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ARTICLE

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

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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 Np^{4+} (neptunium cations) and O^{2-} (oxide ions) in LiCl-KCl eutectic using UV-visible-NIR absorption spectroscopy. O^{2-} is known to react with Np^{4+}, causing precipitation of NpO_2 in the LiCl-KCl melt. However, we observed a new absorption band at ~380 nm upon the addition of Li_2O to the melt containing Np^{4+}. We assigned this absorption signal to the *f-d* transition of Np^{3+} and suggested the possible reduction or disproportionation of Np^{4+} in its reaction with O^{2-}, concomitant with the precipitation of NpO_2 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 (O^{2-}) 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 Np^{4+} and O^{2-} resulted in not only 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

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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 (Li_2O) were obtained from Sigma-Aldrich. Lanthanum chloride and cerium chloride (purity ≥ 99.99%) were purchased from Alfa Aesar. Li_2O-LiCl, $LaCl_3$-LiCl-KCl, and $CeCl_3$-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 NpO_2^+ 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.

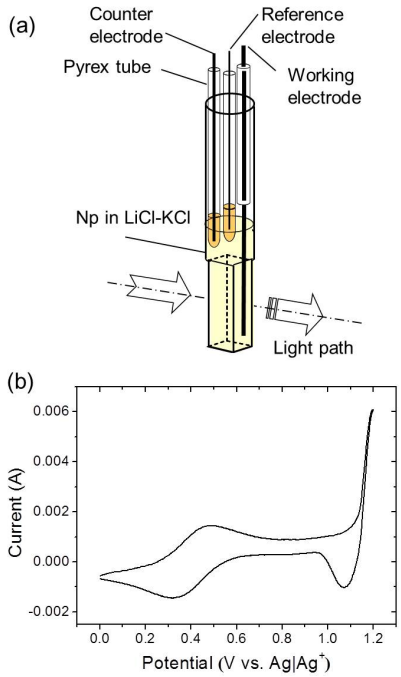

Figure 1. (a) Schematic of the spectroelectrochemical cell. (b) Cyclic voltammogram of Np^{4+} (~15 mM) in LiCl-KCl at 500 °C

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 Np^{3+} to Np^{4+} and the reduction of Np^{4+} to Np^{3+}, 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 Np^{3+} complex, and electrochemical oxidation at 0.8 V versus $Ag|Ag^+$ resulted in a Np^{4+} complex in the melt [5]. The Np^{3+} complex showed a broad absorption band at 383 nm at a concentration of ~1 mM and the Np^{4+} 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].

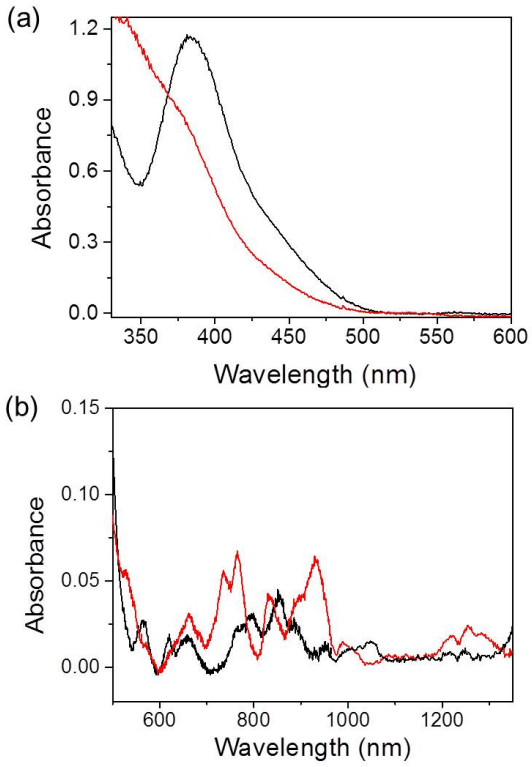

Figure 2. Electronic absorption spectra of Np^{3+} (black) and Np^{4+} (red) in LiCl-KCl at 500 °C recorded using a QEPro spectrometer (a) and after combining the spectra from a QEPro spectrometer and an NIRQuest 512 spectrometer at 970 nm (b). The solution concentrations were ~1 mM (a) and ~4 mM (b).

Figure 3 shows the UV-vis absorption spectra of multicomponent melts prepared by adding $LaCl_3$-LiCl-KCl and $CeCl_3$-LiCl-KCl pellets to the melts containing Np^{4+}. Interestingly, the addition of $LaCl_3$

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 the 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 3b), implying that the lanthanide oxide impurities likely reacted with Np^{4+} in Figure 3a.

