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## Study on the electrodeposition of uranium in chloride molten salt

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This study focuses on the recovery of  $UO_2$  from oxide spent fuel using electrodeposition.  $U_3O_8$  was used as the initial material and dissolved in  $NaCl-2CsCl$  using  $NH_4Cl$  at high temperatures by means of chlorination reaction. The electrolysis process was conducted using a three-electrode system to investigate the effects of cathode material and diameter, electrolysis temperature, electrolysis time, electrolysis voltage, and uranium concentration in the molten salt on the electrolysis reaction. By optimizing the electrolysis conditions, pure  $UO_2$  with a recovery efficiency of 97% was obtained, and the products were characterized using XRD, SEM-EDS, ICP-AES and XPS. It was found that within the scope of this experiment, increasing the cathode diameter, extending the electrolysis time, and increasing the reduction voltage appropriately all led to an improvement in the recovery efficiency of the electrolysis reaction, while other conditions had minimal effect on the reaction. Furthermore, doping of the electrolyte system was performed by adding La, Ce and Nd elements, while the removal of La showed good purification effects, with a maximum decontamination factor of 119. Furthermore, the system showed good purification effects for Nd, with a decontamination factor of 57.

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## 1 Introduction

Nuclear energy is an important clean energy source that can effectively replace fossil fuel power generation, thereby reducing greenhouse gas emissions. In the current stage of sustainable development, the main issues related to nuclear energy include how to maximize the utilization of uranium resources and how to minimize nuclear waste.<sup>1</sup> Dry reprocessing for spent fuel, based on molten salt electrolysis, offers unique advantages such as small-scale operations, low waste generation, high radiation tolerance, a simple process, and effective prevention of nuclear proliferation.<sup>2</sup> It is currently considered one of the most effective methods for spent fuel reprocessing.

Dry reprocessing of spent fuel is one of the critical steps in the nuclear fuel cycle. In recent years, dry reprocessing based on molten salt electrolysis has been considered one of the most effective methods for spent fuel reprocessing due to its unique advantages. The United States has developed molten salt electrorefining technology for spent metal fuel, while Russia has developed molten salt electrodeposition technology for metal oxide spent fuel. The dry reprocessing for oxide spent fuel based on molten salt system electrodeposition technology has a high

maturity.<sup>3</sup> In comparison to electrolytic refining in molten salt, the electrodeposition process is simpler, and the prepared mixed oxide of uranium and plutonium can be applied in the MOX of fast reactors.

Due to the high efficiency, conductivity, and selectivity, molten salt electrolysis method has become a commonly method for depositing metals, purifying metals and synthesizing functional materials in recent years.<sup>4-9</sup> In the electrochemical deposition process, the dissolution and chlorination of oxides are key steps. Effectively chlorinating uranium oxide compounds in molten salt and reducing its corrosiveness to the device remains a significant challenge. For example, the Russian Research Institute of Atomic Reactors (RIAR) used  $Cl_2$  as a chlorinating agent,<sup>10</sup> which generates a large amount of toxic and harmful exhaust gases. On the other hand,  $Cl_2$  as a chlorinating agent, can generate highly volatile  $UCl_5$  and  $UCl_6$  at high temperatures, which may lead to partial loss of uranium.<sup>11</sup>  $UO_2$  exhibits low solubility in molten  $MgCl_2$  or  $CaCl_2$ .<sup>12</sup> Thermodynamic estimates suggest that the chlorination of  $UO_2$  is difficult in the  $ZrCl_4-LiCl-KCl$  molten salt system.<sup>13</sup> Accordingly, the aim of this experiment was to explore the recovery efficiency of  $UO_2$  from spent oxide fuel. First,  $UO_2$  was oxidized to  $U_3O_8$  in an air environment.

Compared to  $NaCl-LiCl$  and  $NaCl-KCl$  eutectic salt,  $NaCl-2CsCl$  has some advantages of higher solubility for  $Cl_2$  and a lower melting point.<sup>4,14</sup> Therefore,  $NaCl-2CsCl$  was chosen as reaction medium in the electrodeposition process. Additionally, the optimal parameters obtained from this work can be applied

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to the engineering field of scale expansion in the future. Considering the aspect of engineering applications,  $\text{U}_3\text{O}_8$  obtained from spent fuel after high-temperature oxidation, and the dissolution of  $\text{U}_3\text{O}_8$  was faster than that of  $\text{UO}_2$  under the air atmosphere.<sup>15</sup> Therefore,  $\text{U}_3\text{O}_8$  was used as a reactant to react with  $\text{NH}_4\text{Cl}$  to generate  $\text{UO}_2\text{Cl}_2$ .<sup>11</sup> Currently, this method proves to be effective for dissolving and chlorinating uranium oxide compounds. After cooling, the mixture was transferred to a glove box for electrolysis, leading to the production of  $\text{UO}_2$ . Herrmann conducted electrolytic reduction refining on oxide spent fuel to recover metal U,<sup>16</sup> and the decontamination factors for neodymium (Nd), cerium (Ce), and lanthanum (La) were only 25, 11, and 24.<sup>17</sup> Considering the low decontamination factors of La, Ce and Nd by electrolytic reduction refining method, combining with the higher content of elements in real spent fuel, La, Ce and Nd were selected as doping elements for electrochemical deposition. The purity and morphology of  $\text{UO}_2$  in the product were analyzed using characterization techniques such as X-ray Diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) and X-ray Photoelectron Spectroscopy (XPS). The recovery efficiency and decontamination factor were calculated based on the initial addition weight of  $\text{U}_3\text{O}_8$  and impurity elements, laying the foundation for the industrial implementation of dry processing for depleted fuel.

