Alternative Anodes for the Electrolytic Reduction of Uranium Dioxide

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

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Abstract

Reprocessing of spent nuclear fuel is an essential step in closing the nuclear fuel cycle. In order to consume current stockpiles, ceramic uranium dioxide spent nuclear fuel will be subjected to an electrolytic reduction process. The current reduction process employs a platinum anode and a stainless steel alloy 316 cathode in a molten salt bath consisting of LiCl–2wt% Li₂O and occurs at 700°C. A major shortcoming of the existing process is the degradation of the platinum anode under the severely oxidizing conditions encountered during electrolytic reduction. This work investigates alternative anode materials for the electrolytic reduction of uranium oxide.

The high temperature and extreme oxidizing conditions encountered in these studies necessitated a unique set of design constraints on the system. Thus, a customized experimental apparatus was designed and constructed. The electrochemical experiments were performed in an electrochemical reactor placed inside a furnace. This entire setup was housed inside a glove box, in order to maintain an inert atmosphere.

This study investigates alternative anode materials through accelerated corrosion testing. Surface morphology was studied using scanning electron microscopy. Surface chemistry was characterized using energy dispersive spectroscopy and Raman spectroscopy. Electrochemical behavior of candidate materials was evaluated using potentiodynamic polarization characteristics. After narrowing the number of candidate electrode materials, ferrous stainless steel alloy 316, nickel based Inconel 718 and elemental tungsten were chosen for further investigation. Of these materials only tungsten was found to be sufficiently stable at the anodic potential required for electrolysis of uranium dioxide in molten salt. The tungsten anode and stainless steel alloy 316 cathode electrode system was studied at the required reduction potential for UO₂ with varying lithium oxide concentrations.
Electrochemical impedance spectroscopy showed mixed (kinetic and diffusion) control and an overall low impedance due to extreme corrosion.

It was observed that tungsten is sufficiently stable in LiCl - 2wt% Li₂O at 700°C at the required anodic potential for the reduction of uranium oxide. This study identifies tungsten to be a superior anode material to platinum for the electrolytic reduction of uranium oxide, both in terms of superior corrosion behavior and reduced cost, and thus recommends that tungsten be further investigated as an alternative anode for the electrolytic reduction of uranium dioxide.
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My family has played a fundamental role in my life, especially in driving my education. I cannot thank any of them enough; I literally owe them a lifetime of gratitude. Thank you!
Finally, this thesis is dedicated to the men and women across the world that have dedicated their lives to the peaceful use of nuclear energy. The wonderful possibilities that lie in the atomic nucleus would not be realized without them.
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Chapter 1: Introduction

1.1 Nuclear Energy

Modern civilization is rapidly approaching a global energy crisis of immense proportions. The increasing living standards of billions of people in developing countries combined with continued reliance on environmentally polluting fossil energy sources will inevitably lead toward a global energy crisis. When choices regarding energy sources for the next decades are examined on an international scale, it becomes clear that the only source of energy currently available on the scale necessary to offset fossil fuel consumption is nuclear energy. On average, nuclear bonds contain ten million times more energy than chemical bonds, and it is this fact that will necessitate the use of nuclear reactions for energy production.

Considering concepts of such magnitude as the global energy supply it is essential to understand the true scale and relative consequences of the ideas being discussed. It is not the point of this research to investigate the feasibility of alternative energy sources; however it is essential to make relative comparisons between nuclear power and other non-fossil fuel based energy sources in order to establish a level of understanding for the layperson. The next few paragraphs provide a brief justification for the continued expansion of nuclear energy.

The three issues that are popular arguments against nuclear energy are: (I) economics, (II) waste management and (III) safety. The facts surrounding these issues are often skewed in relation to nuclear energy, more so than any other industry. These issues are not cut and dry, but all must be understood clearly with a specific understanding of their true repercussions in order to fully grasp the consequences of energy production.
A quick example of the way in which nuclear energy is skewed in the media is in the amount of “waste” produced per unit energy compared to alternative energy sources. A 1000 MW(e) power plant annually consumes either: 2.3 million tons of coal, 9.2 million barrels of oil, 64 million ft³ of natural gas or only 30 tons of nuclear fuel [1]. Due to the conservation of mass, no fuel disappears during energy production (except for mgs of uranium converted by E=mc²). All the fuel that goes into fossil fuel plants come out in the form of CO₂, larger hydrocarbons such as ash, or toxic NOₓ and SOₓ gasses. In the case of coal an average of 6 million tons of CO₂, 27,000 tons of NOₓ and 24,000 tons of SOₓ are produced per 1000MW plant per year [1]. Thus, there is one million times less “waste” mass per unit energy produced from nuclear energy compared to any fossil fueled plant. Because the hydrocarbon wastes are often vaporized and expelled into the atmosphere they are not easily observable, and as a result they are not the source of major controversy. However, the 30 tons of solid Spent Nuclear Fuel (SNF) that results from energy productions is stored securely and often receives bad publicity; moreover, the fossil fuel usage results in polluting the atmosphere with greenhouse gasses that contribute to climate change.

Another misleading point that is often made about nuclear power is that nuclear fuel will stay radioactive for millions of years. This is true, but all elements (besides ⁵⁶Fe) radioactively decay, and the vast majority of them have half-lives in the range of hundreds of thousands of years. It could equally be pointed out that deposits of uranium and its radioactive daughters, including thorium and radon, are present in almost all forms of coal, natural gas and petroleum. These contaminates are not subjected to the same regulations as nuclear energy; in result these radioactive species are expelled as exhaust fumes in quantities that would not be legal if originating from a nuclear plant [1].

The disasters at the Fukushima-Daiichi nuclear plant in Japan, the Three Mile Island plant in Pennsylvania and Chernobyl in the former USSR are often cited as examples of how dangerous nuclear energy is. Yet, to date no individual has died from radiation exposure because of the Fukushima disaster,
and a total of only 30 individuals were exposed to between 100 and 200mSv [2]. After decades of research studying survivors from the nuclear bombings of Hiroshima and Nagasaki, it has been found that acute doses from 100 to 200 mSv result in a 0.35 to 1.25% increased risk of fatality from cancers compared to naturally occurring cancers [3]. Professor Yanch, of the Nuclear Engineering Department at MIT, pointed out that the three highest doses received by workers averaged 180 mSv. Using the highly conservative Linear No Threshold (LNT) model, this would raise these three workers statistical susceptibility of cancer from 22% due to natural causes to 23.7% [4]. The horrific disaster that occurred at Chernobyl in 1986 resulted in 28 prompt deaths, and 19 deaths over the following 20 years that can be directly contributed to radiation exposure [5]. Zero casualties resulted from the Three Mile Island meltdown incident in 1979.

