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Status Report on the Electroreduction of Metal Oxides

T. T. Truong

R. A. Pierce

September 2021

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EXECUTIVE SUMMARY

The U.S. High Performance Research Reactor (USHPRR) Conversion Project supports the conversion of domestic civilian research reactors and isotope production facilities from the use of high enriched uranium (HEU) fuel to low enriched uranium (LEU) fuel. The Savannah River National Laboratory (SRNL) participates in the activities to support identification and validation of options for recovery of LEU metal from fabrication scrap. More specifically, SRNL will assist in the development and demonstration of technologies and equipment for the recovery of USHPRR fuel scrap.

Uranium scrap is generated throughout the fuel fabrication process. In one process, uranium metal or uranium oxide can be dissolved, purified by solvent exchange, the uranium precipitated and converted to U_3O_8 . The U_3O_8 can be converted to U metal through electroreduction. The benefits of electroreduction over the baseline process of hydrofluorination and calciothermic reduction are well-documented. However, gaps in the technology must be resolved prior to its deployment. Corrosion of the platinum anode by intermediate reaction products (and the associated anode replacement costs) has proven to be a major obstacle in full-scale demonstration of the process.

SRNL is working with Argonne National Laboratory to adapt and demonstrate the electroreduction technology to convert uranium oxide to U metal. At SRNL, tungsten trioxide was chosen as a simulant for uranium oxide because of its similarities in density for the reactants and products, and for its similar chemical reduction behavior. This report provides the status on the establishment of an electrochemical reduction test capability at SRNL, and on the evaluation of potential alternate anode materials.

Using designs in the literature, SRNL designed and fabricated an electroreduction system. Because of the limited availability of inert-atmosphere glovebox space, the system is designed to prepare the salt in an inert-atmosphere glovebox, transfer the equipment to a chemical hood, and conduct the electroreduction experiments in the chemical hood while purging the reaction vessel headspace with inert gas.

Although there were some initial concerns about gas impurities affecting the process, testing demonstrated that the design was adequate to perform electroreduction of metal oxides. SRNL performed several cyclic voltammetry (CV) and electroreduction experiments that verify the correct functioning of the equipment. In general, the CVs do not show much oxidation or reduction information because of the narrow electrochemical potential window available for scanning. Nonetheless, the results are consistent with those in the literature.

After functionality of the equipment was shown, SRNL demonstrated that it could reduce WO_3 to W metal. Two experiments successfully produced W metal which established the baseline conditions for evaluating alternate anode materials. In both tests, the anode was visibly degraded during the process. The first alternate anode test was completed with an Ir-coated Pt anode. The experiment passed 105% of the theoretical charge required for complete reduction of WO_3 to W. Analyses show that the product was tungsten metal with a trace iron-tungsten phase.

Microscopy of the Ir-coated Pt anode is planned. Additional alternate anode evaluations are in progress.

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LIST OF ABBREVIATIONS

ANL	Argonne National Laboratory
CC	Cross Cutting
CE	counter electrode
CV	cyclic voltammetry
HEU	high enriched uranium
ICP-AES	inductively coupled plasmas atomic emission spectroscopy
LEU	low enriched uranium
OCP	open circuit potential
RE	reference electrode
SRNL	Savannah River National Laboratory
USHPRR	United States High Performance Research Reactor
WE	working electrode
XRD	x-ray diffraction

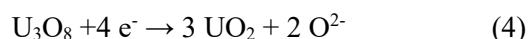
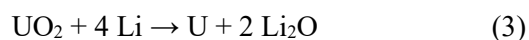
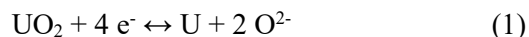
1.0 Introduction

The U.S. High Performance Research Reactor (USHPRR) Conversion Project supports the conversion of domestic civilian research reactors and isotope production facilities from the use of high enriched uranium (HEU) fuel to low enriched uranium (LEU) fuel.^[1] The Savannah River National Laboratory (SRNL) is the lead for Cross-Cutting (CC) Pillar activities that help facilitate fuel qualification, fuel fabrication, and reactor conversion. Within that role, SRNL participates in the activities to support identification and validation of options for recovery of LEU metal from fresh fuel fabrication scrap. More specifically, SRNL will assist in the development and demonstration of technologies and equipment for the recovery of USHPRR fuel scrap.

Uranium scrap is generated throughout the fuel fabrication process. Scrap recovery includes the U-Mo-Zr and aluminum-clad U-Mo-Zr scrap materials that require additional processing (aqueous or pyrochemical) to obtain purified uranium metal. In one process, uranium metal or uranium oxide can be dissolved, purified by solvent exchange, the uranium precipitated and converted to U_3O_8 .^[2] The U_3O_8 would be processed using electroreduction to produce uranium metal from the U_3O_8 .^{[3][4]} Electrowinning will purify the uranium metal stream coming from electroreduction.^[5] Dissolution, solvent extraction, conversion to U_3O_8 , and electrowinning are established technologies. Electroreduction of U_3O_8 to uranium metal requires additional development and demonstration.

Electroreduction of uranium oxide has been under development by several research organizations since at least 2002.^[6] Electroreduction is envisaged as an attractive approach for recycling spent UO_2 nuclear fuel. The benefits of electroreduction over the baseline process of hydrofluorination and calciothermic reduction are well-documented.^[5] The advantages include limited need for chemical reagents because the process uses electrons for the oxide-to-metal conversion; reduced process waste since HF is not used, no use of a reductant metal or one-time-use liners are needed; enhanced process safety due to no HF or steam handling requirements; and reduced process footprint.

The electroreduction process begins by loading uranium oxide into a basket that also functions as the cathode for the electrochemical process. The basket with the uranium oxide is immersed in molten lithium chloride ($LiCl$) containing nominally 1 wt. % lithium oxide (Li_2O) at 650 °C.^[7] Due to $LiCl$ and Li_2O reactivity with water, a high-purity argon environment is required for the process.^[6] According to Equation 1, the Li_2O helps transport the oxide from the uranium oxide to the anode, where it forms O_2 gas. Uranium metal collects in the cathode basket. At the anode, Li^+ ions can be reduced to form Li metal (Equation 2), and Li reacts with UO_2 to form U metal and Li_2O (Equation 3). If U_3O_8 is present, it is reduced to UO_2 (Equation 4) before reacting to form U metal by Equation 1 or 3.



The anode is typically fabricated from platinum and is covered with a ceramic shroud to facilitate withdrawal of the O_2 gas from the system to mitigate equipment corrosion. Corrosion of the platinum anode (and the associated replacement costs) by intermediate reaction products (Li_2PtO_3) has proven to be a major obstacle in full-scale demonstration of the process.^[8]

SRNL is working with Argonne National Laboratory (ANL) to adapt and demonstrate the electroreduction technology. SRNL will also draw on the extensive work cited in the literature and the experience gained at Y-12. Since most of the development efforts have focused on irradiated UO_2 fuel pellets, several noteworthy gaps exist in the technology for processing purified U_3O_8 powder. SRNL research efforts will address some of those gaps.

2.0 Background

This report focuses on two activities. Task 1 is to establish an electrochemical reduction test capability at SRNL. Task 2 is to evaluate potential alternate anode materials.

Task 1: Establish Test Capability

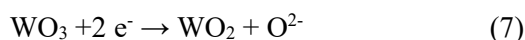
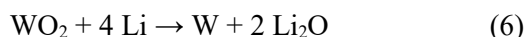
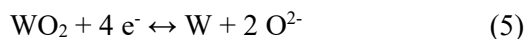
This activity will involve the procurement, set-up, and authorizations for testing. The inert glovebox that will be used for preparations is in Building 999-2W, Lab 142. Chemicals and materials were obtained, and equipment was fabricated in the SRNL Machine Shop.

Task 2: Evaluate Potential Alternate Anode Materials

One way to mitigate the issue of platinum anode corrosion is to identify an alternate anode material. Significant effort was previously given to the use of a carbon anode, but the electrode led to contamination of the salt. A boron-doped diamond electrode was evaluated but had an unsuitable temperature range of operation. Other noble metals (Rh, Pd, Ir, and Au) were also considered but did not differ significantly from Pt in their behavior. There are preliminary indications that tungsten has some potential, but the data supporting the selection of it is very limited. The same study found that 316 stainless steel, Inconel 600 and 718, nickel, molybdenum, and titanium were not good candidates.^{[8][9]}

SRNL has computer modeling capabilities with which to assess other candidate materials. Based on input to the model, other candidates will be identified to be tested in conjunction with platinum and tungsten. This testing should not exclude the use of a sacrificial electrode that corrodes, forms an insoluble oxide, and the oxide is collected and removed from the process as waste.

