

Spectroscopic and Electrochemical Investigation of Reactions of Oxide Ions With U^{3+} and Ln^{3+} ($Ln=Nd, Ce, \text{ and } La$) in LiCl-KCl Melts

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1. Introduction

Lanthanide and actinide elements in spent nuclear fuel coexist as various oxidation states in molten salt of a pyrochemical processing [1]. There is also an oxygen ion in an electro-reduction process of the pyroprocessing. It is well known that the lanthanide and actinide ions may form metal oxide precipitates if the oxygen ion exists in the solution. Therefore, the oxygen ion can give a fatal influence on the operation of electro-refining and electro-winning process. However, reactions between the uranium and the oxygen ions have not been much studied in molten salt yet. In this work, chemical reactions between the U ions and the oxygen ions in LiCl-KCl melts were investigated by electrochemical and UV-vis absorption spectroscopic methods. Raman spectroscopy and X-ray diffraction (XRD) were also employed to characterize the chemical compositions of the resulting uranium oxides.

2. Experimental

All the experiments were carried out in a glove box under Ar, where the O_2 and H_2O levels were maintained at less than 1 ppm. Lithium chloride/potassium chloride (LiCl/KCl) eutectic salts (anhydrous beads), lithium oxide (Li_2O), lithium chloride (LiCl), and silver chloride (AgCl) were obtained from Sigma Aldrich. Neodymium chloride ($NdCl_3$), cerium chloride ($CeCl_3$), and lanthanum chloride ($LaCl_3$) were purchased from Alfa Aesar (purity $\geq 99.999\%$). UCl_3 was prepared with a chemical method from U metal and $CdCl_2$ in a LiCl-KCl melt. Li_2O was added to the molten LiCl-KCl as 5 wt.% Li_2O -LiCl salt due to the low solubility of Li_2O in LiCl-KCl.

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.

3. Results and Discussion

3.1 Electrochemical study

Fig. 1 shows the CVs of UCl_3 and $LnCl_3$ in LiCl-KCl molten salts while adding Li_2O into the melt as a source of O^{2-} . The current-voltage (I-V) curves demonstrate that the electrochemical signals of U^{3+} and Ln^{3+} remained after reacting with the oxide ion in the molten salt. Prior to Li_2O addition, 1 wt.% of U^{3+} and 2wt.% Ln^{3+} show their characteristic deposition and dissolution peaks at -1.4 to -1.6 V and -2.0 to -2.2 V, respectively. Additionally, the redox couple of $U^{3+/4+}$ appears at -0.2 to -0.4 V. Then, we measured the CVs of the melt after adding aliquots of Li_2O (each ~ 0.25 equivalent to the U or Ln ions) to the melt and shaking the mixture to facilitate the reaction. The continuous addition of Li_2O gradually reduced the currents of U^{3+} and Ln^{3+} without inducing new signals, indicating that the U and Ln ions were consumed by the reactions with Li_2O to afford the corresponding insoluble oxide and/or oxychlorides.

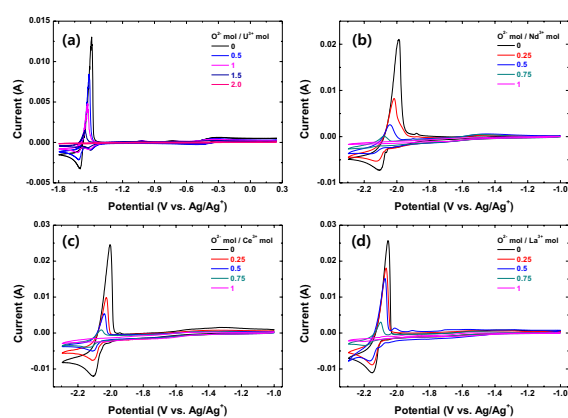


Fig. 1. CVs of LiCl-KCl melts containing (a) 1 wt.% of UCl_3 , and 2 wt.% of (b) $NdCl_3$, (c) $CeCl_3$, and (d) $LaCl_3$, with the addition of Li_2O into the melts at $450\text{ }^\circ\text{C}$. Scan rate = 200 mV/s.

