



## Original Article

## Electrochemical extraction of uranium on the gallium and cadmium reactive electrodes in molten salt

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## ABSTRACT

The electrochemical extraction of uranium in ternary low melting LiCl–KCl–CsCl eutectic on inert and reactive electrodes via different electrochemical techniques was investigated. It was established that the electrochemical reduction process of U(III) ions on the inert W electrode was irreversible and proceeded in one stage. On reactive liquid Ga and liquid Cd electrodes the reduction of uranium ions took place with the considerable depolarization with the formation of UGa<sub>2</sub>, UGa<sub>3</sub> and UCd<sub>11</sub> intermetallic compounds. Thermodynamic characteristics of uranium compounds and alloys were calculated. The conditions for the extraction of uranium from the electrolyte in the form of alloys on both liquid reactive electrodes via potentiostatic electrolysis were found.

## 1. Introduction

Nuclear energy is regarded as one of the few low carbon technologies that can meet future global energy demands, but concerns surrounding its safe use and spent fuel management remain a major challenge. Effective methods for spent fuel reprocessing and metal recovery must be available so as to minimize nuclear waste. A variety of molten salt solvents may be suggested as working media. High radiation stability and the absence of neutron moderators make these media particularly attractive for reprocessing high burn-up spent nuclear fuel (SNF) with short cooling time [1–5]. Pyrochemical reprocessing of SNF of the solid-fuel reactors in molten salts with electrochemical separation of fission products from fissile materials is one of the currently studied options. The electrolysis can be performed on inert or reactive electrodes. The intermetallic reaction process has two advantages; the first is that it prevents nuclear proliferation and the second is that the overall heat and radiation produced from the process is far less [6–10].

Molten salts can also be served as liquid fuel in molten salt reactors [11]. In this case, the amount of radioactive waste will be less, but they will still need to be recycled in the future. To successfully solve the problem of separating fissile materials from fission products, it is necessary to know their electrochemical and thermodynamic properties in molten salts.

Electrochemical behavior of uranium compounds in fused chlorides was reported in a number of works. Electroreduction of UCl<sub>4</sub> and UCl<sub>3</sub> in

molten LiCl–KCl eutectic was studied by different electrochemical methods. It was established that reduction of U(IV) ions proceeded in two steps involving transfer of one and three electrons, respectively. The diffusion coefficients and some thermodynamic properties of uranium compounds in the LiCl–KCl eutectic were determined [12]. The electrochemical behavior of oxygen-free uranium species was investigated on inert electrodes in molten chlorides by different electrochemical methods with the goal to obtain metallic uranium. Two redox peaks were observed on cyclic voltammograms, and these corresponded to two redox reactions, U(IV)/U(III) and U(III)/U, which were found to be reversible and quasi-reversible, respectively [13–18].

The electrochemical behavior of oxygen-free uranium ions in molten chlorides on reactive liquid metal electrodes was studied using various electrochemical techniques [19–31]. In some papers cadmium was considered as the material for the reactive electrode, mainly because of its physical and chemical properties. However, cadmium showed low separation factors (SF) for actinide-lanthanide couples. Aluminum or gallium was reported to be a promising alternative cathode material because of their large SF [32]. In addition, depending on the working temperature, aluminum can be either liquid or solid. It is known that the process of the electrochemical deposition of uranium on reactive cathodes is accompanied by the formation of alloys and proceeds with depolarization.

There are a sufficient number of publications in the literature concerning the electrochemical reduction of uranium in molten chlorides,

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however, the analysis of the presented results shows some differences in the reactions of cathodic reduction of uranium ions to metal, as well as in the formation of intermetallic compounds in molten alkali metal chlorides. There is also no comparative information on the completeness of extraction of fissile materials using reactive electrodes by electrolysis of molten electrolytes.

The main advantages of the LiCl–KCl–CsCl triple eutectic are the low melting point (536 K) and, as a consequence, the possibility of carrying experiments in a wide temperature range. In addition, the presence of cesium chloride increases the strength of the complex compounds of uranium in the melt (i.e. reduces its volatility at high temperatures).