## 2 Results and discussion

### 2.1 Oxidation reaction of $\text{UO}_2$

Heating 9.9 g of  $\text{UO}_2$  at 650 °C for 5.5 h can product 10.0 g of  $\text{U}_3\text{O}_8$  in a yield of 96.3%, as shown in eqn (1).

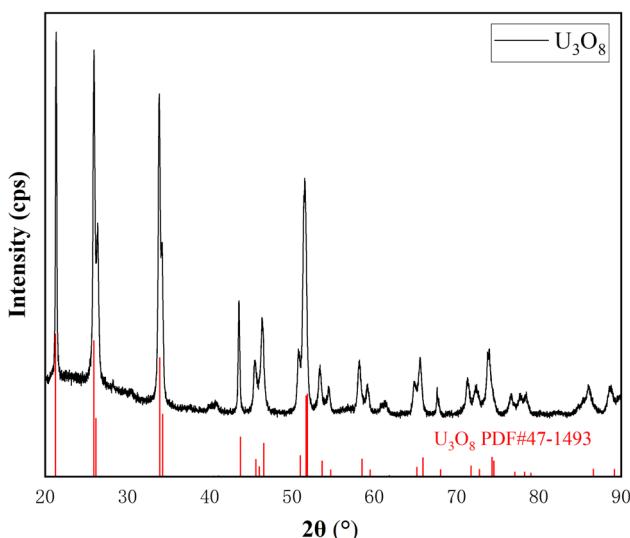
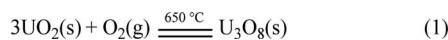
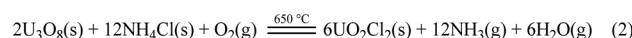


Fig. 1 XRD of oxidation product  $\text{U}_3\text{O}_8$ .

As shown in Fig. 1, the peaks in the XRD spectrum correspond to the standard card of  $\text{U}_3\text{O}_8$ , and there are no other peaks, indicating that  $\text{UO}_2$  has been completely oxidized to pure  $\text{U}_3\text{O}_8$ .

### 2.2 Chlorination reaction of $\text{UO}_2$ (ref. 11 and 15)

Using  $\text{NH}_4\text{Cl}$  to chlorinate  $\text{U}_3\text{O}_8$  to generate  $\text{UO}_2\text{Cl}_2$ , as shown in Fig. 2. Firstly, placed the large crucible ② (which protects the small crucible ③) into a high-temperature well furnace ④ and heated it to 650 °C in a fume hood. Mixed the prepared molten salt,  $\text{U}_3\text{O}_8$ , and  $\text{NH}_4\text{Cl}$  evenly and added them to the small crucible ③. Then, placed the small crucible ③ into the large crucible ②, and installed a quartz condenser cover ① above it. Obviously,  $\text{O}_2$  in the air played an important role in the dissolution process, as it transformed tetravalent uranium into a higher valence state, which was the decisive factor in the formation of  $\text{UO}_2\text{Cl}_2$ .<sup>11,18</sup> The reaction is shown in eqn (2).



### 2.3 Optimization of electrodeposition reaction conditions

The  $\text{Cl}^-$  in the chloride molten salt undergoes an oxidation reaction at the anode, accompanied by the formation of  $\text{Cl}_2$ . While  $\text{UO}_2^{2+}$  gains electrons at the cathode and generates  $\text{UO}_2$ . Different cathode has different reduction processes for  $\text{UO}_2^{2+}$ .<sup>19</sup> When W<sup>20-22</sup> and glassy carbon<sup>23</sup> were used, the reaction took two steps, and the formation of intermediate product  $\text{UO}_2^+$  was found in the molten salt, which was unstable and easily disproportionated into  $\text{UO}_2$  and  $\text{UO}_2^{2+}$ , while  $\text{SnO}_2$ ,<sup>24</sup> Pt,<sup>25</sup> graphite<sup>26</sup> could reduce  $\text{UO}_2^{2+}$  to  $\text{UO}_2$  directly.

In this experiment, the electrode material and diameter, electrolysis time, temperature, uranium concentration in molten salt, and electrolysis voltage were selected to investigate the influence of different conditions of electrodeposition reaction on the recovery efficiency of  $\text{UO}_2$ .

Firstly, dissolved 0.1 g  $\text{U}_3\text{O}_8$  in 10 g of molten salt ( $n(\text{NaCl}) : n(\text{CsCl}) = 1 : 2$ ) at 650 °C, by means of  $\Phi$  6 mm graphite as anode

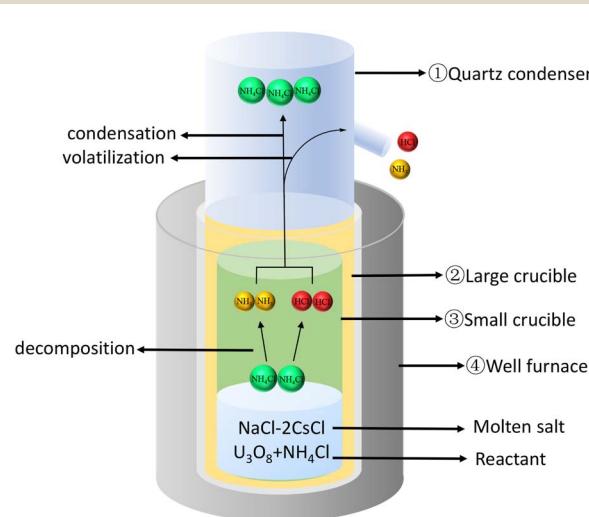


Fig. 2 Chlorination device for  $\text{U}_3\text{O}_8$ .



