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Electrochemical Preparation of UCl_3 -LiCl-KCl Molten Salt in a Frit-Separated Cell

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Abstract

Electrorefining in pyroprocessing requires 3-10 wt.% UCl_3 in the LiCl-KCl molten salt, but current preparation routes rely on CdCl_2 or corrosive chlorinating gases. Here, UCl_3 -LiCl-KCl molten salt was prepared electrochemically at 773 K in a frit-separated cell. The route drives the following reaction $\text{U} + 3\text{LiCl} \rightarrow \text{UCl}_3 + 3\text{Li}$: metallic uranium is dissolved anodically to supply U^{3+} and the Li is generated at the cathode. The suitability of Cd and Bi as the liquid-metal cathode to capture Li was evaluated first. Bi proved better suited than Cd and was adopted for the subsequent runs. Impedance spectroscopy showed that conduction across the frit added 7.1 Ω , increasing the ohmic loss while providing the separation needed to suppress U^{3+} crossover from anode to cathode. Over ten consecutive runs at 0.5 and 1.0 A, the UCl_3 concentration in the anode compartment increased almost linearly to 12.45 and 12.57 wt.%, with comparable apparent current efficiencies of 95.5% and 96.4%. Because UCl_3 is generated electrochemically in situ, this route offers several advantages: it requires no chlorinating reagent, introduces no additional metallic impurity, and allows the UCl_3 concentration to be set directly by the charge passed.

Keywords

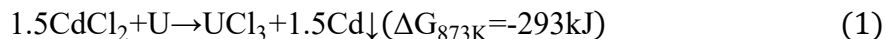
UCl₃; Uranium Chlorination; Pyroprocessing

Introduction

The development of sodium-cooled fast reactor(SFR) in recent years has renewed interest in spent fuel reprocessing, and chloride-salt pyroprocessing has emerged as a promising route. Compared with aqueous reprocessing, molten chloride salt don't contain hydrogen-rich neutron moderators such as water. Consequently, they are well suited to the treatment of highly radioactive spent fuels with short cooling times. These advantages make pyroprocessing well suited to metallic fuels and support the development of more compact reprocessing facilities[1-6].

Electrorefining is the core process in the pyroprocessing flow for the treatment of spent nuclear fuel [7, 8]. Its main objective is to separate actinides, mainly uranium, from lanthanides for reuse. To initiate and maintain stable electrorefining, 3-10 wt.% uranium trichloride(UCl_3) must be added to the molten salt electrolyte [9]. Because uranium trichloride is mainly used in molten salt systems, it is generally prepared directly in the molten salt.

A classic synthetic route[10] involves a high-temperature vessel consisting of a molten LiCl-KCl eutectic upper layer and a liquid Cd pool at the bottom. At 873 K, cadmium metal is first oxidized by chlorine gas to form CdCl_2 . The CdCl_2 then reacts with metallic uranium contained in an immersed basket to form uranium trichloride, which dissolves into the molten salt, while the reduced cadmium settles back into the cadmium pool.

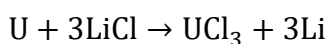


Although metallic cadmium is relatively compatible with containment vessels, there are several drawbacks. For instance, its high vapour pressure can lead to significant volatilisation. Furthermore, the formation of U-Cd intermetallic compounds can cover the reactants and hinder the continuous formation of UCl_3 . Additionally, the residual CdCl_2

decreases the final purity of the synthesised product. Due to these drawbacks, researchers have explored various cadmium-free alternatives based on this synthetic approach. Several metal chlorides have been investigated as potential substitutes, including copper chloride [11], bismuth chloride [12], lead chloride [13], ferrous chloride [14], and zinc chloride [15]. Another well-established method for preparing uranium trichloride is gas chlorination of metallic uranium[16]. This can be achieved either directly with hydrogen chloride gas or indirectly by the thermal decomposition of ammonium chloride to generate hydrogen chloride. This approach avoids the use of metal chlorides, thereby avoiding the introduction of residual metallic impurities and improving product purity. Nevertheless, current approaches still face several critical challenges. For example, the use of copper chloride can result in the formation of uranium tetrachloride as an unwanted by-product. Also, the approach involving ammonium chloride or hydrogen chloride is limited by the corrosive nature of these substances towards metallic containment vessels. Consequently, there is an urgent need to develop a synthesis method for uranium trichloride that is cost-effective and environmentally friendly.

The electrorefining process itself provides an alternative approach. The anodic dissolution of metallic uranium in molten LiCl-KCl is well established and can efficiently generate U^{3+} . Meanwhile, the chloride ions needed to form UCl_3 are already present in the eutectic salt. Therefore, in principle, a UCl_3 containing electrolyte could be prepared directly using only metallic uranium and the molten salt, without adding any external chlorinating agent.

This study presents a unique electrochemical process for preparing UCl_3 -LiCl-KCl molten salt. In this process, the potential of metallic uranium is controlled to drive the following reaction, yielding a purified UCl_3 -LiCl-KCl salt:



To achieve this electrochemical reaction, two key issues must be addressed.