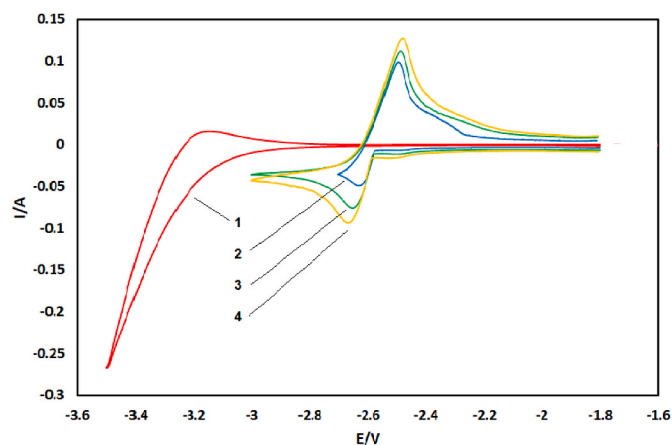
This work was devoted to the study of the mechanism of uranium deposition, electrochemical processes of its alloy's formation with the material of reactive electrodes, calculation of thermodynamic characteristics of uranium compounds and its alloys, and its completeness extraction from low melting triple LiCl–KCl–CsCl eutectic by stationary and non-stationary research methods.

## 2. Experimental

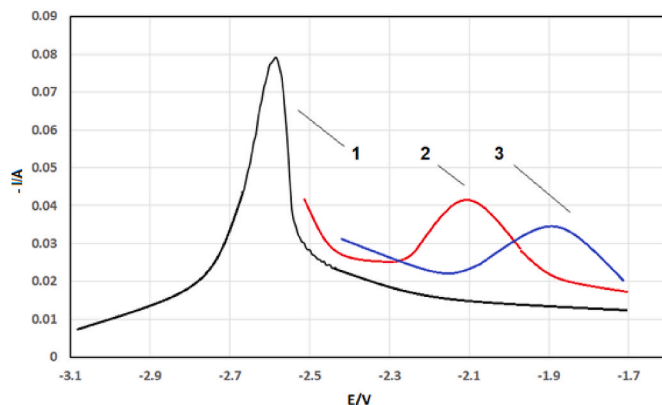
Anhydrous LiCl (Aldrich-Sigma 99.99%), KCl (JSC “Pikalevo alumina plant”, Russia 99.9%), CsCl (JSC “Pikalevo alumina plant”, Russia 99.95%), gallium metal (JSC “Pikalevo alumina plant”, Russia 99.9999%), cadmium metal (JSC “Pikalevo alumina plant”, Russia 99.995%) were used in experiments. All manipulations involving metallic uranium and uranium chloride were performed in an argon filled glovebox SPEKS GB02 (<1 ppm oxygen and <1 ppm moisture content).

Electrolytes containing uranium (III) chloride were prepared by holding molten LiCl–KCl–UCl<sub>4</sub> mixture in contact with uranium bars at 773 K for 4 h. Starting LiCl–KCl–UCl<sub>4</sub> mixture was obtained by dissolving a desired amount of uranium tetrachloride in the alkali chloride eutectic mixture. Uranium tetrachloride was synthesized by reacting uranium trioxide with hexachloropropene. All manipulations involving metallic uranium and uranium chlorides were performed in glove box. Electronic absorption spectra of the melts showed that uranium was present in the oxidation state of +3.

Electrochemical experiments were carried out in a standard quartz cell in the temperature range 653–983 K in an inert atmosphere. A three-electrode electrochemical cell contained working electrode (WE), counter electrode (CE) and reference electrode (RE) was introduced in this work for investigations of molten salts by cyclic voltammetry (CV), square wave voltammetry (SWV) and open circuit potentiometry (OCP). Voltammetric studies were carried out at various scan rates with compensation of the resistance of the electrochemical cell in all experiments. The resistance measurement was realized using an additional device, and then fixed on a potentiostat. Usually these values were in the range from 0.9 to 1.7 Ω. The solid working electrode was a 1 mm diameter tungsten wire which was immersed in the melt to a depth of 4–7 mm. The cathode surface area was determined after experiments. The liquid working electrodes were liquid gallium and cadmium (2–5 g) contained in a silica micro-crucible of 3.0–3.5 mm diameter. The preparation of U–Ga and U–Cd alloys was realized by electrolysis of LiCl–KCl–CsCl–UCl<sub>3</sub> melt directly in the electrochemical cell before the experiments. Preparation was performed in the galvanostatic mode. The resulting U–Ga and U–Cd alloys (dilute solutions) were the single-phase homogeneous liquids. The concentration of uranium in it did not exceed 0.35 wt% and therefore these solutions obey Henry's law [32]. Electrolysis current was equal to 5–10 mA, the duration of electrolysis was 50–80 min. Thin molybdenum wire (0.5 mm diameter) acted as the current conductor to liquid metal. The counter electrode was a 3 mm diameter glassy carbon rod. The measurements were made vs. the standard chlorine reference electrode [33]. Vitreous carbon crucibles were used to contain the electrolytes. Measurements were carried out using an AUTOLAB PGSTAT 302 N potentiostat/galvanostat with NOVA software package (version 1.11).