Because these tests are focusing on the performance of the anode, testing can be effectively performed using a simulant for U_3O_8 . Based on the literature, WO_3 was selected over TiO_2 and Ta_2O_5 for simulant testing. The oxide is attractive because it reduces from WO_3 (8.7 g/mL) to WO_2 (10.8 g/mL), and then undergoes a four-electron transfer to form W metal (19.3 g/mL). Similarly, U_3O_8 (8.3 g/mL) reduces to UO_2 (11.0 g/mL), and then undergoes a four-electron transfer to form U metal (19.0 g/mL). The reactions for W, WO_2 , and WO_3 (Equation 5-7) are comparable to those for U, UO_2 , and U_3O_8 .



3.0 Experimental Procedure

3.1 Process Equipment and Conditions

The reaction vessel was a 1000-mL 316L stainless-steel beaker purchased from Sampling Systems (3.9-in ID and 5.8-in height). A new vessel was used for each experiment. The reaction vessel was fitted with a lid that housed the heat shield, the anode, the cathode, the reference electrode, and a thermocouple. The lid was fabricated from 304L stainless steel and used Swagelok® Ultra-Torr fittings for sealing the equipment

passing through the lid while allowing for the equipment to be raised and lowered during the tests. Figure 3-1 shows the lid with its penetrations on a glass beaker to enable viewing of the reaction vessel contents.

A heat shield was fabricated from 304L stainless steel (Figure 3-2). It contained four layers of baffles with cut-outs for the insertion of the electrodes and thermowell. Three screws and nuts with washers secured the heat shield to the lid. A new heat shield was used for each test.

The anode for most of the tests was 1x4 cm Pt foil spot welded to 18 in of 0.032-in diameter wire [Pt(96%)/Rh(4%)]. For two tests, the Pt foil was sputter coated with a 1 μm layer of either iridium or ruthenium oxide (estimated thickness based on the time and current used to deposit the coating). The anode is housed in a 304L SS anode shroud (Figure 3-3). The shroud is a 14-inch tube, $\frac{3}{4}$ -inch diameter, with porous stainless-steel (100 μm pore size) at the bottom. A $\frac{1}{4}$ -inch Swagelok[®] fitting near the top provides a connection to the off-gas system which draws oxygen generated at the anode out of the reaction vessel. The anode shroud is inserted through an Ultra Torr fitting which is screwed into a piece of machinable ceramic. The machinable ceramic also supports the cathode. The anode is electrically isolated from the anode shroud using machinable ceramics, MgO tubes, and silica gaskets.



Figure 3-1. Lid with Installed Electrodes and Thermocouple

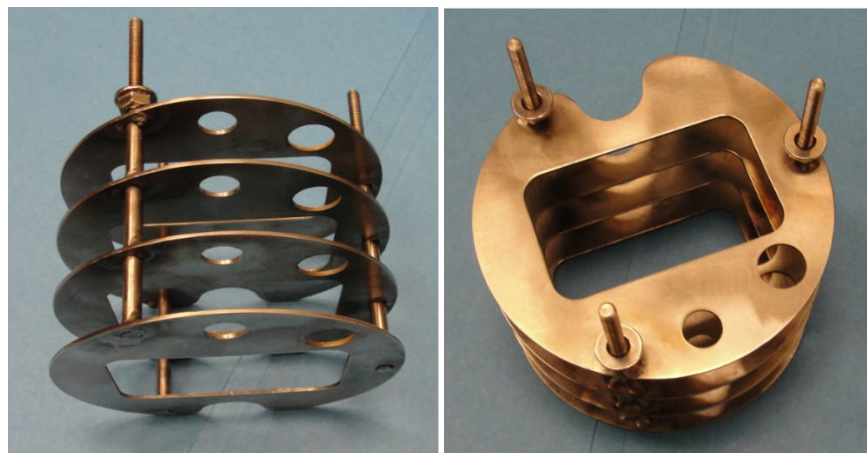


Figure 3-2. Heat Shield

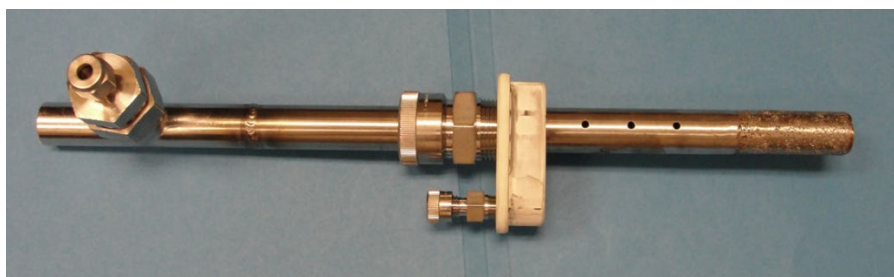


Figure 3-3. Anode Shroud with Fittings and Machinable Ceramic

The cathode was a 1/8-inch 304L stainless steel rod, 8 in long. For some tests, the rod was welded to a ~0.8 inch diameter stainless steel perforated basket (Figure 3-4, left). Other tests contained the perforated basket, but the basket was electrically isolated from the cathode by a ceramic basket bottom. At first, the ceramic bottom was a machinable Al_2O_3 bisque from McMaster-Carr. It was replaced with a MgO bottom piece purchased from MSE Supplies (Tucson, AZ).

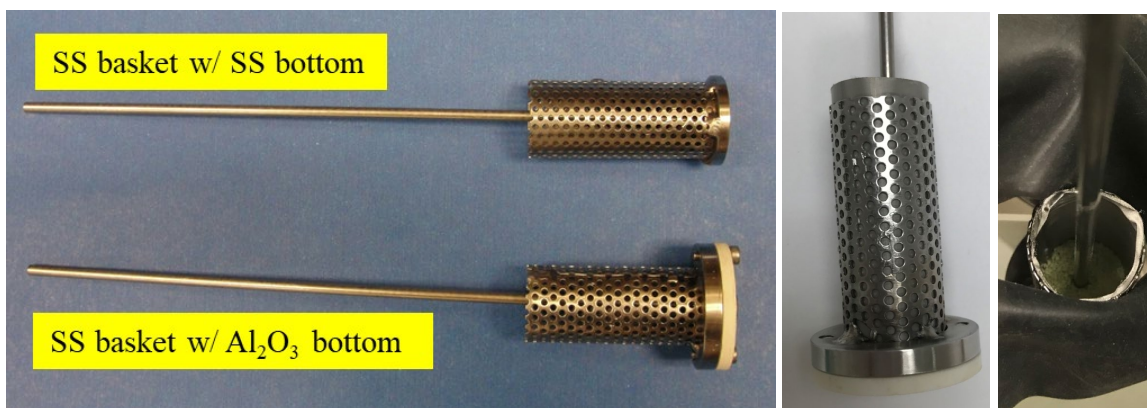


Figure 3-4. Cathode Baskets

Metal oxide (5.0 g) was placed in the cathode basket for electroreduction. Initial tests with WO_3 used a powder from Alfa Aesar with 99.8% purity and 10-25 μm particle size. Due to issues with retaining the powder in the cathode basket, latter tests reacted WO_3 from Kurt J. Lesker Company with 99.99% purity and 300-3000 μm particle size. A spot-welded cylinder of 10 μm opening SS mesh (200x1400 mesh size) was placed in the basket to help retain the WO_3 inside the basket (Figure 3-4, right).

Two reference electrodes were used during testing. The first was a Ni/NiO electrode that used a 1-mm diameter Ni wire inserted into NiO powder inside of a MgO tube with a fritted MgO plug in the end (Tateho Ozark). The MgO porous plug was cut down to ~0.25 inches. Contact between the molten salt the electrode is via the MgO membrane. Regular breakage of the reference electrode led to the consideration of an alternate reference. The second reference electrode was a pseudo reference electrode using a Ni wire inside of an open-ended 0.25-inch MgO tube. The Ni wire is in direct contact with the salt. Slow reaction between the Ni wire and the molten salt causes the reference point to drift during testing, but not enough to significantly affect a short-duration experiment.

A Type-K thermocouple was used to monitor and control the temperature of the salt. The thermocouple was inserted in a 0.25-inch stainless steel tube sealed on one end. The thermocouple was plugged into an HTS/Amptek BT15-B2-K-1-F/C controller. The controller regulates an HTS/Amptek AWH-051-080D heating tape (0.5 in. x 96 in., 624 W) wrapped around the reaction vessel. The heating tape and reaction vessel were covered with additional insulation. The reaction vessel is placed on a piece of insulating blanket to limit heat loss from the bottom of the reaction vessel. A picture of the assembled reaction system is provided in Figure 3-5.

