Absorption spectra and cyclic voltammograms of uranium species in molten lithium molybdate–sodium molybdate eutectic at 550 °C

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Summary. Absorption spectra of uranium species dissolved in molten lithium molybdate–sodium molybdate eutectic of $0.51Li_2MoO_4$–$0.49Na_2MoO_4$ mixture at 550 °C were measured by UV/Vis/NIR spectrophotometry, and their redox reactions were investigated by cyclic voltammetry. We found that the major ions of uranium species dissolved in the melt were uranyl penta-valent. After purging dry oxygen gas into the melt, penta-valent species were oxidized to the uranyl hexa-valent. In the cyclic voltammetry of the melt without uranium species, it was confirmed that the lithium-sodium molybdenum oxide compounds were deposited on the working electrode at the negative potential and the lithium molybdenum oxide compounds were deposited on the counter electrode at positive potential. When UO_2 was dissolved into the melt, the reductive reaction of the uranium species was observed at the reductive potential of the pure melt. This suggests that the uranium species dissolved in the melts could be recovered as mixed uranium-molybdenum oxides by electrolysis.

1. Introduction

The study of a pyrochemical process by using an alkaline molybdate melt has been carried out as a candidate reprocessing process for spent nuclear oxide fuels. This alkaline molybdate melt has a useful characteristic, which is an ability to dissolve uranium oxides, such as UO_2 in a short time. In the previous study [1], the UO_2 pellet was dissolved into molten sodium molybdate mixtures of Na_2MoO_4–$Na_2Mo_2O_7$ at 750 °C in an alumina crucible and uranium species dissolved in the melts were recovered as UO_2 particles by electrolysis at 700 °C. It was confirmed by the X-ray photoelectron spectroscopy (XPS) analysis of the coagulation salt samples that the uranium species in molten Na_2MoO_4–$Na_2Mo_2O_7$ mixtures after dissolving the UO_2 pellet were tetra-valent ions. However, this dissolved uranium species in molten Na_2MoO_4–$Na_2Mo_2O_7$ mixtures might be penta-valent ions since the U $4f_{7/2}$ binding energy of uranium tetra-valent judged in the XPS analysis is close to the binding energy of a uranium penta-valent of a ura-

nium molybdenum compound, $UMoO_5$ [2]. Moreover, the coordination circumstances of uranium species in alkaline molybdate melts have not been studied because the melting point of Na_2MoO_4 is high and the spectrum measurement cell made of quartz is damaged by the salt after melting. So the absorption spectrum has never been reported.

In this study, absorption spectra of uranium species dissolved in molten lithium molybdate–sodium molybdate eutectic of $0.51Li_2MoO_4$–$0.49Na_2MoO_4$ mixture at 550 °C were measured by UV/Vis/NIR spectrophotometry, and their redox reactions were also investigated by cyclic voltammetry. The melting point of Li_2MoO_4–Na_2MoO_4 eutectic is lower than that of Na_2MoO_4 or Na_2MoO_4–$Na_2Mo_2O_7$ mixtures [3], and the corrosion damage of the quartz cell can be avoided.

2. Experimental

2.1 Reagents

Anhydrous Li_2MoO_4 and Na_2MoO_4 of purity 99% up were purchased from Kojundo Chemical Lab. Co., Ltd. and processed by vacuum drying at 150 °C before use. To confirm the chemical composition of Li_2MoO_4–Na_2MoO_4 eutectic, the Li_2MoO_4–Na_2MoO_4 mixtures with mole ratio of $[Li_2MoO_4]/[Na_2MoO_4]$ from $[0.46]/[0.54]$ to $[0.54]/[0.46]$ were melted at 750 °C and melting points of these coagulation salts were measured by the thermal analysis. The simultaneous thermogravimetric and differential thermal analysis instrument, DTG-50H of Shimadzu Co., Ltd. in dry argon atmosphere was used for this thermal analysis. The eutectic composition was $0.51Li_2MoO_4$–$0.49Na_2MoO_4$ as shown in Fig. 1 as a result of the thermal analysis, and it agreed with the reference [3]. The Li_2MoO_4–Na_2MoO_4 eutectic salt utilized in this measurement was prepared by melting the mixed anhydrous reagents of Li_2MoO_4 and Na_2MoO_4 with the above-mentioned eutectic composition.