The first issue concerns the fate of the lithium produced during electrolysis. The amount of lithium generated is determined by Faraday's law and cannot be reduced by changing the cell configuration or operating conditions. The key question, therefore, is how to

effectively manage it. The second issue concerns cathodic selectivity. U^{3+} is reduced at a much more positive potential than Li^+ , so any uranium reaching the cathode is consumed there in preference to lithium. Protecting the dissolved product therefore cannot rely on the difference in reduction potentials, but must instead rely on controlling species transport.

For the first issue, a possible solution is to use a liquid-metal cathode to collect the generated Li through alloy formation. To address the second issue, a porous diaphragm between the anodic and cathodic compartments suppresses U^{3+} transport to the cathode, allowing anodically dissolved uranium to remain in the salt rather than being reduced.

This approach combines three key elements: a metallic uranium anode that dissolves anodically, an active cathode that captures the generated lithium, and a porous frit that limits U^{3+} transport to the cathode compartment. Together, these features enable the direct preparation of a UCl_3 molten salt, which, to our knowledge, has not been reported previously.

In this work, Cd and Bi were assessed as candidate active cathodes through repeated galvanostatic polarization-relaxation measurements. The additional resistance introduced by the porous frit was then determined by electrochemical impedance spectroscopy. Finally, ten consecutive electrolysis cycles were conducted at 0.5 and 1.0 A, respectively, to monitor the accumulation of UCl_3 in the molten salt, and the cathode after electrolysis was characterized by XPS.

Experimental

Materials and salt pretreatment

The electrolyte was a LiCl-KCl eutectic salt (58.5:41.5 mol%), melted at 773 K and then bubbled with HCl gas for 15 min to remove residual moisture. All subsequent experiments were conducted in an argon-filled glovebox in which the oxygen and moisture levels were both kept below 10 ppm. Bi and Cd were selected as candidate active cathode materials. The anode was metallic uranium, prepared by arc-remelting uranium dendrites recovered

from previous electrorefining experiments and then suction-casting the melt. Immediately before use, the anode surface was polished with abrasive paper to remove any oxide layer; the anode was then secured with a Mo wire and immersed in the molten salt. An Ag/AgCl reference electrode was used, comprising an Ag wire immersed in LiCl-KCl containing 1 wt.% AgCl inside a Pyrex tube.

Apparatus

Three-electrode cell for cathode investigation. As Figure 1 shows, each candidate liquid-metal cathode was contained in a bottom-sealed ceramic tube (4 mm inner diameter) with lateral openings. A ceramic-sheathed tungsten wire (1 mm outer diameter) inserted into the metal served as the current collector; the liquid-metal surface exposed to the molten salt had a geometric area of 11.8 mm². More metal than the tube could retain was loaded before heating; on melting, the surplus drained through the lateral openings, ensuring reproducible retained volumes and exposed surface areas across experiments. The positions of the lateral openings were kept identical in all experiments. The resulting differences in meniscus curvature were neglected and the effective exposed areas of the two liquid metals were assumed identical. A graphite rod was used as the counter electrode, and the electrode potential was measured against the Ag/AgCl reference electrode. The cell contained 200 g of LiCl-KCl eutectic salt in an alumina crucible. Electrochemical measurements were performed using a Metrohm Autolab PGSTAT302N electrochemical workstation.

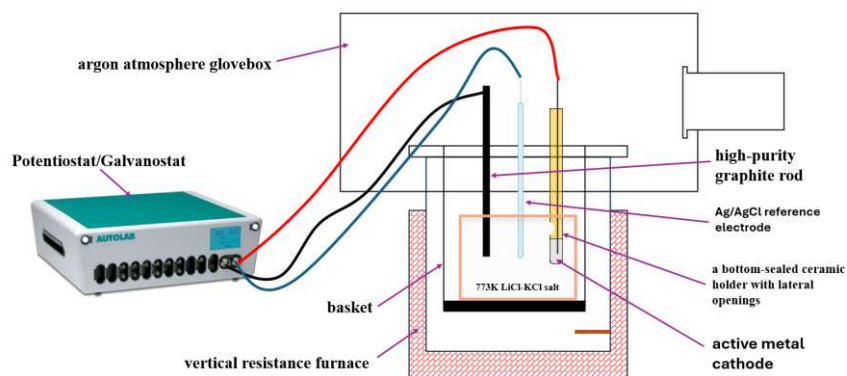


Figure 1 Schematic illustration of the three-electrode electrochemical setup used to investigate active metal cathodes. The cell comprises an active metal cathode held in a

bottom-sealed ceramic holder with lateral openings, a graphite counter electrode and an Ag/AgCl reference electrode.

H-type frit-separated cell. The electrolysis cell (as Figure 2 and Figure 3 show) consisted of two cylindrical quartz compartments (35 mm outer diameter, 60 mm height, and 1 mm wall thickness) connected through a 10 mm opening containing a 2 mm-thick quartz frit. The uranium anode occupied one compartment and the Bi cathode the other. The cathode was 10 g of Bi in a crucible, with a tungsten wire immersed in the melt as the current collector. Each compartment had its own Ag/AgCl reference electrode, so the anode and cathode potentials could be recorded separately with two voltmeters. The electrolysis current was supplied by a DAHUA DH1798 constant-current power supply with a compliance voltage of 40 V. This was sufficient to accommodate the higher cell voltage caused by the added resistance of the frit.

