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Determination of uranium and rare-earth metals separation coefficients in LiCl–KCl melt by electrochemical transient techniques

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Abstract

The main step in the pyrometallurgical process of spent nuclear fuel recycling is a molten salt electrorefining. The knowledge of separation coefficients of actinides (U, Np, Pu and Am) and rare-earth metals (Y, La, Ce, Nd and Gd) is very important for this step. Usually the separation coefficients are evaluated from the formal standard potentials of metals in melts containing their own ions, values obtained by potentiometric method. Electrochemical experiments were carried out at 723–823 K in order to estimate separation coefficients in LiCl–KCl eutectic melt containing uranium and lanthanum trichlorides. It was shown that for the calculation of uranium and lanthanum separation coefficients it is necessary to determine the voltammetric peak potentials of U(III) and La(III), their concentration in the melt and the kinetic parameters relating to U(III) discharge such as transfer and diffusion coefficients, and standard rate constants of charge transfer.

1. Introduction

Pyrometallurgical reprocessing of spent nuclear fuel is now considered as one of the more promising options of an innovative nuclear fuel cycle [1]. Electrorefining in molten chlorides is the main step in this process, where the actinides are separated from the lanthanides [2]. The determination of solution thermodynamic properties, including separation coefficients is crucial for the design of electrochemical cell. Usually separation coefficients are evaluated from the formal standard potentials of metals in melts containing their own ions, values obtained by potentiometric method. The present investigations deal with the study of thermodynamic properties of uranium and lanthanum solutions in molten LiCl–KCl eutectic system by electrochemical transient techniques [3,4].

Various investigations have been carried out on the electrochemistry of the U(III)/U couple in molten LiCl–KCl eutectic [5–16]. In all studies [5–14] oxide materials (glasses and alumina) were used in the construction of electrochemical cell, but our experiments showed that these materials interacted with LiCl–KCl–UCl_3 melt due to the high affinity of uranium to oxygen. Such an interaction can distort experimental results.

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2. Experimental

The electrochemical methods and cell used in present work were described previously [4]. Experiments were carried out in the temperature range 723–823 K. Electrochemical curves were determined with 1 mm diameter tungsten electrodes with respect to a glassy carbon rod as a quasi-reference electrode and vs. the silver–silver chloride reference electrode Ag/LiCl–KCl–AgCl (1 wt%). The glassy carbon plate or ampoule (SU-2000) served as the counter electrode. Potentials vs. silver–silver chloride reference electrode were converted to a Cl^-/Cl_2 reference electrode [15].

Most of our experiments was carried out in AlN or glassy carbon crucibles using tungsten electrode, and glassy carbon as quasi-reference and auxiliary electrodes. Therefore the melt was not in contact with oxide materials during experiments and it only was at the end of experiments that a silver–silver chloride reference electrode was immersed in the melt for a short duration for the determination of peak potential. Furthermore the melt was not re-used after this final potential determination.

Polagraphic-grade LiCl–KCl eutectic and $CdCl_2$ salts were obtained from the Anderson Physics Laboratory. Trichloride of uranium (dark purple colour) was prepared by the oxidation of U with $CdCl_2$ in LiCl–KCl melt at 773 K [16]. The preparation and electrochemical measurements were carried out in glovebox with high purity argon gas atmosphere with moisture and oxygen concentration <2.0 ppm.

3. Results and discussion

3.1. Study of uranium electrodeposition

The voltammetric curves of LiCl–KCl after UCl_3 addition to the melt (Fig. 1) are characterized by the presence of two electroreduction peaks, and two corresponding peaks of electrooxidation. According to the published data [17], we assumed that potentials of R_1, Ox_1 waves correspond to the electrode reaction

$$U(III) + 3e^- \rightarrow U. \tag{1}$$

Electrochemical behavior of prepeak R_1^I was discussed in papers [17,18]. Probably, this wave may be due to surface alloy formation. The prepeak becomes negligible compared to that of process (1) at a relatively high uranium concentration in the melt.

The electroreduction of U(III) to U(0) at tungsten electrode has been studied in details in our investigation [19]. It was found that $0.01 \leqslant v < 0.5$ V s^{-1} the discharge process is quasi-reversible, but increasing the sweep polarization rate from 0.5 to 2.0 V s^{-1} results in irreversible electroreduction.

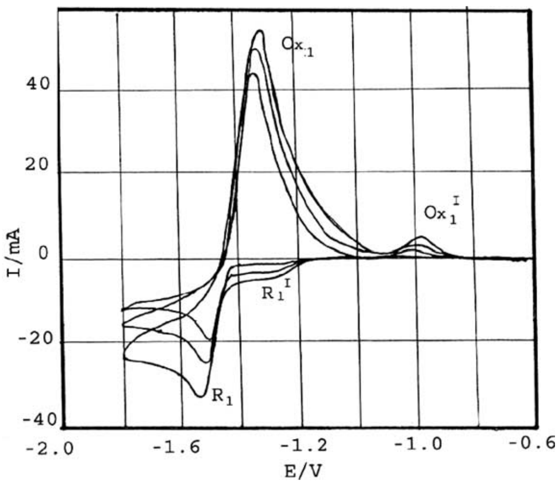

Fig. 1. Cyclic voltammetric curves at a tungsten electrode in LiCl–KCl–UCl_3 melt. Area: 0.322 cm^2. Sweep rates: 0.1; 0.2; 0.25 V s^{-1}. Temperature: 723 K. Concentration of UCl_3: 6.26×10^{-5} mol cm^{-3}. Reference electrode: silver–silver chloride.

