Evaluation of Apparent Standard Potentials of Curium in LiCl-KCl Eutectic Melt

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ABSTRACT

Electrochemical properties of curium (Cm-244) dissolved in LiCl-KCl eutectic melt were studied in the temperature range of 718–823 K. A small electrochemical cell used in the present study was designed to measure electrochemical properties of highly radioactive Cm-244, the maximum handling amount of which is 30 mg in our hot cell, dissolved in molten salts. Apparent standard potentials of Cm3+/Cm couple obtained in the present study, \( E^\circ \) (Cm\(^{3+}\)/Cm) \( = (−3.236 ± 0.011) + (4.86 ± 0.14) \times 10^{-4} ° \) T, reasonably agree with Osipenko’s data (2011) and are lower than Martinot’s data (1975). The validity of the data obtained in the present study was discussed by comparing with the reported data of other transuranic elements.

Keywords : Apparent Standard Potentials, Gibbs Free Energy of Formation, Curium Chloride, Pyrometallurgical Reprocessing

1. Introduction

A pyrochemical process using molten salts is a promising technique for reprocessing of spent nuclear fuels, which has advantages such as its compactness, high radiation resistance and high proliferation resistance. In case of spent metallic fuels, they are dissolved into a molten salt bath (LiCl-KCl eutectic melt) at an anode and uranium is selectively recovered at a solid cathode from the molten salt bath containing dissolved actinides and fission product elements including lanthanides in the electrorefining step. Subsequently, residual uranium, plutonium and minor actinides (MAs: Np, Am, Cm) are selectively recovered at a liquid cadmium cathode by electrorefining. Accurate knowledge about standard potential of actinide elements including MAs in LiCl-KCl eutectic melt is required for designing the pyrochemical process since the standard potential of actinide elements is related to the stability of those ions in LiCl-KCl eutectic melt. Among MAs, reliable apparent standard potential data of Np5+/Np and Am6+/Am in LiCl-KCl eutectic melt were reported. As for Cm, a set of data on the apparent standard potentials of Cm had been reported by Martinot before new data were reported by Osipenko in 2011. Therefore, it is important to determine the reliable apparent standard potentials of Cm3+/Cm couple in LiCl-KCl eutectic melt. In previous studies, Cm\(^{3+}\) ions were introduced into LiCl-KCl as CmH\(_4\)Cl\(_2\) or as curium chloride prepared by the reaction of CmO\(_2\) with chlorine gas in the melt.

In the present study, Cm\(^{3+}\) ions were introduced into LiCl-KCl eutectic melt as CmCl\(_3\) which was synthesized by the solid-state reaction of CmN with CdCl\(_2\). A small electrochemical cell was designed for the electrochemical measurement using a small amount of the highly radioactive MAs (the amount of which is limited lower than 30 mg, because the maximum handling amount of Cm-244 in our hot cell is 30 mg) contained in molten salts. The apparent standard potentials of Cm\(^{3+}\)/Cm couple in LiCl-KCl eutectic melt were measured by using this small electrochemical cell. The validity of the data obtained in the present study was discussed by comparing with the reported data of other transuranic elements.

2. Experimental

Sample preparation of CmCl\(_3\) was briefly given here, since the details of the sample preparation of CmCl\(_3\) were described in Ref. Anhydrous CmCl\(_3\) was synthesized by the solid-state reaction of Curium nitride (CmN) with cadmium chloride (CdCl\(_2\)); other MA chlorides, NpCl\(_3\) and AmCl\(_3\), have been successfully synthesized by similar methods. CmN was synthesized by the carbothermic reduction of CmO\(_2\). CmCl\(_3\) sample used in the present study contained 2% of Am-243 as an impurity, because the sample is mixture of CmCl\(_3\) and Cm (99.95% purity, Nilaco Corp.) immersed into a LiCl-KCl-1 wt%AgCl (99.99% purity, APL) molten salt contained in a closed-end porous mullite tube (50%Al\(_2\)O\(_3\) + 46%SiO\(_2\)) containing 10 ppm of Cm-244 in our hot cell (30 mg) contained in molten salts. Figure 1 shows an experimental setup with the small

Figure 1. Experimental setup of the small electrochemical cell. The picture in this figure is a photograph of a small electrochemical cell used in the present study and the unit of dimensions is in mm.