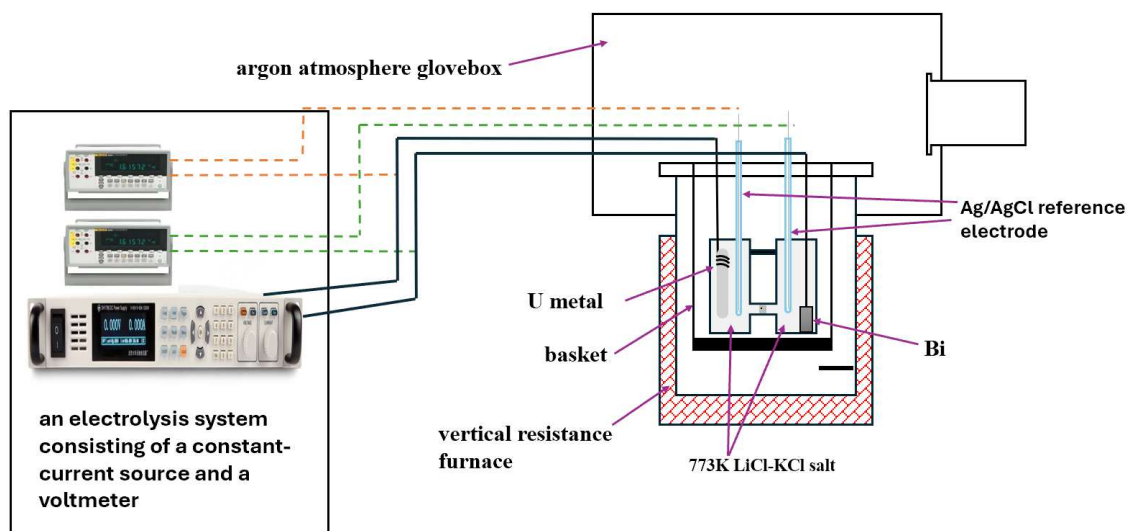


Figure 2 Schematic illustration of the frit-separated H-type electrolysis system used for the electrochemical preparation of UCl_3 - LiCl - KCl molten salt at 773 K. The metallic U anode and Bi active cathode were positioned in separate compartments connected through a porous glass frit. A tungsten wire immersed in the Bi pool serves as the cathodic current collector, and two Ag/AgCl reference electrodes monitor the anode and cathode potentials separately.

145



146

147 Figure 3 Digital photograph of the H-type electrolytic cell assembly. Two cylindrical
148 quartz compartments (35 mm outer diameter, 60 mm high) are connected by a narrow
149 quartz tube (10 mm outer diameter) containing a 2 mm thick glass frit.

150

151 Investigation of the Cathode

152 The two candidate metals were compared by repeated galvanostatic polarization-relaxation
153 cycles in LiCl-KCl eutectic at 773 K. After the open-circuit potential had stabilized, a
154 cathodic current of 50 mA was applied for 5 min to drive the reduction of Li^+ and the
155 incorporation of the generated lithium into the liquid metal, followed by a 5 min relaxation
156 period under open-circuit conditions. The electrode potential was recorded continuously
157 throughout both the polarization and relaxation stages. Identical operating conditions, cell
158 geometry, and salt loading were used for the Cd and Bi experiments, with fresh LiCl-KCl
159 eutectic used for each experiment. For comparison, linear sweep voltammetry (LSV) was
160 also performed using a tungsten wire as an inert working electrode to determine the lithium
161 deposition potential in the LiCl-KCl melt.

162 Galvanostatic electrolysis

163 Each compartment of the H-type cell was loaded with 50 g of dried LiCl-KCl eutectic salt,
164 added in two stages. First, 50 g of salt was added to one compartment, melted at 773 K,
165 and held at this temperature for 12 h to allow the quartz frit to become fully wetted. Wetting
166 of the frit was confirmed by the appearance of a small amount of molten salt in the opposite

compartment. A further 50 g of salt was then added to the other compartment. The metallic uranium anode was placed in one compartment, while an alumina crucible containing approximately 10 g of Bi was placed in the other. The electrodes were then immersed in the molten salt, and the open-circuit potentials were allowed to stabilize before electrolysis.

Before electrolysis, the resistance introduced by the frit was measured by electrochemical impedance spectroscopy. Two reference-electrode configurations were compared: in the first, the reference electrode was placed in the same compartment as the working electrode; in the second, it was placed in the opposite compartment across the frit. The ohmic resistance for each configuration was determined from the high-frequency intercept of the Nyquist plot on the real axis, and the contribution of the frit was taken as the difference between the two values.

Galvanostatic electrolysis was conducted in ten consecutive runs. At 0.5 A, each run lasted 1260 s, whereas at 1.0 A, each run lasted 630 s, so that the same charge was passed in each run under both current conditions. During electrolysis, the anode and cathode potentials were recorded independently against the reference electrode in their respective compartments. After each run, the electrode potentials were recorded for a further 2 min under open-circuit conditions to monitor their relaxation. A molten-salt sample was then withdrawn from the anodic compartment to determine the uranium content. The 0.5 and 1.0 A conditions were investigated in separate experiments using fresh LiCl-KCl eutectic salt and a new Bi cathode for each experiment.