It is a challenging task to rank energy production in terms of fatalities, especially when the statistical nature of radiation exposure is taken into account. By taking an unbiased look at the facts produced by international non-partisan organizations and renowned experts, there are clearly less than one hundred deaths in recorded history that can be directly contributed to commercial nuclear energy. The most blatant contrasting argument regarding energy production hazard is the Banqiao dam disaster that occurred in China in 1975. Due to the restrictions on international monitoring of China at the time, the government issued an official death toll of 86,000; however experts place the number at over 200,000 [6]. To illustrate the dangers of the use of fossil fuels, a very sobering portrayal was recently published by Bergherr et al, a summary of the findings are shown in Figure 1 [7].
Arguments can also be raised about the unavailability of land due to radiological contamination resulting from nuclear meltdowns. The total evacuation zone surrounding the Fukushima-Daiichi reactor complex was 20 km in radius resulted in a the total of 1256 km² (Note that the vast majority of experts consider this level of safety excessively conservative, and that evacuating such a large population likely caused more harm than good [8]). A power station consuming comparable area to this evacuation zone surrounding the Fukushima, the Serra da Mea dam on the Tocantis river in Brazil, displaced 1784 km² of rain forest land to produce 1275 MW(e) and still doesn’t rank in the top 10 largest dams in Brazil [9]. The four reactors at the Fukushima-Daiichi complex had an installed capacity of 4,695 MW(e) resulting in a land consumption rate per unit of electricity production, including the evacuation zone, at roughly one fifth of that of the hydroelectric dam, when including the evacuated zone.

The essential point of these comparisons is that no energy production comes without cost, both in human lives as well as destruction to the environment. Based on history, nuclear energy is by far the
The cleanest and safest form of base load electricity production available in large quantities today. It should be noticed that in these arguments no abstraction was taken into account for global warming, or uncertain death tolls from air pollution. The only statistics employed are from peer reviewed journals, accepted by multinational organizations, and directly display nuclear energy’s impeccable safety record compared to all alternatives.

1.2 Spent Nuclear Fuel

The largest unsettled issue facing the nuclear energy industry today is the long term solution to the disposal of Spent Nuclear Fuel (SNF). Over 65,000 metric tons of SNF has accumulated from commercial nuclear reactors in the United States alone [10]. Since the inception of nuclear power the problem of what to do with SNF has not been one of physics and engineering, but one of politics and economics. It was understood as early as the 1940’s that the vast majority of SNF could be fissioned in reactors; however it was not pursued due to sociological reasons. The severity of this problem, and its key correlation to the success of nuclear power, was first understood by the Nobel laureate Enrico Fermi.

“It is not clear that the public will accept an energy source that produces this much radioactivity and that can be subject to diversion of material for bombs.”

—Enrico Fermi

As of 2008, there were 439 Nuclear Power Plants (NPP) in operation in 31 nations producing, on average, 10,000 tons of SNF annually [10]. The elemental composition of Light Water Reactor (LWR) fuel depends on burn up and irradiation history, but a general example is given in Table 1.
Table 1: Composition of nuclear fuel before and after a standard irradiation cycle in a commercial LWR [1]

<table>
<thead>
<tr>
<th></th>
<th>Fresh Nuclear Fuel atomic %</th>
<th>Spent Nuclear Fuel atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium-238</td>
<td>97</td>
<td>95</td>
</tr>
<tr>
<td>Uranium-235</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Plutonium</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Fission Products</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

The majority of commercial LWR SNF offers almost no practical energy potential in reactors that employ a moderator to “thermalize” the average neutron energy due to the small fission cross section of $^{238}$U for low energy neutrons. Conversely, both $^{238}$U and the majority of the transuranics have larger fission cross sections for incident neutrons of kinetic energy greater than 1keV [11]. Thus, the problem of SNF disposal would be eliminated by building a reactor were the average neutron energy is >1KeV fueled with natural uranium or SNF. It was with this knowledge that the first electricity producing nuclear reactor, Experimental Breeder Reactor I (EBR1), a $^{238}$U fueled fast neutron reactor, was developed in the desert of eastern Idaho.

Fast reactors have been successfully built and operated in the United States, Russia, China, Japan, France, Germany and the United Kingdom [12, 13]. Of specific interest to this study are the Experimental Breeder Reactor 1 and 2 (EBR I & II) as the technological achievements that were overcome at those facilities answered all the major technical questions regarding full scale fast reactor operation. At a fundamental level, EBR1 successfully proved the ability to close the nuclear fuel cycle, consuming the $^{238}$U that makes up more than 97% of SNF, in 1951. Nothing technical has changed since American scientists first closed the nuclear fuel cycle more than 60 years ago. The only obstacle lying in the path to releasing a relatively unlimited amount of energy is the political and economic will to implement the 60 year old technology.
1.3 Pyroprocessing and the Integral Fast Reactor Program

The complete history of the nuclear fuel cycle and fast reactors is simply too complicated to be summarized in this report, so only a few key points relevant to the current research will be discussed. Of significant importance is the electrometallurgical reprocessing process, termed pyroprocessing, developed at Argonne National Laboratory (ANL), for the Integral Fast Reactor (IFR) program.

Pyroprocessing is based on the electrolysis of SNF in molten salt. By employing electrochemical separation, it is possible to extract specific chemical species at various electrodes at specified potentials [14]. This means, SNF can be separated into sets of elements tailored to the specific process at hand. Thus, it is easy to isolate uranium, while leaving the plutonium with various highly radioactive fission products and transuranics. This process, known as “spiking” is one of several inherent nonproliferation aspects of the IFR fuel cycle [15]. In addition to proliferation resistance, pyroprocessing is fundamentally a batch process which avoids the large capital costs involved with industrial scale aqueous reprocessing facilities.

After the US government banned reprocessing in 1974, researchers began to seek a method for reprocessing SNF that was less of a proliferation concern. The proliferation concern that influenced the government’s decision was that aqueous reprocessing isolates plutonium as a waste stream. Plutonium is a highly fissionable element, and any amount of it is classified as weapon’s grade material. In an attempt to minimize the spread of nuclear weapons, any process that isolated plutonium was thus banned in 1974. The solution to this problem is pyroprocessing. Throughout their development, pyroprocessing and the entire IFR fuel cycle were engineered to eliminate political, environmental and economic concerns that were associated with aqueous reprocessing [16].

The IFR program was a research study undertaken at Argonne National Laboratory to find the best way close the nuclear fuel cycle. The study was initiated shortly after the cancellation of the Clinch
River Breeder Reactor in 1983. The termination of the Clinch River reactor signified the end of fast reactor development in the US, and triggered a comprehensive study of the technology, beginning in 1984, termed the IFR initiative. The IFR study lasted for a decade essentially ending with the decommissioning of EBR II in 1994. The key findings of the program was that the safest and most practical method of closing the nuclear fuel cycle was by building a series of sodium cooled fast reactors, each with onsite pyroprocessing facilities capable of processing SNF from several neighboring LWRs. The study was based on the extensive experience gained by our nation’s top nuclear scientists and engineers over four decades of operating fast reactors [17].

