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Development of a Chlorine Cathode and Anode Basket Assembly for Production of Uranium Chloride

Chemical and Fuel Cycle Technologies Division

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Development of a Chlorine Cathode and Anode Basket Assembly for Production of Uranium Chloride

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Abstract

A chlorine cathode has been developed for in situ chlorination of metals, oxides, and oxychlorides in molten chloride electrolytes that could be used to support synthesis of chloride fuel salts for molten salt reactors. The chlorine cathode is designed to electrochemically reduce chlorine gas to generate chloride ions that, when paired with a metal anode, chlorinate that metal as it is oxidized into the salt. The designed porous carbon electrode effectively distributes Cl_2 to the electrode surface and efficiently generates Cl^- ions in the molten chloride electrolyte. This report highlights recent improvements made to the electrode assembly, with a focus on operational control of the anode basket stability. Synthesis tests demonstrated the successful chlorination of uranium metal, resulting in 3.6 wt% uranium generated in the LiCl-KCl base salt in 45 minutes, performed in a bench-scale chlorination apparatus. Higher concentrations could be achieved by applying longer chlorination times or increasing the amount of uranium loaded in the anode basket. Overall, the chlorine cathode can be used with an appropriately designed anode to chlorinate uranium in situ for synthesis of molten salt reactor fuel salts.

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I. Introduction

Molten salt reactors (MSRs) have emerged as attractive candidates for the development of next-generation nuclear energy. High quality molten salts are a crucial component of these reactors, as they function as both a coolant and a fuel source. Deployment of demonstration- and commercial-scale reactors is challenged by the supply chain demand for significant quantities of high-purity actinide chloride salts. Variations in MSR designs complicate this issue further, as they can present different needs in the production of the desired fuel. The adoption of a specific synthetic technique will require the consideration of requirements for salt composition and purity and the available reagents or feedstock (i.e. metal, oxide, oxychloride). Further development of adaptable fuel salt syntheses and purification technologies to address these context-dependent needs will support advancement and deployment of MSR technologies.

Electrochemical chlorination performed directly in a molten salt is one possible method for the synthesis of actinide chloride salts. Chlorination of oxides and oxychlorides that are formed during electrorefining was previously demonstrated by using a Zr-mediated anode (Lichtenstein et al., 2023). In that process, the Zr-mediated anode oxidizes zirconium into LiCl-KCl to form $ZrCl_6^{2-}$ which then reacts with actinide oxide and oxychloride particles to form actinide chlorides and inert ZrO_2. Separately, the electrochemical generation of chloride ions in a molten salt with a chlorine cathode was developed and then demonstrated for use with the Zr-mediated anode or for electrochemical chlorination of actinide metals (Nilles et al., 2024; Nilles et al., 2025). Although the use of the chlorine cathode was effective in chlorinating metals, the design and operation of a paired Nichrome basket anode in the initial scoping tests did not demonstrate that the functionality of the chlorine cathode was sufficient to ensure selective chlorination. While the initial chlorine cathode tests were successful in generating chloride ions and chlorinating metals, optimization of the anode potential is required to control chlorination selectivity.

This report summarizes the continued development of the chlorine cathode toward selective chlorination of actinide metals to support MSR fuel salt synthesis. Electrochemical analysis of the anode was performed during chlorination to determine the operational window for actinide chlorination using a Nichrome anode basket to contain uranium metal and to identify the conditions required for selective and reproducible chlorination of metal actinides in chloride salts.

II. Chlorination Test Apparatus

II.1 Chlorination Assembly

The chlorination assembly was staged in two separate fume hoods. The first fume hood is non-radiological and is used for storage and distribution of chlorine gas and vacuum ventilation of the test apparatus (Figure 1). The second fume hood is radiological and contains the test vessel and chlorine scrubber (Figure 2). A nickel alloy tube was plumbed between the two fume hoods to deliver Cl_2 from a lecture bottle to the chlorination cell. Stainless steel tubing was used for argon gas and vacuum lines between the two fume hoods. The scrubber was filled with stainless steel wool to remove the remaining chlorine gas from the test vessel exhaust before venting into the fume hood. Sensors were placed outside of the fume hood holding the chlorine lecture bottle and downstream of the scrubber to detect any chlorine gas leak.