The theoretical mass of UCl_3 generated from the charge passed was calculated according to Faraday's law:

$$m_{\text{UCl}_3} = \frac{ItM_{\text{UCl}_3}}{3F}$$

where I is the applied current, t is the electrolysis time, M_{UCl_3} is the molar mass of UCl_3 , and F is the Faraday constant. The current efficiency was defined as the ratio of the mass of UCl_3 corresponding to the uranium measured in the anodic compartment to the theoretical mass given above.

Salt samples were taken during electrolysis by quenching. A pre-cooled ceramic rod was briefly immersed in the melt, on which a small quantity of salt solidified and was withdrawn with it. Each sample was weighed, dissolved in dilute HNO₃, and the uranium concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). After the final electrolysis run, the Bi cathode was removed from the cell, and a small amount of powder was scraped from the cathode using a file inside the glovebox. The collected powder was transferred in a vacuum-sealed vial and subsequently analyzed by X-ray photoelectron spectroscopy (XPS).

Results and discussion

Electrochemical behavior of active metal cathodes

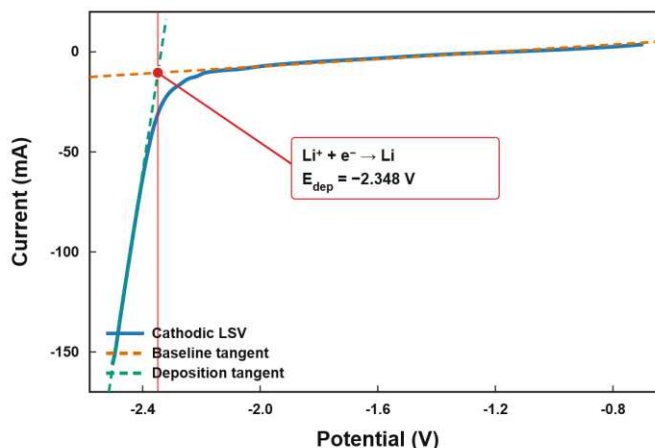
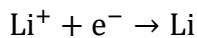


Figure 4 Cathodic linear sweep voltammogram obtained on a W electrode in molten LiCl-KCl. The apparent Li deposition potential (-2.348 V vs. Ag/AgCl) was taken from the intersection of the baseline and the tangent to the rising cathodic current.

To provide a baseline for Li uptake by the Cd and Bi active cathodes, the onset potential of metallic Li deposition was first determined by cathodic linear sweep voltammetry on an inert W electrode in molten LiCl-KCl. As shown in Figure 4, only a small background

current was observed at relatively positive potential. Upon scanning toward more negative potential, the cathodic current increased sharply, marking the onset of Li^+ reduction:



The deposition onset potential was determined using the tangent-intersection method. A tangent was fitted to the approximately linear baseline current, while another tangent was fitted to the steep current increase associated with Li deposition. The intersection of these two tangents gave an apparent Li deposition potential of:

$$E_{\text{dep}} = -2.348 \text{ V vs. Ag/AgCl}$$

The value of -2.348 V was therefore used as an experimental reference for evaluating the behavior of the Cd and Bi active cathodes. In subsequent galvanostatic polarization experiments, cathode potentials more positive than this value would suggest that the generated Li was being accommodated by the liquid metal through dissolution or alloy formation rather than being deposited as a separate metallic Li phase. In contrast, polarization of the active cathode toward or beyond this potential would indicate an increased possibility of free Li deposition.

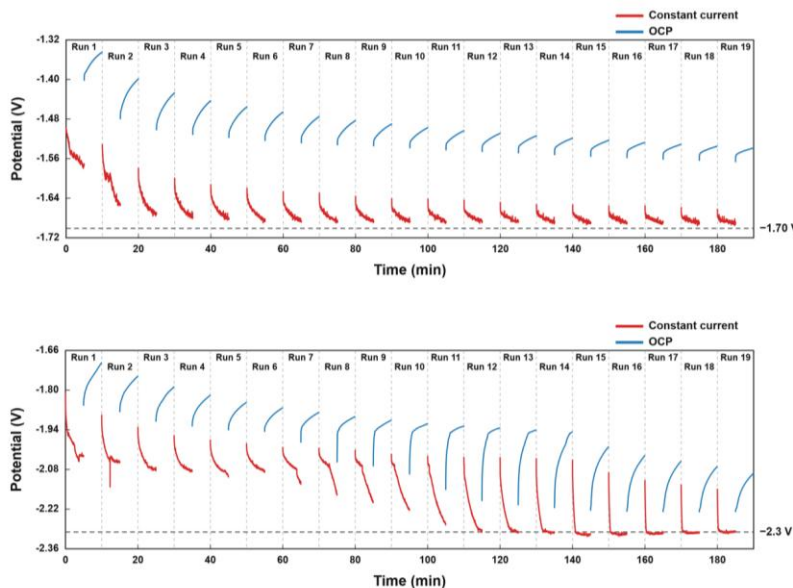


Figure 5 Evolution of the cathode potential during repeated galvanostatic polarization-relaxation cycles for Bi (top) and Cd (bottom) active cathodes in molten LiCl-KCl (773

K). Red and blue curves correspond to constant-current polarization and open-circuit relaxation, respectively.