Table 1 The effect of cathode materials on electrodeposition reactions

No.	Cathode material and diameter (mm)	Temperature (°C)	Electrolysis time (h)	Uranium concentration in molten salt ( $U_3O_8$ : molten salt)	Electrolysis voltage (V)	Recovery efficiency of $UO_2$ (%)
1	Platinum $\Phi 1$	650	2	1 : 100	-1.2	70
2	Platinum $\Phi 2$	650	2	1 : 100	-1.2	90
3	Graphite $\Phi 5$	650	2	1 : 100	-1.2	89

Table 2 The effect of electrolysis time on electrodeposition reaction

No.	Cathode material and diameter (mm)	Temperature (°C)	Electrolysis time (h)	Uranium concentration in molten salt ( $U_3O_8$ : molten salt)	Electrolysis voltage (V)	Recovery efficiency of $UO_2$ (%)
3	Graphite $\Phi 5$	650	2	1 : 100	-1.2	89
4	Graphite $\Phi 5$	650	3	1 : 100	-1.2	92
5	Graphite $\Phi 5$	650	5	1 : 100	-1.2	95
6	Graphite $\Phi 5$	650	6	1 : 100	-1.2	95

and  $\Phi 1$  mm platinum as cathode,  $\Phi 0.5$  mm platinum was used as the reference electrode. Based on the reported Cyclic Voltammetry (CV) curves of  $UO_2Cl_2$ ,<sup>11</sup> the initial electrolysis voltage was selected as -1.2 V. Additionally, electrolyzed the  $U_3O_8$  for 2 h at 650 °C in the argon glove box, which can act as the initial condition. After washing, centrifugation, and drying, pure  $UO_2$  was obtained with a recovery efficiency of 70%.

$$\text{Recovery efficiency of } UO_2 = \frac{m_{U \text{ (in product)}}}{m_{U \text{ (initial in salt)}}} \quad (3)$$

**2.3.1 Optimization of electrode specifications.** Firstly, the cathode material diameter was optimized. When  $\Phi 2$  mm platinum was used as the cathode, the recovery efficiency increased to 90%, indicating that the electrodeposition effect of  $\Phi 2$  mm platinum is better than that of  $\Phi 1$  mm platinum, this may be due to the larger specific surface of  $\Phi 2$  mm platinum, decreasing the current density. Subsequently,  $\Phi 5$  mm graphite was used for testing, and the recovery efficiency of  $UO_2$  was similar to the result obtained with the  $\Phi 2$  mm platinum. Considering potential experimental errors in operation and analysis, the cost-effective  $\Phi 5$  mm graphite with nearly the same recovery efficiency was chosen as the cathode (Table 1).

**2.3.2 Optimization of electrolysis time.** As shown in Table 2, when the reaction time was extended from 2 h to 5 h, the recovery efficiency of  $UO_2$  gradually increased. Further extending the time to 6 h did not result in a significant change in the recovery efficiency, it can illustrate that after 5 h of reaction, the concentration of U in the molten salt has exhausted. Therefore, it

can be observed that prolonging the reaction time appropriately can improve the recovery efficiency of  $UO_2$ . Therefore, the optimal condition for the electrolysis time was determined to be 5 h.

**2.3.3 Optimization of electrolysis temperature.** RIAR found that uranium dioxide with good crystallinity can be obtained at a temperature of 600–650 °C.<sup>27</sup> When the electrolysis temperature was lowered from 650 °C to 600 °C or raised to 700 °C, there was no significant change in the recovery efficiency of  $UO_2$ , which remained at approximately 93–95%. Considering that higher temperature increases the corrosiveness of the electrolysis equipment, and based on the recovery efficiency obtained from the experiments, the optimal electrolysis temperature was determined to be 650 °C (Table 3).

**2.3.4 Optimization of uranium concentration.** By changing the initial concentration of  $U_3O_8$  in the molten salt, the influence of uranium concentration on the electrodeposition reaction was investigated. As shown in Table 4, 0.2 g  $U_3O_8$  was dissolved in 10 g mixed molten salt (NaCl–2CsCl), with other conditions kept constant, the recovery efficiency of  $UO_2$  showed a high value of 96% after electrodeposition. Meanwhile, by decreasing the concentration of  $U_3O_8$  and dissolving 0.1 g of  $U_3O_8$  in 20 g mixed molten salt, a recovery efficiency of 94% was achieved, while the proportion of molten salt components remained unchanged. Considering that increasing the amount of uranium used would decrease the impact on the recovery efficiency due to uranium loss during the experimental process, and there is no significant change in the recovery efficiency of uranium in fact, the mass ratio of 1 : 100 between  $U_3O_8$  and the molten salt was chosen as the optimal concentration. This

Table 3 The effect of electrolysis temperature on electrodeposition reaction

No.	Cathode material and diameter (mm)	Temperature (°C)	Electrolysis time (h)	Uranium concentration in molten salt ( $U_3O_8$ : molten salt)	Electrolysis voltage (V)	Recovery efficiency of $UO_2$ (%)
7	Graphite $\Phi 5$	600	5	1 : 100	-1.2	94
5	Graphite $\Phi 5$	650	5	1 : 100	-1.2	95
8	Graphite $\Phi 5$	700	5	1 : 100	-1.2	93



Table 4 The effect of uranium concentration on electrodeposition reaction

No.	Cathode material and diameter (mm)	Temperature (°C)	Electrolysis time (h)	Uranium concentration in molten salt ( $\text{U}_3\text{O}_8$ : molten salt)	Electrolysis voltage (V)	Recovery efficiency of $\text{UO}_2$ (%)
9	Graphite $\Phi$ 5	650	5	1 : 50	-1.2	96
5	Graphite $\Phi$ 5	650	5	1 : 100	-1.2	95
10	Graphite $\Phi$ 5	650	5	1 : 200	-1.2	94

ensures a reduction in uranium usage as much as possible while maintaining ease of operation.