The diffusion coefficients $D_{U(III)}$ were obtained in the temperature range 723–823 K, at polarization rate $v = 1.0$ V s^{-1}, utilizing the Delahay equation for irreversible electrochemical process [20]. The $D_{U(III)}$ coefficients determined at this polarization rate are described by the following empirical relation:

$$\log D_{U(III)} = -2.52 - 1796/T \pm 0.02. \tag{2}$$

The standard rate constants of charge transfer were determined by impedance spectroscopy method [21]. The diffusion coefficients $D_{U(III)}$ and standard rate constants of charge transfer at different temperatures are presented in Table 1.

The formal standard potentials $E^*_{U(III)/U}$ can be determined by means of the following equation [20], valid for irreversible process:

$$E^*_{U(III)/U} = E_p + RT/\alpha n_\alpha F[0.78 - \ln k_s + \ln(\alpha n_\alpha F v D_{ox}/RT)^{1/2}]. \tag{3}$$

Peak potentials at $v = 0.5$ V s^{-1} and obtained kinetic parameters ($D_{U(III)}$, k_s) values, and the resulting formal standard potentials are reported in Table 1.

Table 1
Experimental and calculated data for determination of $E^*_{U(III)/U}$ in LiCl–KCl melt

Temperature, K	723	773	823
E_p, V	−2.744	−2.722	−2.701
$D_{U(III)}$, cm^2 s^{-1}	1.02×10^{-5}	1.45×10^{-5}	1.97×10^{-5}
k_s cm s^{-1}	1.8×10^{-4}	2.6×10^{-4}	3.4×10^{-4}
$E^*_{U(III)/U}$, V	−2.541	−2.514	−2.487

From the data in Table 1 the following empirical equation for the formal standard potentials $E^*_{\mathrm{U(III)/U}}$ was obtained:

$$E^*_{\mathrm{U(III)/U}}/V = -(2.931 \pm 0.009) + (5.4 \pm 0.2) \times 10^{-4}\ T/\mathrm{K}. \qquad (4)$$

3.2. Electroreduction of uranium and lanthanum in LiCl–KCl melt

A typical voltammogram of the melt LiCl–KCl–UCl_3–$LaCl_3$ obtained on a tungsten electrode is presented in Fig. 2. The uranium peaks location (R_1^I and R_1) on the axis of potentials corresponded to those in individual LiCl–KCl–UCl_3 melt. An additional peak (R_2) appeared on the voltammogram. This peak is related to the process of lanthanum electrodeposition with transfer of three electrons

$$\mathrm{La(III)} + 3e^- \rightarrow \mathrm{La}. \qquad (5)$$

Voltammetric curve had no an extra peaks pointing to the formation of chemical compounds of uranium and lanthanum, which is in an agreement with the equilibrium U–La diagram [22].

It was found that the peak current of process (5) is directly proportional to the square root of the polarization rate at least up to 1.0 V s^{-1}. At the same time the peak potential after compensation of ohmic resistance shifted very slightly to the cathodic direction with increasing scan rate. The peak current of the electroreduction process (5) linearly depends on the $LaCl_3$ concentration. The peak potential shifted to the positive region in accordance with Berzins–Delahay's equation [20], which is valid for reversible process with formation of insoluble product

$$E_p = E^0 + (RT/nF)\ln fN - 0.854RT/nF, \qquad (6)$$

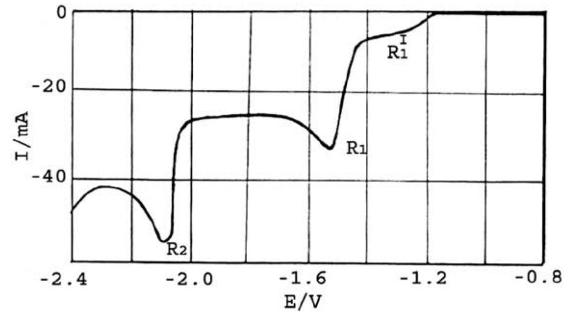

Fig. 2. Voltammogram at a tungsten electrode in LiCl–KCl–UCl_3–$LaCl_3$ melt. Area: 0.322 cm^2. Sweep rate: 0.5 V s^{-1}. Temperature: 723 K. Concentration of UCl_3: 6.26×10^{-5} mol cm^{-3}; concentration of $LaCl_3$: 3.08×10^{-5} mol cm^{-3} and reference electrode: silver–silver chloride.

where f is activity coefficients of La(III), which are constant due to low concentration; N is concentration of La(III) in mole fraction.

