and collimated through another optical fiber connected to a QE65 Pro spectrophotometer and an NIRQuest512 spectrometer (Ocean Optics Inc.) for the wavelength ranges of 200-990 nm and 900-1400 nm, respectively.

Anhydrous LiCl-KCl eutectic beads and lithium oxide (Li₂O) were obtained from Sigma-Aldrich. Lanthanum chloride and cerium chloride (purity ≥ 99.99%) were purchased from Alfa Aesar. Li₂O-LiCl, LaCl₃-LiCl-KCl, and CeCl₃-LiCl-KCl pellets were prepared by dissolving 3-5% of the solutes in the corresponding melts, followed by solidification of the mixtures in thin glass tubes [2]. Np-LiCl-KCl pellets were prepared as described elsewhere [5]. Briefly, electrochemical carbochlorination of NpO₂⁺ in a LiCl-KCl melt, followed by electrodeposition, afforded Np metal, which was then electrochemically dissolved in a fresh LiCl-KCl melt and solidified at ambient temperature in a thin glass tube. These cylindrical pellets were added to LiCl-KCl melts for the absorption spectroscopic and electrochemical studies.

3. Results and discussion

Figure 1b shows the cyclic voltammogram of the Np ion in a LiCl-KCl melt. Anodic and cathodic peak currents appeared at 0.50 and 0.33 V versus Ag/Ag⁺, which were attributed to the oxidation of Np³⁺ to Np⁴⁺ and the reduction of Np⁵⁺ to Np⁴⁺, respectively. No significant peaks other than that for chloride oxidation were observed at more positive potentials, indicating that soluble neptunyl species was not present in the melt [5].

Figure 2 displays the absorption spectra of the neptunium ions in LiCl-KCl melts. The dissolution of the Np-LiCl-KCl pellets afforded a Np³⁺ complex, and electrochemical oxidation at 0.8 V versus Ag/Ag⁺ resulted in a Np⁴⁺ complex in the melt [5]. The Np⁴⁺ complex showed a broad absorption band at 383 nm at a concentration of ~1 mM and the Np⁵⁺ complex showed a monotonic increase in absorbance below 500 nm (Figure 2a). Both Np complexes exhibited several discrete absorption bands at 500-1350 nm but showed much lower absorbance even at higher Np concentrations (~4 mM, Figure 2b) because of their f-f transition characteristics [5].

Figure 3 shows the UV-vis absorption spectra of multicomponent melts prepared by adding LaCl₃-LiCl-KCl and CeCl₃-LiCl-KCl pellets to the melts containing Np⁴⁺. Interestingly, the addition of LaCl₃,
resulted in a new absorption shoulder at 350-400 nm (Figure 3a), although La$^{3+}$ has no electronic transitions in the region recorded [2]. The subsequent addition of CeCl$_3$ not only gave rise to a characteristic f-d transition band of Ce$^{3+}$ at 300-350 nm [2], but also enhanced absorbance of the band at ~380 nm, indicating that both lanthanide pellets probably yielded the same product after reacting with Np$^{4+}$.

However, different batches of pellets led to dissimilar results in terms of appearance and intensity of the new absorption signal, which could be due to traces of impurities such as oxide in the pellets. To remove the oxide impurities, we dissolved the pellets again and treated them with electrochemically generated Cl$_2$ gas [5]. Notably, the addition of purified lanthanide pellets to a melt containing Np$^{4+}$ did not result in a significant absorption signal around 380 nm (Figure 3a), implying that the lanthanide oxide impurities likely reacted with Np$^{4+}$ in Figure 3a.

![Figure 3. Electronic absorption spectra of Np$^{4+}$ (black) in LiCl-KCl melts with subsequent addition of LaCl$_3$ (red) and CeCl$_3$ (blue) before (a) and after (b) purification of lanthanide chlorides.](image)

- The reactions of actinide and lanthanide ions with oxide impurities are of interest because the oxide impurities in the electrorefining salt precipitate the metal ions as metal oxychloride or metal oxide species, and thus are likely to affect pyroprocessing [2]. Np$^{4+}$ is known to react with O$_2^-$ in LiCl-KCl eutectic melt, precipitating NpO$_2$, as described in Eq. (1) with a high $\Delta G^\circ$ of 20 at 660 °C [4].

$$\text{Np}^{4+} + 2 \text{O}_2^- \rightarrow \text{NpO}_2\text{(s)} \tag{1}$$

This leads to the assumption that Np$^{4+}$ reacts with the oxide impurity in the lanthanide chloride salts to yield a soluble species concomitant with NpO$_2$ in the LiCl-KCl melt.