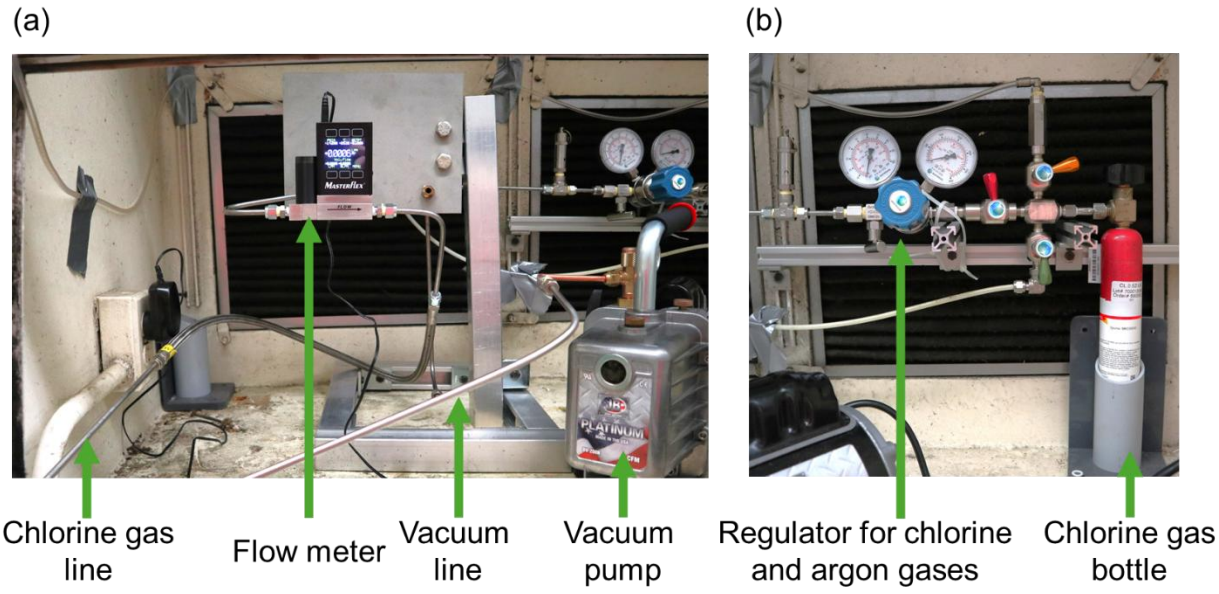

Figure 1. Non-radiological hood used for chlorination and vacuum pump for the chlorination test vessel. (a) Left side of the hood showing chlorine gas line, flow meter used to monitor chlorine flow, vacuum line, vacuum line, vacuum pump. (b) Right side

