



Electrochemical separation of uranium from lanthanide (La, Eu, Gd) fluorides in molten LiCl-KCl

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ABSTRACT

The electrochemical behaviors of a series of lanthanide fluorides in molten LiCl-KCl were investigated, and the results on the separation of uranium from molten LiCl-KCl-UF₄-LaF₃-GdF₃-EuF₃ by electrolysis were provided. On the basis of the cyclic voltammetry and square wave voltammetry measurements, LaF₃ and GdF₃ undergo a three-electron reduction to metal in molten LiCl-KCl while the fluoride of europium (III) can only be reduced to europium (II) via single electron transfer. Compared with the relatively simple electrochemical behaviors of individual LaF₃, GdF₃ or EuF₃ in molten LiCl-KCl, the cyclic voltammograms of LaF₃, UF₄, GdF₃ and EuF₃ coexisting in the LiCl-KCl melt are complicated by the presence of F⁻ ions which cause the appearance of new peaks especially in the oxidation processes. Potentiostatic electrolysis of the LiCl-KCl-UF₄-LaF₃-GdF₃-EuF₃ melt using the tungsten sheet electrode resulted in the formation of metallic deposits that are composed of uranium as well as small amount of UO₂ according to the X-ray diffraction and scanning electron microscope analysis, suggesting that uranium can be successfully separated from lanthanide fluorides in the LiCl-KCl molten salt.

1. Introduction

Actinide fluorides can be employed as liquid fuel for the molten salt reactor. However, the amount of fission products keeps increasing as long as the reactor is in operation, and the liquid fuel eventually contains certain amount of fission products such as lanthanide fluorides, the presence of which significantly affects the occurrence of chain reactions of actinide fluorides. As a result, it is necessary to separate and recover actinides from the fission products such that the actinide fluorides can be further utilized as liquid nuclear fuel [1]. A series of investigations have been carried out on the recovery of actinides such as uranium from molten fluorides by using electrochemical methods in the past few decades. For example, the possibility for the electrochemical separation of uranium and thorium from lanthanides was assessed in FLiNaK using inert molybdenum electrode [2]. It was also demonstrated that uranium can be obtained either as metallic state or alloy in FLiNaK or LiF-CaF₂ depending on the nature of electrode [3,4].

Compared with molten fluorides, chloride melt such as LiCl-KCl is also a suitable molten medium because of its lower melting point, wider electrochemical window and structure material friendly character [5]. Experimental investigations have shown that uranium can be successfully separated from lanthanide chlorides in LiCl-KCl molten salt by electrolysis using inert Mo and stainless steel electrodes or reactive

electrodes such as aluminum and liquid cadmium [6–10]. Besides the results obtained in pure fluoride and chloride melts, molten salt systems that contain both chlorides and fluorides have attracted attention as well since the electrochemical behaviors of metal ions such as titanium, zirconium and niobium in molten chlorides are significantly influenced by the presence of fluoride ions.[11–13] The advantages of the LiCl-KCl melt make it an ideal medium for the separation of thorium and lanthanide fluorides by electrochemical methods.[14] For uranium, there is no systematic study regarding the electrochemical separation of uranium from lanthanide fluorides as high purity metal in the LiCl-KCl melt although the electrochemical behavior of UF₄ in molten LiCl-KCl has been reported.[15]

In this paper, we provide a detailed experimental study on the electrochemical separation of uranium from multiple lanthanide fluorides in the LiCl-KCl melt. The electrochemical behaviors of individual LaF₃, GdF₃ or EuF₃ in molten LiCl-KCl were investigated by using cyclic voltammetry (CV) and square wave voltammetry (SWV), and the influences of F⁻ ions on the electrochemical behaviors of LaF₃, GdF₃, EuF₃ and UF₄ coexisting in the same melt were also probed. Potentiostatic electrolysis was employed to demonstrate the feasibility for the separation of uranium from LiCl-KCl-UF₄-EuF₃-GdF₃-LaF₃, and the composition and morphology of the deposited products were characterized by X-ray diffraction (XRD) and scanning electron

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microscope (SEM).