electrochemical cell. 3.54 g of LiCl-KCl mixed with 4.13 mg of CmCl3 \((X(CmCl_3) = 2.96 \times 10^{-4})\) was used for the electrochemical measurements where \(X\) is the mole fraction of the solute in LiCl-KCl eutectic melt. The sample was introduced in a high-purity alumina crucible (99.9% Al_2O_3, Nikkato Corp.) with an inner diameter of 18 mm which had been inserted in a Mo container. This container was attached to a cover of the furnace to fix the position of the alumina crucible. An electrodes separator was used to prevent the contacts of the electrodes. The temperature of the molten salt was measured with a calibrated Chromel-Alumel thermocouple (precision: \(\pm 1 K\)) inserted in a closed-end alumina tube (99.5% Al_2O_3, Nikkato Corp.) immersed into the melt. The uncertainty in the electrochemical measurements was \(\pm 5\%\). All electrochemical measurements such as cyclic voltammetry, galvanodynamic measurements,\(^{2,3}\) potentiostatic and open-circuit chronopotentiometry were carried out using a Princeton Applied Research (PAR) 263A Potentiostat/Galvanostat controlled with the Scribner Associates Inc. CorrWare software.

3. Results and Discussion

To confirm the accuracy of the data obtained from electrochemical measurements using the small electrochemical cell, preliminary measurements using the small electrochemical cell were performed using LiCl-KCl-CeCl3 at 723 K. 7.50 g of LiCl-KCl mixed with 9.8 mg of CeCl3 \((X(CeCl_3) = 2.96 \times 10^{-4})\) was used for this experiment. The mole fraction of CeCl3 \((X(CeCl_3))\) in this experiment is similar to that of CmCl3 \((X(CmCl_3))\) in the experiment using Cm; the accuracy of our measurements is considered not to affected by such small difference of concentration of the solute \((X(CeCl_3))\). Figure 2 shows a typical cyclic voltammogram measured at 723 K in LiCl-KCl-CeCl3. The anodic and cathodic peaks attributed to the reaction of Ce\(^{3+}/\text{Ce}\) couple were observed. The apparent standard potential of Ce\(^{3+}/\text{Ce}\) couple was determined from the equilibrium potential measured by the galvanodynamic technique as shown in Fig. 3. The apparent standard potential (vs. Cl\(_2\)/Cl\(^{-}\)) is related to the equilibrium potential by the Nernst equation:2

\[
E_{eq}(M^{3+/M}) = E^{\infty}(M^{3+/M}) + \frac{RT}{1F} \ln(X(MCl)) + E_{ref},
\]

\((M = \text{Ce or Cm}), \) (1)

where \(E_{eq}(M^{3+/M})\) and \(E^{\infty}(M^{3+/M})\) are the equilibrium potential and the apparent standard potential given in V (vs. Cl\(_2\)/Cl\(^{-}\)). \(R\) and \(T\) are the ideal gas constant and temperature, respectively. The potential of the Ag/AgCl reference electrode, \(E_{ref}\) (vs. Cl\(_2\)/Cl\(^{-}\)), is expressed by the following equation:

\[
E_{ref} = E^{\infty}(Ag^{+}/Ag) + \frac{RT}{1F} \ln(X(AgCl)),
\]

(2)

where \(E^{\infty}(Ag^{+}/Ag)\) is the apparent standard potential of Ag\(^{+}/Ag\) couple (vs. Cl\(_2\)/Cl\(^{-}\)) and \(X(AgCl)\) is the mole fraction of AgCl in the reference electrode. \(X(AgCl) = 0.0039\) in the present study. The apparent standard potential of Ag\(^{+}/Ag\) couple is expressed with Eq. (3).\(^{2,23}\)

\[
E^{\infty}(Ag^{+}/Ag) = -1.0910 + 2.924 \times 10^{-4} \times T.
\]

(3)

The apparent standard potential of Ce\(^{3+}/\text{Ce}\) couple relative to the Cl\(_2\)/Cl\(^{-}\) reference electrode, \(E^{\infty}(Ce^{3+/Ce})\), was determined to be \(-3.101 \pm 0.005\) V at 723 K. This value was in agreement with the reported values, \(-3.085 \pm 0.005\) V\(^{24}\), \(-3.092\) V\(^{25}\), and \(-3.098 \pm 0.006\) V.\(^{26}\) From this result, it was judged that the electrochemical data obtained using this small electrochemical cell has a sufficient accuracy.

