Understanding the chemical reactions in chloride-based molten salts at high temperatures is of fundamental importance for developing pyroprocessing technologies, which have been extensively examined over the last 30 years as a promising solution for accumulated spent nuclear fuel. In particular, the electrochemical behaviors of actinides and lanthanides in LiCl-KCl melts have been widely studied to explain the fundamental electrochemical reactions in the electrorefining process, which partitions reusable metals and highly radioactive fission products. However, before the commercialization of this technology, it is necessary to obtain comprehensive insight of the molten salt chemistry of trace elements dissolved from the spent nuclear fuel, and the additives and/or impurities that enter during the process.

Li2O is a critical ingredient for the electrochemical reduction of spent oxide fuel. It affords O2− ions that diffuse to the anode at the beginning of the reduction process, and controls the O2− concentration in the LiCl melt to prevent the Pt cathode from dissolving. However, a trace amount of Li2O likely remains in the reduced fuel, even after distilling out the molten salt at the end of the oxide reduction process, and can enter the next process. During the electrorefining process, the oxide ion may react with trivalent actinide and lanthanide ions in the LiCl-KCl eutectic melt, affording insoluble oxides and oxychlorides which contain the salt and reduce the purity of recovered uranium. In addition, unreduced lanthanide oxides in the metal fuel feed play the role of oxo-donor in the LiCl-KCl melt. Therefore, knowledge of the reactions between the actinide/lanthanide ions and the oxide ion in the molten salt could lead to improvement in the electrorefining technology. Several research groups have studied such reactions by potentiometric titration of the oxide ion in the melt and product characterization, in order to estimate the thermodynamic properties for oxide reduction and to partition lanthanides and actinides from the melt.

In the present work, we focused monitoring the chemical behaviors of ions of interest (U3+, Nd3+, Ce4+, and La3+) in situ during their reactions with O2− in the LiCl-KCl molten salt by means of electrochemical and spectroscopic tools. The chronological cyclic voltammograms (CVs) and absorption spectra elucidated the chemical reactions of the actinide/lanthanide and oxide ions, in combination with the characterization of the precipitates using Raman spectroscopy and X-ray diffraction (XRD) analysis. Moreover, the in situ CV monitoring of the precipitation reaction of a mixture of uranium and lanthanides evaluated the relative sensitivity of the ions to precipitation in the LiCl-KCl melt.

Experimental

All the experiments were carried out in a glove box under Ar, where the O2 and H2O levels were maintained at less than 1 ppm. Lithium chloride/potassium chloride (LiCl/KCl) eutectic salts (anhydrous beads), lithium oxide (Li2O), lithium chloride (LiCl), and silicious beads), lithium oxide (Li2O), lithium chloride (LiCl), and silver chloride (AgCl) were obtained from Sigma Aldrich. Neodymium chloride (NdCl3), cerium chloride (CeCl3), and lanthanum chloride (LaCl3) were purchased from Alfa Aesar (purity ≥ 99.9%). UC1 was prepared with a chemical method from U metal and CdCl2 in a LiCl-KCl melt. Li2O was added to the molten LiCl-KCl at 5 wt% Li2O-LiCl salt due to the low solubility of Li2O in LiCl-KCl.

Electrochemical studies were performed using a quartz tube (20 mm in outer diameter and 2 mm in wall thickness), whereas the absorption spectroscopic studies used 350 mm long quartz tubes (outer diameter of 10 mm) finished with a quartz cuvette (path length 1 cm). W wire (Alfa Aesar, diameter 0.2 mm) and glassy carbon (Alfa Aesar, diameter 3 mm) electrodes were used as the working and counter electrodes, respectively. The W wire electrode was mechanically polished with sand paper prior to use. The reference electrode was Ag wire dipped into a Pyrex tube including 1 mol % AgCl in the LiCl-KCl eutectic melt.

Cyclic voltammetry was performed using a Gamry Reference 3000 instrument. The ultraviolet-visible (UV-vis) spectra were measured with an Ocean Optics assembly (QE65 Pro, DH-2000). Raman spectra and XRD patterns were measured using UniRam (Uninotech Co.) and D8 Advanced (Brucker AXS) systems, respectively. Because samples containing LiCl-KCl eutectic were very hygroscopic, they were encapsulated in a Pyrex tube and a Kapton film for the Raman and XRD measurements, respectively. The 632.8 nm radiation from a He/Ne laser with a radiation power of 20 mW was used as the excitation source for Raman spectroscopy. Results and Discussion