**Fig. 1.** Cyclic voltammograms of fused LiCl–KCl–CsCl eutectic (1 – red line) and LiCl–KCl–CsCl–UCl<sub>3</sub> solution (2 – blue line,  $\nu = 0.10 \text{ V s}^{-1}$ ; 3 – green line,  $\nu = 0.35 \text{ V s}^{-1}$ ; 4 – yellow line,  $\nu = 0.50 \text{ V s}^{-1}$ ) at 733 K. Working electrode: W ( $S = 0.31 \text{ cm}^2$ ).  $[\text{U(III)}] = 3.1 \cdot 10^{-2} \text{ mol kg}^{-1}$ .



**Fig. 2.** Square wave voltammetry curves of LiCl–KCl–CsCl–UCl<sub>3</sub> molten salt solution at 721 K. Pulse height: 25 mV; potential step: 1 mV; frequency: 12 Hz;  $[\text{U(III)}] = 2.8 \cdot 10^{-2} \text{ mol kg}^{-1}$ . WE – W (1 – black line); WE – Ga (2 – red line); WE – Cd (3 – blue line).

Uranium concentration in the melts and alloys was determined by atomic emission method on an OPTIMA 4300 DV spectrometer with inductively coupled plasma.

## 3. Results and discussion

The electrochemical extraction of uranium from molten LiCl–KCl–CsCl–UCl<sub>3</sub> solutions was investigated by cyclic and square wave voltammetry, as well as open circuit potentiometry in a wide temperature range. Cyclic voltammograms of fused LiCl–KCl–CsCl eutectic (1 – red line) and LiCl–KCl–CsCl–UCl<sub>3</sub> ( $3.1 \cdot 10^{-2} \text{ mol kg}^{-1}$ ) solution (2 – blue line,  $\nu = 0.10 \text{ V s}^{-1}$ ; 3 – green line,  $\nu = 0.35 \text{ V s}^{-1}$ ; 4 – yellow line,  $\nu = 0.50 \text{ V s}^{-1}$ ) at 733 K on W electrode was shown in Fig. 1. In the range of potentials from –1.8 to –3.6 V for the molten eutectic solvent (red line) only one peak of the reduction of alkali metal ions and one peak of its oxidation were recorded. After adding uranium trichloride to the melt in the potential scale from –1.7 to –3.0 V additional signals were appeared on cyclic voltammogram, Fig. 1 (2–4), which can be associated with the reactions of uranium deposition (–2.65 V) and its dissolution (–2.50 V). In addition, at the cathode potential about –2.40 V and the corresponding anode potential about –2.30 V, weak signals were recorded, which may be associated with the presence of some impurities in the electrolyte. No other redox signals were observed in

**Table 1**Apparent standard potentials of U(III)/U system and base thermodynamic characteristics of UCl<sub>3</sub> in molten LiCl–KCl–CsCl eutectic.

T (K)	$E_{U(III)/U}^*$ (V)	$\Delta G_{UCl_3}^*$ (kJ·mol <sup>-1</sup> )	$\Delta G_{UCl_3}^0$ (kJ·mol <sup>-1</sup> )	$\log \gamma_{UCl_3}$	$\gamma_{UCl_3}$
653	-2.670	-773.055	-718.952	-4.33	$4.62 \cdot 10^{-5}$
710	-2.628	-761.009	-706.891	-3.98	$1.03 \cdot 10^{-4}$
758	-2.593	-750.865	-696.748	-3.73	$1.84 \cdot 10^{-4}$
802	-2.561	-741.566	-687.801	-3.50	$3.11 \cdot 10^{-4}$
860	-2.519	-729.308	-675.702	-3.26	$5.48 \cdot 10^{-4}$
920	-2.475	-716.628	-663.438	-3.02	$9.44 \cdot 10^{-4}$
983	-2.429	-703.314	-650.454	-2.81	$1.54 \cdot 10^{-3}$

this potential range. Therefore, it can be concluded that the electrochemical reduction of U(III) ions to metal on the inert W electrode is a one-step process in molten LiCl–KCl–CsCl eutectic at 733 K. It was shown that the cathodic potential peak is not constant and shifts to more negative values with the increasing of scan rate and the cathodic peak current is directly proportional to the square root of the polarization rate. According to the theory of the cyclic voltammetry technique [34, 35] the redox system U(III)/U(0) is irreversible and proceeds in one stage. Square wave voltammetry was used to confirm the single step reduction of U(III) ions to metal on the solid tungsten electrode. Square wave curve recorded in LiCl–KCl–CsCl–UCl<sub>3</sub> ( $2.8 \cdot 10^{-2}$  mol kg<sup>-1</sup>) molten salt on W electrode (black line) at 721 K was presented in Fig. 2 (1). The voltammogram consists of a single Gaussian shape reduction peak and confirms that U(III)/U(0) redox process was carried out in a single step at the peak potential around  $-2.6 \pm 0.1$  V vs. Cl<sup>-</sup>/Cl<sub>2</sub> reference electrode. Taking into account the previously obtained data it can be assumed that the cathodic reaction of the electrochemical deposition of metallic uranium on inert solid electrode can be written as:



The apparent standard potential of the redox couple U(III)/U(0) was determined at several temperatures by OCP mode. A short cathodic polarization (15–30 s) with current 100–200 mA was applied in order to form in situ a metallic deposit of U on the W electrode, and then pseudo-equilibrium potential of the couple U(III)/U(0) was measured versus time. The apparent standard potential was determined using the Nernst equation:

$$E_{U(III)/U} = E_{U(III)/U}^* + \frac{RT}{nF} \ln X_{UCl_3} \quad (2)$$

being,

$$E_{U(III)/U}^* = E_{U(III)/U}^0 + \frac{RT}{nF} \ln \gamma_{UCl_3}, \quad (3)$$

where  $E_{U(III)/U}$  is the equilibrium potential of the system, V;  $E_{U(III)/U}^*$  is the apparent standard potential of the system, V;  $X_{UCl_3}$  is the concentration of uranium in mole fraction.

The experimental values can be satisfactorily described by the following linear equation obtained using the least squares fit with the confidence level of 0.95:

$$E_{U(III)/U}^* = -(3.147 \pm 0.005) + (7.3 \pm 0.1) \cdot 10^{-4} T \pm 0.004 \text{ V} \quad (4)$$

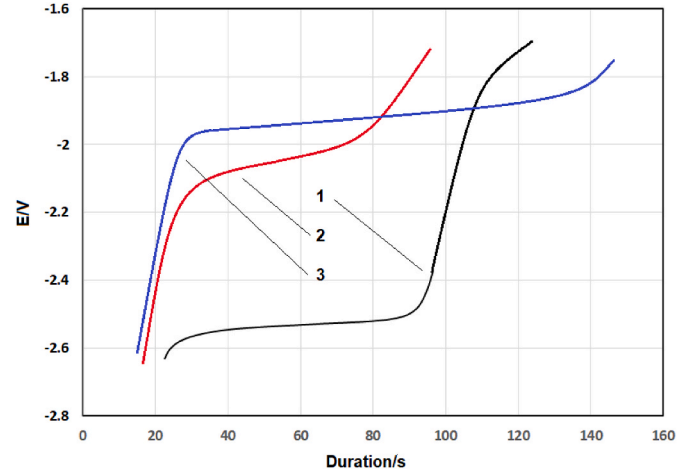
Thermodynamic properties of UCl<sub>3</sub> from the elements dissolved in LiCl–KCl–CsCl eutectic melt were calculated using Eq. (5):

$$\Delta G_{UCl_3}^* = -nFE_{U(III)/U}^* \quad (5)$$

$$\Delta G_{UCl_3}^* = -(911 \pm 4) + (0.21 \pm 0.02)T \pm 3.55 \text{ kJ} \cdot \text{mol}^{-1} \quad (6)$$

The examination of the temperature dependence of an apparent standard Gibbs energy change of UCl<sub>3</sub> formation allowed us to determine the enthalpy  $\Delta H^*$  and entropy  $\Delta S^*$  of this reaction. The plot of  $\Delta G_{UCl_3}^*$  as a function of temperature shows a linear dependence.

The activity coefficient of uranium trichloride in molten salt gives



**Fig. 3.** The potential–time dependences after a short cathodic polarization of different working electrodes in LiCl–KCl–CsCl–UCl<sub>3</sub> melts at 721 K. [U(III)] =  $2.8 \cdot 10^{-2}$  mol kg<sup>-1</sup>. Galvanostatic electrolysis: I = 100–200 mA; duration: 10–30 s.