The UO_2 powder was loaded into molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C in a quartz tube by adding MoO_3 of twice mole amount of UO_2, and argon gas was purged into the melt until the UO_2 dissolution was completed. Then this source material containing uranium species was added into the measurement melts used in the absorption spectrophotometry and cyclic voltammetry.

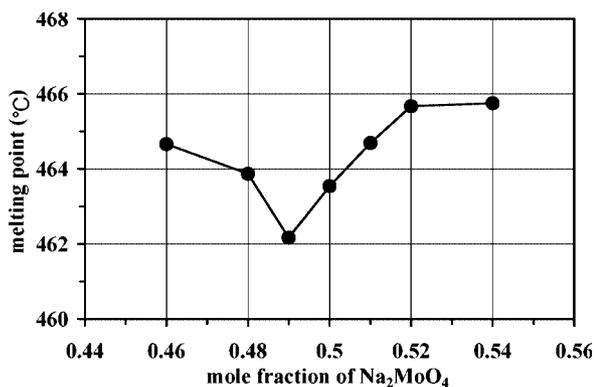*Author for correspondence
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Fig. 1. Melting point of Li_2MoO_4–Na_2MoO_4 mixtures.

Fig. 2. An absorption spectrum of Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C.

2.2 Apparatus and procedure

All the measurements were carried out in a glove box filled with dry argon where humidity and oxygen impurity were kept less than 1 ppm. The optical measurement system for the molten salt sample is described in detail elsewhere [4]. The sample temperature was kept at 550 ± 1 °C by an automatically controlled electric furnace.

The absorption spectrophotometry was carried out by using the sample cell of a quartz tube, 350 mm in length and 13 mm in inner diameter. At the bottom of the tube an optical cell having a 10 mm light path was welded. About 10 g of the prepared Li_2MoO_4–Na_2MoO_4 eutectic salt was put into the sample cell and they were heated to 550 °C. After taking the background absorption spectrum of pure Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C, a portion of the source material containing uranium species was added into the melt and the absorption spectrum of uranium species in the Li_2MoO_4–Na_2MoO_4 eutectic was measured. A self-registering spectrophotometer, V-350 of JASCO Co. was used for the absorption spectrophotometry over the wavenumber from 5000 to 25 000 cm^{-1}.

In the cyclic voltammetry, about 10 g of the Li_2MoO_4–Na_2MoO_4 eutectic and the source material containing uranium species were put into the measurement cell made of quartz tube of 13 mm in inner diameter and heated to 550 °C. After melting was completed, three electrodes were all inserted into the measurement cell: a working, a counter and a reference electrode. Two platinum wires of 1 mm diameter were used as the working and counter electrodes, and these electrodes were inserted to a depth of 10 mm into melts for the measurements. The reference electrode utilized was composed of a PYREX tube with about 1 g of 12.17 mol % MoO_3 in Li_2MoO_4–Na_2MoO_4 eutectic and a platinum wire, referring to the electrode structure that Smolenskii *et al.* had reported [5]. An electrochemical measurement system, HAG-5001 of Hokuto Denko Co. was used for the cyclic voltammetry.

3. Results and discussion

3.1 Absorption spectra of uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic

Fig. 2 shows the absorption spectrum of Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C. This Li_2MoO_4–Na_2MoO_4 eutectic has
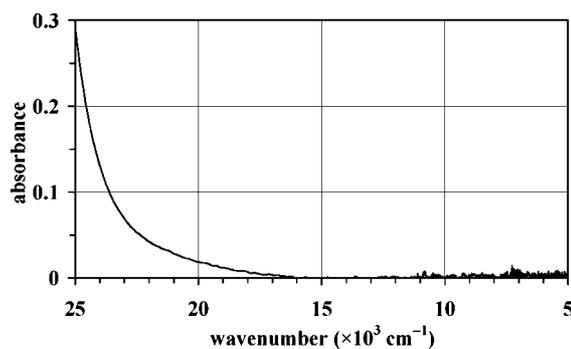
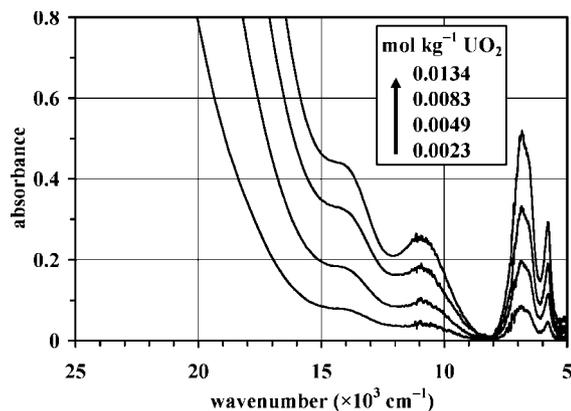**Fig. 3.** Absorption spectra of uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C.