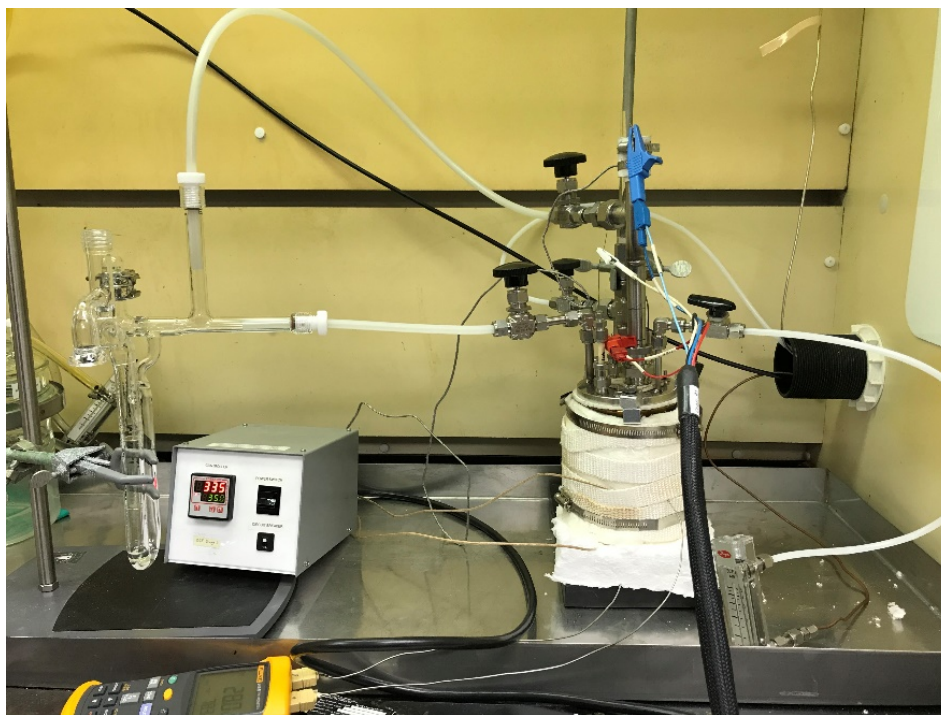


Figure 3-5. Assembled Reaction Vessel

Cyclic voltammetry (CV) experiments were conducted using the BioLogic VSP potentiostat with VMP3 Booster. When the electroreduction experiments were conducted, the potentiostat was disconnected and the power supply connected. The power supply was a BK Precision Model 1696B. A Fluke handheld voltmeter was used to measure the anode and cathode potentials versus the reference electrode during electroreduction experiments.

3.2 Test Methodology

A series of six experiments were completed measuring cyclic voltammetry and/or performing electroreduction of a metal oxide to a metal. Different anode, cathode, and reference electrode

configurations were evaluated. Two different particle size ranges of WO_3 were reduced. A list of the process conditions is provided in Table 3-1.

Table 3-1. Conditions for Cyclic Voltammetry and Electroreduction Experiments

Test*	LiCl (g)	Li ₂ O (g)	Anode	Cathode	Cathode Bottom [#]	WO ₃ (g)	WO ₃ (μm)	RE
ER-01	400	---	Pt	SS Rod	n/a	n/a	n/a	Ni/NiO
ER-02	600	6.0	Pt	SS Basket	SS	5	10-25	Ni/NiO
ER-03	601	6.0	Pt	SS Basket	SS	5	10-25	Ni/NiO
ER-04	600	6.0	Pt	SS Basket	Al ₂ O ₃	5	10-25	Ni
ER-05	600	6.0	Pt	SS Basket	Al ₂ O ₃	5	300-3000	Ni
ER-06	600	6.0	Ir-Pt	SS Basket	MgO	5	300-3000	Ni
* All tests completed with the salt at 650 °C								
[#] For MgO and Al ₂ O ₃ bottoms, the basket is electrically isolated from the rod								

The test methodology was completed in three phases spread across three or more days. First, the salt is melted and prepared in the reaction vessel in an inert atmosphere glovebox. Next, the reaction vessel is transferred to an air-atmosphere chemical hood with an inert gas purge for the electroreduction experiment. Last, the products of the experiment are sampled in an air- or inert-atmosphere environment.

3.2.1 Melt Salt in Inert-Atmosphere Glovebox

First, the salt must be melted and dried in an inert glovebox. Prior to putting items into the glovebox, the components of the electroreduction cover/insert are assembled with the cathode in the “raised” position and the anode, reference electrode, and thermocouple in the “lowered” position. The cover/insert and process vessel are transferred into the inert glovebox. The process vessel is already wrapped with heating tapes and insulation. The lithium salts, lid, funnel, and stir rod for melting the salts are already in the glovebox.

Tungsten oxide (~5 g) is weighed and transferred to the cathode basket. Lithium chloride (~600 g) is weighed and loaded into the reaction vessel. Lithium oxide (~6 g) is weighed and stored in a separate vial. The vessel cover, funnel, and funnel cover used for melting the salt are placed on the top of the reaction vessel and the vessel is secured. A Type-K thermocouple in a thermowell is inserted through the hole in the cover and plugged into a digital readout.

The salt is dried by gradually heating to 250 °C in 50 °C increments and held at temperature for about 5 hours. It is then gradually heated to 450 °C in 50 °C increments and held at temperature for about 3 hours. The salt is cooled overnight. In the morning, the Li₂O in the vial is added to the reaction vessel. The LiCl/Li₂O is gradually heated to 650 °C in 50 °C increments. Once at temperature, the funnel is removed, a stir rod is inserted through the hole, and the salt is stirred. Next, the heating is turned off, the funnel cover is removed, and a salt sample is collected on a quartz rod. The electroreduction cover/insert is placed on the reaction vessel with a high-temperature fiber gasket between the reaction vessel and the cover/insert. The electrochemical cell is cooled overnight.

3.2.2 Conduct Electrochemical Reduction Experiment

When cooled, the electroreduction lid is secured to the reaction vessel with clamps. The reaction vessel is enclosed in a plastic bag, making sure that the argon inlet line passes through the wall of the bag. The process vessel is transferred from the inert glovebox to a chemical hood, and immediately argon gas flow is connected to the inlet line. Argon flow is initiated at 0.5 scfh. After 5 minutes, the bag around the reaction vessel is removed. The reaction vessel and its services are connected, and the vessel is secured with ring stands and clamps. Argon flow to the reaction vessel is maintained throughout testing.

Using the heating tape controller, the reaction vessel is heated in 50 °C increments to 650 °C and held at temperature for about an hour. The cathode basket is lowered into the molten salt and the electrical leads to the BioLogic potentiostat are connected to the electrodes. The open circuit potential of the electrodes is monitored. About 10 minutes after lowering the cathode basket, CV tests are performed with the cathode basket as the working electrode. After the CV tests are complete, the potentiostat is disconnected, and the electrodes are connected to the power supply.

Electroreduction of the metal oxide in the cathode basket is completed by intermittently applying power to the electrodes and turning off the power to allow accumulated Li in the salt to react. While the power supply is off, the open circuit potential of the cathode is monitored. When the reduction test is complete, the anode, cathode, and reference electrode are moved to the “raised” position. The reaction system is cooled, the heating tape controller turned off, and the thermocouple moved to the “raised” position. The reaction vessel cools overnight under a continuous stream of Ar.

3.2.3 Disassembly and Sampling

After the electrochemical cell is cooled to ambient temperature, the vessel is disassembled, and the components are removed from the vessel. Samples of the salt were submitted for analysis by ICP-AES. The cathode basket was cut into using a Dremel with a cutting blade attachment. The product was removed, and the large chunks were immersed in EtOH to remove residual surface LiCl. After gentle stirring at room temperature in EtOH for several hours, the product was filtered and dried under vacuum overnight. Some of the product was transferred into the inert glovebox. The sample was ground with a mortar and pestle and then submitted for X-ray diffraction (XRD) analysis. For some tests, the anode and reference electrode were cleaned and examined using microscopy.

4.0 Results and Discussion

The electroreduction experiments had two distinct phases. The first phase involved CV using the potentiostat connected to the electrodes. This quick scan observes reactions which occur as a function of electropotential. The second phase connects a power supply to the anode and cathode in place of the potentiostat. A current is applied between the electrodes to reduce the metal oxide in the cathode basket to its corresponding metal.