1 – quasi-equilibrium potential of U(III)/U(0) couple  $-2.592$  V (WE – W); 2 – quasi-equilibrium potential of U–Ga alloy  $-2.096$  V (WE – Ga); 3 – quasi-equilibrium potential of U–Cd alloy  $-1.961$  V (WE – Cd).

information about the complexation of the uranium ions by the melt. The activity coefficients,  $\gamma$ , were calculated comparing the Gibbs energy of the formation  $\Delta G_{UCl_3}^*$ , (determined using OCP method) with the Gibbs energy of formation for solid pure compounds,  $\Delta G_{UCl_3}^0$ . The activity coefficient of UCl<sub>3</sub> at different temperatures was calculated by the following equation:

$$\log \gamma = \frac{\Delta G_{(exp)}^* - \Delta G_{(pure\ compounds)}^0}{2.303RT} \quad (7)$$

The standard Gibbs energy of formation for solid pure compounds was obtained from the thermochemical data published in the literature [35]. Activity coefficients of uranium (III) ions in molten LiCl–KCl–CsCl eutectic was calculated at different temperatures in the range 653–983 K and was describe by the following expression:

$$\log \gamma = 0.197 - \frac{2969}{T} \pm 0.02 \quad (8)$$

The values indicate a marked deviation from the ideal solution behavior, which indicates that U(III) ions form strong complexes with chloride ions from the melt. It is also observed from Table 1 that there is an increase of  $\gamma$  with the temperature; that is, U(III) ions are less solvated by molten chloride as the temperature increase.

For clearer understanding of the electrochemical reduction processes of U(III) ions on reactive electrodes leading to the formation of U–Ga and U–Cd intermetallic compounds, the cathode processes were investigated on Ga and Cd reactive electrodes in the ternary low-melting LiCl–KCl–CsCl eutectic by square-wave voltammetry. Additional cathodic current peaks were appeared on the SWV curves (red and blue

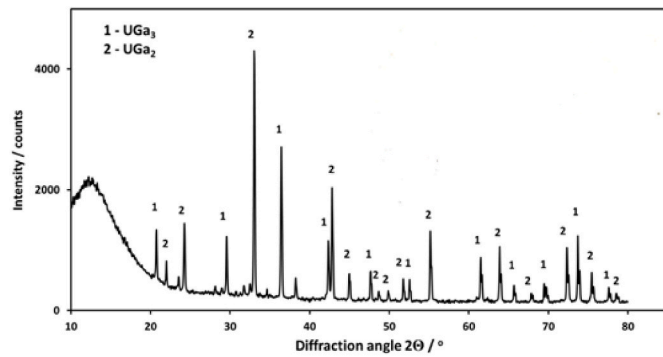


Fig. 4. XRD patterns of gallium cathode after electrolysis of LiCl–KCl–CsCl–UCl<sub>3</sub> melt at 736 K. [U(III)] = 3.1·10<sup>-2</sup> mol kg<sup>-1</sup>. Deposition potential: –2.1 V; duration: 360 min.

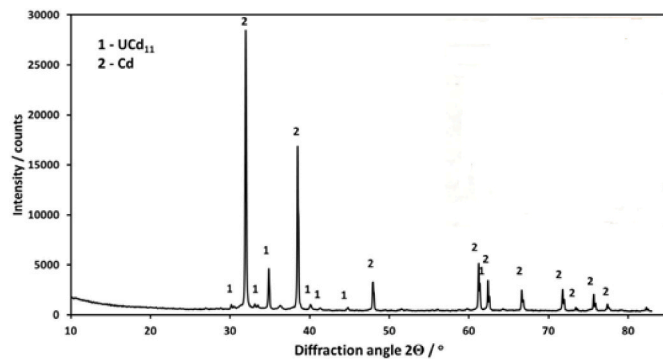


Fig. 5. XRD pattern of cadmium cathode after electrolysis of LiCl–KCl–CsCl–UCl<sub>3</sub> melt at 708 K. [U(III)] = 3.6·10<sup>-2</sup> mol kg<sup>-1</sup>. Deposition potential: –1.9 V; duration: 360 min.

lines, Fig. 2 (2, 3)) at more positive potentials than the deposition of metallic uranium. These potentials shift likely was a result of the formation of alloys or intermetallic compounds of uranium with the material of the reactive electrodes, similar to the observations reported in the literature [18–21,30]. The effect of the cathode material on the process of uranium extraction was illustrated in Fig. 3. Only one plateau was formed on the “potential – time” dependence recorded on the inert tungsten electrode after a short cathodic polarization. This plateau reflected deposition of metallic uranium during short galvanostatic electrolysis. The potential of the plateau was equal to –2.592 V at 721 K and corresponded to the equilibrium potential of U(III)/U(0) couple. Similar experiments at the reduction of U(III) ions on liquid Ga and liquid Cd reactive electrodes showed that deposition of uranium was proceeded with significant depolarization. The value of depolarization on gallium electrode was about 0.5 V and on cadmium electrode was about 0.6 V. The depolarization was associated with the alloy formation of uranium with the surface of electrode material during electrolysis and its value was depended on the nature of the active metal, i.e. in its location in the Periodic Table of Elements.