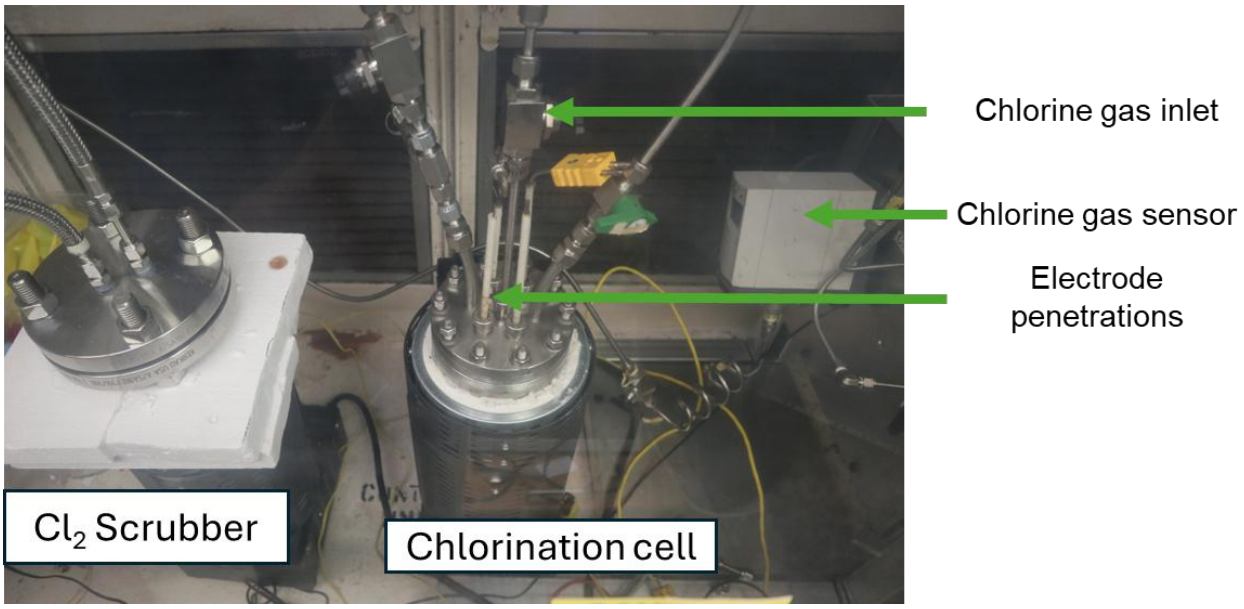

Figure 2. Chlorination and scrubber apparatus in the radiological hood.

II.2 Operation of the Chlorination Assembly

Chlorination of uranium metal was performed using a chlorine cathode (Figure 3) with a 100 pores per inch carbon foam electrode surface and a Nichrome anode basket containing uranium metal (U-10Mo foil) in a LiCl-KCl eutectic salt mixture. Chlorine gas was directly supplied to the foam material through slits along the side of the nickel tube. This method of gas delivery maximizes the amount of chlorine that contacts the carbon material during chlorination, thereby minimizing the amount of unreacted chlorine gas leaving the test vessel. An alumina crucible was filled with 150 g of fresh LiCl-KCl eutectic and placed in the bottom of the chlorination test vessel in an argon-atmosphere glovebox. Electrodes were held in the cell above the salt level during cell assembly. The chlorination vessel was assembled and sealed in the glovebox, then moved to the fume hood, connected to the gas lines and scrubber, and placed under vacuum.

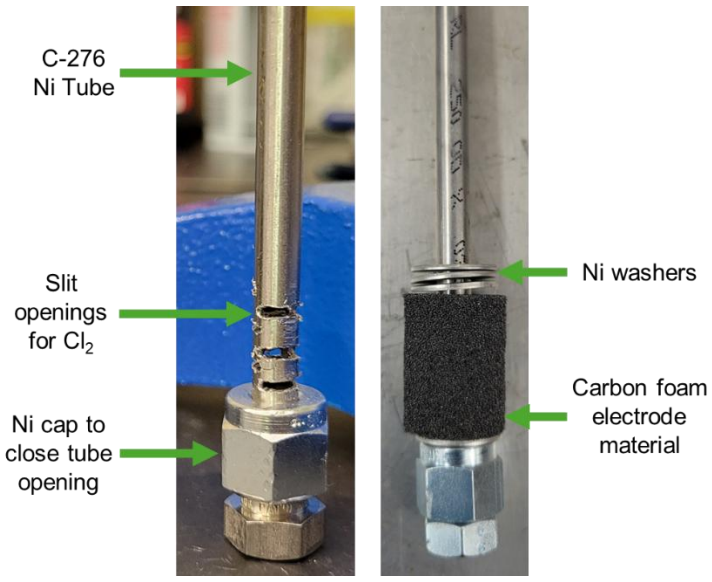

Figure 3. Assembly of chlorine cathode composed of nickel tubing and caps with slit openings for chlorine gas (left) shrouded by a porous carbon layer and held in place with nickel washers (right).

The assembled chlorination test cell was heated under vacuum at 250 °C for 12 h to remove any moisture absorbed in the salt and crucible. After drying, the test vessel was heated to 500 °C under a continuous argon blanket to melt the salt, and then the electrodes were lowered into the salt. Argon gas was flowed through the cathode prior to and during immersion. After the immersed chlorine cathode had thermally equilibrated with the salt, the gas mixture was switched to chlorine gas and chlorination was initiated. An argon gas blanket was maintained in the cell headspace to sweep unreacted chlorine gas out of the chlorination vessel and through the scrubber, which was held at 300 °C.

A potentiostat (Gamry Reference 5000E) was used to apply either current or voltage between the chlorine cathode and anode basket. The anode basket was used as the working electrode, the chlorine cathode as the counter electrode, and a tungsten wire immersed in the salt was used as a quasi-reference electrode. Voltage measurements were made relative to the open circuit potential (OCP) of the quasi-reference electrode. Two separate uranium chloride synthesis tests were conducted with different applied current and charge passed to partially chlorinate the U-10Mo foil. The shorter synthesis run was performed at 1.8 A for 10 minutes with a targeted uranium concentration of 0.5 wt % based on charge passed. A longer synthesis was conducted at current ranging from 2.5 – 1.5 A over 45 minutes with a targeted uranium concentration of 2.7 wt % based on charged passed. After tests were completed, the chlorine flow was stopped, the electrodes were removed from the salt, and the vessel was allowed to cool under continuous argon gas flow. The cooled vessel was then moved from the fume hood to a glovebox for disassembly and post-test examination. Salt samples were collected from the bulk material by mechanical separation using a chisel and stored in vials for ICP-MS analysis.