4.1 Cyclic Voltammetry

Cyclic voltammetry is a tool that reveals the occurrence of electrochemical reactions in a chemical system as a function of electrochemical potential. The cyclic nature of the method identifies both oxidation and reduction reactions. To conduct effective CVs, it is best if the working electrode (WE) has significantly less surface area than the counter electrode (CE) so that the CE can readily receive the current from the WE at a range of electropotentials. For these studies, the WE was the SS cathode and the CE was the Pt anode.

In most of the experiments, the WE was a cathode basket with surface area comparable to that of the CE. This was because the system was set up to measure the CV of the system first and then transition directly to the electroreduction of the metal oxide. Furthermore, the potentiostat used to measure the CV has an operating current limit of 5 amps. As a result, most of the CVs collected (Tests ER-02 through ER-06) were limited to a narrow electrochemical potential window that did not contain reaction peaks for the tungsten and lithium components.

4.1.1 Test ER-01

Test ER-01 was completed using a SS rod for the cathode (also the WE) and Pt for the CE (Figure 4-1). The CV was cycled twice from ~ -0.36 V vs. Ni/NiO to -2.0 V vs. Ni/NiO and back. For the first scan, two reduction peaks were observed and one oxidation peak which includes one redox couple at ~ -0.48 V and the reduction peak at -1.92 V. The second scan had similar results except the current decreased. The

expected Li/Li^+ couple was not observed within this window of -2.0 to -0.36 V. Herrmann and Li reported the onset of lithium formation was at -2 V vs. Ni/NiO .^[10]

A third and fourth scans expanded electrochemical window to -2.5 V and saw the expected Li/Li^+ couple. The onset of lithium formation was at -2.25 V. The difference between the observed Li/Li^+ couple (-2.25 V) and the one reported in the literature (-2 V) is likely due to the RE not reaching equilibrium with the molten salt. The RE was in the salt at temperature for 2-3 hours. The recommended time the Ni/NiO RE, with the porous MgO plug, is ~12 hours.^[11] The redox couple at -0.5 V and the reduction peak at -1.8 V is not known at this time. They might be due to impurities in the salt such as LiOH or from the SS WE.

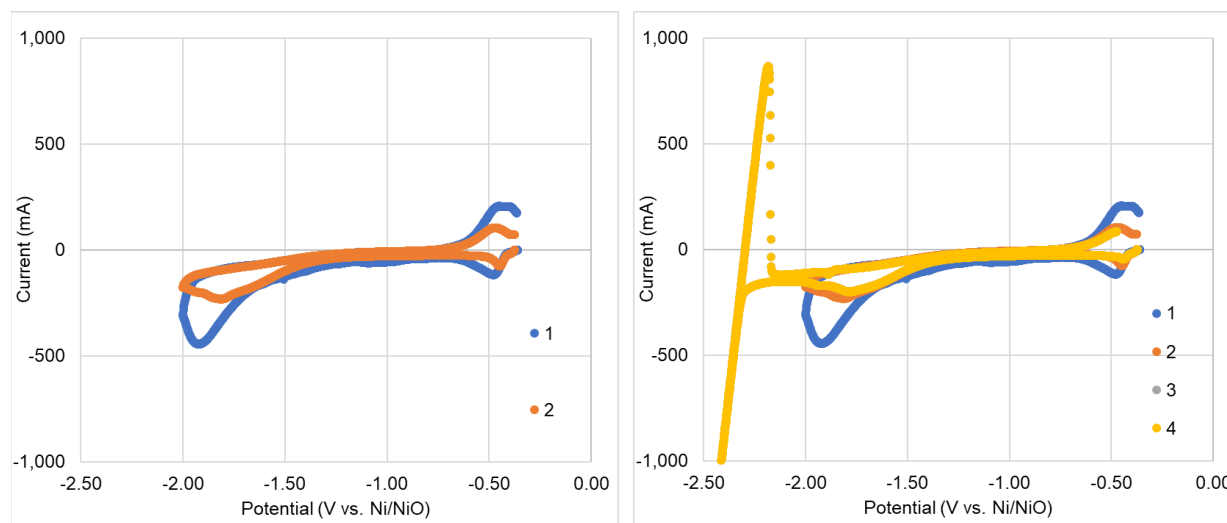


Figure 4-1. Cyclic Voltammetry for Test ER-01

When the electrodes were raised above the electrodes for disassembly, the MgO tube of the RE was broken near the molten salt interface. This might be caused by thermal shock during lowering and/or raising the RE into the molten salt. It is unclear when this occurred. Due to repeated breaking of the MgO tube for the RE in Tests ER-02 and ER-03, experiments switched to using a Ni-wire pseudo-RE. From Test ER-01, the baffles were covered in black gunk on the bottom layer, but there was no evidence of salt accumulation on the top layers. A picture of the black residue on the anode is provided in Figure 4-2. The source of the black residue is not known.



Figure 4-2. Black Residue on Anode after Test ER-01

4.1.2 Tests ER-02 through ER-06

Tests ER-02 through ER-06 used a SS basket for the cathode (and WE). Consequently, the electrochemical potential window for the CVs was limited. One of the wider potential windows tested was for Test ER-04. The potential between the Ni pseudo-RE and the Pt anode or the SS vessel was monitored using a voltmeter.

After 20 minutes of monitoring the open circuit potential (OCP) at 650 °C, the OCP was stable at ~0.51 V vs. Ni wire.

When the CV was set to scan between -1.7 V and 0.5 V. The potential was swept cathodically, but it encountered issues around -1 V due to hitting the 5 A current limit of the potentiostat. There appeared to be a reduction peak at 0.17 V. The window was reduced to between -0.7 and 0.5 V, and three successive CV scans (Part C) showed a redox couple around 0.1 V vs. Ni wire (Figure 4-3). The redox couple becomes more prominent with additional scans. It is likely that this redox couple is due to the corrosion of Ni into the salt matrix.

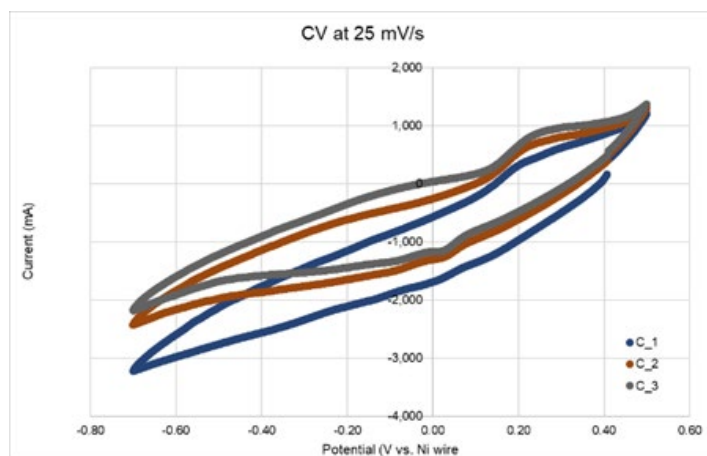


Figure 4-3. Test ER-04 CV Scans, Part C

The window for CV scans was eventually widened to between -1.2 and 0.7 V (Part E). The first scan resembled the previous CV curves with a reduction peak at 0 V (very symmetrical peak which indicates a deposited material) and an oxidation peak at ~0.3 V (Figure 4-4). On the second scan, the reduction peak shifted more negative to -0.04 V and another small reduction peak was observed at -0.16 V. The third CV scan was like to the second scan.

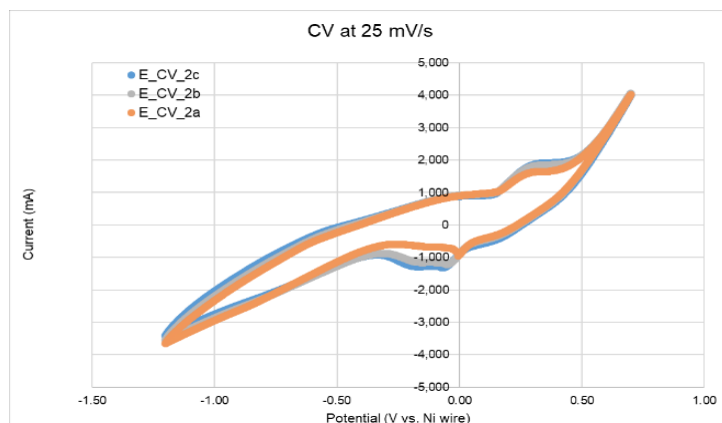


Figure 4-4. Test ER-04 CV Scans, Part E

Cyclic voltammetry scans were also conducted at the start of Tests ER-05 and ER-06. Three scans were completed as part of each test, and the results were similar. The CV scans from Test ER-06 were between 0 and 0.71 V at 25 mV/s. The CVs do not show any distinguishable redox peaks. In previous tests, the CV did show small redox peaks within this electrochemical window. These peaks might be due to nickel redox couples as the nickel reference electrode is not inert in the molten salt, and the peaks appear near 0 V vs.