In summary ANL’s research has accomplished all necessary features of an IFR at the scale required for full development of a closed nuclear fuel cycle [16, 18, 19]. EBR II was a sodium cooled fast reactor that operated for 30 years with no insurmountable safety problems. EBR II operated at 20 MW(e), burned transuranic elements and was fueled with reprocessed uranium and plutonium in the form of mixed oxide fuel and metallic fuel. In addition, a full pyroprocessing facility was developed, capable of separating SNF into desirable components. As of 2012 more than 4.26 metric tons of SNF had been pyroprocessed at Idaho National Laboratories (INL) [20].

1.4 Electrolytic Reduction of UO₂

LWR’s employ ceramic oxide fuel consisting of uranium oxide, UO₂, clad with a zirconium alloy. In order for this fuel to be reprocessed using pyroprocessing the ceramic uranium must be stripped from its cladding and converted to its metallic form through a reduction process [21]. The process, developed by ANL, is an electrolytic reduction process that takes place in molten LiCl. Reaction (1) shows the reduction of UO₂ and the required electrode potential in LiCl-2wt%Li₂O at 700°C [22].

\[
\text{UO}_2 \rightarrow \text{U}(m) + \text{O}_2 \quad E_\theta = -2.396 \text{ V vs Pt} \quad \text{Reaction 1 [22]}
\]
LiCl-2wt% Li₂O was chosen as the electrolyte for the reduction process due to its thermodynamic stability, and compatibility with container materials at the required temperature. In addition the Li⁺ content facilitates faster reduction times [21]. The process has been demonstrated on a full engineering scale of kg basis by several organizations in at least four nations, most notably South Korea [23-27]. Essentially every organization currently studying this process employs a stainless steel 316 cathode basket to hold the SNF and a platinum anode to apply the required anodic potential to achieve the reduction of UO₂.

In order for pyroprocessing and the IFR technologies to be feasible, the economics of the process must show advantages over alternatives such as the PUREX process [28]. Thus cost effective production of components and their stability for a significant amount of time before replacement is necessary. The currently practiced process consumes platinum at a significant rate. In addition to its cost, platinum has been shown to be susceptible to lithium attack and anodic dissolution [29]. Platinum is known to form compounds such as Li₂PtO₃ when anodically polarized in LiCl–Li₂O [30-33]. The consumption and degradation of the platinum anode is not desirable as it decreases the economic viability of the process and could potentially lead to the failure of the reduction circuit. For these reasons it is desirable to find an alternative anode material for this process [28].

Boron doped diamond has recently been shown to be a viable alternative anode [28]. However, these anodes are likely to be expensive thus negating the economic advantage over platinum. Recent research has also shown that underpotential deposition of Li on the cathode could assist the kinetics of UO₂ reduction; however this leads to higher current densities at both electrodes [33].

In the highly oxidizing conditions encountered at the anode during the reduction of UO₂, corrosion of the anode material emerges as a major technical challenge. In addition, decreasing the cathode/anode area ratio has been suggested to increase the current density on the uranium cathode
thus accelerating the process [34]. Furthermore, as soluble fission products accumulate in the salt, the rate of UO₂ reduction has been shown to decrease, necessitating longer electrolysis times [35]. Both of these processes would require increased oxidation at the anode. For the above reasons, identifying an inexpensive alternative anode that is also relatively inert at high current densities is essential.

This study explores the use of various alternative anode materials for the electrolytic reduction of UO₂. Finding an alternative anode that can act as a stable substitute for platinum will be vital to the development of an economically attractive IFR program and a closed nuclear fuel cycle for the United States and across the globe.
Chapter 2: Experimental

The electrolytic reduction of UO₂ is currently carried out in LiCl-2wt% Li₂O at 700°C. In order to study the degradation of candidate electrodes in this process, a unique experimental setup had to be established. The design constraints for the system required: a potentiostat for electrochemical testing, an inert atmosphere to minimize unwanted secondary reactions, a high purity salt and a consistent method for exposing the sample surface to the salt melt. The experimental parameters of this research will be discussed in this chapter, while details on their development and implementation are given in chapter 3.

2.1 Materials

The composition of the various alloys investigated is shown in Table 2. The purity of all metals was greater than 99wt%. All alloys were factory annealed, while metals were studied as drawn. All electrode metals and alloys were purchased from the Goodfellow Corporation.

Table 2: The composition in weight percent as given by the commercial supplier of the alloys studied in weight percent.

<table>
<thead>
<tr>
<th></th>
<th>Fe wt%</th>
<th>Cr wt%</th>
<th>Ni wt%</th>
<th>Mo wt %</th>
<th>Minor Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel 600</td>
<td>8</td>
<td>15.5</td>
<td>72</td>
<td>-</td>
<td>Mn/Si/Co</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>19</td>
<td>19</td>
<td>53</td>
<td>-</td>
<td>Nb/Mo/Ti</td>
</tr>
<tr>
<td>SS 316</td>
<td>balance</td>
<td>18</td>
<td>10</td>
<td>3</td>
<td>Mn</td>
</tr>
<tr>
<td>Hastelloy B</td>
<td>1.5</td>
<td>1.5</td>
<td>65</td>
<td>28.5</td>
<td>-</td>
</tr>
</tbody>
</table>
Anhydrous LiCl and Li₂O were procured from VWR Scientific and was of >99wt% purity. The salts were packed in an argon atmosphere and opened in a controlled environment with <50 ppm O₂ and <1 ppm H₂O. No pretreatment was undertaken for further purification of the salts. All the salts used in this study were procured for the same batch to ensure the same amount of impurities existed in all experiments.

The salt melt was contained inside a high purity graphite crucible with a 4.13cm internal diameter. The graphite contained a <100 ppm ash. Crucibles were used for a single melt cycle, consisting of two polarizations, then were boiled in water to remove the salt ingot after solidification. After the bulk salt was removed the crucibles underwent a thorough cleaning with distilled water and ethanol. After cleaning, the crucibles were baked at 150°C for three hours to remove any moisture trapped in the graphite.

2.2 Sample Preparation

An electrode geometry of 1mm diameter wire was chosen to minimize the size of the apparatus. Electrodes were polished using 400 and 600 grit sandpaper successively, followed by a rinse with acetone prior to exposure of the electrolyte. Samples were purposely not polished to a mirror finish to simulate real world conditions.

After polishing, the samples were loaded into 1.54mm inner diameter alumina tubes, leaving 1cm exposed out of the working end. Thus an area of 34.5mm² (including the tip) was exposed to the salt during each experiment. Electrodes were arranged in a triangular symmetry with 1 cm in-between each vertex. The electrodes were exposed to vapors given off by the molten salt for 15 seconds before and after immersion while they were lowered into and removed from the melt.