After establishing the Li deposition potential on the W electrode, repeated galvanostatic polarization-relaxation cycles were performed on the Cd and Bi cathodes to evaluate their ability to accommodate Li. Figure 5 shows the evolution of the cathode potential during the current pulses (red) and the subsequent open-circuit relaxation periods (blue).

For both active cathodes, the potential shifted rapidly toward more negative values when the current was applied. This cathodic polarization reflects the reduction of Li^+ and the incorporation of Li into the liquid metal cathode. When the current was interrupted, the electrode potential relaxed gradually toward more positive values. This recovery indicates that Li diffused from the electrode surface into the bulk of the active metal, allowing the potential to recover toward the equilibrium potential of the Li-containing alloy.

For the Bi cathode (Figure 5, top), the potential during the current pulses remained relatively stable over repeated cycles, and even at the end of polarization it stayed significantly more positive than the Li deposition potential on W. The relaxation potential also recovered reproducibly after each pulse. This behavior indicates that Bi effectively accommodates the electrochemically generated Li through Li-Bi alloy formation. The relatively mild polarization and good recovery behavior suggest that the Li activity in Bi remained low throughout the test, demonstrating good buffering capability of the Bi cathode. Notably, the potential approached -1.7 V during repeated polarization, which is close to the potential reported in previous studies [17] for the formation of Li_3Bi during the electrochemical lithiation of Bi.

In contrast, the Cd cathode (Figure 5, bottom) showed much stronger negative polarization during repeated current pulses. As the experiment proceeded, the cathode potential shifted progressively toward more negative values and eventually approached -2.3 V, which is close to the Li deposition potential determined on W. At the same time, the open-circuit potential also shifted to more negative values and the extent of potential recovery during relaxation decreased. This trend indicates continuous accumulation of Li in the Cd cathode

and a gradual increase in Li activity. Once the cathode potential approaches the Li/Li⁺ equilibrium region, the active metal can no longer efficiently buffer newly generated Li, and free metallic Li is increasingly likely to deposit. Therefore, compared with Bi, Cd exhibits poorer stability as a Li-absorbing cathode under repeated electrolysis conditions.

Overall, the polarization-relaxation results show that Bi has a greater ability to accommodate Li and better electrochemical stability than Cd. The Bi cathode remained well above the Li deposition potential and showed reproducible relaxation behavior, whereas the Cd cathode gradually polarized toward the Li deposition potential, suggesting a lower Li capacity. These results support the use of Bi as the active cathode for the electrochemical preparation of UCl₃.

Resistance of the frit-separated cell

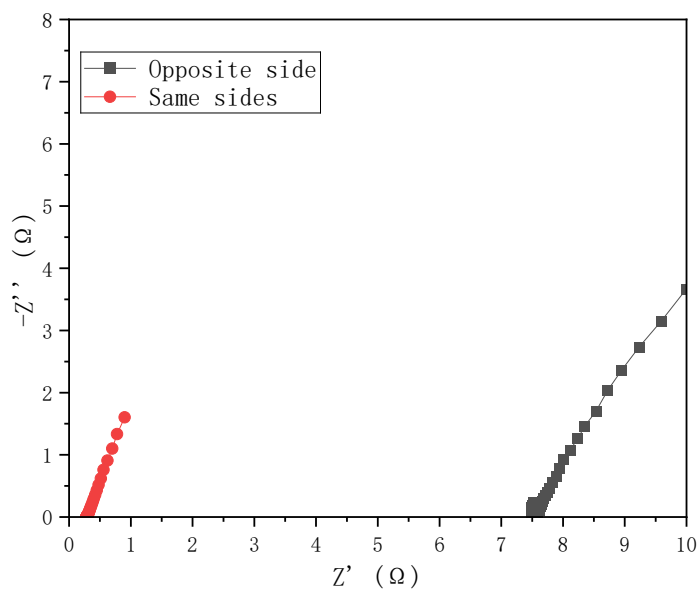


Figure 6 Nyquist plots measured with the reference electrode positioned on the same side and the opposite side of the porous frit relative to the working electrode.

Before the preparation electrolysis, the ohmic resistance introduced by the fritted diaphragm was evaluated. Figure 6 compares the Nyquist plots obtained with two reference-electrode configurations: one with the reference and working electrodes in the same compartment, and the other with the reference electrode in the opposite compartment. The two spectra show similar overall shapes but their high-frequency intercepts on the real axis differ by 7.1Ω . Because the two configurations differ only in the position of the reference electrode, this offset is attributed to the fritted diaphragm and was used as an estimate of the diaphragm resistance in the following analysis.

The influence of this additional resistance on the preparation process can be directly obtained from Ohm's law. At a current of 1 A, this resistance alone would produce a voltage drop of 7.1 V. Therefore, the use of a fritted diaphragm to separate the anodic and cathodic compartments entails an additional energy cost. In this system, the factor that determines the overall voltage of the electrolytic cell may not be the electrode reactions themselves, but rather this extra ohmic resistance, which is also the reason why a power supply with a relatively high compliance voltage is required in the experiments.

Accumulation of UCl_3

Figure 7 shows the change in UCl_3 concentration in the anodic compartment over ten electrolysis runs. At both currents, the UCl_3 concentration increased approximately linearly, reaching 12.45 wt.% and 12.57 wt.% at 0.5 A and 1.0 A, respectively. Because an identical amount of charge was passed in each run, this linear increase indicates that the mass of uranium dissolved per run remained essentially constant. Hence, within the concentration range investigated here, the efficiency of the uranium conversion process shows no appreciable decline.