2. Experimental details

2.1. Materials

LiCl, KCl (99%, Sigma-aldrich), LaF₃, GdF₃, EuF₃ (99.99%, Sigma-aldrich) and UF₄ were used without further purification. The LiCl-KCl eutectic was prepared according to the procedures reported previously. [16,17] The LiCl-KCl-LaF₃, LiCl-KCl-GdF₃, LiCl-KCl-EuF₃ and LiCl-KCl-UF₄ melts were prepared by mixing LiCl-KCl eutectic and LaF₃/GdF₃/EuF₃/UF₄ at room temperature followed by being heated and kept at 723 K for 2 h. The concentration of UF₄ is 1.00 wt% for the electrochemical behavior study and 5.00 wt% for the electrochemical separation study. The melts containing uranium and multiple lanthanide fluorides were obtained by adding certain amount of UF₄ and LnF₃ into the LiCl-KCl eutectic in the glovebox, and the mixture was heated to 723 K and kept at this temperature for 4 h.

2.2. Electrochemistry

The electrochemical experiments were performed on an apparatus that was described in detail elsewhere. [3,18-20] The apparatus (Scheme 1) is composed of an argon glovebox, an electric resistance furnace with stainless steel vessel and an off-gas treatment unit. The concentrations of O₂ and H₂O are less than 1 ppm inside the box. The molten salt mixture was loaded into a graphite crucible (50 ml) placed in the vessel, and it was heated to 723 K in a furnace (temperature deviation within ± 1 K) for all of the electrochemical studies.

A three-electrode system was used in all the electrochemical experiments. The working electrode for CV and SWV measurements is tungsten wire (99.9%, Φ1, Alfa-Aesar) which was cleaned by ultrasonic treatment in concentrated HNO₃ before use. Graphite rod (Φ5) and Ag/AgCl (4.76 mol% AgCl in LiCl-KCl) electrode were used as auxiliary and reference electrodes respectively. The Ag/AgCl reference electrode was made according to the literature. [15] For convenience, all of the potentials obtained from the experiments are referenced to the dynamic Li⁺/Li reduction potential in the same system unless otherwise specified. Tungsten sheet electrode (10 mm in width and 50 mm in length) was used as the deposition substrate for the potentiostatic electrolysis in molten LiCl-KCl. The active electrode surface area was determined by measuring the depth of the electrode immersed into the melt after each experiment. All of the electrochemical measurements were performed using the Autolab PGSTAT N302 (Metrohm) electrochemical workstation controlled by NOVA (version 1.11).

2.3. Sample analysis

Powder XRD spectrum was obtained on a X'Pert Pro 98 MPD diffractometer using Cu Kα₁ radiation. The morphology and element distribution of the deposits were analyzed by SEM (LEO 1530VP, Zeiss,

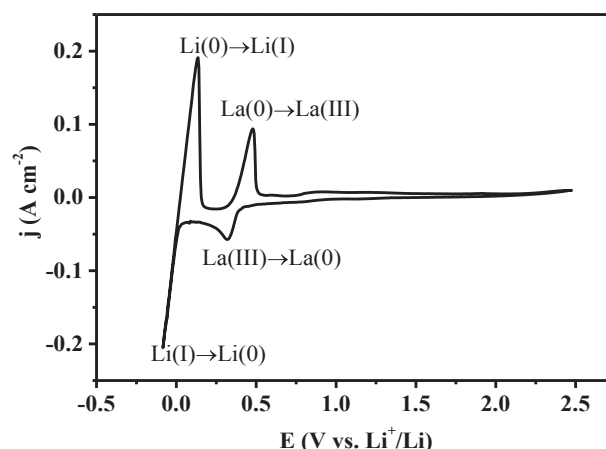


Fig. 1. Cyclic voltammogram of the LiCl-KCl-LaF₃ (2.00 wt%) melt at a scanning rate of 0.10 V s⁻¹ at 723 K. Working electrode: tungsten wire (Φ1).

Germany) and energy dispersive spectrometer (EDS). The raw deposits were rinsed by the ethanol/water (volume ratio: 1:1) mixture three times in order to remove the adhered chloride salts.