Ni wire. The more time the nickel wire is in the molten salt, the more likely that nickel dissolves into the molten salt and appears in the CV. Because the nickel wire for Test ER-06 was immersed in the molten salt less than 10 minutes for the CVs, then the nickel redox couple did not appear in the CV.

4.2 Electroreduction Experiments

Of the six experiments completed to date, five were configured to reduce WO_3 to W metal. Of those five, two were discontinued (ER-03 and ER-04) due to degradation of the anode prior to switching from CV scans to electroreduction studies. In both cases, the electrochemical potential was sufficiently high to dissolve the anode wire, causing the Pt foil to become disconnected from the power supply.

4.2.1 Test ER-02

Test ER-02 was completed using WO_3 powder in a SS cathode basket, a Pt anode, and a Ni/NiO reference electrode. After the CV experiments, the BK Precision power supply was connected to electroreduce WO_3 to W metal. Because the potential limits were not known from the CV experiments, the initial parameters chosen was a series of cycles that applied 3 A (with a cell voltage upper limit of 3 V) to the anode and cathode for 12 min followed by 4 min of “rest” (no applied current) [Figure 4-5]. The rest period allows accumulated Li metal to react and oxidize. Accumulated Li can attack the anode or impede access of current to the WO_3 .^[6]

During the first cycle, the cell voltage increased with time and hit the set upper voltage limit of 3 V. Following this first cycle, for four subsequent cycles, the cell voltage was set to 3.2 V and the experiments were run with cell voltage control. As can be seen in the following plots, under applied voltage control, the current decreased with time during the 12 minutes when current was flowing. The total time that current was flowing through the reactor was 62 minutes. The calculated charge was 2.64 amp-hr. The applied charge corresponds to 75% of the theoretical charge needed to fully reduce WO_3 to W metal.

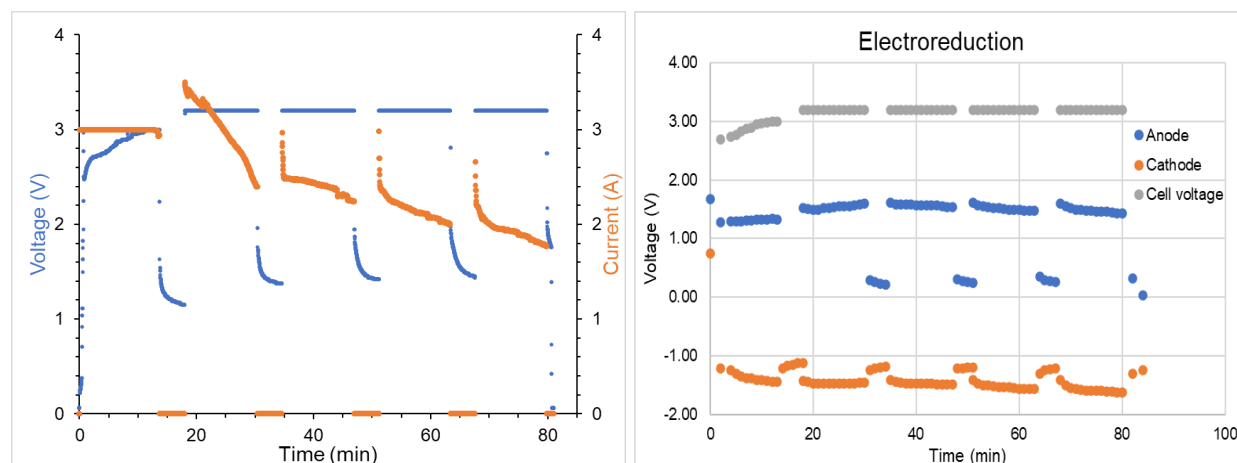


Figure 4-5. Test ER-02 Voltage and Current Profiles

The potentials of the anode and cathode were monitored using a voltmeter (against the Ni/NiO RE). The potential of the anode was initially ~1.3 V, but for subsequent cycles it was ~1.5 V. During the rest period, the anode potential was ~0.25 V. As for the cathode, it was initially ~-1.3 V and then ~-1.5 V in subsequent cycles and at ~-1.2 V at rest. During the 4 min rest period, the cathode potential became more positive with time.

After the electroreduction experiment, the electrodes and thermowell were raised and the reactor cooled overnight under Ar flow. When the lid was raised, the cathode basket remained embedded in the salt. The reference electrode was intact but the MgO tube that was immersed in the LiCl salt was discolored. The Pt

foil was partially consumed from a 1cm x4cm Pt foil to a thin black section. The cathode basket and other surfaces were covered with a black film (Figure 4-6).



Figure 4-6. Test Equipment after Test ER-02

The cathode basket was cut into using a Dremel tool and snippers. The black material at the bottom of the cathode basket was crushed and the larger chunks were immersed in EtOH to remove residual LiCl. The smaller black particles were observed to turn bronze in the chemical hood. These smaller particles were bagged and placed in the desiccator. Both compounds were dried under vacuum overnight and transferred into an inert glovebox. Tungsten dioxide (WO_2) is bronze-colored while WO_3 is yellow-green, and tungsten metal is gray. The color change for the small particles might be oxidation of W to form WO_2 .

In the argon-atmosphere glovebox, the black chunks and particles were ground using a mortar and pestle then pressed into an XRD sample holder. Two samples were submitted: 1) black material rinsed in EtOH (TT-ER-cathode- WO_3) and 2) the smaller particles that contained some powder that had turned bronze without an EtOH rinse (TT-ER-cathode- WO_3 _air).

TT-ER-cathode- WO_3 (Figure 4-7): Analysis of the XRD spectrum identified lithium tungsten oxide ($\text{Li}_2(\text{WO}_4)$), lepidocrocite ($\text{FeO}(\text{OH})$), iron oxide (Fe_7O_9), tungsten (W), and lithium chloride (LiCl). The sample is predominantly tungsten metal. The presence of $\text{Li}_2(\text{WO}_4)$ is consistent with the passing of 75% of the theoretical current for complete conversion of WO_3 to W.