The slopes in coordinates E_p vs. $\ln N_{\mathrm{La(III)}}$ averaging 0.022–0.023 V decade^{-1} at different polarization rates (0.1–1.0 V s^{-1}) are in agreement with the theoretical value 0.021 V decade^{-1} expected for a three-electron process. Therefore this proves that the La(III)/La system is reversible up to polarization rate 1.0 V s^{-1}. This conclusion is in agreement with study [23], where it was found that electrochemical reaction (5) is rapid.

The magnitude of the formal standard potential is related to the value of the peak potential by the equation

$$E^*_{\mathrm{La(III)/La}} = E_p^{\mathrm{La}} - (RT/nF)\ln N + 0.854RT/nF. \qquad (7)$$

The experimental values for the $E^*_{\mathrm{La(III)/La}}$ were satisfactory fitted by the linear relation

$$E^*_{\mathrm{La(III)/La}}/\mathrm{V} = -(3.520 \pm 0.006) + (5.7 \pm 0.1) \times 10^{-4} T/\mathrm{K}. \qquad (8)$$

Our results for the formal standard potentials of $E^*_{\mathrm{La(III)/La}}$ (mole fraction scale) agree well with literature data [23]. Our values in temperature range 723–823 K are 7–9 mV more positive than in [23]. In our opinion, this difference can be explained by the formation of solid solutions of lanthanum in uranium [22], because the process (5) proceeds on the surface of uranium. Usually the value of depolarization due to formation of solid solutions with insignificant solubility does not exceed 20 mV [24].

3.3. Separation coefficients

The effectiveness of electrochemical separation of metals during their deposition at the cathode is commonly characterised by the value of distribution or separation coefficient θ, which is the quotient of the ratios of the mole fraction of the separated metals M_1 and M_2 in the electrolyte (N_1, N_2) and in the alloy (x_1, x_2)

$$\theta = N_2x_1/N_1x_2. \qquad (9)$$

The refined metal activity coefficient is close to unity ($\gamma_1 \rightarrow 1$). At a nonsymmetrical normalization of thermodynamic functions of diluted solutions formed on electrorefining, the activity coefficient is $\gamma_2 \rightarrow 1$ at $x_2 \rightarrow 0$. In our case the oxidation states of uranium and lanthanum are the same ($n_1 = n_2 = 3$), and the separation coefficients are determined by the difference of formal standard potentials of metals only [25]

$$\ln\theta^* = 3F(E_1^* - E_2^*)/RT. \qquad (10)$$

Using the temperature dependence of uranium formal standard potentials (4) and lanthanum (8) the following equation for separation coefficients was obtained

$$\ln\theta^* = -1.045 + 20509/T. \qquad (11)$$

As can be seen from Eq. (11), separation coefficients decreased at increasing temperature. Thus for effective separation of uranium from lanthanum, the lower temperatures should be preferred.

As discussed above for the system LiCl–KCl–UCl_3–$LaCl_3$, at polarization rate $v \geqslant 0.5\ \mathrm{V\,s^{-1}}$, an irreversible process for uranium discharge and reversible for lanthanum electrodeposition were determined. In this case the common equation for the separation coefficients of actinides (An) from lanthanides (Ln) is

$$\ln\theta^* = \frac{3F}{RT}\left[\left(E_{\mathrm{p}}^{\mathrm{An}} - E_{\mathrm{p}}^{\mathrm{Ln}}\right) + 0.78\frac{RT}{F}\left(\frac{1}{\alpha_1 n_1}\right) + \frac{RT}{F}\left\{\frac{1}{\alpha_1 n_1}\ln\left(\frac{\alpha_1 n_1 F v D_{\mathrm{An(III)}}}{RT}\right)^{1/2}\right\} - \frac{RT}{F}\left(\frac{1}{\alpha_1 n_1}\ln k_{S_1}\right) + \frac{RT}{n_2 F}\ln N_{\mathrm{Ln}} - 0.854\frac{RT}{n_2 F}\right]. \tag{12}$$

So, for determining separation coefficients of actinides from lanthanides it is necessary to know not only the thermodynamic parameters, but also the kinetic parameters.

The utilization of quasi-reference electrode instead of reference electrode is possible, because it is necessary to know the difference of potential peaks for the determination of separation coefficients using electrochemical transient techniques. This is especially very significant for chloride–fluoride and fluoride melts due to the absence of reliable reference electrode for these media.

4. Conclusions

Study of uranium and lanthanum electroreduction in LiCl–KCl–UCl_3–$LaCl_3$ melt showed that $LaCl_3$ does not influence on uranium electrochemical behavior. At the same time, due to the formation of lanthanum–uranium solid solution during electrodeposition of lanthanum on the uranium surface, some depolarization was observed. Empirical equation for separation coefficients of uranium from lanthanum was obtained by electrochemical transient techniques.

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