The experimentally measured UCl_3 concentrations can also be compared with the theoretical values calculated from the charge passed. According to Faraday's law, a cumulative charge of 6300 C corresponds to the formation of 7.50 g of UCl_3 , which is equivalent to a UCl_3 concentration of 13.04 wt.% in the anodic compartment. On this basis,

the apparent current efficiencies at 0.5 A and 1.0 A were calculated to be 95.5% and 96.4%, respectively.

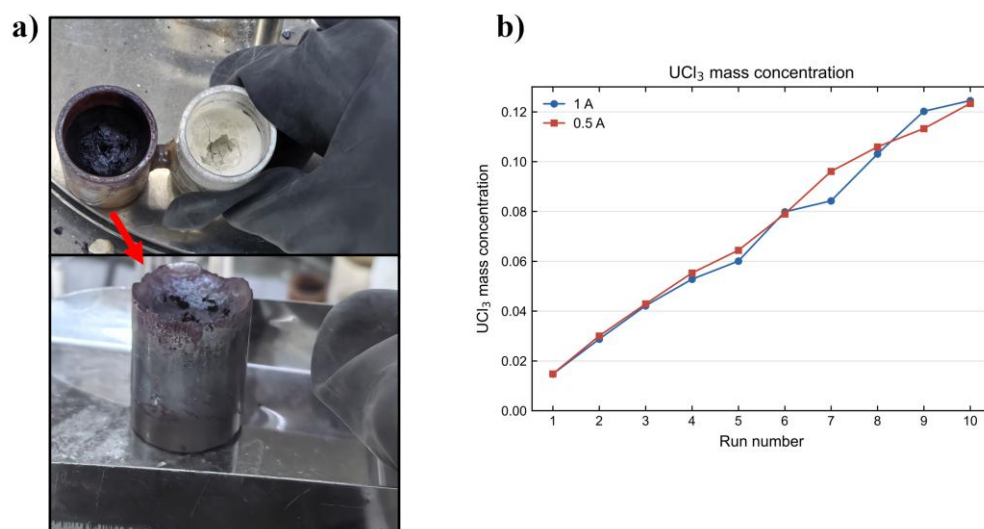


Figure 7 Product of the electrolysis and the accumulation of UCl_3 . **a)** The recovered $\text{UCl}_3\text{-LiCl-KCl}$ salt; **b)** UCl_3 mass fraction in the anodic compartment, determined after each of the ten runs at 0.5 and 1.0 A.

Behavior of the uranium anode

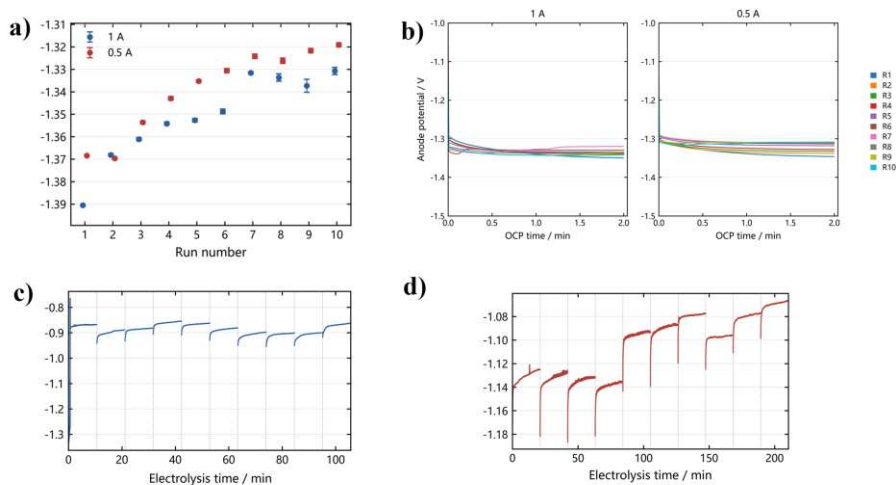


Figure 8 Behavior of the uranium anode potential during repeated electrolysis at 1.0 A and 0.5 A. **a)** Open-circuit anode potential measured before each of the ten runs; each

point is the mean over the 2-min open-circuit period, with error bars showing the spread about that mean. **b)** Relaxation of the anode potential during the 2-min open-circuit period before each run (R1-R10) at 1.0 A (left) and 0.5 A (right). **c), d)** Anode potential profiles recorded during galvanostatic electrolysis over the ten runs at 1.0 A (c) and 0.5 A (d).

The linear accumulation of UCl_3 described above already indicates that the anodic dissolution process remains stable over repeated electrolysis runs. To examine this behavior further, the anodic potential was analyzed in detail. Figure 8 summarizes the variations in anodic potential before, during, and after each electrolysis run.