**2.3.5 Optimization of electrolysis voltage.** To investigate the influence of electrolysis voltage on the electrodeposition reaction, the voltage was adjusted to -1.6 V and -0.8 V. When the voltage was set at -1.6 V, the recovery efficiency of  $\text{UO}_2$  was 97%. When the reduction voltage was -0.8 V, low applied voltage leads to a decrease in current during the electrolysis process. As the number of electrons transferred per unit time decreases, the electrolysis rate will decrease, resulting in a higher current generated after 5 h of electrolysis. Therefore, the electrolysis time was extended to 9 h, resulting in a recovery efficiency of 91%. By adjusting the electrolysis voltage, it was found that reducing the reduction voltage would decrease the rate of electrodeposition, which is unfavourable for the progression of the reaction. Although increasing the reduction voltage would slightly improve the recovery efficiency of  $\text{UO}_2$ , excessive higher reduction voltages may cause side reactions, leading to the reduction of impurity ions and mix them into the  $\text{UO}_2$  product. Hence, the electrolysis voltage should be set based on the actual reduction voltage of the doping elements present.

## 2.4 Characterization of $\text{UO}_2$

Factors such as cathode material and electrolysis voltage can influence the morphology and composition of the deposition. In this experiment, XRD, SEM-EDS, ICP-AES and XPS characterization were performed on the electrolytic product  $\text{UO}_2$  to study the deposition of different types and morphologies of particles on the electrode.

Fig. 3 shows the XRD spectrum of the  $\text{UO}_2$  product obtained when using  $\Phi$  5 mm graphite and  $\Phi$  2 mm platinum as the cathodes. All peaks correspond to the standard XRD pattern of  $\text{UO}_2$ , and no other peaks are observed. This confirms that both material of electrodes can produce pure  $\text{UO}_2$  in the electrodeposition reaction.

The surface morphology of  $\text{UO}_2$  deposition formed under different cathodes and electrolysis voltages were analyzed using SEM-EDS. Fig. 4 presents the SEM images of the  $\text{UO}_2$  deposition obtained by electrolyzing at a constant potential of -1.2 V for 2 h in  $\text{NaCl}-2\text{CsCl}$  molten salt at 650 °C. When  $\Phi$  5 mm graphite was used as the cathode,  $\text{UO}_2$  were observed as dendritic particles (as shown in Fig. 4(a) and (b)). Conversely, when  $\Phi$  2 mm platinum was used as the cathode,  $\text{UO}_2$  products with blocky or powdered particles were obtained (as shown in Fig. 4(c) and (d)), this phenomenon was attributed to the different electrode surface roughness and solid electrolyte interface exhibited by graphite and platinum, which will affect

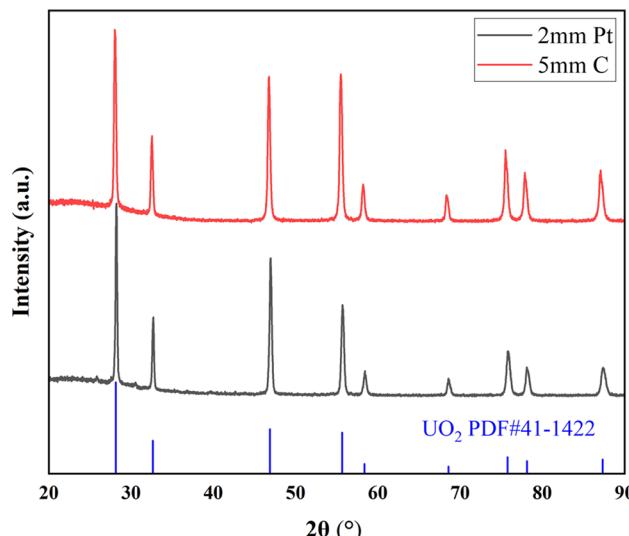


Fig. 3 XRD spectra of products obtained by electrodeposition with different electrodes.

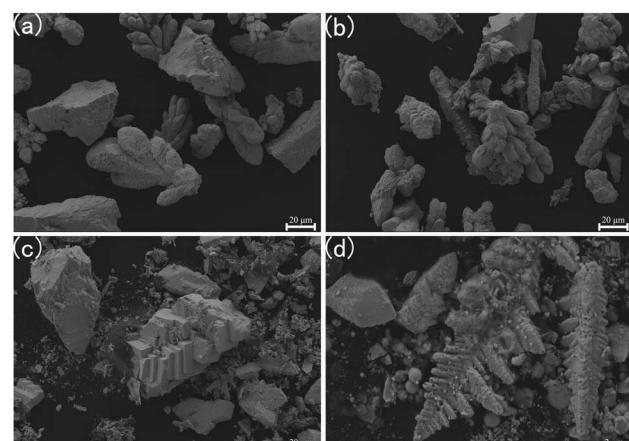


Fig. 4 SEM image of the product after 2 h of electrolysis at 650 °C and -1.2 V; (a) and (b) deposition on  $\Phi$  5 mm graphite; (c) and (d) deposition on  $\Phi$  2 mm platinum.

the growth of dendrites.<sup>28</sup> The particles size of both types of cathode depositions was in the micrometre range.