3. Results and discussion

3.1. Electrochemical behaviors of individual LaF₃, UF₄, GdF₃ or EuF₃ in molten LiCl-KCl

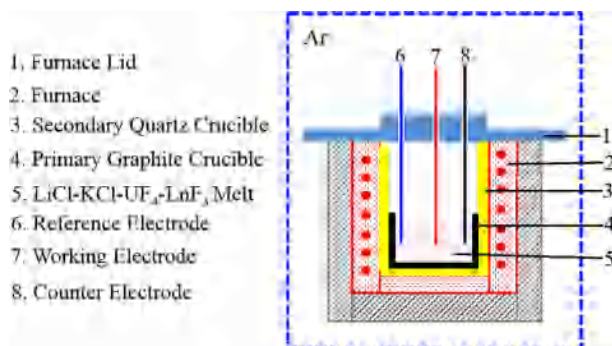
Fig. 1 shows the cyclic voltammogram of LiCl-KCl-LaF₃ at 723 K. A pair of redox peaks was observed at 0.32 and 0.48 V within the potential window (Li⁺/Li) range. Compared to the electrochemical behaviors of LaF₃ in molten fluorides and LaCl₃ in molten chlorides [16,21-23], this pair of redox peaks should arise from the La(III)/La(0) couple. The I_{pa}/I_{pc} ratio of 1.65 indicates that this three-electron redox reaction is quasi-reversible, which is consistent with the difference of 0.16 V between E_{pa} and E_{pc}. [24,25] A series of cyclic voltammograms were obtained by varying the potential scanning rate in the range of 0.10–0.30 V s⁻¹ (Figure S1), and the reduction peak current increases with the increase of scanning rate. Simultaneously, the peak potential slightly shifts to the negative direction due to ohmic drop. [22,26] The quasi-reversible character of such redox process involving deposition of metal ion and stripping of metal was observed in the LiCl-KCl-UCl₃, LiCl-KCl-PuCl₃ and LiCl-KCl-GdCl₃ systems as well. [27-29]

In order to confirm the assignment of the redox peaks in Fig. 1, SWV measurement was performed on the LiCl-KCl-LaF₃ system (Fig. 2). Similar to the results from the cyclic voltammogram, a one-step reaction was observed as indicated by the single reduction peak in the square wave voltammogram within the scanning range. The quasi-reversible character of this reaction is further confirmed by the fact that the peak potential is independent of the frequency [30]. For a quasi-reversible process, the number of exchanged electrons can be obtained according to equation (1) [29,31,32].

$$W_{1/2} = 3.52RT/nF \quad (1)$$

where W_{1/2} is the half width of the current peak which can be determined by curve fitting, R is the universal gas constant, T is the temperature in K, n is the number of exchanged electrons, F is the Faraday constant. The value of n was calculated to be 2.73 according to equation (1), which confirms that the number of exchanged electrons for the redox reactions involved in the LiCl-KCl-LaF₃ system is 3. As a result, La(III) fluoride undergoes a three-electron reduction to metallic lanthanum in LiCl-KCl. This is similar to the electrochemical behaviors of La(III) in LiCl-KCl [16,21,22] and FLiNaK melts [23] where one-step reduction mechanism was established as well.

The electrochemical behaviors of GdF₃, EuF₃ and UF₄ in LiCl-KCl



Scheme 1. Electrochemical experimental apparatus.

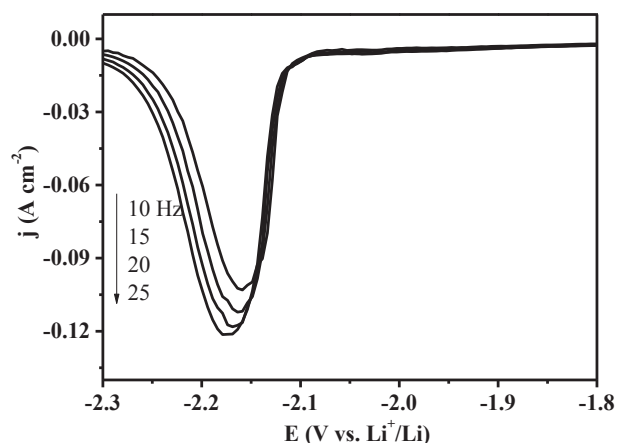


Fig. 2. Square wave voltammograms of the LiCl-KCl-LaF₃ (2.00 wt%) melt recorded at different frequencies at 723 K (Amplitude: 10 mV; step potential: 5 mV). Working electrode: tungsten wire (Φ 1).

were also studied, and the results (Table 1) are similar to those reported previously.[15,33]