Figure 1 shows the CVs of UCl3 and LnCl3 in LiCl-KCl molten salts while adding Li2O into the melt as a source of O2−. The current-voltage (I-V) curves demonstrate that the electrochemical signals of
U\textsuperscript{3+} and Ln\textsuperscript{3+} remained after reacting with the oxide ion in the molten salt. Prior to Li\textsubscript{2}O addition, UCl\textsubscript{3} and LnCl\textsubscript{3} show their characteristic cathodic deposition and anodic dissolution peaks at \(-1.4\) to \(-1.6\) V and \(-2.0\) to \(-2.2\) V, respectively.\textsuperscript{19,23} Additionally, the redox couple of U\textsuperscript{3+/4+} appear at \(-0.2\) to \(-0.4\) V. Then, we measured the CVs of the melt after adding aliquots of Li\textsubscript{2}O (each \(\sim 0.25\) mole ratio (O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+})) to the melt. Although the amount of Li\textsubscript{2}O added occasionally exceeded the solubility,\textsuperscript{21} the addition of the 5 wt\% Li\textsubscript{2}O-dispersed LiCl salt and frequent shakings of the mixture before measurements facilitated the reaction between the oxide ion and the metal ion. The continuous addition of Li\textsubscript{2}O gradually reduced the currents of U\textsuperscript{3+} and Ln\textsuperscript{3+} without inducing new signals, indicating that the U and Ln ions were consumed by the reactions with Li\textsubscript{2}O to afford the corresponding insoluble oxide and/or oxychlorides. In addition, the oxide addition shifted the peak potentials cathodically, as a result of the consumption of the metal ions. This can be explained by the Nernst equation below

\[ E = E^0 - \frac{RT}{zF} \ln \frac{1}{[Ln^{3+}]} \]

where E is the measured potential, E\textsuperscript{0} is the apparent standard reduction potential, R is the gas constant, T is the reaction temperature, z is the number of electrons, and F is the Faraday constant.

Figure 2 shows the charges of the anodic dissolution current computed from the CVs in Figure 1. For comparison, the charges are normalized with the initial charge prior to Li\textsubscript{2}O addition. For Ln\textsuperscript{3+}, the charges nearly disappeared after adding 1:1 mole ratio (O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+}) of Li\textsubscript{2}O was added. On the other hand, the anodic dissolution charge of U\textsuperscript{3+} decreased relatively slowly. The dissolution/deposition and U\textsuperscript{3+/4+} signals remained after the addition of 1:1 mole ratio (O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+}) of Li\textsubscript{2}O, but the currents disappeared after adding 2:1 mole ratio (O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+}) of Li\textsubscript{2}O. Given the amount of Li\textsubscript{2}O consumed, the

\[ O_2^- \text{ mol} / U^{3+} \text{ mol} \]

\[ 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2.0 \]

\[ O_2^- \text{ mol} / Nd^{3+} \text{ mol} \]

\[ 0 \quad 0.25 \quad 0.5 \quad 0.75 \quad 1 \]

\[ O_2^- \text{ mol} / Ce^{3+} \text{ mol} \]

\[ 0 \quad 0.25 \quad 0.5 \quad 0.75 \quad 1 \]

\[ O_2^- \text{ mol} / La^{3+} \text{ mol} \]

\[ 0 \quad 0.25 \quad 0.5 \quad 0.75 \quad 1 \]

Figure 2. Electric charges vs. molar ratio O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+} with the addition of Li\textsubscript{2}O into the LiCl-KCl melts. The dotted lines indicate theoretical values based on the stoichiometry of O\textsubscript{2}\textsuperscript{-}/M\textsuperscript{3+} = 2:1 and 1:1.
Absorbance of U3+ with the addition of Li2O (black square, 450 nm; red circle, 900 nm).

Figure 3. UV-vis absorption spectra of LiCl-KCl melts containing (a) 0.05 wt% of UCl3, (c) 1 wt% of NdCl3, and (d) 0.032 wt% of CeCl3 with the addition of Li2O at 450°C. (b) Normalized absorbance of U3+ with the addition of Li2O (black square, 450 nm; red circle, 900 nm).

Absorption spectroscopy has been widely used to identify chemical species and in particular to monitor reactions in molten salts.19,22,26,27 Figure 3 shows the electronic absorption spectra of LiCl-KCl eutectic melts containing UCl3, NdCl3, and CeCl3. Prior to Li2O addition, U3+ and Ce3+ exhibit their characteristic f-d transitions at 400–700 nm and 200–350 nm, respectively. In addition, U3+ and Nd3+ show their respective f-f transitions at 700–900 nm and 300–900 nm.28,29 The molar absorptivities of uranium and lanthanide cations were consistent with those in the literatures.28,29 However, La3+ displayed no absorption signal in the range of 200–950 nm.30 For the absorption study with an optical cell with 1-cm path length, the solution concentrations were adjusted to the optical cell with 1-cm path length, the solution concentrations were accordingly adjusted to ~0.05 wt% for UCl3 and CeCl3, and ~1 wt% for NdCl3 based on their absorbance. Therefore, while Nd3+ was used at very similar concentrations in both absorption and electrochemical studies, the concentrations of UCl3 and CeCl3 in the absorption study were much lower than those in the electrochemical study.