Fig. 5 illustrates the SEM images of the  $\text{UO}_2$  depositions obtained by electrolyzing at a constant voltage for 5 h using  $\Phi$  5 mm graphite as cathode in  $\text{NaCl}-2\text{CsCl}$  molten salt at 650 °C. Fig. 5(a) and (b) depict the products obtained at -1.6 V, exhibiting a morphology of large blocky dendritic particles.



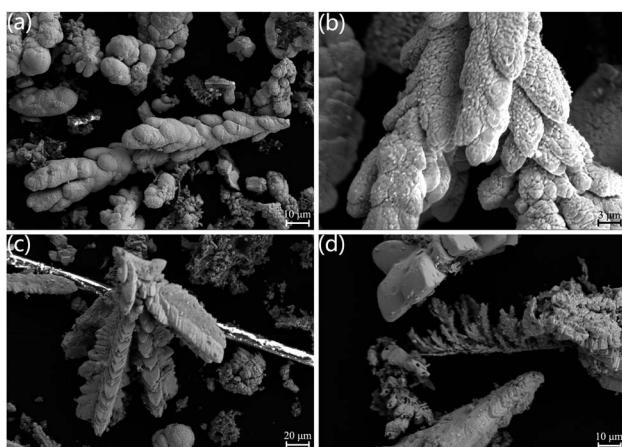


Fig. 5 SEM image of the product obtained from electrolysis of 5 mm graphite at 650 °C for 5 h; (a) and (b) products deposited at  $-1.6$  V; (c) and (d) products deposited at  $-0.8$  V.

Fig. 5(c) and (d) show the products obtained at  $-0.8$  V, consisting of smaller dendritic particles.

The uranium–oxygen ratio of the electrodeposited products under different conditions was determined by ICP-AES. A standard curve for uranium was prepared in the range of 0–10 ppm. As shown in Table 6 (with the same number as Tables 1–5), the mass of the electrodeposited products under different conditions was accurately weighed and dissolved in

5 mL of 6 mol L<sup>-1</sup> HNO<sub>3</sub>. Then, 75  $\mu$ L of the solution was taken and diluted with deionized water to a volume of 900  $\mu$ L, resulting in a 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution. This solution was further diluted 66.7 times with 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>. The concentration of uranium after dilution was measured, and the masses of uranium and oxygen in the products were calculated accordingly. The uranium–oxygen ratio was determined to be 1 : 2, confirming that the electrodeposited products were UO<sub>2</sub>.

The uranium content in the molten salt after electrolysis under different conditions were determined using ICP-AES. A standard curve for uranium was prepared in the range of 0–2 ppm. The mass of the molten salt after electrolysis under different conditions were accurately weighed and dissolved in 10 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>. The uranium concentration after dilution was measured, and the mass and content of uranium in the molten salt after electrolysis were calculated accordingly. The results are shown in Table 7.

## 2.5 Doping experiment

To investigate the influence of La, Ce, and Nd on uranium electrodeposition, these three elements were introduced into the reaction separately. Firstly, the doped La system was studied. Under the optimized conditions mentioned above, electrolysis was conducted at  $-1.2$  V or  $-1.6$  V, and the resulting products were characterized by XRD, ICP-AES, SEM-EDS, and

Table 5 The effect of electrolysis voltage on electrodeposition reaction

No.	Cathode material and diameter (mm)	Temperature (°C)	Electrolysis time (h)	Uranium concentration in molten salt (U <sub>3</sub> O <sub>8</sub> : molten salt)	Electrolysis voltage (V)	Recovery efficiency of UO <sub>2</sub> (%)
11	Graphite $\Phi$ 5	650	9	1 : 100	$-0.8$	91
5	Graphite $\Phi$ 5	650	5	1 : 100	$-1.2$	95
12	Graphite $\Phi$ 5	650	5	<b>1 : 100</b>	<b><math>-1.6</math></b>	<b>97</b>

Table 6 Determination of uranium–oxygen ratio of products

No.	Mass of the sample/mg	Measured concentration of uranium/ppm	Mass of uranium in the sample/mg	Uranium–oxygen ratio
2	22.38	4.8755	19.50	$0.46 \approx 1 : 2$
5	20.01	4.4464	17.79	$0.54 \approx 1 : 2$
8	20.69	4.5441	18.18	$0.49 \approx 1 : 2$
9	20.85	4.6974	18.79	$0.61 \approx 1 : 2$
11	20.14	4.4071	17.63	$0.47 \approx 1 : 2$
12	20.65	4.5109	18.04	$0.46 \approx 1 : 2$

Table 7 The content of uranium in molten salt

No.	Mass of molten salt sample/mg	Measured concentration of uranium/ppm	Mass of uranium in molten salt sample/mg	The content of uranium in molten salt/%
2	71.51	0.9363	0.009363	0.010
5	63.82	0.4825	0.004825	0.008
8	41.62	0.3483	0.003483	0.008
12	57.36	0.3304	0.003304	0.006



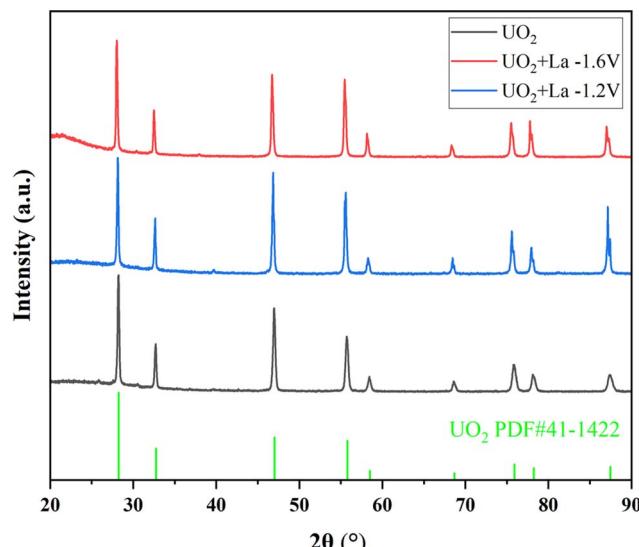


Fig. 6 XRD spectra of products in doped La experiments.