a broad absorption band over 17 000 cm^{-1} in UV/Vis regions, and this absorption was similar to the case of a sodium molybdate solution [6].

Absorption spectra of uranium in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C were observed as shown in Fig. 3. The absorption peaks were found at 14 000, 11 000, 6700, and 5700 cm^{-1} in Vis/NIR regions. The absorption profile was similar to that of uranyl penta-valent ion, UO_2^+, in molten chlorides [7], and corresponded to the f–f electronic transitions that had been identified in molten NaCl–CsCl [8]. A huge absorption band observed over 16 000 cm^{-1} in UV/Vis regions was similar to that of UO_2^+ in sodium silicate glass [9]. Therefore, the predominant uranium species in the molten Li_2MoO_4–Na_2MoO_4 eutectic is UO_2^+ when UO_2 is dissolved into the melt.

To confirm the stability of UO_2^+ in molten Li_2MoO_4–Na_2MoO_4 eutectic, dry oxygen gas was purged into the melt and absorption spectra were measured. After purging oxygen gas, the characterized absorption peaks of UO_2^+ at 14000, 11000, 6700, and 5700 cm^{-1} disappeared and a huge charge transfer absorption band appeared over 17 000 cm^{-1} in UV/Vis regions, as shown in Fig. 4. In addition to this huge absorption band, a small absorption peak by the uranyl-type electronic transition can be seen at 22 500 cm^{-1}, as a shoulder on the huge absorption. The absorption profile was similar to that of uranyl hexa-valent ion, UO_2^{2+}, in molten LiCl–KCl [10, 11], NaCl–CsCl [4] eutectics and sodium silicate glass [9]. This suggests that UO_2^+ in the molten Li_2MoO_4–Na_2MoO_4 eutectic was oxidized to UO_2^{2+} by oxygen in the melt.
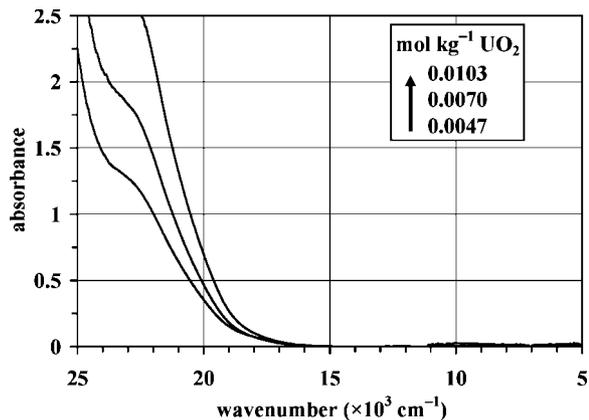
Fig. 4. Absorption spectra of uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C after oxygen gas purging into the melt.
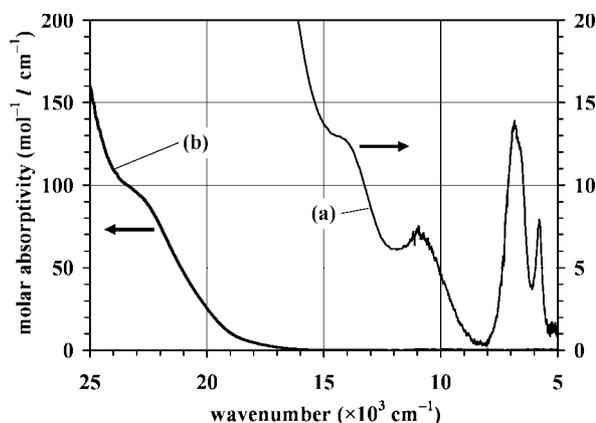
Fig. 5. Molar absorptivity of uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C, (a) before and (b) after oxygen gas purging.