Figure 3 shows the spectra recorded after being sufficiently stabilized after adding Li2O and shaking the mixture. The subsequent additions of Li2O portions (~0.25 mole ratio (O2−:M3+) each) to the melt containing UC13 led to a gradual disappearance of the absorption signal, and the spectral features markedly disappeared after adding ~2:1 mole ratio (O2−:M3+) of Li2O. Figure 3b displays the change of U3+ absorbance at 459 and 900 nm with Li2O addition. Due to slight baseline fluctuation during the measurements, the absorbance was corrected using the value at the wavelength where U3+ scarcely absorbs light. Then, these values were normalized with the initial absorbance for comparison. The absorbance at both wavelengths showed a gradual decrease as the mole ratio of O2−/M3+ approaches 2. The absorption at 459 nm still marginally remains even after adding 2:1 mole ratio (O2−:M3+) of Li2O, probably due to the high molar absorptivity of the f-d transition and the influence of precipitation formation. In contrast, the absorbance of the f-f transition at 900 nm nearly vanishes after adding 2:1 mole ratio (O2−:M3+) of Li2O. Therefore, the results indicate that the reaction formed a 1:2 adduct (UO2), which agrees well with the electrochemical study.

The reactions of NdCl3 and CeCl3 with Li2O not only steadily diminished the absorption features, but also greatly increased the spectral background as more Li2O was added (Figures 3c and 3d). We speculate that such different behaviors between uranium and lanthanides probably resulted from the different densities of their precipitates.31,32 The lanthanides afforded oxychloride colloidal solids, a part of which could remain suspended in the melt and scatter the light. In contrast, uranium likely formed heavier oxide precipitates that mostly sank in the melt and only moderately affected the absorption measurement. Meanwhile, the absorption features of Nd3+ nearly disappeared with the addition of 1:1 mole ratio (O2−:M3+) of Li2O as observed in the electrochemical study, suggesting the formation of 1:1 adduct such as NdOCl. On the other hand, the relative magnitude of the Ce3+ transition persisted moderately, even after adding much more than 1:1 mole ratio (O2−:M3+) of Li2O. Although the scattering and peak broadening greatly affected the absorbance, the high molar...
absorptivity of the f-d transition allowed for the detection of a trace amount of the ion, and the result might suggest the formation of a different product from the oxychloride expected from the electrochemical study.

The addition of Li2O quickly led to a turbid melt in all the molten salt samples, and the precipitates slowly settled down to the bottom of the reaction vessel as shown in the insets of Figure 4. A dark purple melt of U3+ resulted in a dark brown solid after the reaction. A blue melt containing NdCl3 presented a blue precipitate, and colorless melts of CeCl3 and LaCl3 afforded white solids. After solidifying the melts at ambient temperature, the bottom parts of the salts were analyzed using Raman spectroscopy and XRD.

In the Raman spectra in Figure 4, the uranium precipitate exhibits a broad peak at 448 cm⁻¹, which is attributable to the U-O stretching mode of UO2.38 On the other hand, the neodymium precipitate presents a very intense signal. The excitation wavelength (632 nm) is very close to one of the f-f transitions of Nd³⁺ (Figure 3c) and the Raman signals of the blue precipitate can be enhanced by resonance. On the basis of literature, the Raman modes can be assigned to NdOCl: the mode at 185 cm⁻¹ has A1g symmetry, the modes at 122 and 461 cm⁻¹ have Eg symmetry, and that at 355 cm⁻¹ can be assigned to phonons with A1g or B2g symmetry.34,36 Despite the slightly noisy Raman signals, the spectra of Ce and La show Raman shifts very similar to those of NdOCl, indicating that the precipitates also have the same oxychloride structure.34–36 However, the broad Raman shift of the Ce precipitate at 465 cm⁻¹ is at much higher energy than that observed in the literature (439 cm⁻¹), even though the Raman shifts of the other modes are nearly identical.36 Interestingly, CeO2 has a Raman active Ce-O-Ce symmetric vibration at ~465 cm⁻¹.37 Therefore, the Raman and electronic spectroscopy studies suggest that the Ce precipitate also contains CeO2.