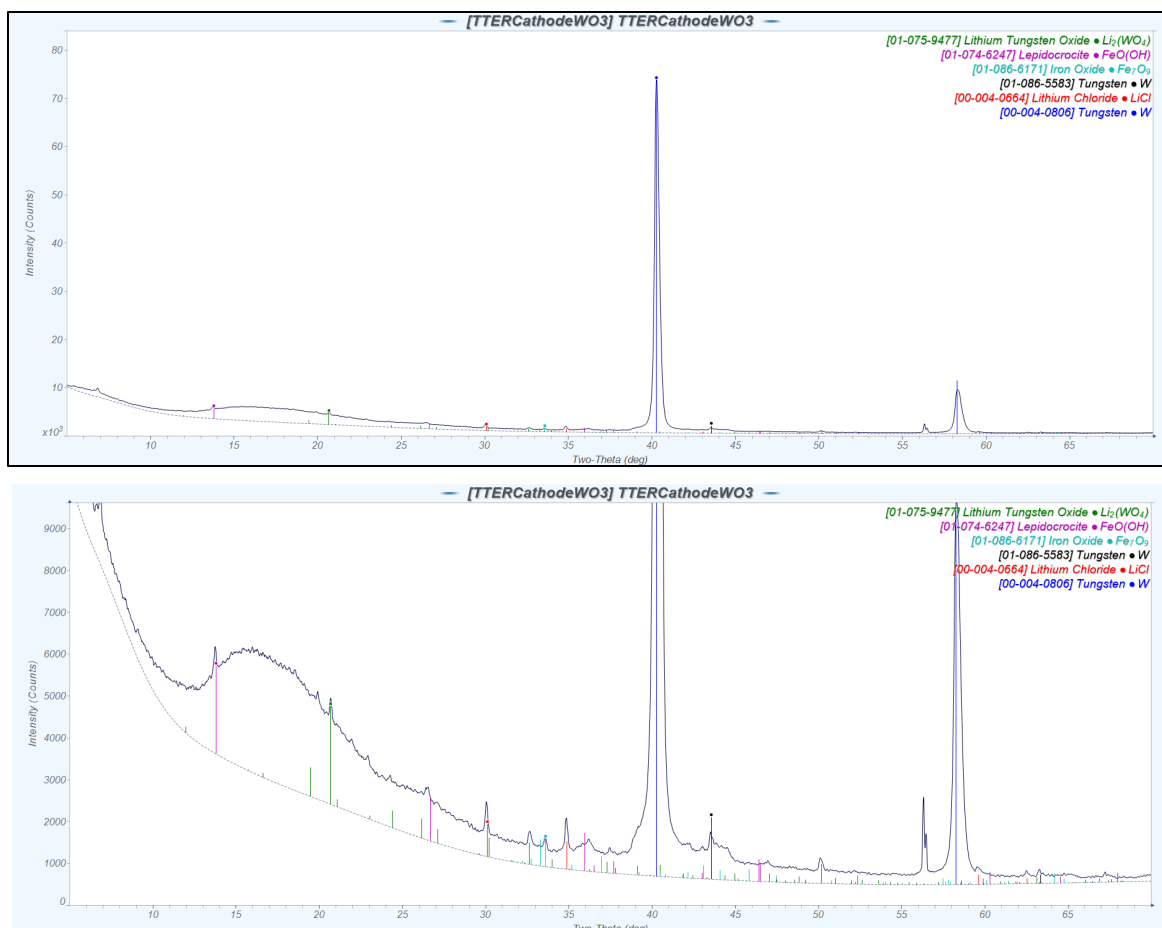


Figure 4-7. XRD Analysis of Product from Test ER-02

TT-ER-cathode-WO₃_air: Analysis of the XRD spectrum identified lithium chloride (LiCl), tungsten (W) and iron (Fe). It does not show WO₂, as expected based upon observation of the color change from black particles to bronze particles. However, the color change was only observed for a small amount of the sample and probably was not enough of the sample to show up in XRD analysis.

4.2.2 Test ER-05

Test ER-05 was completed using WO₃ particles in a SS/Al₂O₃ cathode basket, a Pt anode, and a Ni wire pseudo-RE. After the CV measurements, the BK Precision power supply was used to electroreduce WO₃ to W metal. As the potential limits were not known due to the limited potential window for the CV experiments, the initial parameters were chosen to limit the cell voltage to 2.9 V. The current was increased from 0.5 to 2.5 A until the cell voltage approached 2.9 V. During the change of applied current from 1.5 to 2.0, the parameters were accidentally entered incorrectly, and the electrochemical cell operated at 4.0 V and 7 A for ~6 sec. The applied current was intermittently interrupted after 12 min and the system power was off for 4-6 min to allow depletion of accumulated Li.

During the first cycle, the cell voltage increased with applied current and reached a maximum of 2.55 V at 2.5 A. The second cycle applied 2.0 A and the maximum cell voltage of 2.5 V. The anode and cathode potentials were monitored using a voltmeter vs. Ni wire. For the first cycle, the anode potential was around 1.5 V vs. Ni wire. It decreased to around 0.73 V vs. Ni wire for the second cycle. The cathode potential decreased steadily during the first cycle from 0.18 V to -1.1 V vs. Ni wire. Note that during the current interruption, the cathode voltage did not significantly increase which indicates the absence of lithium metal

on the cathode basket. The cathode potential was around -1.55 V for the second cycle, and the cathode potential increased to -1.2 V during the current interruption period. The data for the first two cycles are provided in Figure 4-8.

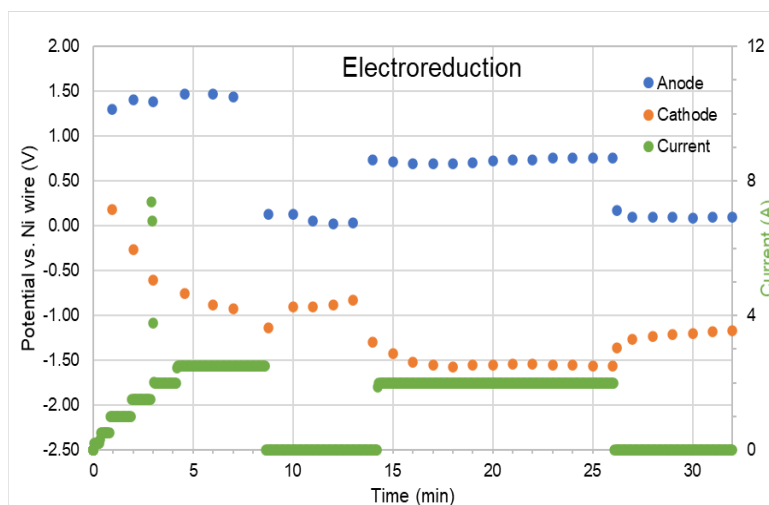


Figure 4-8. Cycles 1 and 2 of Test ER-05

The current and voltage data for the rest of the electroreduction experiment are shown in Figure 4-9. The current was decreased to maintain the cell voltage below 2.9. The anode potential was steady during the subsequent cycles and slightly decreased from 0.75 V to 0.61 V. The cathode potential decreased during each cycle and generally plateaued during the 12-min cycle at ~ -2.1 V. During the current interruption cycles, the cathode potential was monitored to make sure the potential reached -1.4 V before turning the current on. The potential -1.4 V was assumed to correspond to the oxidation of lithium metal from the cathode basket.

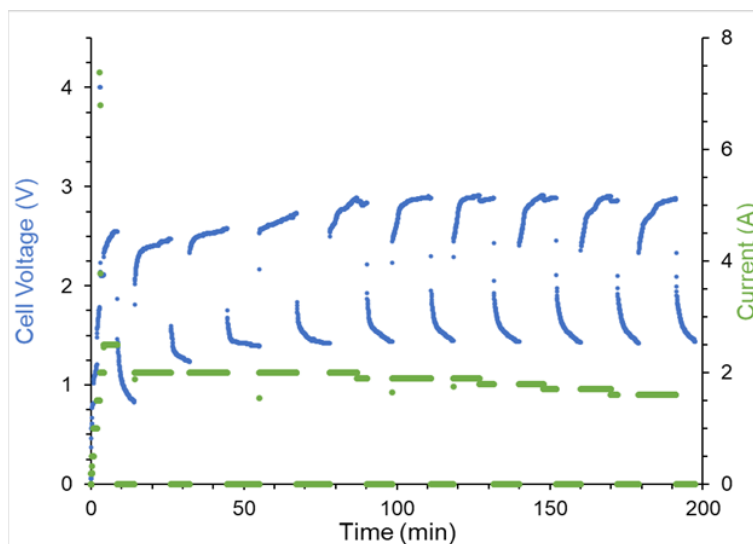


Figure 4-9. Voltage and Current Data for All Cycles of Test ER-05

The total time that current was flowing through the electrodes was 119 min. The calculated charge was 3.72 amp-hr. The charge applied corresponds to 107% of the theoretical charge needed to fully reduce WO_3 to W metal. After the electroreduction experiment, the electrodes and thermowell were raised and the reactor cooled overnight under Ar flow.

When the lid was raised, all components were intact but covered with a black film. Pictures of the cathode, anode, and cathode product are provided in Figure 4-10. After wiping the Ni wire pseudo-RE, the surface of the wire looked rough, indicating nickel was not stable during the electroreduction process or in the molten salt. The Pt foil anode was intact but covered in black residue. The SS/ceramic cathode basket was cut into using a Dremel tool. The black product was around the SS rod and not at the ceramic bottom of the basket. Some particles on the black product were observed to turn bronze during handling indicating the formation of WO_2 . The black product was removed, and the large chunks were immersed in EtOH to remove residual surface LiCl.