In order to verify this assumption, we monitored the reaction of Np$^{4+}$ and O$_2^-$ using absorption spectroscopy. **Figure 4a** displays the change in the absorption spectrum of Np$^{4+}$ (~0.2 mM) with the subsequent addition of Li$_2$O (~20 $\mu$g$\times$3). As observed for the lanthanide pellets, the addition of Li$_2$O resulted in a new band at ~380 nm. However, consecutive additions of Li$_2$O decreased the absorbance of the new band and resulted in a featureless spectrum due to the precipitation of NpO$_2$. Interestingly, the energy of the new absorption band was similar to that of the f-d transition band of Np$^{3+}$ at 383 nm, whose high molar absorptivity probably allows Np$^{3+}$, if present, to be observed even at high dilution.

Further, we investigated the f-f transitions of the Np ions at a higher concentration (~1 mM). In **Figure 4b**, the red line (iii) displays the spectrum of the reaction mixture of Np ions, which was obtained during the electroreduction of Np$^{4+}$ (ii, blue) to Np$^{3+}$ (iv, black) [5]. Therefore, the spectrum exhibited absorption features of both species. On the other hand, the pink trail (i) in Figure 4b shows the spectrum obtained after adding Li$_2$O (~100 $\mu$g) to the Np$^{4+}$ solution. Notably, the characteristics of spectra (i) and (iii) were similar, indicating the presence of unreacted Np$^{4+}$ as well as newly formed Np$^{3+}$ in the melt. Although the reaction of Np$^{4+}$ and O$_2^-$ thermodynamically favors the precipitation of NpO$_2$ (Eq. 1), the higher formal potential of Np$^{3+}$|Np$^{4+}$ (~0.42 V) compared to that of O$_2$|O$_2^-$ (~0.1 V vs. Ag|Ag+) in the LiCl-KCl melt [5, 7] may trigger the reaction described in Eq. (2).

$$2 \text{Np}^{4+} + \text{O}_2^- \rightarrow 2 \text{Np}^{3+} + 1/2 \text{O}_2 \tag{2}$$

Moreover, it has been reported that the disproportionation of Np$^{4+}$ in a RuCl-CsCl melt at 660-770 °C yields Np$^{3+}$ and NpO$_2$ by controlling $p$O$_2$ of the solution using a HCl-H$_2$O gas mixture [8]. NpO$_2^+$ is not clearly evident in the spectrum (Figure 4b-i), probably due to its low concentration and superimposition of transitions with Np$^{3+}$ and Np$^{4+}$ [8, 9, 10]. However, a disproportionation reaction, as suggested in Eq. (3), might also produce Np$^{3+}$.

$$2 \text{Np}^{4+} + 2 \text{O}_2^- \rightarrow \text{NpO}_2^+ + \text{Np}^{3+} \tag{3}$$

Therefore, the absorption signals at ~380 nm in Figures 3 and 4 could be attributed to the f-d transition of Np$^{3+}$ resulting from the reaction of Np$^{4+}$ and O$_2^-$ in the LiCl-KCl melts. However, further studies will be carried out to unambiguously authenticate such a minor by-product or intermediate in the reaction mixture.
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4. Conclusion

Here, we studied the reaction between \( \text{Np}^{4+} \) and \( \text{O}^{2-} \) in \( \text{LiCl-KCl} \) eutectic using absorption spectroscopy. Although \( \text{NpO}_2 \) precipitation is thermodynamically favorable, we observed a new soluble species upon the addition of \( \text{Li}_2\text{O} \) to the melt containing low concentrations (less than a few mM) of \( \text{Np}^{4+} \). Interestingly, an absorption band was seen at \( \sim 380 \) nm, which was energetically very similar to the \( f-d \) transition of \( \text{Np}^{3+} \). In addition, the absorption spectrum of the reaction mixture closely resembled that of a mixture of \( \text{Np}^{4+} \) and \( \text{Np}^{3+} \) prepared electrochemically. On the basis of these results, we assigned the new absorption signal to \( \text{Np}^{3+} \) and proposed redox reactions occurring in parallel with the precipitation reaction of \( \text{NpO}_2 \).

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References