Absorbance at several peaks shown in Figs. 3 and 4 was proportional to the concentration of uranium. Fig. 5 shows the molar absorptivities of uranium species in the melt before/after the purging dry oxygen gas that were calculated from the measured spectra in Figs. 3 and 4. The density of molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C was approximated as 2.781 g cm^{-3} from the calculation by using the density of molten pure Li_2MoO_4 and Na_2MoO_4 [12], as shown in Eqs. (1) and (2).
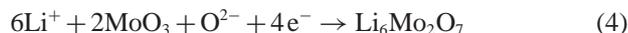
$$\rho_{Li_2MoO_4}(\text{g cm}^{-3}) = 2.886 - 0.2380 \times 10^{-3}T \quad (°C) \quad (1)$$

$$\rho_{Na_2MoO_4}(\text{g cm}^{-3}) = 3.168 - 0.6542 \times 10^{-3}T \quad (°C) \quad (2)$$

In our previous analysis of uranyl ions in molten NaCl–CsCl eutectic at 650 °C [4], the molar absorptivities of UO_2^+ were determined to be 12.5 mol^{-1} l cm^{-1} at 16 100 cm^{-1} and 15.9 mol^{-1} l cm^{-1} at 12 900 cm^{-1}, and that of UO_2^{2+} 57.2 mol^{-1} l cm^{-1} at 22 200 cm^{-1}. The dissolved uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic after purging oxygen gas can be assigned to UO_2^{2+}, because there were no peaks corresponding to UO_2^+. The molar absorptivity of the shoulder peak at 22 500 cm^{-1} of UO_2^{2+} in molten Li_2MoO_4–Na_2MoO_4 eutectic, as shown line (b) in Fig. 5 ($\varepsilon = 88.3$), was larger than those of UO_2^{2+} in molten NaCl–CsCl [4] and LiCl–KCl eutectics [10, 11].

3.2 Cyclic voltammograms of uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic

Fig. 6 shows cyclic voltammograms in molten pure Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C. The deposition of lithium-sodium molybdenum oxide compounds on the working electrode was observed below -1.0 V (*vs.* reference electrode), as shown 1 c in Fig. 6. The deposited compounds were analyzed by the X-ray diffraction (XRD) and they were various alkali molybdenum oxides such as the lithium molybdenum oxides and the lithium-sodium molybdenum oxides. The oxygen gas could have been generated from the working electrode surface over 0.8 V of 3a in Fig. 6, since the deposition of molybdate compounds was observed on the counter electrode and these compounds were identified by the XRD analysis to be lithium molybdenum oxides of Li_2MoO_3 and $Li_6Mo_2O_7$. These are presumed to be generation with the reactions of Eqs. (3) and (4) corresponding to the oxygen gas generation Eq. (5).

$$2Li^+ + MoO_3 + 2e^- \rightarrow Li_2MoO_3 \quad (3)$$

$$6Li^+ + 2MoO_3 + O^{2-} + 4e^- \rightarrow Li_6Mo_2O_7 \quad (4)$$

$$2O^{2-} \rightarrow O_2 + 4e^- \quad (5)$$

The oxidizing reaction peak of 1a in Fig. 6 was a re-dissolution of deposited lithium-sodium molybdenum oxides on the working electrode, and the reductive reaction of 3c in Fig. 6 was thought to be re-dissolution of adhering oxygen bubbles on the working electrode. The reactions of 2c at -0.5 V and 2a at -0.3 V in Fig. 6 were deposition and dissolution of molybdate compounds, because the thin deposit was observed on the working electrode surface after the experiment.

From measured cyclic voltammograms as shown in Fig. 6, it was found that the potential width of electrochemical window in molten Li_2MoO_4–Na_2MoO_4 eutectic was about 1.8 V at 550 °C. This potential width was narrower than that in the molten chlorides, since the deposition potential of lithium-sodium molybdenum oxides was more positive than that of the alkali metals.
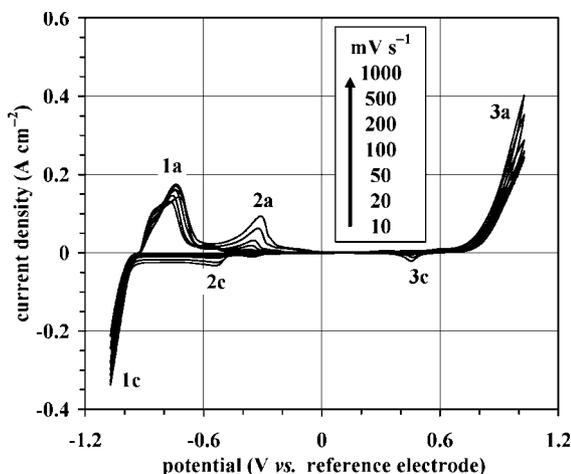