III. Optimization of Electrode Assembly

The test results discussed in previous reports (Nilles et al. 2024, Nilles et al. 2025) demonstrated that the chlorine cathode is highly effective in chlorinating most metals and that selective chlorination of metals can be controlled by the anode configuration and cell operation. The non-selective chlorination observed in the previous tests could have been caused by differences in surface area of the chlorine cathode and the anode basket. The chlorine cathode used in tests described in earlier reports (Nilles et al. 2024, Nilles et al. 2025) had a large surface area originating from the porous carbon layer. As a result, reaction in the anode basket became current-limiting and drove the anode toward strong oxidative potentials, leading to the Nichrome basket decomposition. Therefore, further testing described in this report employed the anode basket as the working electrode to enable careful potential control toward selective chlorination of uranium metal.

Galvanodynamic measurements at the anode were used to establish the operating current and potential window for selective chlorination of uranium metal and protection of the Nichrome basket (Figure 4). During these measurements, chlorine gas was flowed through the cathode at 50 mL/min and electrochemically reduced to chloride ions. The current was scanned at a rate of 25 mA/cm^2 from 0 mA to 5A and the change in the anode potential was monitored vs a tungsten quasi-reference electrode. This potential was normalized to the $Li^{+/0}$ reduction potential, which was determined from cyclic voltammograms that were collected on the tungsten electrode prior to chlorine introduction into the cell. Three anode configurations were tested in the galvanodynamic measurements: an empty Nichrome basket without uranium metal present, a Nichrome basket with a U-10Mo foil with low surface area, and a Nichrome basket with a U-10Mo foil with high surface area (Figure 4).

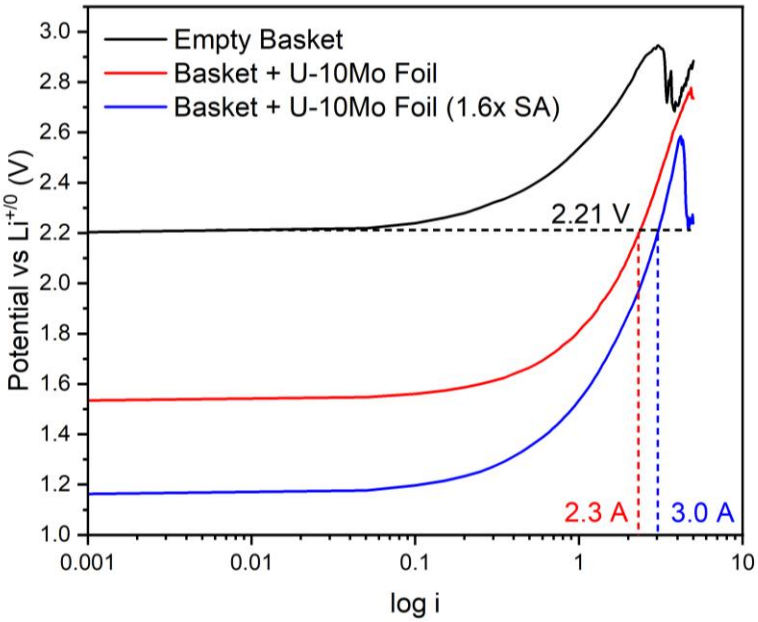

Figure 4. Galvanodynamic polarization curve of an empty anode basket (black) and anode baskets containing U-10Mo foils (red, blue) during chlorination. The surface area of the U-10Mo foil in the measurement shown by the blue trace was 1.6 times greater than the surface area of the U-10Mo foil represented in the measurement shown by red trace.