3.2. Electrochemical behaviors of LaF₃, UF₄, GdF₃ and EuF₃ coexisting in molten LiCl-KCl

A key factor for the successful separation of uranium and lanthanide by using electrochemical method is the difference between the reduction potentials of the corresponding redox couples. It has been demonstrated that two steps are involved in the reduction from U(IV) to U(0), and the U(III)/U(0) couple is directly associated with the formation of metallic uranium. The reduction potential of U(III)/U(0) becomes more negative due to the decrease in U(III) concentration as electrolysis continues, and the uranium and lanthanide ions start to codeposit on the cathode when the reduction potential of U(III)/U(0) approaches that of Ln(III)/Ln(0). According to the results reported before,[34] the difference of the reduction potentials before and after electrolysis for a certain couple depends on the separation rate (η) as described by the following equation:

$$\Delta E = E_{\text{initial}} - E_{\text{final}} = \frac{RT}{nF} \ln \frac{\alpha_{\text{initial}}}{\alpha_{\text{final}}} = \frac{RT}{nF} \ln \frac{1}{1 - \eta} \quad (2)$$

where ΔE is the difference of reduction potentials before and after electrolysis, T , R and F are the same as those in equation (1). α_{final} and α_{initial} are the molality of the metal ion before and after electrolysis. The separation rate (η) is defined by equation (3).

$$\eta = 1 - \frac{\alpha_{\text{final}}}{\alpha_{\text{initial}}} \quad (3)$$

According to equation (2), ΔE should be larger than 0.143 V in theory in order to obtain a separation rate more than 99.99%.

Compared with the studies regarding the electrochemical separation of actinide and lanthanide chlorides in molten chlorides,[8-10] no systematic study has been carried out on the separation of uranium and

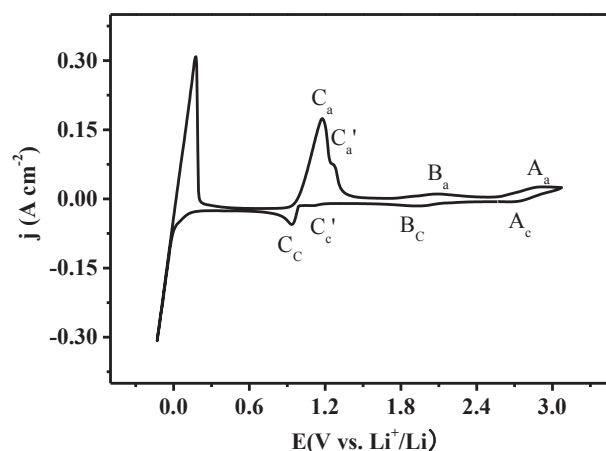


Fig. 3. Cyclic voltammogram of the LiCl-KCl-UF₄ (1.00 wt%)-EuF₃ (1.00 wt%) melt at a scanning rate of 0.10 V s⁻¹ at 723 K. Working electrode: tungsten wire (Φ 1).

lanthanide fluorides coexisting in LiCl-KCl molten salt, which could reveal some difference from the behaviors of individual ions due to the presence of additional fluoride ions as found in other systems. [35,36] As a result, the electrochemical behaviors of UF₄ and EuF₃ coexisting in molten LiCl-KCl were first studied. Fig. 3 shows the cyclic voltammogram of molten LiCl-KCl-UF₄-EuF₃ at a scanning rate of 0.10 V s⁻¹ at 723 K, and three redox peaks located at 2.73/2.87 V, 1.88/2.09 V and 0.92/1.18 V (vs. Li⁺/Li) were observed. Based on the results listed in Table 1, the A_c/A_a, B_c/B_a and C_c/C_a couples are readily assigned to the Eu(III)/Eu(II), U(IV)/U(III) and U(III)/U(0) couples respectively. In addition to these peaks, an additional shoulder labeled C_a' appears at 1.27 V which was not observed in LiCl-KCl-EuF₃ and very weak in the LiCl-KCl-UF₄ melt.[15,33] To understand the origination of the C_a' peak, the cyclic voltammogram of LiCl-KCl-UF₄-LiF was recorded in which the molar concentration of LiF is three times as much as EuF₃ in LiCl-KCl-UF₄ (1.00 wt%)-EuF₃ (1.00 wt%). It can be found that the intensity of the C_a' peak (1.26 V in Figure S2) is significantly enhanced due to the increase in the amount of free F⁻ ions provided by LiF added into the LiCl-KCl-UF₄ melt, suggesting that the appearance of C_a' should result from the formation of UF_xCl_{6-x}²⁻ that are in equilibrium with F⁻ and UCl₆²⁻ ions.[37] It should be noted that the intensity of the C_a' peak in Fig. 3 is lower than that in Figure S2, which is due to the fact that the free F⁻ ions provided by EuF₃ is less than LiF. Different from the C_a' peak, the corresponding reduction peak C_c' is very weak and observed at 1.10 V. Apart from the C_c'/C_a' peaks, the cyclic voltammogram of molten LiCl-KCl-UF₄-EuF₃ resembles the sum of LiCl-KCl-EuF₃ and LiCl-KCl-UF₄. Unlike U(IV) that can be eventually reduced to U(0) in LiCl-KCl, Eu(III) can only be reduced to Eu(II) while further reduction to Eu(0) is impossible in the same molten salt since the reduction potential of Eu(II)/Eu(0) is out of the potential window. As a result, the presence of EuF₃ has negligible effect on the reduction of UF₄ to metallic uranium on tungsten electrode in molten LiCl-KCl.