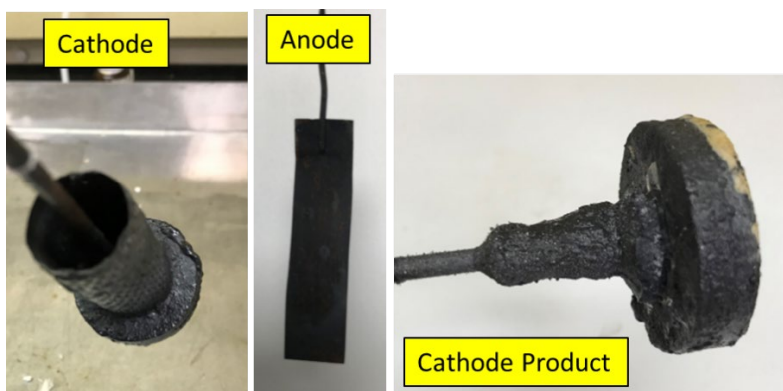


Figure 4-10. Cathode, Anode, and Cathode Product from Test ER-05

The product from ER-05 was transferred into an Ar atmosphere glovebox. The chunks appeared light gray on the surface but were dark gray after crushing. The sample was ground using a mortar and pestle and then pressed into an XRD sample holder. Analysis of the XRD spectrum identified tungsten (W), lithium chloride (LiCl), and trace iron tungsten ($\text{W}_{0.016}\text{Fe}_{0.9}$) (Figure 4-11). The sample is predominantly tungsten. No unreacted WO_3 was identified, consistent with the passing of 107% of the theoretical current.

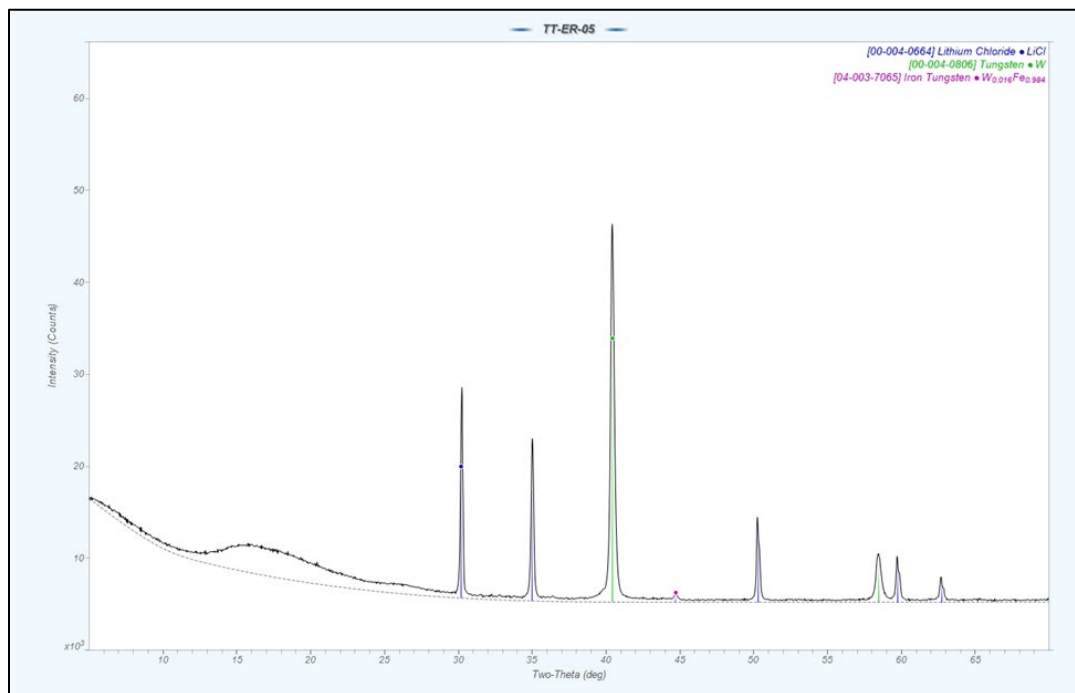


Figure 4-11. XRD Analysis of Cathode Product from Test ER-05

The electrodes were examined using a Keyence VR-3200 microscope. The unused nickel wire is unblemished and shiny under the microscope. For the nickel wire used as the pseudo-RE, the surface has been significantly attacked (Figure 4-12). Similarly, the Pt anode looked rougher and rusted (Figure 4-13).

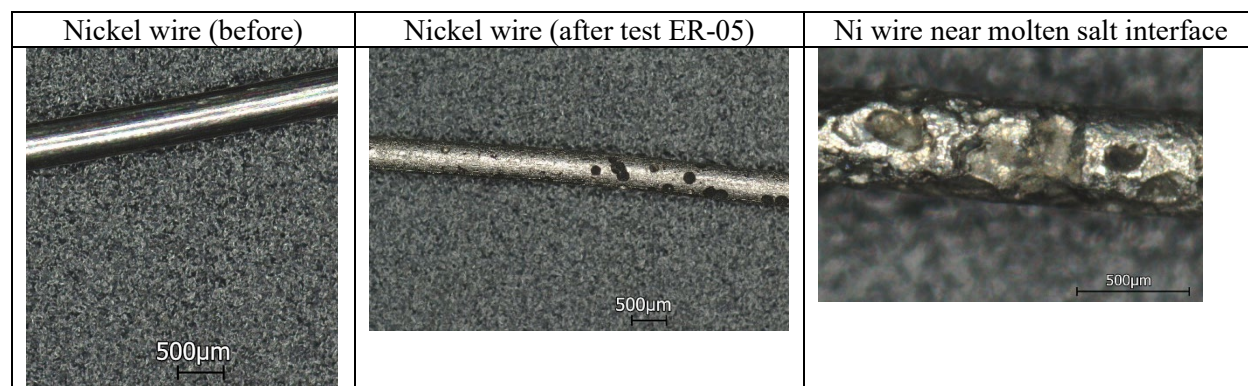


Figure 4-12. Nickel Pseudo-RE from Test ER-05



Figure 4-13. Platinum Anode from Test ER-05

The successful formation of W metal from WO_3 in Tests ER-02 and ER-05 provides a technical basis for having established a baseline condition. The baseline condition enables comparison of the performance of alternate anode materials with that of the baseline Pt anode.

4.2.3 Test: ER-06

Test ER-06 was completed using WO_3 particles in a SS/MgO cathode basket, an Ir-coated Pt anode, and a Ni wire pseudo-RE. After the CV experiment, the power supply was used to electroreduce WO_3 to W metal under constant current. For ER-06, the cell voltage limit was increased to 3.0 V (vs 2.9 V for ER-05). Initially, the current was 2.2 A, and the cell voltage was ~1.6 V. Therefore, the current was increased to 2.5 A. As the cell voltage approached 3.0 V during the run, the current was decreased to maintain the cell voltage below 3.0 V. The applied current was routinely interrupted after 15 min for 5-min rest period. The anode and cathode were monitored using a Fluke voltmeter and the cathode potential was verified to reach ~-1.4 V before current was resumed.

For the first applied current cycle (2.5 A), the cell voltage increased and leveled off at ~2.8 V (Figure 4-14). In the second cycle (2.5 A), the cell voltage increased steadily. The current was decreased to 2.4 and then 2.3 A for the third cycle to ensure the cell voltage remained below 3.0 V. For the first three cycles, the anode potential was steady around 0.73 V vs. Ni wire. The cathode potential was steady around -1.83 V vs. Ni wire in the first cycle and slowly decreased to -1.97 V by the end of the third cycle. During the five-minute current interruption for all three cycles, the cathode potential increased and leveled at ~-1.4 V. The data for the remaining cycles show more changes as the current was decreased multiple times to maintain the cell voltage below 3.0 V

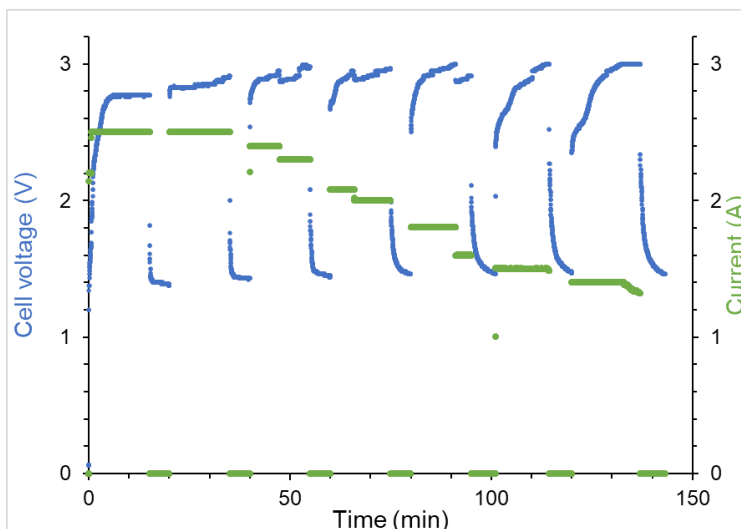


Figure 4-14. Voltage and Current Data for All Cycles of Test ER-06

The total time that current was flowing through the electrochemical cell was 105 minutes. The calculated charge was 3.51 amp-hr. The theoretical charge needed to reduce 5 grams WO_3 is 3.47 amp-h. The charge applied corresponds to 105% of the theoretical charge needed to fully reduce WO_3 to W metal. After the electroreduction experiment, the electrodes and thermowell were raised and the reactor cooled overnight under Ar flow.