Fig. 6. Cyclic voltammograms in molten pure Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C. 1c, 2c, and 3c: reductive reactions, 1a, 2a, and 3a: oxidizing reactions.
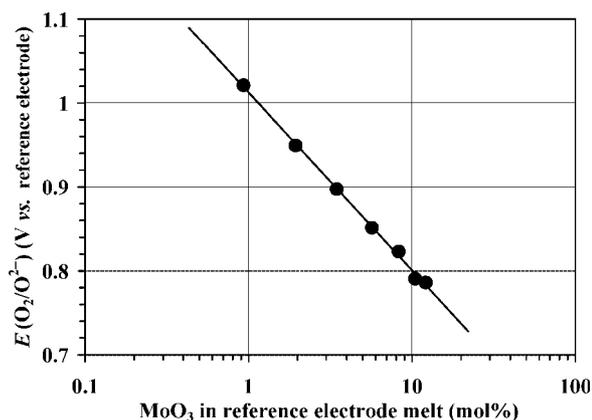
Fig. 7. Influence of the oxygen overvoltage of $E(O_2/O^{2-})$ in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C with MoO_3 concentration in reference electrode melt.

Fig. 8. Cyclic voltammograms of dissolved uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C for various measuring potential ranges. UO_2 concentration in the melt was 1.02 mol %. Potential sweep rate: 10 mV s^{-1}. Ic, IIc, and IIIc: reductive reactions. Ia, IIa, IIIa, and IIIa': oxidizing reactions.

Fig. 9. Cyclic voltammograms of dissolved uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C for various potential sweep rates. UO_2 concentration in the melt was 1.02 mol %.

To confirm the validity of the reference electrode potential at the electrochemical measurement, the cyclic voltammograms were measured on the condition of 0.93 to 12.17 mol % MoO_3 in the reference electrode salt. Fig. 7 shows the relation of the MoO_3 concentration in the reference electrode salt to the oxygen overvoltage, $E(O_2/O^{2-})$, in molten pure Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C. This $E(O_2/O^{2-})$ was defined as the potential that the tangent of the oxygen generating reaction 3a in Fig. 6 was intersected with current density of 0 A cm^{-2}. The relation of $E(O_2/O^{2-})$ to the logarithm of MoO_3 concentration in reference electrode salt has a good linearlity as shown in Fig. 7, but the redox reaction in the reference electrode could not be clarified accurately in this study. The slope of this line in Fig. 7 is equivalent to 0.75 electron exchange reactions when calculating from the Nernst's relation.

To confirm the stability of the reference electrode potential with 12.17 mol % MoO_3 in the electrode used in this study, the cyclic voltammograms were measured repeatedly for 150 min. The cyclic voltammogram after 150 min corresponded to the initial result, and the stability of the cyclic voltammetry was confirmed.

Fig. 8 shows the cyclic voltammograms of dissolved uranium species in molten Li_2MoO_4–Na_2MoO_4 eutectic at 550 °C for various measuring potential ranges. The UO_2 concentration of the melt was 1.02 mol %. The reductive reactions of dissolved uranium species in the melt were observed in a potential range that was more negative than −0.1 V (*vs.* reference electrode) as shown Ic, IIc and IIIc in Fig. 8, and the oxidizing reactions were observed in Ia, IIa, IIIa, and IIIa' in Fig. 8.