Salt solutions varied in mass from 25 g to 28 g depending on required Li₂O concentration. The balance used to measure the salt mass had a precision of 0.1 g, resulting in an uncertainty of 0.4wt%Li₂O
in the melt. The salt was ground and mixed thoroughly in a mortar and passel prior to loading into the graphite crucible.

### 2.3 Furnace and Temperature

A furnace was procured from the Mellen Company specifically for compatibility with thermal insulation specifications and with operation inside a glove box. The furnace insulation was chosen to be aluminosilicate fiber, and was outfitted with an Omega PID programmable temperature control system. The furnace thermocouple was positioned on the wall of the central furnace chamber and was used as a rough temperature scale for the furnace only, not as a calibrated reference of the salt temperature.

The temperature of the salt was measured using an insulated thermocouple. Temperature measurements were made at the electrode positions varying in height, and less than a 10°C temperature gradient was found to exist along the length of the electrode. The variation in electrode position in each experiment resulted in a temperature uncertainty of ± 5°C. All experiments, with the exception of the system validation, were conducted at 700°C.

### 2.4 Electrochemical Testing

A Gamry PC4 750 potentiostat was employed for all electrochemical tests. The potentiostat was calibrated by the manufacturer immediately before the beginning of this research. The potentiostat was located externally of the glove box, and connected through an electrical feedthrough to insulated copper wires and connected to the electrodes with alligator clips.

#### 2.4.1 Potentiodynamic Polarization

Potentiodynamic polarization was used as an initial method of classifying candidate materials on their electrochemical potential in the molten LiCl-Li₂O. Potentiodynamic polarization is a powerful technique for accelerated corrosion testing. It was specifically used to yield electrochemical potential ranking of the materials, and to study the anodic passivation behavior of candidate anodes.
Hastelloy B wire was used as the reference and counter electrodes for potentiodynamic polarization experiments. Hastelloy B was chosen due to its noble potential compared to candidate materials, see results section 4.1.

Open circuit potential (OCP) was recorded for 30 seconds after the samples were immersed in the salt melt which was followed by potentiodynamic polarizations. It should be noted that sample’s OCP did not always stabilize during this time period. Preliminary investigation showed that many materials never approached an equilibrium state, but continued to corrode due to the formation of corrosion products that were soluble in molten LiCl-Li₂O. In order to establish a consistent experimental procedure an arbitrary exposure time of 30 seconds was chosen. This ensured an equivalent surface reaction time for each material with the salt prior to polarization.

Potentiodynamic polarizations were scanned from -0.4 V to +1.5 V vs OCP at a scanning rate of 1 mV/s. Scans were conducted in duplicate to ensure reproducible measurements were recorded. Gamry Echem Analyst software was used to analyze the potentiodynamic data.

2.4.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was used as a method of further classifying candidate anodes electrochemical stability, and to study the surface phenomena involved in molten salt corrosion. EIS was performed using a Hastelloy B reference and counter electrode in the same configuration as potentiodynamic polarizations. EIS was conducted with a 10 mV rms AC voltage at OCP. For EIS the OCP was monitored for 60 seconds in attempt to reach a more consistent equilibrium state. The frequency was swept from 10kHz to 10 mHz. Attempts to collect data at frequencies lower than 10 mHz failed due to the dynamic state of the electrode surface resulting in inconclusive data, and an inability to monitor the furnace at temperature long period of time without exceeding temperature limits inside the glove box.
2.4.2 Potentiostatic Polarization

After a specific metal was chosen as a promising candidate alternative anode, potentiostatic polarization was used to study its stability at the required potential for the reduction of UO₂. In order to simulate the industrial process, a single SS 316 electrode was used as the counter and reference electrode at a cathodic potential of -2.5 V. The polarization began immediately after the electrodes were submersed in the molten salt and were conducted for 600 seconds. The current was recorded by the potentiostat during these polarizations. Polarizations were run at varying oxide concentrations from 0wt% to 8wt% Li₂O in 1wt% intervals to study the effect of oxide concentration on accelerated electrode oxidation.

2.5 Post Exposure Analytical Methods

2.5.1 Microscopic Imaging

Following polarization, samples were removed from the apparatus and mechanically cut to remove the polarized section of material from the unexposed material. Samples were then removed from the glove box and quickly imaged using a digital camera to capture a macroscopic image of the bulk deformation and salt coat formation that was formed during the exposure to the salt. Images were taken against a white background at a 1x magnification to display a non-distorted view of the samples.

2.5.2 Scanning Electron Microscopy

A Hitachi S-4700 Field-Emission Scanning Electron Microscope (FESEM) was used to study the morphology of the material surface before and after polarization. Micrographs were recorded from 30x to 15,000x to display morphology at various magnification levels. A qualitative elemental composition of the surface was obtained using energy dispersive X-ray spectroscopy (EDS). The FESEM was operated at 20 kV for microscopic imaging and 15 kV during EDS measurements.
2.5.3 Raman Spectroscopy

Raman spectroscopy was conducted to study the chemical composition of the corrosion products formed during polarization in the molten salt. A Thermo-Scientific DXR dispersive Raman microscope was used to measure the Raman vibrational spectroscopy of the surfaces. The DXR was used with a 532nm wavelength laser at 10mW with 20 second exposure times and averaging 15 exposures per spectra. The DXR facilitated spectral mapping of sample surfaces as well. The step sizes and details of the various mapping programs are discussed with their respective results in section 4.8.
Chapter 3: System Development

Several fundamental design constraints forced the experimental regime for studying corrosion in molten salts into a unique system: (I) molten chloride salts react spontaneously with oxygen in air, necessitating the controlled atmosphere of a glove box, (II) Extremely high temperatures and oxidizing conditions encountered require specific materials to be used. This requirement alone forbids the use of common electrical insulators, which complicates the electrochemical testing aspects of the experiment. Lastly, and perhaps most importantly, the hazardous chemical products that can result from reactions with the salt, such as chlorine gas, require a level of safety that tightens all of the above design constraints and limits the flexibility that is enjoyed by countertop experiments.

The development of the Molten Salt Electrochemical Reactor (MoSER) began in January 2012, and is continuing to strive for increased safety and efficiency today. Since its inception, the MoSER has progressed toward a completely automated system. With the hope of future experiments involving hazardous materials in mind, it is seen as a major priority to achieve an experimental system with minimal direct human involvement. This goal has played a key role in the decisions made during the MoSER design. The development began with the choice of a certain furnace and glove box, and then through a series of electrochemical equipment, automation tools, exotic temperature measurement systems, exhaust plumbing development and wireless control system programming.