The open-circuit potential recorded before each electrolysis run shifted gradually in the positive direction with increasing run number. At 1.0 A, the open-circuit potential shifted from -1.39 V to -1.33 V; at 0.5 A, it shifted from -1.37 V to -1.32 V. This is consistent with the expected result of gradual U^{3+} accumulation in the anodic compartment: the equilibrium potential of the U^{3+}/U couple follows the Nernst equation, and at 773 K, for a three-electron transfer reaction, the equilibrium potential shifts by approximately 51 mV per decade change in activity. The error bars in the figure represent the deviation of the measured potential from its final value over the open-circuit period.

During galvanostatic electrolysis, the anodic potential is maintained between -1.19 and -1.07 V at 0.5 A, and between -0.96 and -0.85 V at 1.0 A; in both cases, the most negative potential values correspond to the transient response immediately following the application of the current step. Over the course of ten consecutive electrolysis sessions, the anodic potential remains stable under both conditions. Therefore, the anodic potential shows no indication of continuously increasing kinetic resistance, indicating that the uranium anode is able to dissolve steadily and consistently throughout the entire series of experiments.

The relaxation of the anodic potential after current interruption was also relatively rapid. Therefore, the different electrolysis behaviors to be discussed in the next section mainly need to be examined from the perspective of the cathodic process.

Behavior of the bismuth cathode

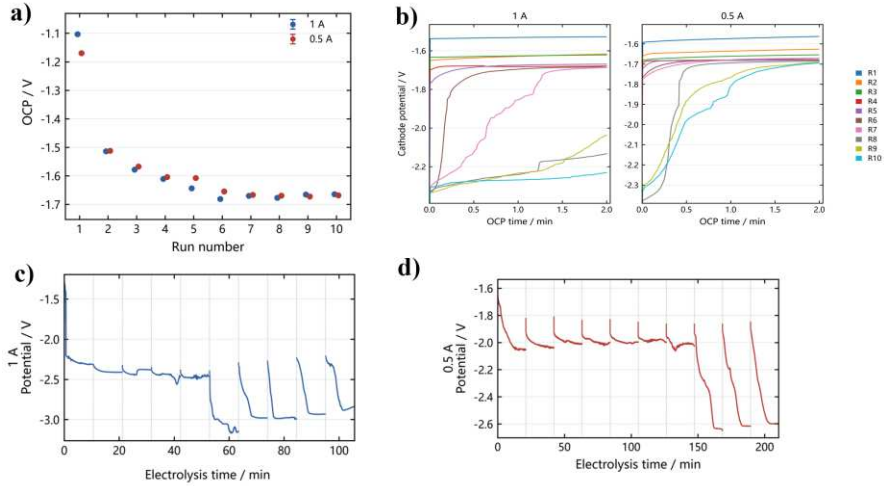


Figure 9 Behavior of the bismuth cathode potential during repeated electrolysis at 1.0 A and 0.5 A. **a)** Open-circuit cathode potential measured before each of the ten runs; each point is the mean over the 2-min open-circuit period, with error bars showing the spread about that mean. **b)** Relaxation of the cathode potential during the 2-min open-circuit period before each run (R1-R10) at 1.0 A (left) and 0.5 A (right). **c), d)** Cathode potential profiles recorded during galvanostatic electrolysis over the ten runs at 1.0 A (c) and 0.5 A (d).

The open-circuit potential measured before each electrolysis run shifted gradually in the negative direction with increasing cumulative charge. At 1.0 A, the open-circuit potential decreased from an initial value of -1.1 V to -1.6 V by the fourth run; at 0.5 A, it decreased from -1.17 V to a similar level. Beyond approximately the sixth run, the open-circuit potential changed little and stabilized at -1.65 to -1.68 V under both current conditions. Since this potential is close to the reported equilibrium potential of Li_3Bi , the stabilized value is attributed to the formation of this alloy phase.

Throughout the entire process, the relaxed cathodic potential remained approximately 0.68 V more positive than -2.35 V, the reference potential for the deposition of free metallic lithium. Therefore, on a bulk thermodynamic basis, the cathode never reached the condition required for a separate metallic lithium phase to be stable, indicating that the Bi cathode was still able to accommodate the lithium generated subsequently while maintaining a relatively low lithium activity.

During the electrolysis process, the cathodic potential exhibited distinctly different variation characteristics depending on the applied current. At 0.5 A, the cathodic potential remained stable at -1.9 to -2.1 V during most of the runs and only shifted negatively to -2.60 to -2.65 V in the later runs. At 1.0 A, the cathodic potential was in the range of -2.2 to -2.5 V from the very beginning and dropped abruptly to approximately -3.0 V at an earlier run. A higher current therefore led to stronger cathodic polarization and caused the polarization to deteriorate earlier.

In the first few runs, the cathodic potential recovered rapidly to -1.55 to -1.70 V after current interruption. At 0.5 A, even during the later runs, the recovery of the cathodic potential remained largely complete. Although the potential shifted negatively to -2.65 V during electrolysis, it still recovered to -1.69 to -1.72 V within 2 min after current cessation. In contrast, at 1.0 A, the potential recovery became progressively slower; after the last few runs, even after the same 2 min relaxation period, the cathodic potential still remained at -2.0 to -2.25 V. Thus, Bi is still considered a promising medium for Li collection, its performance could be improved by measures such as stirring.