Figure 4 shows a typical cyclic voltammogram in LiCl-KCl-CeCl3 measured at 823 K. The anodic and cathodic peaks, \(P_a\) and \(P_c\), were observed around \(-1.85\) V relative to the Ag/AgCl reference electrode. It was supposed that these peaks are attributed to the redox reaction of Cm\(^{3+}/Cm\) couple. Small peaks which are not assigned to any electrochemical reactions were observed around \(-1.3\) V (vs. Ag/AgCl). The anodic peak observed around \(-1.3\) V can be attributed to the oxidation reaction of Am\(^{3+}/Am\) couple since a small amount of Am was contained in this molten salt bath as mentioned in Sec. 2. It was checked whether it is attributed to the oxidation reactions of Am or not, as below. The apparent standard potential of Am\(^{3+}/Am\) couple, \(E^{\infty}(Am^{3+/Am})\), is expressed by the following equation:10

\[
E_{ref} = E^{\infty}(Ag^{+}/Ag) + \frac{RT}{1F} \ln(X(AgCl)),
\]

(2)

where \(E^{\infty}(Ag^{+}/Ag)\) is the apparent standard potential of Ag\(^{+}/Ag\) couple (vs. Cl\(_2\)/Cl\(^{-}\)) and \(X(AgCl)\) is the mole fraction of AgCl in the reference electrode. \(X(AgCl) = 0.0039\) in the present study. The apparent standard potential of Ag\(^{+}/Ag\) couple is expressed with Eq. (3).\(^{2,23}\)

\[
E^{\infty}(Ag^{+}/Ag) = -1.0910 + 2.924 \times 10^{-4} \times T.
\]

(3)
In addition, reported standard potentials of Np$^{3+}$/Np, Pu$^{3+}$/Pu and Am$^{3+}$/Am couples were compared to investigate the validity of the data. Here, it is well-known that the reaction of Am$^{3+}$ to Am metal in LiCl-KCl is a two-step reaction which consists of those of Am$^{3+}$/Am$^{2+}$ and Am$^{2+}$/Am couples. Thus, apparent standard potential of Am$^{3+}$/Am couple was calculated from those of Am$^{3+}$/Am$^{2+}$ and Am$^{2+}$/Am couples using the following equation:

$$3E^{\circ}(\text{Am}^{3+/\text{Am}}) = E^{\circ}(\text{Am}^{3+/\text{Am}^{2+}}) + 2E^{\circ}(\text{Am}^{2+/\text{Am}}).$$

As shown in Figs. 7, 8, and 9, in all cases, Martinot’s data were about 0.4–1.0 V higher than other reported data. In Ref. 23, it has been mentioned that the results of Pu$^{3+}$/Pu couple evaluated by Martinot must be erroneous although the reason for a discrepancy is not known. The apparent standard potentials of Pu$^{3+}$/Pu couple reported by Serp were in very good agreement with those by Roy and Masset and close to those by Campbell and Leary and Shirai. The dependency of the apparent standard potential on temperature was almost same in the case of Np, Pu, Am, and Cm, as shown in Figs. 6–9. The apparent standard potential in an An$^{3+}$/An system (Here, An denotes Np, Pu, Am, or Cm) is defined by the following equation:

$$E^{\circ}(\text{An}^{3+/\text{An}}) = E^{\circ}(\text{An}^{3+/\text{An}^{2+}}) + \frac{RT}{F} \ln(\gamma_{\text{An}^{2+}}) \times T,$$

where $E^{\circ}(\text{An}^{3+/\text{An}})$ and $\gamma_{\text{An}^{2+}}$ are the standard potential in the An$^{3+}$/An system and the activity coefficient of M$^{3+}$ ion in LiCl-KCl eutectic melt, respectively. Under the assumption that the standard potential is intrinsic to each element, namely, the standard potential is independent of experimental conditions, the coefficient of the

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**Table 1.** Apparent standard potentials of Cm$^{3+}$/Cm relative to the Cl$_2$/Cl$^-$/ reference electrode in V with reported values.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>This work</th>
<th>Martinot$^{[12]}$</th>
<th>Osipenko$^{[13]}$</th>
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<tr>
<td>673</td>
<td>−1.833</td>
<td>−1.937</td>
<td>−1.888</td>
</tr>
<tr>
<td>718</td>
<td>−2.287</td>
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<td>723</td>
<td>−1.777</td>
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<td>773</td>
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<td>−2.836</td>
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<td>873</td>
<td>−1.636</td>
<td>−1.636</td>
<td>−1.636</td>
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<tr>
<td>923</td>
<td>−2.805</td>
<td>−2.805</td>
<td>−2.778</td>
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</tbody>
</table>

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**Figure 4.** Cyclic voltammogram of Cm$^{3+}$/Cm couple in LiCl-KCl eutectic melt at 823 K with the scan rate of 0.1 V/s.

**Figure 5.** Open-circuit chronopotentiogram of Cm$^{3+}$/Cm couple in LiCl-KCl eutectic melt after the controlled potential electrolysis with applied potential of −2.30 V and duration time of 10 s at 718 K, −2.20 V and 10 s at 773 K, −2.15 V and 10 s at 823 K.
second term on the right side of Eq. (9) indicates the slope of temperature dependency of apparent standard potential. This suggests that the activity coefficients of each element in LiCl-KCl eutectic melt were almost same in previous studies.