The reductive reaction of Ic and oxidizing reaction of Ia are presumed to be the redox reaction of the UO_2^{2+}/UO_2^+ couple, because the existence of the uranyl ions, UO_2^+ and UO_2^{2+}, was confirmed by the above-mentioned absorption spectrophotometry. To confirm that this redox reaction is a soluble–soluble reaction, cyclic voltammograms in potential range of −0.25 to 0.4 V were measured for various potential sweep rates ranging from 5 to 500 mV s^{-1}, as shown in Fig. 9. The reductive current of reaction Ic included other reactions, but the current density of this redox couple increased with an increase of the potential sweep rate. As for oxidizing reaction of Ia, the relation between the square root
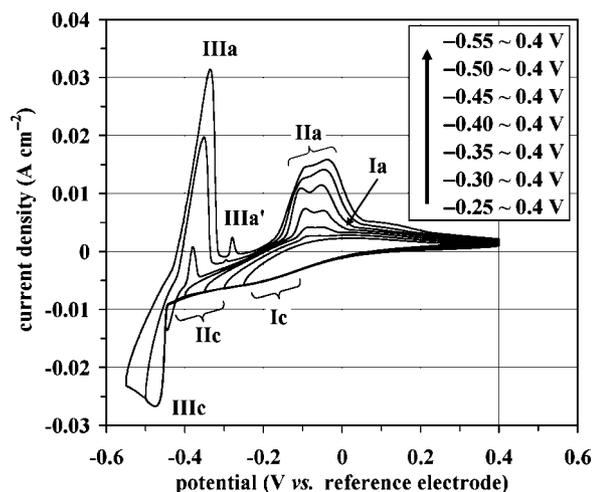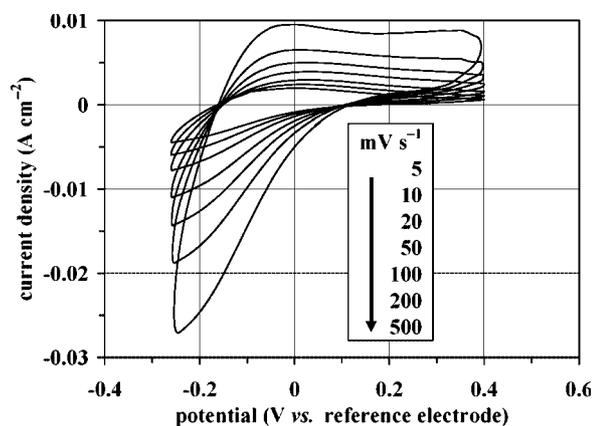
of potential sweep rate and the oxidizing current density showed a good linearity.

The deposition current peak of dissolved uranium species in the melt was observed in a potential range that was more negative than −0.45 V shown as IIIc in Fig. 8, and the dissolution current peak of deposited uranium compounds on the working electrode was observed below −0.3 to −0.4 V shown as IIIa and IIIa' in Fig. 8. And reductive reaction of IIc below −0.4 to −0.3 V and oxidizing reaction of IIa over −0.15 to 0 V accounted for deposition of other uranium species and dissolution of uranium compounds. Since these deposit samples by reactions of IIc and IIIc were so small, they were not identified by the XRD analysis.

However, the deposition potential of uranium compounds as shown IIIc in Fig. 8 is close to the potential that was deposited molybdate compounds shown as 2c in Fig. 6. Therefore, it was suggested that the uranium species in this molten Li_2MoO_4–Na_2MoO_4 eutectic are recovered as mixed uranium-molybdenum oxides by electrolysis. In following investigations, several grams of the compound could be collected and identified the phase.

4. Conclusion

In this study, the absorption spectrophotometry and cyclic voltammetry of dissolved uranium species in the molten lithium molybdate–sodium molybdate eutectic at 550 °C were carried out. This melt is the binary alkaline molybdate mixture with the lowest melting point, and the corrosion damage of the quartz cell could be avoided in these measurements.

As the results of spectrophotometry, it was found that the major ions of uranium species dissolved in the melt were uranyl penta-valent ions of UO_2^+, whose observed absorption spectra were similar to those of UO_2^+ in molten chlorides. After purging dry oxygen gas into the melt, the absorption peaks of UO_2^+ decreased and UO_2^+ was oxidized to the uranyl hexa-valent ion of UO_2^{2+}.

In the cyclic voltammetry, it was found that the potential width of electrochemical window in the melt was narrower than that in the molten chlorides. When UO_2 was dissolved into the melt, the reductive reaction of the uranium species was observed. It was suggested that the uranium species in the melt are recovered as mixed uranium-molybdenum oxides by electrolysis, since the reduction potential of uranium species is close to the deposition potential of the molybdenum oxide compounds.

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