When the lid was raised, all components were intact but covered in black residue. As previously observed, the nickel wire pseudo-reference electrode was corroded. The Ir-coated Pt foil anode was intact but appeared rough with an uneven black/gray/tan surface (Figure 4-15). Sections of the anode were tan/brown, and several spots were light gray. A black residue covered the cathode basket. The basket was sectioned to recover the product. The product was all at the bottom of the cathode basket in contrast to ER-05 which had the product around the SS rod. The black product was stirred in EtOH for several hours to remove residual LiCl and dried under vacuum.

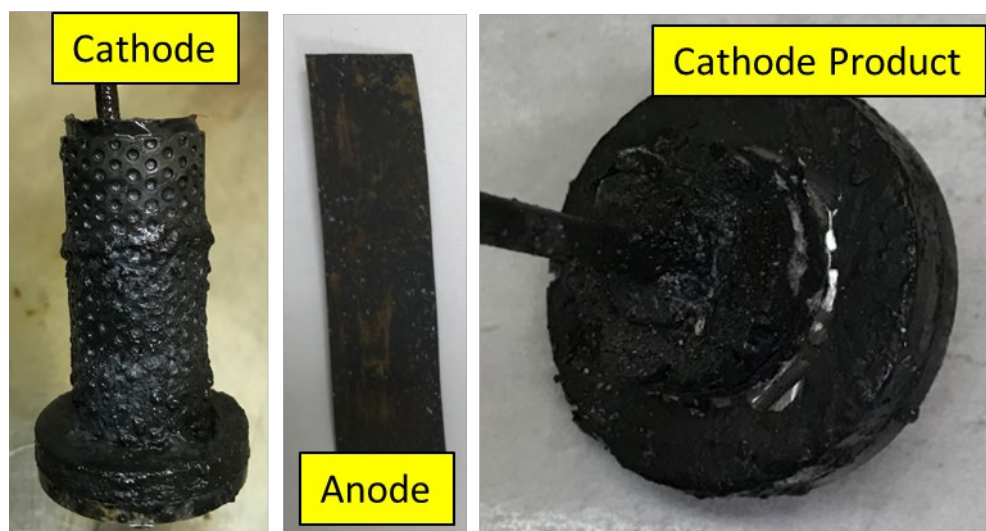


Figure 4-15. Cathode Basket, Anode, and Cathode Product from Test ER-06

The product from ER-06 was transferred into an Ar atmosphere glovebox. The dark gray sample was ground using a mortar and pestle and then pressed into an XRD sample holder. Analysis of the XRD spectrum identified tungsten metal with a trace Fe-W phase (Figure 4-16).

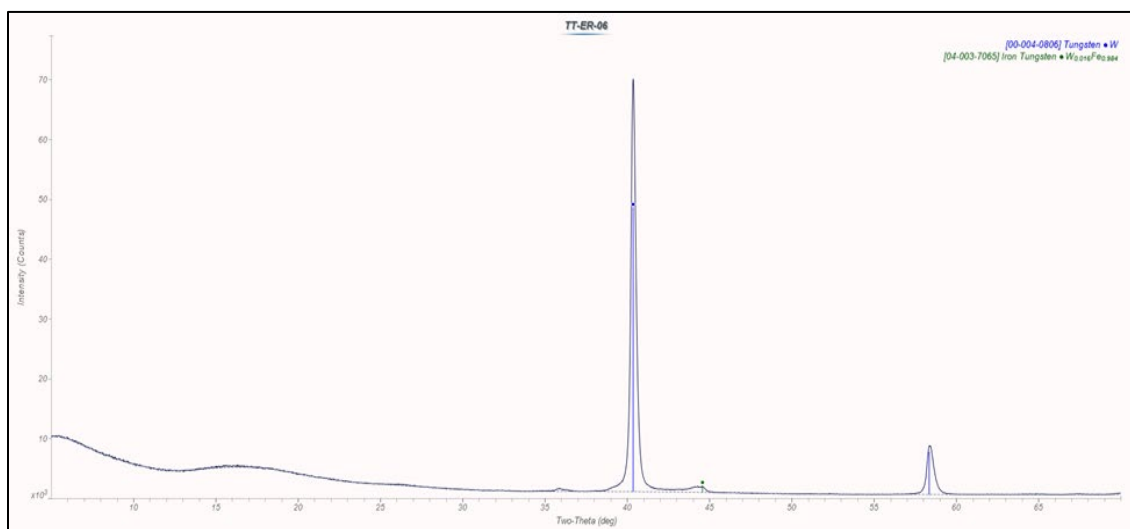


Figure 4-16. XRD Analysis of Cathode Product from Test ER-06

Samples of the salt after the experiments ER-05 and ER-06 (Figure 4-17) were submitted for elemental analysis. The samples were prepared for ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) by acid dissolution and peroxide fusion. The ICP-AES results show that SS and W were not in the salt (Table 4-1). However, nickel from the pseudo-RE was detected. This is not surprising because the nickel wire was visibly reacted after the tests, and corrosion of SS also contributes Ni to the salt. It is not understood why it was found in ER-06 but not ER-05 as the nickel wires were visually similar after both tests. However, it could be a function of sample location or increased vessel corrosion for ER-06. Even for the value of Ni reported, it is not much above the detection limit.



Figure 4-17. Salts in the Reaction Vessel after Tests ER-05 and ER-06

Table 4-1. Elemental Analyses of Salts from Tests ER-05 and ER-06

<i>Elemental wt.%</i>								
<u>Sample ID</u>	<u>Lab ID</u>	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Mn</u>	<u>Mo</u>	<u>Ni</u>	<u>W</u>
TT-ER-05	S-13048	<0.0500	<0.0500	<0.0500	<0.0100	<0.0500	<0.0500	<0.0500
TT-ER-05	S-13048	<0.0500	<0.0500	<0.0500	<0.0100	<0.0500	<0.0500	<0.0500
TT-ER-06	S-13084	<0.0500	<0.0500	<0.0500	<0.0100	<0.0500	0.0638	<0.0500
TT-ER-06	S-13084	<0.0500	<0.0500	<0.0500	<0.0100	<0.0500	0.0640	<0.0500

5.0 Conclusions

SRNL is working with ANL to adapt and demonstrate the electroreduction technology to convert U_3O_8 to U metal. This report provides the status of two activities. The first is the establishment of an electrochemical reduction test capability at SRNL. The second is the evaluation of potential alternate anode materials. Because these tests are focusing on the performance of the anode, testing can be effectively performed using a simulant for U_3O_8 . Tungsten trioxide was used as a simulant for U_3O_8 because of its similarities in density and chemical reduction behavior.

Using concepts in the literature, SRNL designed and fabricated an electroreduction system. The system is designed to prepare the salt in an inert-atmosphere glovebox, transfer the equipment to a chemical hood, and conduct the electroreduction experiments in the chemical hood while purging the reaction vessel headspace with inert gas. Although there were some initial concerns about gas impurities affecting the process, testing demonstrated that the design was adequate to perform electroreduction of metal oxides.

SRNL has performed several CV and electroreduction experiments that verified the correct functioning of the equipment. In general, the CVs do not show much oxidation or reduction information because of the narrow electrochemical potential window available due to the limited current of the potentiostat. A separate test will be performed with a low-surface anode to obtain a CV within the capabilities of the potentiostat. A CV scan of the initial salt is consistent with what is expected based on the literature.

After functionality of the equipment was demonstrated, SRNL proved that it could reduce WO_3 to W metal. Two experiments successfully produced W metal. One experiment, which passed 75% of the theoretical charge for complete conversion of WO_3 to W, yielded a product that was predominantly W metal with minor amounts unreduced tungsten oxide as $Li_2(WO_4)$. The second experiment, which passed 107% of the theoretical charge, yielded a metal product with a trace Fe-W impurity. These two results established the baseline conditions for evaluating alternate anode materials. In both tests, the anode was visibly degraded during the process, and the degradation is clearly represented in micrographs.

The first alternate anode test was completed with an Ir-coated Pt anode. The experiment passed 105% of the theoretical charge required for complete reduction of WO_3 to W. Analyses show that the product was W metal with a trace Fe-W phase. Microscopy of the Ir-coated Pt anode is planned. Additional alternate anode evaluations are in progress.

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