At the test onset, the empty Nichrome basket had a positive potential of 2.21 V vs $Li^{+/0}$. This potential is indicative of the onset of basket decomposition and should be used as the anode potential limit when performing actinide chlorination in a Nichrome basket. The measured potential gradually increased as higher currents were applied, which drove the electrode to stronger oxidative potentials. This method was repeated for the anode basket configurations that contained U-10Mo foils having different surface areas. The galvanodynamic polarization of the U-10Mo anode basket with low uranium foil surface area had a similar trace as the empty basket but began at the more negative potential of 1.53 V vs $Li^{+/0}$ (Figure 4, red trace). The polarization curve for the low surface area uranium foil reached the empty Nichrome basket onset potential (2.21 V) at 2.3 A. The test was repeated with a U-10Mo foil with a surface area 1.6 times greater than the foil used in the previous test (Figure 4, blue trace). The electrode containing the larger foil behaved similarly to the low surface area electrode but achieved a higher current value limit of 3.0 A before basket decomposition.

The electrodes remained structurally intact following the galvanodynamic chlorination testing with operational control of the anode (Figure 5). The chlorine cathodes from the empty basket test and U-10Mo tests displayed little to no clogging from frozen salt when cooled (Figure 5A&C). A small degree of corrosion was observed for the empty basket electrode as evidenced by the black discoloration towards the bottom of the electrode, but the basket remained intact after the galvanodynamic test, indicating that potential control will prevent basket dissolution during chlorination (Figure 5B). With U-10Mo present within the basket electrode, a small amount of red-orange colored salt was adhered to the Nichrome basket (Figure 5D) and was enriched in iron

and nickel based on ICP-MS analyses (Table 1).

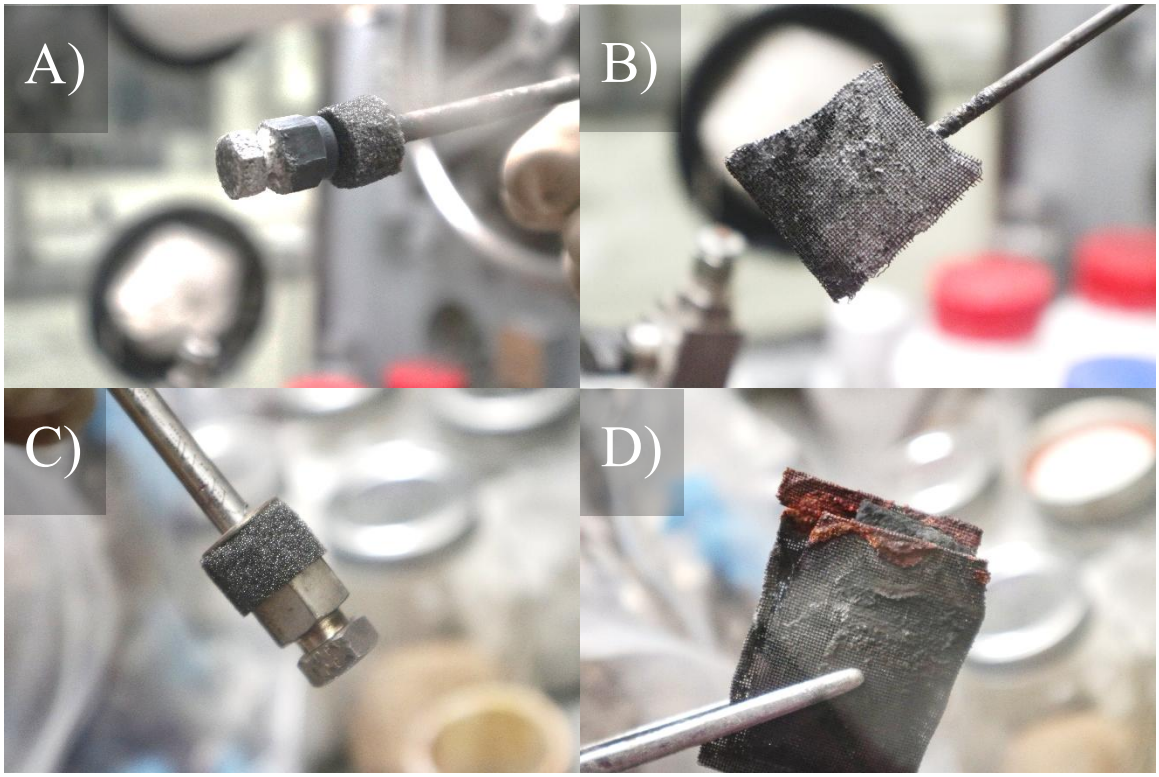

Figure 5. Chlorine cathode and anode following chlorination testing for empty basket test (A&B) and U-10Mo with low surface area (C&D). Both sets of electrodes were used in the galvanodynamic polarization (Figure 4). Additionally, the U-10Mo electrodes were also used in synthesis Test 1 (1.8 A for 10 minutes).