3.1 The Furnace

In order to reach the required temperatures to study molten salts, up to 900° C, a custom furnace was designed and procured from the Mellen Company. With the aid of advice from previous researchers, it was apparent that thermal insulation and size of the furnace would be the main concern for operation inside a glove box. A design for a furnace specific to these constraints was developed in
conjunction with the engineers at Mellen. The final design was based on a stainless steel frame for heat conduction to the glove box base, with a thick aluminumsilicate insulating wall and lid over the experimental chamber. The central chamber was made as small as possible to reduce variations in temperature along the depth of the chamber. The furnace was made with highly efficient heating coils that wrap the experimental chamber radially. This design was chosen to ensure an even azimuthal temperature profile, and to minimize the height and diameter of the heating element. The furnace included an additional aluminumsilicate jacket that fits snugly between the crucible and the heating coil walls. This jacket provides stability to the salt containing crucible, in addition to insuring that the crucible sits in the center of the chamber and is heated evenly from all sides. The resulting schematic drafted by Mellen, and the final product containing molten salt is shown in Figure 4.

Figure 4: The furnace engineering draft schematic provided by Mellen, and the actual furnace containing molten LiCl.

3.2 The Glove Box

An Omni-Lab glove box, complete with a custom gas circulation and cooling system manufactured by Vacuum Atmospheres Company, was used in this study. The glove box was installed in the lab and was retrofitted with new vacuum, inert gas and exhaust plumbing systems. Special care was
taken to ensure that under all possible scenarios, the glove box would automatically expel any internal gas into the exhaust system which flows directly into a UNR EH&S certified chemical exhaust system. The glove box atmosphere was maintained at less than 10 ppm O₂ and 1 ppm H₂O during all experiments. A new Omni-lab glove box is shown in Figure 5.

![Figure 5](image)

**Figure 5:** The Omni-Lab glove box that contains the furnace that housed all this study’s experiments [36].

The glove box atmosphere purification system employs an activated carbon molecular sieve in addition to a purification system. In order to minimize the consumption of the purification catalyst, the main chamber of the glove box was isolated from the circulation system while the furnace was in operation. After an experimental run was completed, the main chamber was purged with nitrogen and outgassed into the exhaust system. In this manner a significant amount of salt vapor was deposited on internal components in the main chamber. After several months of operation significant corrosion was
noticed on the stainless steel lining of the chamber. To resolve this issue the glove box was dismantled, and all internal components were ground to a fresh bulk metallic finish, then thoroughly coated with clear acrylic paint. In addition a sacrificial stainless steel plate was placed across the floor of the chamber to avoid any spilled salt from contacting the frame of the glove box.

To avoid further system corrosion issues an internal box, kept at negative gauge pressure relative to the glove box chamber, was fabricated out of stainless steel. This box houses the furnace itself along with the electrodes throughout the experiment. The box is vented directly into the glove box exhaust system and is kept at a negative pressure relative to the glove box by continuously purging inert gas through the main chamber and out of the exhaust system.

### 3.3 Temperature Measurements

Temperature has been shown to have a strong correlation to corrosion in molten salts [37]. Accurate determination of temperature inside the salt melt can prove to be difficult due to the oxidizing nature of the salt and caustic vapors given off by it. Initially a system of Inconel and magnesium oxide insulated thermocouples were purchased from Omega Engineering. These thermocouples were expected to function in the molten LiCl due to Inconel’s and MgO’s relative stability in molten chloride salts [38, 39]. It was later found that during the insertion and removal of the thermocouple, the porous MgO insulation allowed for the diffusion of Cl⁻ vapors into the thermocouple, compromising its ability to function as calibrated. A subsequent system was employed using OMEGA CLAD® insulated thermocouples that are completely encased, including electrical connections, in a solid nickel-chrome alloy jacket that can withstand up to 1335°C and has an accuracy of ±2.5°C at 815°C. These thermocouples have shown no signs of degradation due to exposure of the salt vapors.

Considering the design goal of complete automation of the MoSER, an automatic temperature monitoring system was developed. Due to a limited number of electrical feedthroughs into the main
glove box chamber, a wireless system was employed to record the temperature at multiple locations in the glove box continuously throughout operation. This system component will be discussed in section 3.5 with the wireless monitoring and control system of the MoSER.

### 3.4 Electrode Submersion System

Due to the phase transformation undergone by the salt at roughly 350°C, a system for immersing the electrodes into the salt once the desired temperature was reached needed to be designed and instrumented. A key design constraint in this aspect was the heat given off by the furnace throughout extended experimental runs. The electronics powering the submersion system had be far enough from the furnace not to exceed their maximum operating temperature; however as the distance is increased the torque on the motor is increased as the arm extending to the furnace lengthens. A final design was put in place using a Zaber Industries linear translation stage mounted vertically to the internal negative pressure box. An aluminum tube was used as the armature to maintain strength and keep the system weight down. A custom quick connect system was designed such that identical armatures could be swapped out during operation. This proved advantageous in salt consumption because multiple polarization experiments could be achieved in the same salt melt safely without cooling the electrolyte to solidification temperatures.

The mounting of the electrodes into the submersion rack was achieved through a number of design iterations. The main design limitation in this aspect was avoiding electrical shorting between the electrodes, the walls of the furnace and the submersion system. 1.5mm ID alumina tubes were used as guides down the 15cm from the armature to the salt melt. These tubes serve the additional function of electrical insolation between the sample wires and the submersion system, and could easily be positioned in the desired configuration of the experiment in question. The translation stage, quick connect armature and electrode holding system is shown in Figure 6.
Figure 6: The electrode immersion system developed for accurate placement of electrodes and quick exchange of electrode armatures. This picture was taken prior to the installation of the internal containment box.

3.5 LabVIEW Programing and the Wireless Sensory Network

Foreseeing more complex experiments with the MoSER system, it was desirable to develop a complete wireless control and automation system for the operation of the MoSER. The goal was to develop a system such that a user could simply load an electrode into place and then run the entire experiment from a computer. The main advantage of such a system is the elimination of human errors that could lead to the exposure of extreme heat, release of toxic gasses, the spilling of caustic
substances and or the miss alignment of components. The wireless system was developed on three principle categories; electrode control, temperature monitoring, and safety.

A system of Wireless Sensory Network (WSN) devices developed by National Instruments was chosen for ease of compatibility with LabVIEW. The WSN network is built off a gateway hardwired by an Ethernet cable to the computer running LabVIEW. The gateway communicates wirelessly to a series of end nodes that serve a specified function. The MoSER WSN system required three components; a WSN 9791 gateway, a WSN 3202 four channel thermocouple receiver and a WSN 3230 RS-232 programmable node. The thermocouple receiver and gateway required a fairly straight forward connection procedure, and quickly facilitated wireless temperature readings from four thermocouples. The four channels were designated for the temperature of the negative pressure box, the electronics and two OMEGAACLAD® salt specific thermocouples.