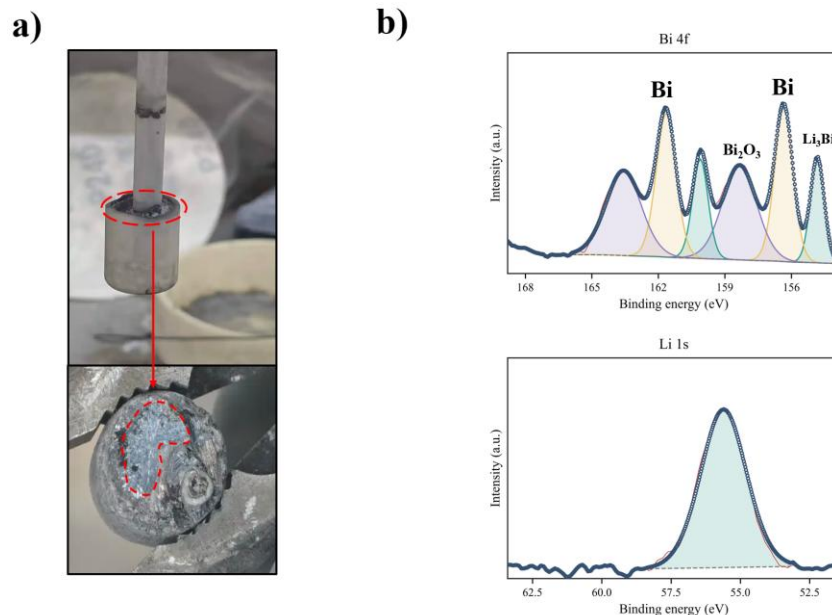


Figure 10 Post-electrolysis characterization of the bismuth cathode. **a)** Photographs of the cathode recovered after electrolysis: the crucible lifted out together with the current lead (top; red dashed circle, solidified cathode surface), and the purple phase exposed by grinding the bismuth ingot (bottom; red dashed outline). **b)** XPS spectra of powder

collected from the ground bismuth: the Bi 4f region (top) fitted with three spin-orbit doublets, corresponding to metallic Bi, Bi₂O₃ and a low-binding-energy component assigned to Li₃Bi; and the Li 1s region of the same sample (bottom).

During the removal of the cathode at the end of both experiments, the crucible holding the bismuth was lifted out together with the current lead, indicating that the cathode had solidified rather than remained liquid at that stage. After cooling, grinding the solidified bismuth revealed a purple phase embedded within it (Figure 10a). A small amount of metallic powder was then collected from the 1.0 A cathode by filing for XPS analysis.

XPS analysis of the Li 1s spectrum (Figure 10c) further confirmed the presence of Li in the same sample. The Bi 4f spectral region (Figure 10b) showed that Bi was present in multiple chemical states and was therefore fitted with three spin-orbit doublets, each constrained to a 4f_{7/2}-4f_{5/2} splitting of 5.3 eV and a peak area ratio of 4:3. Among these, the 4f_{7/2} peak of the third component was located at 155.0 eV. Such a shift to lower binding energy indicates a more electron-rich chemical environment for Bi. This position also agrees with values reported for Li₃Bi[18], and the component is therefore assigned to the Li₃Bi phase.

Taken together with the other experimental observations—the solid phase observed in the cathode at the operating temperature, the open-circuit potential plateau near the reported Li₃Bi equilibrium potential, and the purple region visible in the cathode—the low-binding-energy Bi 4f component indicates that Bi does not act merely as an inert current collector, but participates in the cathodic reaction. The Li generated during electrolysis is therefore retained in the Bi cathode as a Li-Bi alloy phase rather than being released as free metallic lithium.

Conclusions

Metallic uranium was electrochemically converted to UCl₃ in LiCl-KCl molten salt at 773 K in an electrolytic cell whose anodic and cathodic compartments were separated by a porous frit. This chlorine required for UCl₃ formation was supplied by the molten salt itself

rather than by an external chlorinating agent, while the lithium generated at the cathode was immobilized as a Li-Bi alloy. This process therefore consumes no additional chlorinating reagent and requires no sacrificial metal chloride.

Among the two candidate cathode metals, Bi exhibits better suitability. XPS of the recovered cathode identifies a phase as Li_3Bi . Impedance measurements indicate that the ionic conduction path through the porous frit introduces an additional resistance of approximately $7.1\ \Omega$. During ten consecutive electrolysis runs, the UCl_3 concentration in the anodic compartment increases approximately linearly, ultimately reaching 12.45 wt.% and 12.57 wt.% at 0.5 A and 1.0 A, respectively, with corresponding apparent current efficiencies of 95.5% and 96.4%. Therefore, the final UCl_3 concentration is primarily determined by the cumulative charge passed and can be preset by controlling the total charge amount. Increasing the current from 0.5 A to 1.0 A does not reduce the charge utilization, but it does enhance cathodic polarization during electrolysis and slows the recovery of the cathodic potential between electrolysis cycles. Nevertheless, after sufficient relaxation, the cathodic potential can recover to a plateau at approximately -1.67 V under all conditions. These results demonstrate the potential of this electrochemical strategy for the controlled preparation of UCl_3 molten salts.

Overall, a frit-separated cell pairing a metallic uranium anode with an active Bi cathode converts the metal into dissolved UCl_3 at a current efficiency approaching the theoretical value, without any external chlorinating agent. This offers an alternative route to the preparation of UCl_3 molten salts.

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