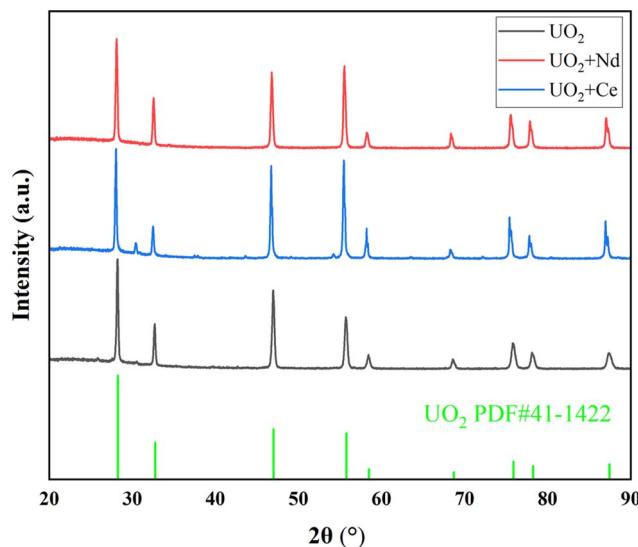


Fig. 7 XRD spectra of products doped with Ce or Nd experiments.

XPS technologies to explore their effects on uranium recovery and decontamination factor.

As shown in Fig. 6, when  $\text{La}_2\text{O}_3$  was introduced into  $\text{U}_3\text{O}_8$  and electrolysis was performed at  $-1.2$  V or  $-1.6$  V after chlorination, the obtained  $\text{UO}_2$  products exhibited negligible impurity peaks in the XRD spectra, the data with black line represents the  $\text{UO}_2$  product obtained under optimal conditions. To analyze the content of the doped element in the product, ICP-AES measurements were performed on the products obtained at different electrolysis voltages. As shown in Table 8, compared to the undoped blank sample, the introduction of La had no significant effect on the recovery efficiency of product. After doping with  $\text{La}_2\text{O}_3$  and electrolysis at  $-1.2$  V or  $-1.6$  V, the La content in the  $\text{UO}_2$  products was determined to be  $0.2\%$  and  $0.3\%$ , respectively. The decontamination factors of La were calculated as  $\text{DF}(\text{La}) = 119$  at  $-1.2$  V and  $\text{DF}(\text{La}) = 79$  at  $-1.6$  V, respectively. The results indicate that electrolysis at  $-1.2$  V is more favorable for the separation of impurity elements. The decontamination factor (DF) is calculated using the following equation.

$$\text{DF}(\text{La}) = \frac{m_{\text{La}} \text{ (initial in salt)} / m_{\text{U}} \text{ (initial in salt)}}{m_{\text{La}} \text{ (in product)} / m_{\text{U}} \text{ (in product)}}$$

Table 8 The effect of doping elements on electrodeposition reaction

Entry	Doped element	Electrolysis voltages (V)	Recovery efficiency of $\text{UO}_2$ (%)	Impurity metal content in the product (%)	Decontamination factor
1	$\text{La}_2\text{O}_3$	$-1.2$	95	0.2	$\text{DF}(\text{La}) = 119$
2	$\text{La}_2\text{O}_3$	$-1.6$	93	0.3	$\text{DF}(\text{La}) = 79$
3	$\text{CeO}_2$	$-1.2$	88	1.2	$\text{DF}(\text{Ce}) = 27$
4	$\text{Nd}_2\text{O}_3$	$-1.2$	91	0.7	$\text{DF}(\text{Nd}) = 57$
5 (blank)	—	$-1.2$	95	—	—

On the other hand, under an electrolysis voltage of  $-1.2$  V, electrodeposition reactions were carried out for the doped  $\text{CeO}_2$  or  $\text{Nd}_2\text{O}_3$  systems, and the XRD spectra of the resulting products are shown in Fig. 7, the data with black line represents the  $\text{UO}_2$  product obtained under optimal conditions. In Fig. 7, the main product was  $\text{UO}_2$ , but trace impurity peaks can be observed, which may be the generation of  $\text{CeOCl}$ .<sup>29</sup> As shown in Table 8, the recovery efficiency of the  $\text{UO}_2$  products were  $88\%$  and  $91\%$  for Ce and Nd, respectively, and the Ce and Nd contents in the  $\text{UO}_2$  products were determined to be  $1.2\%$  and  $0.7\%$ , respectively. The calculated decontamination factors were  $\text{DF}(\text{Ce}) = 27$  and  $\text{DF}(\text{Nd}) = 57$ . The results indicate that the system doped with lanthanide elements, under the given electrolysis conditions, the recovery efficiency of  $\text{UO}_2$  was slightly reduced. This could be attributed to the formation of a thin film of lanthanide elements on the surface of  $\text{UO}_2$ , which inhibits the growth of  $\text{UO}_2$  crystals.<sup>30-32</sup> As a result, some extremely fine  $\text{UO}_2$  particles were lost during centrifugation and washing processes, leading to a decrease in the recovery efficiency of  $\text{UO}_2$ . Regarding the aspect of separation, the separation of La from uranium is relatively easier, while the separation of Ce from uranium is relatively poorer.