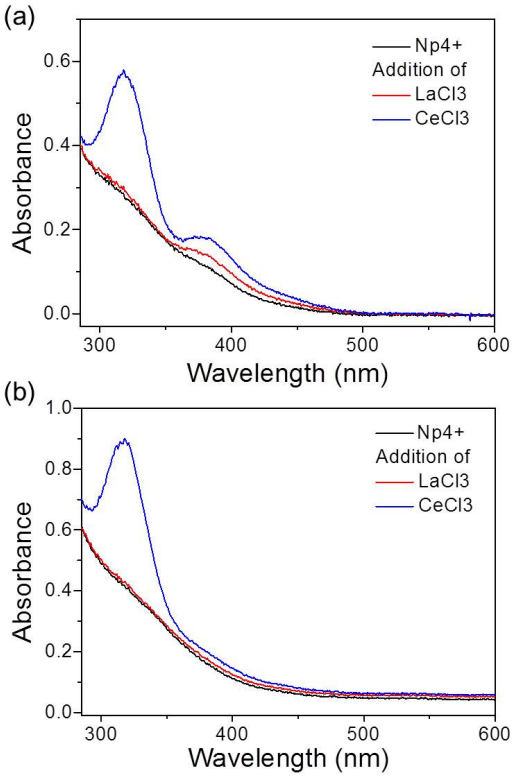

Figure 3. Electronic absorption spectra of Np^{4+} (black) in LiCl-KCl melts with subsequent addition of $LaCl_3$ (red) and $CeCl_3$ (blue) before (a) and after (b) purification of lanthanide chlorides.

The reactions of actinide and lanthanide ions with oxide ions are of interest because the oxide ions 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 pK_{sp} ~20 at 660 °C [4].

$$Np^{4+} + 2\ O^{2-} \rightarrow NpO_2\ (s) \quad (1)$$

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 consecutive addition of Li_2O (~20 μg×3). As observed for the lanthanide pellets, the addition of Li_2O resulted in a new band at ~380 nm. However, consecutive additions of Li_2O 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 very 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_2O (~100 μg) 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).

$$2\ Np^{4+} + O^{2-} \rightarrow 2\ Np^{3+} + 1/2\ O_2 \quad (2)$$

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 pO^{2-} of the solution using a $HCl\text{-}H_2O$ 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+}.

$$2\ Np^{4+} + 2\ O^{2-} \rightarrow NpO_2^+ + Np^{3+} \quad (3)$$

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.

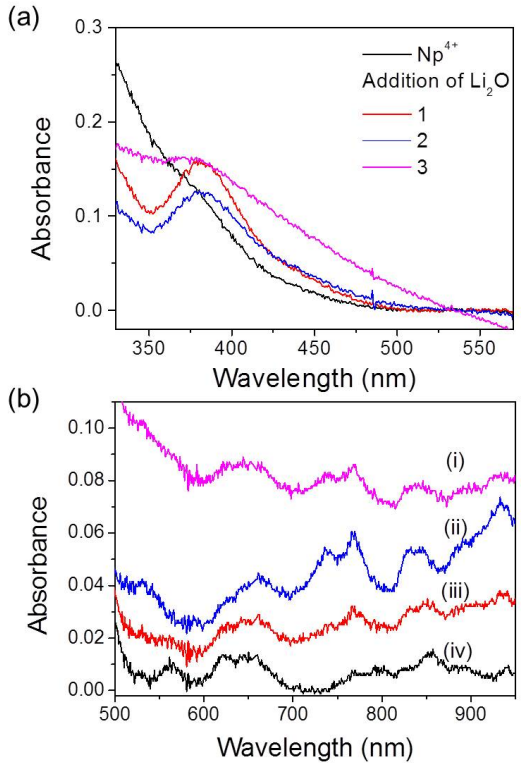

Figure 4. (a) Absorption spectra with sequential addition (1 to 3) of Li_2O to the LiCl-KCl melt including Np^{4+} (~0.2 mM). (b) Absorption spectra of a mixture of Np^{4+} and Li_2O in a LiCl-KCl melt (i) and absorption spectra recorded while electrochemically reducing Np^{4+} to Np^{3+} in LiCl-KCl melt for comparison: Np^{4+} (ii), a mixture of Np^{4+} and Np^{3+} (iii), and Np^{3+} (iv). [Np] ~ 1 mM.

4. Conclusion

Here, we studied the reaction between Np^{4+} and O^{2-} in LiCl-KCl eutectic using absorption spectroscopy. Although NpO_2 precipitation is thermodynamically favorable, we observed a new soluble species upon the addition of Li_2O to the melt containing low concentrations (less than a few mM) of Np^{4+}. Interestingly, an absorption band was seen at ~380 nm, which was energetically very similar to the *f-d* transition of Np^{3+}. In addition, the absorption spectrum of the reaction mixture closely resembled that of a mixture of Np^{4+} and Np^{3+} prepared electrochemically. On the basis of these results, we assigned the new absorption signal to Np^{3+} and proposed redox reactions occurring in parallel with the precipitation reaction of NpO_2.

Acknowledgements

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