To identify the cathode deposits, potentiostatic electrolysis was carried out at the potentials of the current peaks of the reactive electrodes shown in Fig. 2. It is known that there are 3 intermetallic compounds (UGa<sub>3</sub>, UGa<sub>2</sub>, U<sub>2</sub>Ga<sub>3</sub>) on U–Ga phase diagram in the studied temperature range [36]. The potentiostatic electrolysis of the molten LiCl–KCl–CsCl–UCl<sub>3</sub> (3.1·10<sup>-2</sup> mol kg<sup>-1</sup>) solution was carried out for 4 h at a potential of –2.1 V vs. Cl<sup>-</sup>/Cl<sub>2</sub> reference electrode on a gallium reactive electrode. After electrolysis, the crucible contained a solid spongy mass of gray color, which could be easily broken into fragments. X-ray diffraction analysis showed that the deposit was mainly a mixture of two intermetallic compounds of gallium-uranium, UGa<sub>3</sub> and UGa<sub>2</sub>,

Table 2

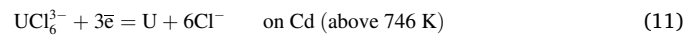
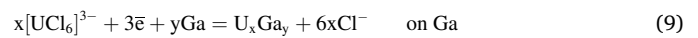
Activity coefficients of solid U in liquid Ga and liquid Cd metals in molten LiCl–KCl–CsCl eutectic at various temperatures.

T (K)	log γ <sub>U(Ga)</sub>	γ <sub>U(Ga)</sub>	log γ <sub>U(Cd)</sub>	γ <sub>U(Cd)</sub>
653	–7.78	1.63·10 <sup>-8</sup>	–4.17	6.75·10 <sup>-5</sup>
710	–7.04	9.13·10 <sup>-8</sup>	–3.48	3.29·10 <sup>-4</sup>
758	–6.49	3.17·10 <sup>-7</sup>	–2.98	1.04·10 <sup>-3</sup>
802	–6.05	8.73·10 <sup>-7</sup>	–2.58	2.63·10 <sup>-3</sup>
860	–5.54	2.83·10 <sup>-6</sup>	–2.11	7.76·10 <sup>-3</sup>
920	–5.08	8.16·10 <sup>-6</sup>	–1.68	2.06·10 <sup>-2</sup>
983	–4.66	2.16·10 <sup>-5</sup>	–1.29	5.05·10 <sup>-2</sup>

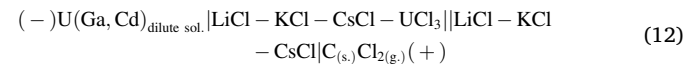
Fig. 4.

Potentiostatic electrolysis on a cadmium reactive electrode in molten LiCl–KCl–CsCl–UCl<sub>3</sub> (3.6·10<sup>-2</sup> mol kg<sup>-1</sup>) solution was carried out for 4 h at a potential of –1.9 V vs. Cl<sup>-</sup>/Cl<sub>2</sub> reference electrode at the temperature 708 K. It should be particularly noted that according to the U–Cd phase diagram [36], the existence of a single intermetallic compound UCd<sub>11</sub> is possible only at low temperatures. The solidified alloy was formed as a compact ingot. X-ray diffraction analysis of the deposit showed that the cathode product was consisted of a mixture of cadmium and an intermetallic compound UCd<sub>11</sub>, Fig. 5.

Based on the above results it can be concluded that the electrolysis of molten LiCl–KCl–CsCl–UCl<sub>3</sub> solutions on reactive electrodes leads to the formation of intermetallic compounds according to the following reactions:



A standard electrochemical cell was used to measure the equilibrium potentials of double U–Ga and U–Cd alloys by open circuit potentiometry:



It is known that when the concentration of the metal ions in the molten salts does not exceed (3–5)·10<sup>-2</sup> m.f. (dilute solutions) [33], then their activity coefficient can be considered as constant. The same statement is true for the dilute solutions of U–Ga and U–Cd alloys [32]. The value of the apparent standard potential of the alloy was described by the following expression [32]:

$$E_{\text{U}(\text{Me})} = E_{\text{U}(\text{Me})}^{**} + \frac{RT}{nF} \ln \frac{C_{\text{U}(\text{III})}}{X_{\text{U}(\text{Me})}}, \quad (13)$$

where Me = Ga or Cd;  $E_{\text{U}(\text{Me})}$  is the equilibrium potential of the alloy, V;  $E_{\text{U}(\text{Me})}^{**}$  is an apparent standard potential of the alloy, V;  $C_{\text{U}(\text{III})}$  is the concentration of uranium ions in solution in mole fraction;  $X_{\text{U}(\text{Me})}$  is the concentration of uranium in the alloy in atomic fraction.