GdF₃ was then added into the LiCl-KCl-UF₄-EuF₃ melt, and the

Table 1

Reduction peak potentials (vs. Li⁺/Li) of individual LaF₃, GdF₃, EuF₃ or UF₄ in LiCl-KCl melt.

electrode reaction	U(IV) + e → U(III) (1) U(III) + 3e → U(0) (2)	La(III) + 3e → La(0)	Gd(III) + 3e → Gd(0)	Eu(III) + e → Eu(II)
reduction potential/V	1.96 (1), 0.95 (2) [-1.58 (1), -0.62 (2)] ^a	0.32	0.38 (-2.18 ^b)	2.75 (0.14 ^b)
reversibility	reversible (1) quasi-reversible (2)	quasi-reversible	quasi-reversible	reversible

^a In reference to Ag/AgCl (5 mol%), from Ref. [15].

^b In reference to Ag/AgCl (5 mol%), from Ref. [33].

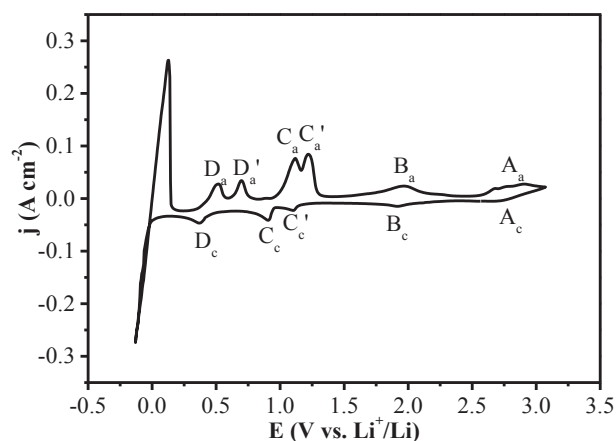


Fig. 4. Cyclic voltammogram of the LiCl-KCl-UF₄ (1.00 wt%)-EuF₃ (1.00 wt%)-GdF₃ (0.15 wt%) melt at a scanning rate of 0.10 V s⁻¹ at 723 K. Working electrode: tungsten wire (Φ1).