Controlling the Zaber translation stage required significantly complicated programing. Existing LabVIEW Virtual Instruments (VIs) were accessible for direct manipulation of the stage when using a hardwire RS-232 cable; however this architecture needed to be adapted to the WSN communication system. The WSN 3230 serial node was designed for serial communication, however due to the recent release of the device, the implemented programing to deliver serial code from a user to the output of the 3230 node in real time had not been previously developed. The details of the LabVIEW programming are not vital to this research so they will be omitted, however key features can be observed in Figures 7 and 8.
Figure 7: The LabVIEW program written onto the WSN 3230 Node. The program takes in 8 bit strings used to communicate between the WSN devices, and converts it into the RS-232 serial output that controls the translation stage.

The WSN node operates similar to a master / slave archetechture, except that the slave functions are programed to the node prior to receiving the command from the master. In the current scenario, the node is programed to receive an 8 bit serial code in the WSN language, then convert it into a RS-232 signal that is interpreted by the Zaber translation stage. This programing written onto the 3230 node is shown in Figure 7.
Figure 8: The LabVIEW Virtual Instrument developed to take user input, convert it into the RS-232 serial code usable by the translation stage, and then convert it into 8-bit strings that are sent between the WSN devices.

Figure 8 shows the “master” computer side of the program where the input command from the user is converted into the end RS-232 signal. This signal is then converted into 8-bit strings that are communicated between the WSN gateway and the node. Although the programming is complex and appears confusing, the outcome is a simplistic user control panel shown in Figure 9.
The user interface of the MoSER WSN system is shown in Figure 9. Understanding and using the interface is straightforward, and can be learned quickly without understanding its programming details. The temperature of each thermocouple is shown in real time while a history of each is plotted continuously. The data obtained by the temperature charts is automatically saved, and can be opened using Microsoft Excel®. The translation stage control is equally simplistic, with a single click switch to go from the electrodes being submerged to complete removal from the furnace. A manual override stop switch and numerical positioning control (not shown) is also available for specific uses.
Chapter 4: Results and Discussions

4.1 System Validation

Prior to scientific use the MoSER needs to be validated against previously published work. This was achieved by performing a potentiodynamic polarization of molybdenum against a tungsten reference electrode with a stainless steel counter in LiCl-2wt%Li₂O at 670°C; an experiment identical to one conducted by Ruppert et al. [32]. The result of this experiment is shown in Figure 10 (A) and (B).

Figure 10: Potentiodynamic polarizations used for a system validation compared to previously observed polarization data for Mo in LiCl-2wt%Li₂O at 670°C. (A) is the result of a polarization carried out in the MoSER, (B) was previously reported [32].

The comparison made in Figure 10 to validate the MoSER system must be considered appropriately. As will be shown in the section 4.4, even consecutive identical experiments do not produce identical polarization plots. This is a result of the dynamic surface reactions and instabilities associated with electrolysis in any molten salt system. The interactions between the electrodes and the salt, as well as ionic motion in the electrolyte, are extremely dynamic due to high temperature and thus give rise to significant electrochemical noise. These issues make reproducibility challenging; certain characteristics and more importantly the trends observed need to be considered to evaluate reproducibility. Thus the consistency shown in Figure 10 serves as sufficient system validation.
4.2 Electrodes for Electrochemical Tests

Once the MoSER had been validated against previous work, a single reference electrode had to be chosen for use in subsequent experiments. In order to choose a proper reference electrode potentiodynamic scans of all available materials was run against Ni. This test facilitated a rough electrochemical potential ranking of the candidate materials investigated. Ni was chosen as the initial reference due to its reported inert nature in chloride salts [40]. A plot of potentiodynamic polarizations for all materials using a nickel reference and a nickel counter electrode in this experiment is shown in Figure 11.

**Figure 11:** Potentiodynamic polarization scans of all candidate materials measured against a Ni reference electrode using a Ni counter electrode. The electrolyte was LiCl–2wt% Li$_2$O at 700°C. The samples were exposed to the salt solution for 30 seconds prior to polarization. The sample was polarized from -0.5 V to +0.5 V vs the open circuit potential at a rate of 5mV/S.
As depicted in the potentiodynamic scans shown in Figure 11 Hastelloy B was determined to have the most noble electrochemical potential against the nickel reference in the molten salt. These initial experiments were conducted in LiCl–2wt% Li2O at 700°C at a scan rate of 5mV/s in order to determine the electrochemical potential ranking of the various materials in the electrolyte encountered during the reduction of UO₂. Based on results shown in Figure 11, Hastelloy B was used as reference electrode for all subsequent experiments (unless otherwise specified). This choice of reference electrode was later confirmed when no positive E_{corr} value was observed for other materials investigated in subsequent experiments; these results are shown in section 3.4. This observation confirms that the electrochemical reactions measured in subsequent experiments were always that of the working electrode, rather than the reference. If a positive E_{corr} value were ever measured the oxidation of the reference would be the reaction being studied rather than that of the working electrode.

An additional study was undertaken to investigate the effect of varying the counter electrode on polarization measurements. Two potentiodynamic polarizations of SS 316 were run from -0.4 to +1V vs Hastelloy B in LiCl-2wt%Li2O at 700°C. The polarization plots are shown in Figure 12.
Figure 12: Potentiodynamic polarization scans of SS 316 measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode (blue) and a nickel counter electrode (blue) in LiCl–2wt% Li₂O at 700°C.

Polarization results were interpreted in terms of corrosion potential \(E_{corr}\), and passivation characteristics. The result shown in Figure 12 is explainable because ideally the counter electrode plays no role in the electrochemical reactions being studied; it only acts as a conduit for the flow of electrons necessary to maintain the potential specified by the potentiostat. Ideally changing the counter electrode material only has an effect on the speed at which electrons are provided to the circuit (current) and plays no role in the electrochemistry of the working / reference electrode interactions. The interpretation of Figure 12 is contestant with this theory in that only the current changed when using the alternate counter electrodes, while the \(E_{corr}\) and passivation behavior of the SS 316 remained constant.
As a result of studying the candidate materials nobility, and the effect of altering the counter electrode, Hastelloy B was chosen as the counter and reference electrodes in all subsequent experiments, unless otherwise stated.

4.3 Comparison to the Platinum Standard

In order to properly compare alternative metals to the anode currently used in industry, a benchmark comparison had to be established by studying platinum. Platinum was subjected to identical polarization and microscopy studies that would later be used to study alternative materials. The potentiodynamic polarization plot for platinum against a Hastelloy B reference is shown in Figure 13.