The experimental values can be satisfactorily described by the following linear expressions:

$$E_{\text{U}(\text{Ga})}^{**} = -(2.746 \pm 0.005) + (6.3 \pm 0.1) \cdot 10^{-4} T \pm 0.005 \text{ V} \quad (14)$$

$$E_{\text{U}(\text{Cd})}^{**} = -(2.778 \pm 0.004) + (4.4 \pm 0.1) \cdot 10^{-4} T \pm 0.004 \text{ V} \quad (15)$$

The activity coefficients of solid γ-U in liquid Ga and liquid Cd metals were calculated according to the following expression [32]:

$$\log \gamma_{\text{U}(\text{Me})} = \frac{nF}{2.303RT} \left( E_{\text{U}(\text{III})/\text{U}}^* - E_{\text{U}(\text{Me})}^{**} \right), \quad (16)$$

where  $E_{\text{U}(\text{III})/\text{U}}^*$  is an apparent standard potential of U(III)/U couple, V;  $E_{\text{U}(\text{Me})}^{**}$  is an apparent standard potential of the alloy, V.

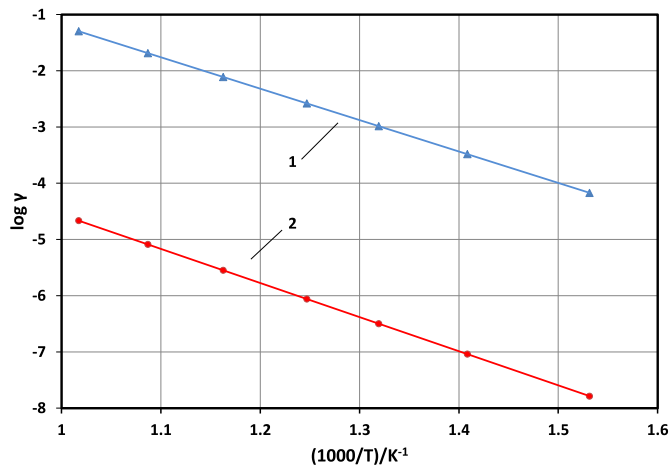


Fig. 6. The dependence of the activity coefficients of solid U in liquid Cd (1) and liquid Ga (2) vs. the temperature in molten LiCl–KCl–CsCl eutectic.

Variation of the activity coefficients of solid  $\gamma$ -U in liquid Ga and liquid Cd metals as a function of the temperature in molten LiCl–KCl–CsCl eutectic were described by the following linear equation obtained using the least squares fit with the confidence level of 0.95 and was presented in Table 2:

$$\log \gamma_{U(\text{Ga})} = 1.51 - \frac{6070}{T} \pm 0.10 \quad (17)$$

$$\log \gamma_{U(\text{Cd})} = 4.39 - \frac{5590}{T} \pm 0.14 \quad (18)$$

Low values of the activity coefficients show a strong interaction between components. The results of the studies, Table 2, showed that the value of the activity coefficients of uranium in liquid active metals strongly depend on the nature of the reactive cathode material, Fig. 6.

The results of investigations of the electrochemical behavior of uranium compounds in molten salts were put in the basis of the practical electrochemical extraction of uranium from molten LiCl–KCl–CsCl eutectic by potentiostatic electrolysis. For determination the degree of uranium extraction from molten salt, potentiostatic electrolysis was carried out at potentials of  $-1.9$  V on cadmium and  $-2.1$  V on gallium electrodes vs.  $\text{Cl}^-/\text{Cl}_2$  reference electrode at a temperature of 727 K for 12 h. Square wave voltammograms after different duration of potentiostatic electrolysis of LiCl–KCl–CsCl– $\text{UCl}_3$  solutions on liquid Ga (initial  $[\text{U}(\text{III})] = 1.63 \cdot 10^{-1} \text{ mol kg}^{-1}$ ) and liquid Cd (initial  $[\text{U}(\text{III})] = 1.57 \cdot 10^{-1} \text{ mol kg}^{-1}$ ) electrodes were presented in Fig. 7. The obtained