resulting cyclic voltammogram is shown in Fig. 4. The redox peaks A_c/A_a, B_c/B_a and C_c/C_a due to the Eu(III)/Eu(II), U(IV)/U(III) and U(III)/U(0) couples are close in position to the corresponding peaks in Fig. 3, suggesting these processes are not significantly influenced by the addition of GdF₃. The additional C_c'/C_a' peaks also exist in Fig. 4 but with higher intensities (vs. C_c/C_a), indicating that GdF₃ can serve as a F⁻ source as well although the amount of free F⁻ ions provided by GdF₃ is different from that provided by EuF₃. The most notable difference between Figs. 3 and 4 is the region between Li(I)/Li(0) and U(III)/U(0) where the gadolinium related peaks appear. The D_c/D_a peaks at 0.37 and 0.51 V can be readily assigned to the Gd(III)/Gd(0) couple by comparison with the data in Table 1. In addition, a new oxidation peak at 0.71 V (D_a') appears on the positive side of the peak arising from Gd(0) → Gd(III) (D_a) with equal intensity. This peak was not observed in the cyclic voltammogram of LiCl-KCl-GdF₃-EuF₃ (Figure S3), suggesting that it should be related to the presence of UF₄ in the molten salt. Since no additional peak was observed between the Gd(0) → Gd(III) and U(0) → U(III) peaks in the cyclic voltammogram of LiCl-KCl-UCl₃-GdCl₃, [38] it is unlikely that the D_a' peak at 0.71 V arises from the stripping of gadolinium from alloys such as Gd-U alloy. Instead, formation of the GdF_xCl_{6-x}³⁻ [39] ions should be responsible for this additional feature as confirmed by the increase of the D_a' peak intensity when LiF was added into the LiCl-KCl-GdF₃-EuF₃ melt (Figure S4). Note that the D_a' peak in Figure S4 (0.65 V) is 0.06 V lower than that in Fig. 4, which can be attributed to the formation of multiple GdF_xCl_{6-x}³⁻ ions with different numbers of coordinated F⁻ as observed in the chromium system. [35] As for the reduction counterpart of D_a', it most likely overlaps with peak D_c, and therefore not resolved in the experiment. On the basis of above analysis, the gap between the reduction potentials of U(III)/U(0) and Gd(III)/Gd(0) is 0.53 V, suggesting uranium can be well separated from gadolinium in molten LiCl-KCl-UF₄-EuF₃-GdF₃ according to equation (2).

Fig. 5 shows the cyclic voltammogram of U(IV), Eu(III), Gd(III) and La(III) fluorides coexisting in the LiCl-KCl melt. Besides the peaks of the Eu(III)/Eu(II), U(IV)/U(III), U(III)/U(0) and Gd(III)/Gd(0) couples, a new reduction peak (E_c) that is slightly negative to the Gd(III)/Gd(0) peak (D_c) appears at 0.32 V, and it is due to the reduction of La(III) to La(0). It is worth noting that the C_a'/C_c' peaks are even more intense than C_a/C_c in comparison to the relative intensities shown in Fig. 3 as more F⁻ ions can be provided by LaF₃ and GdF₃ when they were both added to the LiCl-KCl-UF₄-EuF₃ melt, which further confirms that the UF_xCl_{6-x}²⁻ ions are responsible for the appearance of the C_a'/C_c' peaks. The difference between the reduction potentials of La(III)/La(0) and U(III)/U(0) is 0.63 V, even larger than that between Gd(III)/Gd(0) and U(III)/U(0). Therefore, it is theoretically feasible to separate uranium from the

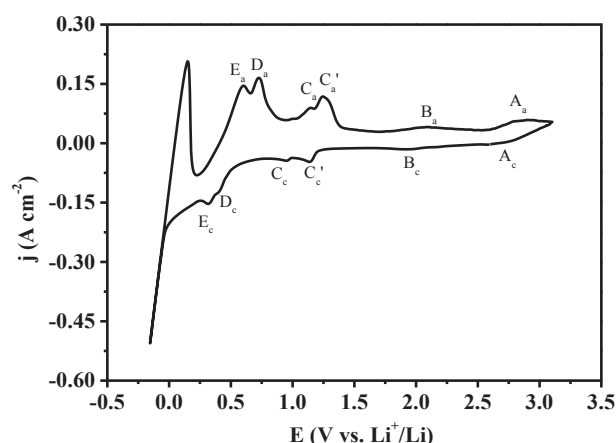


Fig. 5. Cyclic voltammogram of the LiCl-KCl-UF₄ (1.00 wt%)-EuF₃ (1.00 wt%)-GdF₃ (0.15 wt%)-LaF₃ (0.15 wt%) melt at a scanning rate of 0.10 V s⁻¹ at 723 K. Working electrode: tungsten wire (Φ1).

LiCl-KCl-UF₄-EuF₃-GdF₃-LaF₃ melt by electrolysis.