Uranium chloride synthesis was demonstrated in two separate galvanostatic tests. For these syntheses, U-10Mo foils providing high surface areas were used, and the chlorination conditions were determined from the galvanodynamic test with U-10Mo foils providing the higher surface area (Figure 4, blue curve). During synthesis Test 1, the cell was held at 1.8 A for 10 minutes with chlorine gas flowing through the cathode The resulting salt was grey in color and had a uranium concentration of 1.35 wt %, as measured by using ICP-MS (Table 1). Synthesis Test 2 was conducted over 45 minutes (Figure 6). In synthesis Test 2, high currents (2.5 A – 1.5 A) were applied and were adjusted over the course of the test to maintain an anode potential that was approximately 500 mV lower than the basket decomposition potential indicated in Figure 4 (2.21 V vs. W quasi-reference). The electrodes remained structurally intact during both synthesis tests, similar to the electrodes shown in Figure 5. The upward trend in the potential response is attributed to drift in the quasi reference electrode resulting from changes in salt composition during the test. A more stable reference or quasi reference electrode is recommended

for longer synthesis tests to ensure appropriate anode operation at larger scales or longer synthesis durations.

Table 1. ICP-MS Analysis of salt samples following chlorination syntheses, wt %*

Element	U	Mo	Ni	Cr	Fe
Test 1, base salt (grey)	1.35	2.33 E-03	0.02	0.03	< 0.06
Test 2, salt adhered to basket (red-orange)	0.85	0.35	7.56	3.14	5.25
Test 2, base salt top layer (brown-grey)	1.35	0.01	0.05	0.19	0.51
Test 2, base salt middle layer (green)	1.48	4.52 E-03	0.03	0.16	0.40
Test 2, base salt bottom layer (purple-black)	6.35	4.37 E-03	0.02	0.06	<0.11

*balance LiCl/KCl.

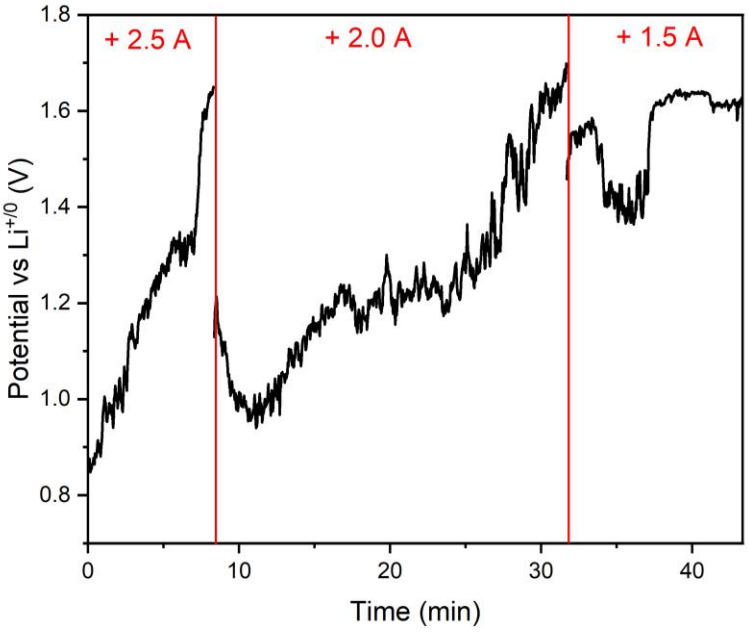

Figure 6. Galvanostatic measurement of U-10Mo basket anode during chlorination (Test 2).