results made it possible to control the extraction and separation processes at different stages. It was found that the peak current of U(III) ions on SWV curves decreases with increasing electrolysis duration at both electrodes, indicating that the concentration of U(III) ions in molten salts was gradually decreased, which means that uranium is continuously extracted from the molten salt. When the electrolysis time reached 12 h, the peak signal was disappeared, indicating that the concentration of U(III) ions was below the detection limit. Salt samples were taken at regular intervals and analyzed for determination of the concentration of uranium in the melt during electrolysis. The degree of uranium extraction on liquid reactive electrodes was calculated using the following equation:

$$\eta = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100\% \quad (19)$$

The separation degree of uranium on liquid Ga and liquid Cd electrodes at different durations were estimated and summarized in Table 3. Based on these data, the uranium has been extracted from the molten salts and the high extraction degrees were obtained on Ga and Cd electrodes. They were above 97% according to the chemical analysis. Also the products were characterized by XRD methods as the stable intermetallic compound obtained by potentiostatic electrolysis.

#### 4. Conclusions

Stationary and non-stationary research methods were used for study

Table 3

Concentration and separation degree of uranium in molten salt during potentiostatic electrolysis.

Electrode	Duration (h)	Concentration ( $\text{mol} \cdot \text{kg}^{-1}$ )	Current (A)	Charge (C)	Separation degree (%)
Ga	0	0.163	0	0	0
	1	0.146	0.0423	152	10.42
	2	0.133	0.0385	429	18.40
	4	0.107	0.0309	875	34.36
	6	0.071	0.0205	1319	56.44
	8	0.055	0.0159	1778	66.26
	10	0.029	0.0083	2080	82.21
Cd	12	0.002	0.0006	2105	98.77
	0	0.157	0	0	0
	1	0.145	0.0414	149	7.64
	2	0.133	0.0386	426	15.29
	4	0.109	0.0316	880	30.57
	6	0.081	0.0234	1387	48.41
	8	0.061	0.0176	1895	61.15
10	0.037	0.0107	2281	76.43	
12	0.004	0.0011	2331	97.51	

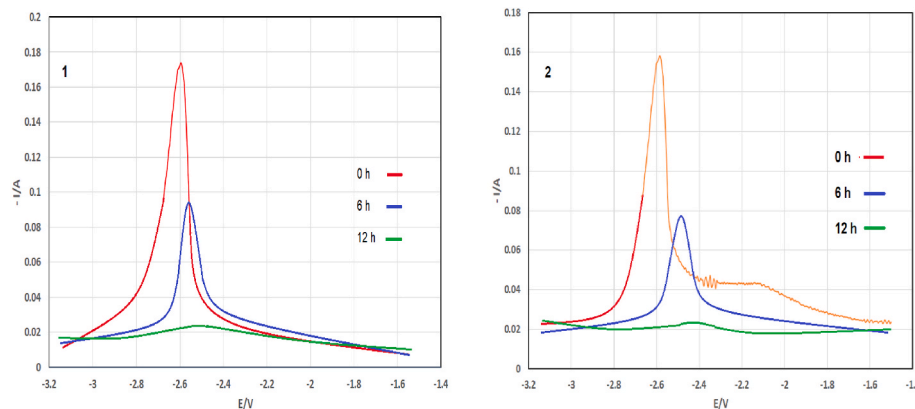


Fig. 7. Square wave voltammograms of U(III) ions registered on W electrode after potentiostatic electrolysis in molten LiCl–KCl–CsCl– $\text{UCl}_3$  solutions at 727 K. (1) – Ga liquid electrode; potential of deposition:  $-2.1$  V;  $[\text{U}(\text{III})] = 1.63 \cdot 10^{-1} \text{ mol kg}^{-1}$ ; (2) – Cd liquid electrode; potential of deposition:  $-1.9$  V;  $[\text{U}(\text{III})] = 1.57 \cdot 10^{-1} \text{ mol kg}^{-1}$ .

the electrochemical reduction of U(III) ions on inert W and reactive Ga, Cd electrodes in molten LiCl–KCl–CsCl eutectic in the temperature range of 673–973 K. The mechanism of the cathodic reaction during the electrochemical reduction of U(III) ions to the metal on the inert electrode was irreversible and took place in one stage. The extraction of uranium on the reactive electrodes took place with the considerable depolarization with the formation of  $UGa_2$ ,  $UGa_3$  and  $UCd_{11}$  intermetallic compounds. The conditions of the electrochemical production of alloys of a given composition were found. Thermodynamic properties of uranium compounds and alloys were calculated. The electrochemical extraction of uranium in the form of U–Ga and U–Cd alloys in ternary low melting LiCl–KCl–CsCl eutectic via potentiostatic electrolysis was determined. The obtained results may be of interest in the development of pyrochemical technology for reprocessing spent nuclear fuel of fast neutron reactors.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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