3.3. Electrochemical separation of uranium from molten LiCl-KCl-UF₄-EuF₃-GdF₃-LaF₃

On the basis of the electrochemical behaviors of uranium and some lanthanide fluorides that coexist in the LiCl-KCl melt, potentiostatic electrolysis was carried out at 0.75 V (vs. Li⁺/Li). Fig. 6 shows the variation of current versus the electrolysis time. At the beginning, the current sharply decreases from 560 to 270 mA due to the formation of uranium nucleus on the surface of tungsten sheet electrode that was used as the deposition substrate. The current then gradually increases to 600 mA during the next 600 s as a result of the fact that the active surface area of the electrode becomes larger as more and more metal particles are deposited on the tungsten sheet. At the end of the electrolysis process, the tungsten sheet was immediately removed from the molten electrolyte, and cooled down to room temperature in an argon glovebox. The black raw products deposited on the tungsten sheet electrode is shown in the inset of Fig. 6. A small amount of purple species was found on the surface of the deposits, which are due to U(III) species resulting from the reaction between metallic uranium and U(IV) in the LiCl-KCl melt. [40-42]

The XRD spectrum (Fig. 7) of the deposits after salt removal reveals

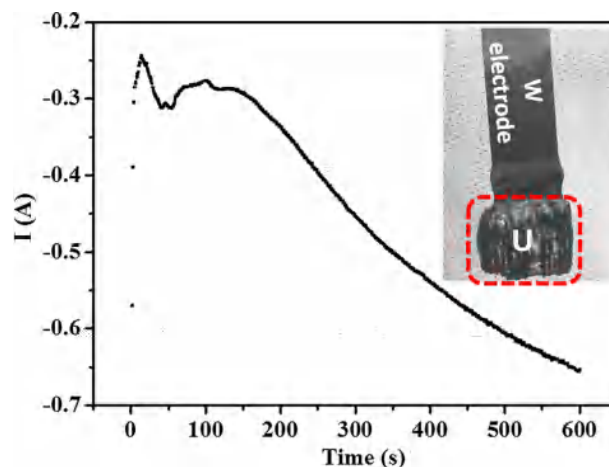


Fig. 6. Chronoamperogram for uranium deposition from LiCl-KCl-UF₄ (5.00 wt%)-EuF₃ (1.00 wt%)-LaF₃ (0.15 wt%)-GdF₃ (0.15 wt%) at 0.75 V (vs. Li⁺/Li) on the tungsten sheet (area immersed in the melt: 1.0 cm²) at 723 K. The image of the deposited products is shown in the red rectangle in the inset.

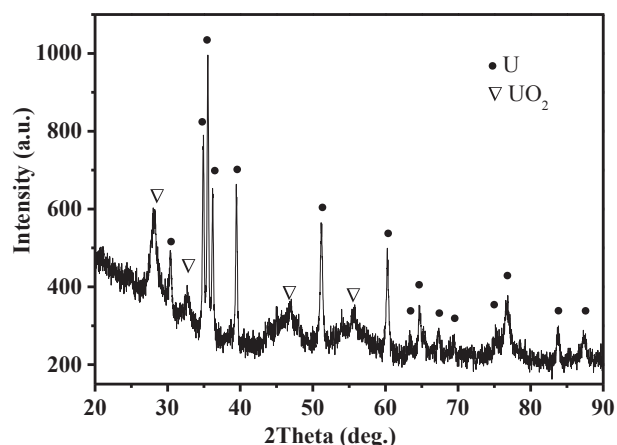


Fig. 7. XRD pattern of the deposits on the tungsten sheet after electrolysis of the LiCl-KCl-UF₄ (5.00 wt%)-EuF₃ (1.00 wt%)-GdF₃ (0.15 wt%)-LaF₃ (0.15 wt%) melt.

the presence of two sets of peaks. The major diffraction peaks can be well indexed to metallic uranium (PDF# 24-0748), and the other set of peaks with lower intensities results from UO₂ which is presumably formed via the oxidation of metallic uranium during the salt removal process. No diffraction peak due to europium, gadolinium and lanthanum was found in the same XRD spectrum, suggesting that uranium can be separated as metallic state without contamination from detectable lanthanides.