Figure 5 shows the XRD results of the mixtures of salt and precipitates obtained after the reactions. The major component LiCl and KCl exhibit much more intense signals than the reaction products. The salt containing U displays peaks of 32.7°, 55.7°, 58.4°, and 87.3°, which are attributed to UO2.25 Like the Raman results, the XRD patterns of the three lanthanides were very similar and were assigned to the corresponding oxychloride structures. These data are in good agreement with the literature.11,38 Therefore, the vibrational and XRD analyses of the precipitates, combined with the electrochemical and absorption spectroscopic studies, confirm that U³⁺ and Ln³⁺ (Nd³⁺, Ce³⁺, and La³⁺) react with O²⁻ to produce UO2 and LnOCl, respectively. Meantime, it was difficult to find evidence of CeO2 in the XRD result of the salt-precipitate mixture. After removing the salt with water,39 the remaining Ce precipitate was measured again by XRD. The result (shown in red in Figure 5c) displays a clear pattern of CeO2, indicating the reaction of Ce³⁺ and Li2O to form CeO2 as a by-product, as observed in the Raman spectra. The formation of CeO2 seems very sensitive to reaction conditions, such as the concentration and source of the oxide ion.11,13,14,17

An assay of the chemical behaviors of individual ions in a multi-component system is necessary for understanding the chemical reactions during the pyroprocessing. Next, we electrochemically studied the precipitation reaction at 450 °C in a LiCl-KCl mixture containing 1 wt% UC1 and 1.2 wt% LnCl3 (0.4 wt% each of NdCl3, CeCl3, and LaCl3). Figure 6 shows the CVs of the mixture and the anodic dissolution charge variation of uranium and the lanthanides. Prior to Li2O addition, the uranium presents its U⁴⁺/³⁺ and U⁴⁺/²⁺ redox couples at potentials nearly identical to those in Figure 1. On the other hand, the three lanthanides lead to a combined I-V curve of their individual CVs, due to the closeness of their redox potentials. Notably,
Figure 5. XRD patterns of LiCl-KCl containing (a) U, (b) Nd, (c) Ce, and (d) La precipitates. The red trace in (c) was obtained from the solid after washing the precipitate with water.

Upon adding Li$_2$O up to 2:1 mole ratio (O$^{2-}$:M$^{3+}$), the redox currents of U$^{3+}$ gradually decreased and nearly disappeared. Meanwhile, the Ln$^{3+}$/0 redox couple was nearly intact, although further addition of Li$_2$O began to reduce the current of the lanthanides. These results demonstrate that uranium and lanthanides react independently with Li$_2$O in the LiCl-KCl melt, and concentration control of the oxide ion can separate uranium from a chloride molten salt containing several lanthanide ions. In addition, the electrochemical measurement tool used in this study has potential for on-line monitoring of the chemical reactions in the melt.

Figure 6. (a) CVs of the melt containing 1 wt% UCl$_3$ and 1.2 wt% LnCl$_3$ (0.4 wt% each of NdCl$_3$, CeCl$_3$, and LaCl$_3$) with the addition of Li$_2$O at 450°C. Scan rate = 200 mV/s. (b) Variation of electric charge with the addition of Li$_2$O into the LiCl-KCl melt. The dotted lines indicate the theoretical amounts of Li$_2$O based on the stoichiometry of U$^{3+}$:O$^{2-}$ = 1:2 and Ln$^{3+}$:O$^{2-}$ = 1:1.
Conclusions

Here, we studied the chemical reactions of $\text{U}^{3+}$, $\text{Nd}^{3+}$, $\text{Ce}^{3+}$, and $\text{La}^{3+}$ with $\text{Li}_2\text{O}$ in the $\text{LiCl-KCl}$ melt using electrochemical and spectroscopic tools. The CV and UV-vis spectroscopic measurements enabled in situ monitoring of the reactions upon the addition of oxide ions, demonstrating that $\text{U}^{3+}$ and $\text{Ln}^{3+}$ react with 2:1 and 1:1 mole ratios ($\text{O}_2^{-}\cdot\text{M}^{3+}$) of the oxide ion, respectively. Raman spectroscopy and XRD analyses of the products confirmed that the precipitation reactions presented $\text{UO}_2$ and $\text{LnOCl}$. Both analyses detected a trace of $\text{CeO}_2$, which likely resulted from the oxidation of $\text{CeOCl}$ during the reaction. Finally, we electrochemically monitored the precipitation reactions in a mixture containing uranium and different lanthanides, and demonstrated that the uranium ions can be selectively precipitated from the melt by the control of the oxide ion concentration.

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