**Figure 13:** Potentiodynamic polarization scans of Pt measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode. The electrolyte was LiCl–2wt% Li₂O at 700°C. The samples were exposed to the salt solution for 30 seconds prior to beginning the test and the scan was sampled at a rate of 1 mV/s from -0.4 V to +1.5 V vs the open circuit potential. Two duplicate scans are shown.
Table 3: $E_{\text{corr}}$ potentials from duplicate potentiodynamic polarizations for platinum.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{corr}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt 1</td>
<td>-6</td>
</tr>
<tr>
<td>Pt 2</td>
<td>-6</td>
</tr>
<tr>
<td>Average</td>
<td>-6</td>
</tr>
</tbody>
</table>

The potentiodynamic polarization curve for platinum in LiCl–2wt% Li$_2$O at 700°C shown in Figure 13 provides several significant insights into the metals behavior when subjected to polarization in the LiCl-Li$_2$O electrolyte. First the $E_{\text{corr}}$ potential is very low and consistent at -6mV vs Hastelloy B suggesting an inert surface chemistry. This noble potential suggests platinum’s stability in the electrolyte at no applied voltage; however this is not necessarily suggestive of the metal’s ability to function as an electrode at an applied anodic potential.

The second notable feature of this data is the formation of pseudo-passive region at +20mV vs Hastelloy B. This formation appears to be stable between +20mV and +1V. The current density observed is not suppressed by more than a factor of five from the primary passivation potential of +20mV. This minimal reduction in current density indicates a thin, non-insulating film. A clear transpassive breakdown is observed ~ +1V, however the increase in current density is relatively slow, rising by an order of magnitude with a 300mV rise in potential. The tendency for the protective surface film to partially survive above the transpassive potential would suggest that some of the film remains after the polarization is completed. This prediction is supported by the observation of a brownish coat on the platinum shown in Figure 14.
The image shown in Figure 14 depicts the platinum anode after it was subject to potentiodynamic polarization from -400mV to +1.5V vs Hastelloy B. The appearance of the electrode is typical of what was observed of platinum after polarization. The observed yellow / brownish coat is proposed to be Li$_2$PtO$_3$. A recent report on the anodic behavior of platinum in molten LiCl-Li$_2$O recorded the formation of Li$_2$PtO$_3$ via Reaction (2) [30].

\[
2\text{Li}^+ + \text{Pt} + 3\text{O}^{2-} \leftrightarrow \text{Li}_2\text{PtO}_3 + 4\text{e}^- \quad \text{Reaction 2} \quad [30]
\]

The relationship between Li$_2$O concentration and the potential at which Reaction (2) occurs has been demonstrated; $E_0=2.5V$ vs liquid Li-Bi with [Li$_2$O]=0.1wt% and $E_0=1.9V$ vs liquid Li-Pb (32at% Li) with [Li$_2$O]=0.5wt% [30, 41]. Other studies report the formation of Li$_2$PtO$_3$ at slightly lower potentials [29]. Considering this effect, and noting the 2wt% Li$_2$O concentration in the salt during the polarization shown in Figure 13, it is thus hypothesized that Li$_2$PtO$_3$ is the surface oxide film formed on platinum during the anodic polarization shown in Figure 14. The platinum anode was micrographed using a FESEM in order to further characterize the surface. The micrographs obtained from the FESEM are shown below in Figure 15.
Figure 15: Micrographs of platinum subjected to cathodic to anodic polarization studies of magnification varying from 50x to 15,000x

FESEM micrographs of the Pt wire after anodic potentiodynamic polarization are shown in Figure 15 (A – E). At lower magnification, Figure 15(A) shows areas of increased degradation in irregular patterns. As the magnification is increased, the morphology is seen continuing to exhibit selective degradation, with areas of severe degradation surrounded by relatively unaffected regions. This morphology is typical of Intergranular Corrosion Cracking (IGCC). IGCC has been observed as the degradation pathway for platinum under anodic polarization in pure LiCl while oxidation of platinum to Li$_2$PtO$_3$ is suspected to occur when Li$_2$O is present in the molten salt [22]. A hypothesis for the observation of IGCC in Figure 15 is the breakdown of the Li$_2$PtO$_3$ film along grain boundaries at potentials exceeding 1.1V. This would expose highly anodically polarized platinum, which previously hadn’t been exposed to the electrolyte, to the molten salt resulting in rapidly oxides.
4.4 Potentiodynamic Polarization Studies

Following control experiments with platinum, candidate materials were subjected to identical polarization tests; potentiodynamic polarization sweep from -0.4 V to +1.5 V vs Hastelloy B at a scan rate of 1 mV/s in molten LiCl–2wt% Li₂O at 700°C. The data obtained from the potentiodynamic polarization experiments of all candidate materials is shown in the following Figures. The \(E_{\text{corr}}\) potentials determined from these studies are shown in accompanying Tables for each material. The alloys investigated will be discussed first followed by the pure metals. The surface morphology post polarization microscopy is provided in section 4.7.

Figure 16: Potentiodynamic polarization plots of Inconel 718 measured in LiCl–2wt% Li₂O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.
Table 4: $E_{\text{corr}}$ potentials from duplicate potentiodynamic polarizations for Inconel 718.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{corr}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel 718 1</td>
<td>-39</td>
</tr>
<tr>
<td>Inconel 718 2</td>
<td>-32</td>
</tr>
<tr>
<td>Average</td>
<td>-35.5</td>
</tr>
</tbody>
</table>

The polarization of Inconel 718, shown in Figure 16 and summarized in Table 4, provided promising results. The alloy exhibited a slightly more active $E_{\text{corr}}$ than Pt. The anodic passivation behavior shows a constant oxidation reaction rate just below 20mA/cm$^2$ from +0.1 to above +1.2 V vs Hastelloy B. The passivation does not show a strong primary passivation state followed by a significant reduction in current density, suggesting that a stable surface film does not form. It is more likely that an equilibrium surface reaction occurs at a quasi-constant rate between Inconel 718 and the molten LiCl between +0.1 and +1.2 V. Above the transpassive potential the current density raises very rapidly, roughly an order of magnitude in a potential range of 100 mV.
Figure 17: Potentiodynamic polarization plots of Inconel 600 measured in LiCl–2wt% Li2O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.

Table 5: $E_{corr}$ potentials from duplicate potentiodynamic polarizations for Inconel 600.

<table>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel 600 1</td>
<td>-20</td>
</tr>
<tr>
<td>Inconel 600 2</td>
<td>-23</td>
</tr>
<tr>
<td>Average</td>
<td>-21.5</td>
</tr>
</tbody>
</table>

The differences in polarization behavior between Inconel 718 and Inconel 600 are quickly seen when comparing Figures 16 and 17. With a comparable $E_{corr}$ values the nobility of the two alloys are only slightly different. The difference in polarization behavior lies in Inconel 600’s passivation behavior. Around +100mV the current density drops by almost an order of magnitude from what appears to be a primary passivation potential. The current density sharply rises back to 10mA at +500 mV, signifying that whatever oxide surface formed at +100mV was not stable after +500mV. A transpassive potential of
+1.2 V is observed, lower than Inconel 718 by roughly 25 mV, however, 25 mV is within range of reproducibly in this experiment.