The microstructures and elemental distribution of  $\text{UO}_2$  products obtained in the doping system were characterized by



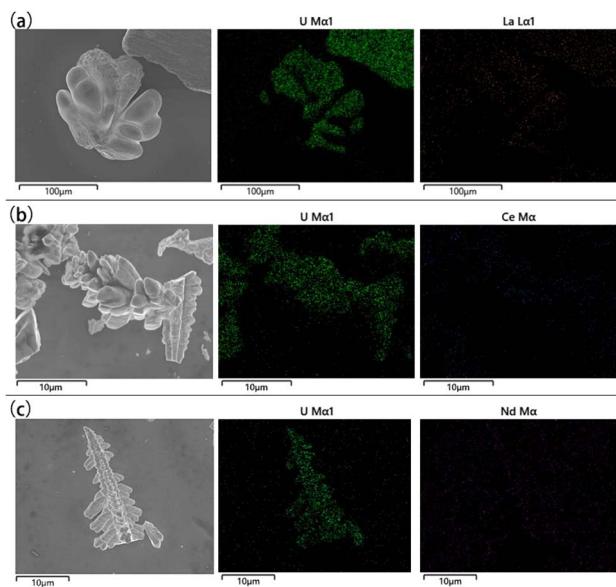


Fig. 8 SEM-EDS spectra of different doping systems; (a) doping system with La; (b) doping system with Ce; (c) doping system with Nd.

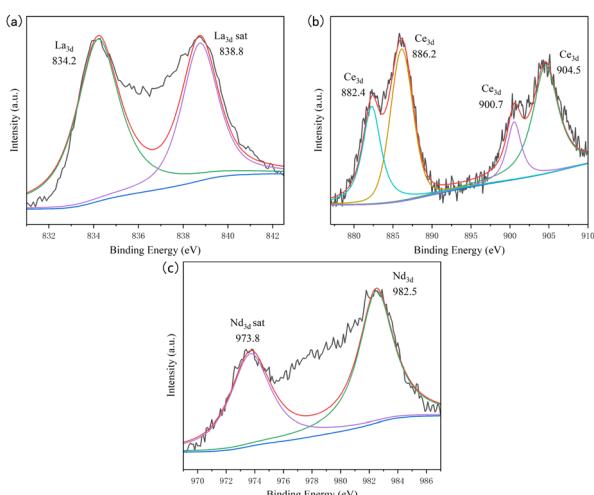


Fig. 9 XPS spectra of different doping systems; (a) doping system with La; (b) doping system with Ce; (c) doping system with Nd.

SEM-EDS respectively. As shown in Fig. 8, the electrolysis products of different doped elements were all relatively pure  $\text{UO}_2$ , with the low content of impurity elements. The distribution of impurity elements was almost invisible in the EDS spectrum, which further proves the reliability of ICP-AES.

The valence states of impurity elements in the  $\text{UO}_2$  product obtained from the doped system were analyzed by XPS, and the analysis data was fitted with peak deconvolution, as shown in Fig. 9. In the product of the doped La system, the binding energy of the La element was determined to be 834.2 eV, corresponding to the characteristic peak of La, and exist in the form of  $\text{LaOCl}$ .<sup>33</sup> In the product of the doped Ce system, the binding energies of the Ce element were determined to be 882.4, 886.2, 900.7, and 904.5 eV, all corresponding to the

characteristic peaks of Ce.<sup>34</sup> When Nd was introduced, the binding energy of Nd element was 982.5 eV, which corresponding to the characteristic peak of Nd.<sup>35,36</sup> Considering the high temperature and the presence of trace amounts of  $\text{H}_2\text{O}$  and  $\text{O}_2$  in the chloride molten salt, during the electrolysis process,  $\text{LaOCl}$ ,  $\text{CeOCl}$ ,  $\text{NdOCl}$  could be formed and mixed with the  $\text{UO}_2$  product.<sup>37,38</sup>

### 3 Conclusions

In this study, electrodeposition technology was used to investigate the recovery of  $\text{UO}_2$  from spent oxide fuel. Dissolution of  $\text{U}_3\text{O}_8$  was achieved through chlorination using  $\text{NH}_4\text{Cl}$ . By means of a three-electrode system, the effects of cathode material and diameter, electrolysis temperature, electrolysis time, electrolysis voltage and uranium concentration in the molten salt on the electrolysis reaction had been explored. Consequently, increasing the cathode diameter, extending the electrolysis time, and appropriately increasing the reduction voltage can all contribute to improving the recovery efficiency of the electrolysis reaction. When using  $\varnothing$  5 mm graphite as the cathode,  $\varnothing$  6 mm graphite as the anode, and  $\varnothing$  0.5 mm platinum as the reference electrode, the temperature of 650 °C, the mass ratio of  $\text{U}_3\text{O}_8$  and molten salt is 1 : 100, pure  $\text{UO}_2$  was obtained by electrolytic reaction at  $-1.6$  V for 5 h with a recovery efficiency of 97% and was characterized using XRD, SEM-EDS, ICP-AES and XPS.

Furthermore, doping experiments were conducted in this electrolyte system by introducing La, Ce, and Nd elements separately. Electrolysis voltage was performed at  $-1.2$  V and  $-1.6$  V, respectively. For introduction of La, the system exhibited better removal of La at  $-1.2$  V, a decontamination factor as high as 119, which is superior to the  $-1.6$  V (the decontamination factor decreased to 79). The system showed good purification effects for Nd, with a decontamination factor of 57 at an electrolysis voltage of  $-1.2$  V. However, it was not effective in removing Ce, with a decontamination factor of only 27.

The further research work will be conducted on the removal of Ce in the future to achieve higher purification efficiency. Additionally, scaling up the research on electrodeposition and research on corrosion-resistant materials will be conducted to accelerate the research progress of electrolysis technology in the dry reprocessing of spent nuclear fuel.