3.2 Precipitations Analysis

In the Raman spectra in Fig. 2, the uranium precipitate exhibits a broad peak at 448 cm^{-1} , which is attributable to the U-O stretching mode of UO_2 . On the basis of literature, the Raman modes can be assigned to NdOCl : the mode at 185 cm^{-1} has A_{1g} symmetry, the modes at 122 and 439 cm^{-1} have E_g symmetry, and that at 315 cm^{-1} can be assigned to phonons with A_{1g} or B_{2g} symmetry. 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. Interestingly, CeO_2 has a Raman active Ce-O-Ce symmetric vibration at $\sim 465\text{ cm}^{-1}$. Therefore, the Raman and electronic spectroscopy study suggest that the Ce precipitate also contains CeO_2 .

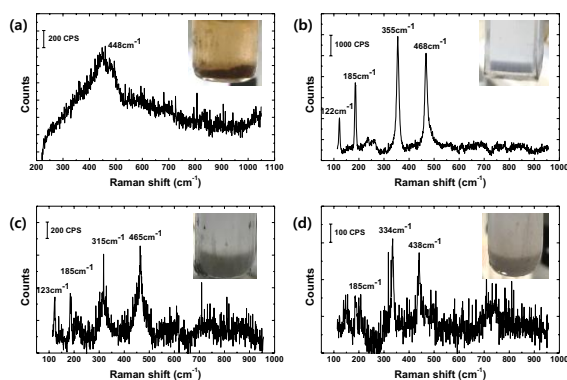


Fig. 2. Raman spectra of LiCl-KCl containing precipitates of (a) U, (b) Nd, (c) Ce, and (d) La ($\lambda_{\text{ex}} = 625.8\text{ nm}$, 20 mW ; acquisition time, 1 s). Insets: photos of molten salts containing the precipitates.

Fig. 3 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 UO_2 . Like the Raman results, the XRD patterns of the three lanthanides were very similar and were assigned to the corresponding oxychloride structures. Meantime, it was difficult to find evidence of CeO_2 in the XRD result of the salt-precipitate mixture. After removing the salt with water, the remaining Ce precipitate was measured again by XRD. The result (shown in red in Fig. 3c) displays a clear pattern of CeOCl with trace signatures of CeO_2 , indicating the reaction of Ce^{3+}

and Li_2O can also form CeO_2 as a by-product, as observed in the Raman spectra. The formation of CeO_2 seems very sensitive to reaction conditions, such as the concentration and source of the oxide ion.

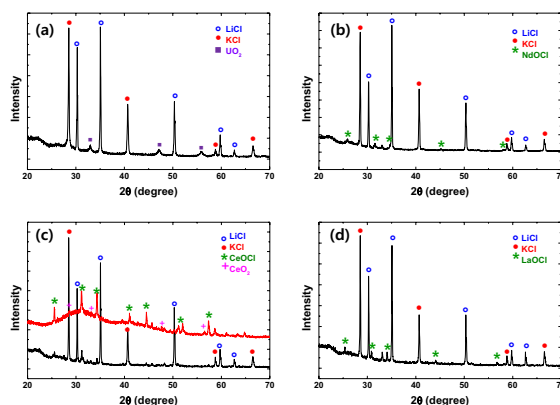


Fig. 3. XRD patterns of LiCl-KCl containing (a) U, (b) Nd, (c) Ce, and (d) La precipitates. The red trace in (c) was obtained from the solid after washing the precipitate with water.

4. Conclusions

Here, we studied the chemical reactions of U^{3+} , Nd^{3+} , Ce^{3+} , and La^{3+} with Li_2O in the LiCl-KCl melt using electrochemical tools. The CV measurements enabled in-situ monitoring of the reactions upon the addition of oxide ions, demonstrating that U^{3+} and Ln^{3+} react with two and one equivalents of the oxide ion, respectively. Raman spectroscopy and XRD analyses of the products confirmed that the precipitation reactions presented UO_2 and LnOCl . Both analyses detected a trace of CeO_2 , which likely resulted from the oxidation of CeOCl during the reaction.

REFERENCES

- [1] H. Lee, G.-I. Park, K.-H. Kang, J.-M. Hur, J.-G. Kim, D.-H. Ahn, Y.-J. Cho, and E.-H. Kim, "Pyroprocessing Technology Development at KAERI", Nuclear Engineering and Technology, 43 (4), 317-328 (2011).