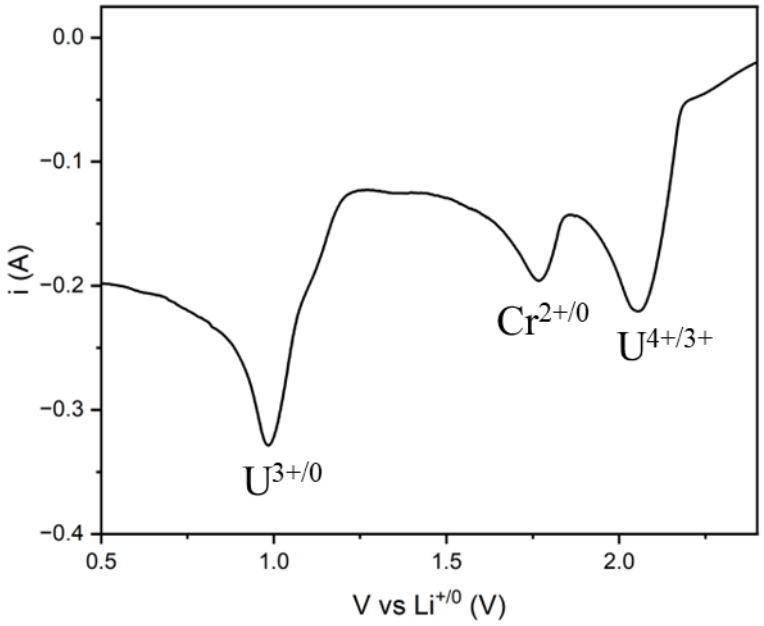

Figure 7. Linear sweep of post-Test 2 salt synthesis using tungsten electrodes at 500 mV/s.

Before disassembly of synthesis Test 2, the salt composition was characterized by using linear sweep voltammetry (LSV) with tungsten wires as the working, counter, and reference electrodes (Figure 7). Reduction peaks associated with $U^{3+/0}$ and $Cr^{2+/0}$ were identified and are consistent with previous chlorination tests (Nilles et al. 2025). Additionally, a peak approximately 1 V more positive to the $U^{3+/0}$ peak was detected that corresponds to $U^{4+/3+}$ reduction (Masset et al. 2005).

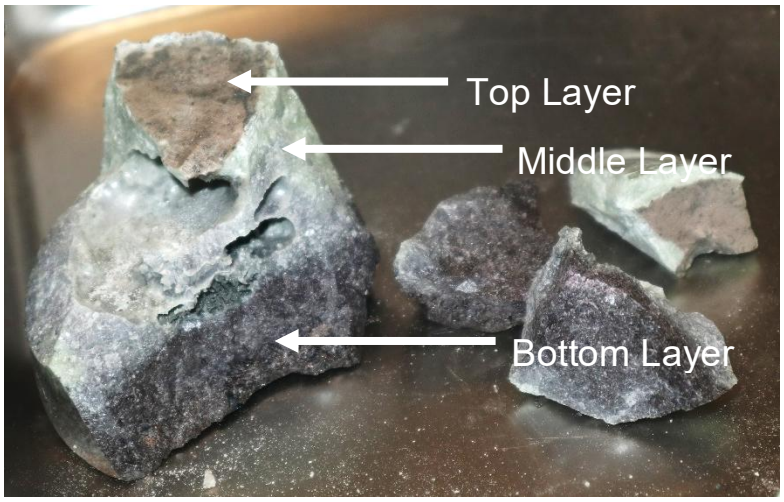

Figure 8. Salt layers resulting from chlorination synthesis Test 2 of U-10Mo foil over 45 minutes with applied currents from 2.5 to 1.5 A.

Once cooled, three layers were observed in the solidified salt (Figure 8). A thin brown/grey layer was detected on top of the salt, a thicker green layer in the middle, and a purple-black colored salt at the bottom. The salt layers were separated mechanically using a chisel and then individually melted to further characterize the components of the green and black salt layers. The $U^{3+/0}$ reduction peak was used to quantify the concentration of uranium in the salts through the operation of a four-probe electrode sensor (Guo et al. 2021). The sensor consisted of four tungsten wires at sequential lengths differing by 5 mm each. Linear sweep voltammograms (LSVs) were conducted at 2000, 1000, and 500 mV/s on each tungsten wire and the peak currents were recorded to determine the concentration. Corrections for uncompensated ohmic resistance were implemented in the analysis of peak currents and widths through the use of current multipliers that had been developed previously for sensor implementation (Shaheen et al. 2024). The concentration of uranium in the bottom layer of the salt measured by using the sensor was calculated to be 8.7 wt %. ICP-MS analysis of the bottom layer measured a uranium concentration of 6.35 wt %. The difference between the two measured concentrations could be a result of inhomogeneity of the cooled salt layer when sampling or analytical uncertainty associated with ICP-MS analysis. The top green layer contained a lower concentration of uranium, calculated to be 1.3 wt % using the sensor, which is similar to the ICP-MS data measuring 1.48 wt %. The green colored salt in this layer is characteristic of uranium tetrachloride. Excess Cl_2 gas in the cell could explain the generation of UCl_4, as gaseous chlorination reactions are known to make higher-valent uranium chlorides (Canning 1957). While uranium trichloride is the desired species, reduction of U^{4+} to U^{3+} is straightforward and can be accomplished by adding excess uranium metal to the salt. When considering the total volume of the base salt, the total concentration of uranium produced by chlorination was determined to be 3.6 wt %, and the synthesis test consumed approximately 50% of the loaded uranium before the test was terminated. Based on the charge passed during the electrochemical synthesis, the theoretical maximum concentration of uranium in the volume of salt used was predicted to be 2.7 wt %. The chlorination synthesis tests were intended to evaluate anode control schemes and intentionally did not aim for complete conversion of metal to UCl_3. It is possible that some unreacted Cl_2 gas from the chlorine cathode chemically reacted with the U-10Mo metal to generate additional uranium chloride. Alternatively, uranium could have been generated through reaction of the U-10Mo foil with corrosion products such as $FeCl_2$ or $CrCl_2$. The corrosion-mediated production of uranium (III) from a stainless-steel vessel has been reported (Choi et al. 2025), defined by the equations:

$$FeCl_3 + U \rightarrow Fe + UCl_3 \qquad \Delta G = -431.31 \text{ kJ @ } 773 \text{ K}$$

$$1.5FeCl_2 + U \rightarrow 1.5Fe + UCl_3 \qquad \Delta G = -329.07 \text{ kJ @ } 773 \text{ K}$$

$$CrCl_3 + U \rightarrow Cr + UCl_3 \qquad \Delta G = -343.24 \text{ kJ @ } 773 \text{ K}$$

$$1.5CrCl_2 + U \rightarrow 1.5Cr + UCl_3 \qquad \Delta G = -249.67 \text{ kJ @ } 773 \text{ K}$$

Small amounts of iron and chromium were detected in the salt using ICP-MS, and we hypothesize that a small quantity of uranium chloride was generated following this mechanism. The iron and

chromium detected in the salt post-testing could have originated from portions of the stainless-steel vessel over repeated use with chlorine gas or the Nichrome anode basket. The additional chlorination from unreacted Cl_2 gas with the uranium metal can be moderated with optimization of the chlorine cathode geometry gas flow rate for more efficient conversion to chloride ions, which would correspond with higher selectivity for uranium metal.

These tests have demonstrated improved operational control and stability of the anode basket electrode during the chlorination of uranium metal. However, some drift in the potential measured using the quasi-reference that occurred during galvanostatic polarization (Figure 6) could, if uncontrolled or uncompensated for, lead to conditions resulting in oxidation of the anode basket over long operating times. Further development of electrochemical chlorination to produce MSR salt should employ a more stable reference electrode to improve control of electrode operation and selectivity in product generation.

IV. Conclusions and Recommendations

The use of the chlorine cathode and anode basket assembly for chlorination of metals in molten LiCl-KCl has been successfully demonstrated and anode basket control requirements have been identified to maximize selectivity during chlorination to support development of MSR salt synthesis technology. This report summarizes results of tests used to develop and implement anode operational controls needed to prevent anode basket dissolution. In particular, the Nichrome anode basket voltage must be maintained at a potential lower than 2.2 V vs. a tungsten quasi-reference electrode to prevent anode basket dissolution. Further, this operational upper-limit will be dependent on the anode material. Utilization of a stable reference electrode would enhance operational control over longer operating times needed for engineering-scale syntheses.

Additional tests are required to further improve the selectivity and efficiency of actinide metal and oxide chlorination using this electrode assembly, with a particular emphasis on developing process controls for non-pure feedstocks to ensure that a pure salt is produced and developing operational parameters at engineering scale. This electrode assembly could be applied to the synthesis of UCl_3 from oxide precursors by coupling the chlorine cathode with a Zr-mediated anode. Implementation of a Zr-mediated anode for efficient chlorination of oxide precipitate will require additional optimization to match the output of the Zr-mediated anode and chlorine cathode. Tests demonstrating actinide oxide chlorination should identify the electrode voltages, operation times, and cell configurations needed to provide effective chlorination of oxide precipitates and minimize contamination levels. Tests for actinide metal chlorination should be performed to optimize the cell configuration and operating times to maximize yield and identify design and operational requirements needed for process scale up. With additional development, the chlorine cathode and anode basket assembly is expected to provide an effective method for the synthesis of actinide chlorides salts relevant to nuclear fuels for molten salt reactors.

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