## 4 Experimental section

### 4.1 Reagents and instruments

Sodium chloride ( $\text{NaCl}$ , anhydrous, 99.8% purity, Zancheng (Tianjin) Technology Co., Ltd.), cesium chloride ( $\text{CsCl}$ , anhydrous, 99.9% purity, Anhui Senrise Technology Co., Ltd.), and ammonium chloride ( $\text{NH}_4\text{Cl}$ , anhydrous, GR grade, Aladdin Reagent (Shanghai) Co., Ltd.) were purchased.  $\text{NaCl}$  and  $\text{CsCl}$  were dried at 180 °C for over 12 h to minimize the amount of adsorbed water before use.

The phases composition was analyzed and tested by X-ray diffraction (XRD) diffractometer using Miniflex 600 (Rigaku Corp.) with  $\text{Cu K}\alpha$  radiation at 40 kV and 40 mA. Scanning



electron microscopy (SEM, ZEISS GeminiSEM 360, Zeiss Germany Inc.) was used to investigate morphology and size of samples. Energy dispersive X-ray spectroscopy (EDS, AZtecone, Oxford Instruments) was used to analyze the products' composition with SEM. And the concentrations of the uranium were tested by inductively coupled plasma atomic emission spectrometer (ICP-AES, ARCOS FHS12, Spectro Scientific). The valence states of the products were analyzed by an X-ray photoelectron spectrometer (XPS, Escalab250Xi, ThermoFisher Scientific Inc.) equipped with an Al K $\alpha$  source.

## 4.2 Experiment

**4.2.1 Oxidation of uranium dioxide.** 9.99 g of UO<sub>2</sub> placed in a quartz crucible, heating at 650 °C for 5.5 h, with the formation of black powder.

### 4.2.2 Chlorination reaction

**4.2.2.1 Chlorination reaction of pure U<sub>3</sub>O<sub>8</sub>.** 1.48 g NaCl, 8.52 g CsCl, 2 g NH<sub>4</sub>Cl, and 0.1 g U<sub>3</sub>O<sub>8</sub> were grinded thoroughly, the mixture was transferred to a corundum crucible, and heat at 650 °C for 2 h to obtain an orange solution. Then cool to room temperature yielding a yellow block solid.

**4.2.2.2 Chlorination reaction of U<sub>3</sub>O<sub>8</sub> with doping elements.** Three systems were prepared with different doping elements:

(1) Doping with La element: 1.48 g NaCl, 8.52 g CsCl, 3 g NH<sub>4</sub>Cl, 0.1 g U<sub>3</sub>O<sub>8</sub>, and 49.7 mg La<sub>2</sub>O<sub>3</sub> were accurately weighed, thoroughly mixed, and transferred to a corundum crucible. The crucible was then heated at 650 °C for 2 h and cooled to room temperature.

(2) Doping with Ce element: 1.48 g NaCl, 8.52 g CsCl, 3 g NH<sub>4</sub>Cl, 0.1 g U<sub>3</sub>O<sub>8</sub> and 52.1 mg CeO<sub>2</sub> were accurately weighed, thoroughly mixed, and transferred to a corundum crucible. The crucible was then heated at 650 °C for 2 h and cooled to room temperature.

(3) Doping with Nd element: 1.48 g NaCl, 8.52 g CsCl, 3 g NH<sub>4</sub>Cl, 0.1 g U<sub>3</sub>O<sub>8</sub> and 49.5 mg Nd<sub>2</sub>O<sub>3</sub> were accurately weighed, thoroughly mixed, and transferred to a corundum crucible. The crucible was then heated at 650 °C for 2 h and cooled to room temperature.

**4.2.3 Electrodeposition reaction.** The electrodeposition reaction used a three-electrode system, all electrodes were submerged in deionized water and sonicated for 10 min, followed by cleaning them with ethanol. The platinum was polished with sandpaper and dried. At 650 °C, 0.1 g of U<sub>3</sub>O<sub>8</sub> was chlorinated and dissolved in 10 g of molten salt ( $n$ (NaCl) :  $n$ (CsCl) = 1 : 2) in a corundum crucible with the method in Section 4.2.2.  $\Phi$  6 mm graphite was used as the anode,  $\Phi$  1 mm platinum was used as the cathode,  $\Phi$  0.5 mm platinum was used as the reference electrode, and electrolysis at -1.6 V for 5 h inside the glovebox. A black solid product was formed, most of which fell into the molten salt, leaving only a small amount of product on the electrodes. After cooling to room temperature, added 50 mL of deionized water, stirred for 20 min to dissolve all molten salt on the cathode or in the crucible, centrifuged at 3000 rpm for 2 min, pour off the supernatant, and then wash the solid with deionized water (50 mL × 2) and anhydrous

ethanol (50 mL × 2). Dry the solid at 50 °C overnight to obtain a black solid powder.

## Author contributions

Pei Wu: conceptualization, methodology, validation, investigation, formal analysis, software, writing – original draft. Liqin Wang: conceptualization, data curation, software, writing – review & editing. Jinrui Wang: investigation, writing – original draft. Junhan Luo: methodology, resources, investigation. Yuexiang Lu: resources, methodology, formal analysis. Xiaopeng Song: methodology, supervision. Jilian Liu: investigation, formal analysis, conceptualization, writing – review & editing. Yongquan Qin: supervision, project administration, funding acquisition, writing – review & editing. Liudong Hou: conceptualization, resources, supervision, funding acquisition, project administration. Jing Ma: conceptualization, resources, supervision, project administration, funding acquisition, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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