The Gibbs free energy of formation of CmCl$_3$ in LiCl-KCl eutectic melt $\Delta G_f^{\circ}$(CmCl$_3$) is related to the apparent standard potential of Cm$^{3+}$/Cm couple by the following equation:

$$\Delta G_f^{\circ}$(CmCl$_3$) = 3FE^{\circ}$(Cm$^{3+}$/Cm). \hspace{1cm} (10)$$

The Gibbs free energy of formation is also expressed with the enthalpy of formation $\Delta H_f^{\circ}$(CmCl$_3$) and the entropy of formation $\Delta S_f^{\circ}$(CmCl$_3$) in LiCl-KCl eutectic melt by the following equation:

$$\Delta G_f^{\circ}$(CmCl$_3$) = $\Delta H_f^{\circ}$(CmCl$_3$) – $T \Delta S_f^{\circ}$(CmCl$_3$). \hspace{1cm} (11)$$

As shown in Fig. 10, a linear dependence of Gibbs free energy of formation of CmCl$_3$ on temperature enables us to evaluate the enthalpy and entropy of formation of CmCl$_3$. The enthalpy and entropy of formation of CmCl$_3$ in LiCl-KCl eutectic melt are listed in Table 2. The enthalpy and entropy of CmCl$_3$ in the present study were good agreement with those reported by Osipenko$^{13}$ and lower than those reported by Martinot.$^{12}$ Furthermore, the standard enthalpy of formation of CmCl$_3$ in solid state at 298.15 K$^{30}$ and the standard entropy of formation of CmCl$_3$ in solid state which has been calculated using a semi-empirical method$^{31}$ are much closer to those derived from the data obtained in the present study and Osipenko’s data than those derived from Martinot’s data.

In addition, reported Gibbs free energy of formation of NpCl$_3$, PuCl$_3$, AmCl$_3$, and CmCl$_3$ in LiCl-KCl eutectic melt and those in solid at 298.15 K were compared to investigate the validity of the data. Gibbs free energies of formation of these chlorides in LiCl-KCl eutectic melt at 298.15 K were

Table 2. Enthalpy of formation of CmCl$_3$ and entropy of formation of CmCl$_3$ in LiCl-KCl eutectic melt with reported values$^{12,13}$ and those of CmCl$_3$ in solid.$^{30,31}$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_f^{\circ}$(kJ mol$^{-1}$)</th>
<th>$\Delta S_f^{\circ}$(J K mol$^{-1}$)</th>
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<tbody>
<tr>
<td>This work</td>
<td>$-936.4 \pm 15.4$</td>
<td>$141 \pm 20$</td>
</tr>
<tr>
<td>Martinot$^{12}$</td>
<td>$-753.7$</td>
<td>$315$</td>
</tr>
<tr>
<td>Osipenko$^{13}$</td>
<td>$-950.5$</td>
<td>$182$</td>
</tr>
<tr>
<td>Solid</td>
<td>$-974 \pm 40$</td>
<td>$163.1 \pm 631$</td>
</tr>
</tbody>
</table>

evaluated by extrapolating. As shown in Fig. 11, our data and reported Gibbs free energies of formation in LiCl-KCl eutectic melt have a same tendency to the atomic number of metal element in the chlorides, namely, as the atomic number of metal element in the chlorides is increased, the Gibbs free energy of formation of the chlorides in LiCl-KCl eutectic melt and that in solid is decreased. From these results, it was concluded that the apparent standard potentials of Cm$^{3+}$/Cm couple evaluated in the present study and those reported by Osipenko are reliable.

4. Conclusions

Electrochemical properties of curium in LiCl-KCl eutectic melt were investigated using the small electrochemical cell designed for the electrochemical measurements of a small amount of highly radioactive minor actinides. Before the measurements using curium samples, the accuracy for the data of electrochemical measurements using the small electrochemical cell was confirmed by the electrochemical measurements carried out in LiCl-KCl-CeCl$_3$ at 723 K.

Apparent standard potentials of Cm$^{3+}$/Cm couple in LiCl-KCl eutectic melt were evaluated in the temperature range of 718–823 K. The obtained apparent standard potentials had a linear tendency on temperature in this temperature range and were accordance with Osipenko’s data. Considering the result of comparing the apparent standard potentials of Pu, Np, Am and Cm and Gibbs free energy of formation of CmCl$_3$, it was concluded that the apparent standard potentials of Cm$^{3+}$/Cm couple evaluated in the present study and reported by Osipenko are reliable.

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References