The SEM images of the electrolysis products are shown in Fig. 8a and 8b, which reveal the formation of irregular aggregations of metallic uranium. According to the results from the mapping image and EDS spectrum (Fig. 8c and d), uranium is the only metal element in the explored region, and it is homogeneously distributed. The presence of fluorine in the EDS spectrum is mainly due to the residual fluorides that are not easily soluble in water. Both the XRD and SEM results demonstrate that the deposited uranium is not contaminated by gadolinium, europium and lanthanum, and it is therefore feasible to obtain high

purity uranium from the LiCl-KCl-UF₄-EuF₃-GdF₃-LaF₃ melt by using electrochemical method.

4. Conclusions

The feasibility for the electrochemical separation of uranium from molten LiCl-KCl containing UF₄, LaF₃, GdF₃ and EuF₃ was investigated. According to the CV and SWV measurements, LaF₃ and GdF₃ can be reduced to the corresponding metals via one-step reduction while only the redox peaks of the Eu(III)/Eu(II) couple were observed for europium fluoride. U(IV) fluoride is reduced to metallic uranium via a two-step process mediated by U(III). Addition of EuF₃ into the LiCl-KCl-UF₄ melt resulted in the appearance of additional features in the cyclic voltammogram due to the influence of F⁻ ions on the coordination environment of the uranium ions. Such effect also accounts for the observation of the new oxidation peak when GdF₃ was added into the LiCl-KCl-UF₄-EuF₃ melt. The reduction processes of UF₄, LaF₃, GdF₃ and EuF₃ coexisting in LiCl-KCl are not significantly affected in comparison to those of individual metal fluorides.

By applying a suitable voltage, uranium can be separated from the LiCl-KCl-UF₄-EuF₃-LaF₃-GdF₃ molten mixture and deposited as metal on the tungsten sheet electrode. The XRD results show that the deposits are mainly metallic uranium with small amount of uranium oxide while no lanthanides were detected, which is also consistent with the SEM analysis. The experimental results demonstrate that it is feasible to separate uranium from lanthanide fluorides in molten chloride as metallic state with high purity, which could serve as an alternative route for the reprocessing of fluoride based nuclear fuel by electrochemical methods.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgments

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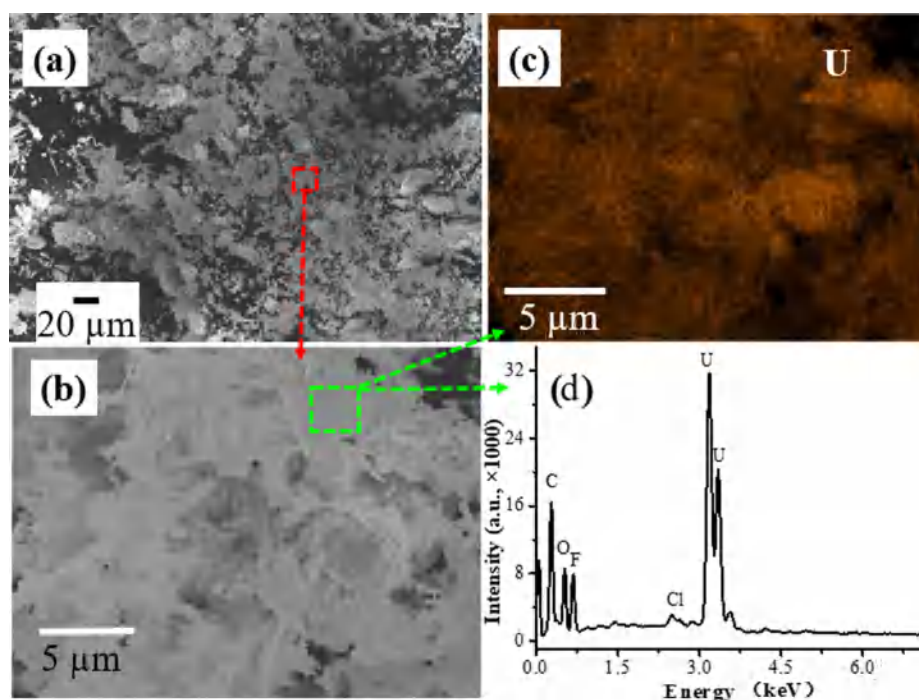


Fig. 8. (a) SEM image of the deposited products after being rinsed by water/ethanol mixture, (b) SEM image of the region inside the red square in (a), (c) EDS mapping image of the region inside the green square in (b), (d) EDS analysis of the region inside the green square in (b).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.116227>.

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