The difference in alloying composition between Inconel 600 and 718 is shown in Table 2. Inconel 600, with half of the iron content and a 19 wt% increase in nickel compared to 718, appears to have formed a more stable surface film. This is observed in the brief passivation region between +100 - 400 mV and 600 mV – 1.2, however if such a film was formed it was not stable at higher potential. Inconel 600 has slightly superior corrosion behavior compared to Inconel 718 in LiCl-2 wt% Li₂O molten salt, probably due to lower iron and higher content, but it is not significantly superior to Inconel 718.

**Figure 18:** Potentiodynamic polarization plots of SS 316 measured in LiCl–2wt% Li₂O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.
Table 6: $E_{corr}$ potentials from duplicate potentiodynamic polarizations for SS 316.

<table>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 316 run 1</td>
<td>-60</td>
</tr>
<tr>
<td>SS 316 run 2</td>
<td>-47</td>
</tr>
<tr>
<td>Average</td>
<td>-53.5</td>
</tr>
</tbody>
</table>

Potentiodynamic polarization of SS 316 is shown in Figure 18. The anodic portion of the curve shown in Figure 18 contains two broad current density peaks between +100 - 200mV and +600 - 700mV. After these peaks the current density drops by a factor of five and three, respectively. These reductions in current density can be interpreted as different surface oxidation reactions occurring at different rates between the two potential ranges. As expected from the comparatively low nickel content the SS 316, $E_{corr}$ values averaging -53.5mV are slightly more active than either of the Inconel alloys. A comparatively gradual transpassive behavior is also observed, raising an order of magnitude in current density over more than 500mV.
Figure 19: Potentiodynamic polarization plots of titanium measured in LiCl–2wt% Li₂O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.

Table 6: \( E_{corr} \) potentials from duplicate potentiodynamic polarizations for titanium.

<table>
<thead>
<tr>
<th></th>
<th>( E_{corr} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti run 1</td>
<td>-357</td>
</tr>
<tr>
<td>Ti run 2</td>
<td>-276</td>
</tr>
<tr>
<td>Average</td>
<td>-316.5</td>
</tr>
</tbody>
</table>

The first of the metals to be discussed, namely titanium, provided both promising and negative results. The average \( E_{corr} \) of -316.5mV displays titanium’s highly active nature in the molten LiCl. At a first glance, this active characteristic proves the metal’s lack of ability to act stably in the electrolyte. Titanium’s passivation observed between -100mV to +600mV vs Hastelloy B is remarkably stable at 14mA/cm² and consistent between the duplicate polarizations. In addition there was no obvious transpassive breakdown up to +1.5V vs OCP. As a result of this lack of transpassive nature subsequent
polarizations were run to a higher potential to characterize the metal’s stability at a more anodic potential. In order to determine titanium’s ability to passivate under the conditions encountered in the reduction of UO₂ this experiment used a SS 316 reference electrode. The result from the subsequent polarization is shown in Figure 19.

![Figure 19: potentiodynamic polarization scan of titanium from -0.4V to +2.5V measured against a SS 316 reference electrode using a Hastelloy B counter electrode in LiCl–2wt% Li₂O at 700°C.](image)

The investigation of titanium polarized to highly anodic potential shown in Figure 19, proved titanium’s inability to operate in the high potential region. Although a sharp transpassive potential was never observed, the current density continued to rise after +1.5V, resulting in so much oxidation that at +1.95V the titanium anode fully degraded. The residual current density observed past 2V in Figure 19 is thought to be the remaining connection of salt from the bulk electrode above the salt surface to the salt melt.
Figure 20: Potentiodynamic polarization plots of molybdenum measured in LiCl–2wt% Li2O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.

Table 7: $E_{corr}$ potentials from duplicate potentiodynamic polarizations for molybdenum.

<table>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo run 1</td>
<td>-2</td>
</tr>
<tr>
<td>Mo run 2</td>
<td>-58</td>
</tr>
<tr>
<td>Average</td>
<td>-30</td>
</tr>
</tbody>
</table>

Despite the desirable nobility of molybdenum, as shown by the $E_{corr}$ potential of -30mV shown in Table 7, the behavior under anodic polarization proved highly unfavorable. Rather than maintaining at a constant oxidation rate over a wide potential range, the molybdenum oxidation followed a fairly constant decade of current density increase per volt of anodic potential. The rate of oxidation approached 300mA/cm² at +1.5V, and the electrode visually showed excessive loss of mass. Considering these results molybdenum was ruled out as a candidate anode material.
Figure 21: Potentiodynamic polarization plots of nickel measured in LiCl–2wt% Li<sub>2</sub>O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.

Table 8: $E_{\text{corr}}$ potentials from duplicate potentiodynamic polarizations for nickel.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{corr}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni run 1</td>
<td>-146</td>
</tr>
<tr>
<td>Ni run 2</td>
<td>-96</td>
</tr>
<tr>
<td>Average</td>
<td>-121</td>
</tr>
</tbody>
</table>

The potentiodynamic polarization behavior of nickel shown in Figure 21 exhibited several characteristics of interest. Despite initial beliefs about the nobility of nickel in molten chloride salts, the $E_{\text{corr}}$ potential averaged -121mV vs Hastelloy B. The passivation behavior of nickel was very similar to that of Inconel 600, which is explainable due to the 70wt% nickel in the alloy. The primary passivation potential at +100mV vs Hastelloy B and the secondary increase in current density at +500mV vs Hastelloy B were recorded at the same potential for nickel as Inconel 600, however the degree to which
current density was suppressed as the potential increased beyond them was higher for pure nickel. This suggests that the passivation of Inconel 600 was greatly due to the oxidation of nickel on the surface, and that the alloying elements resulted in secondary reactions causing the deviation from the smooth curve observed with nickel. An alternative positive aspect of the alloying elements is the observed +100mV potential shift in the transpassive potential from pure nickel. At the slightly lower potential the nickel suffered from similar rapid transpassive breakdown as the Inconel alloys, increasing the oxidation rate by an order of magnitude with a 100mV potential increase.

Figure 22: Potentiodynamic polarization plots of tungsten measured in LiCl–2wt% Li2O at 700°C. Hastelloy B served as the reference electrode and additionally Hastelloy B served as the counter electrode. Two duplicate scans are shown.
Table 9: \( E_{\text{corr}} \) potentials from duplicate potentiodynamic polarizations for tungsten.

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{corr}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W run 1</td>
<td>-146</td>
</tr>
<tr>
<td>W run 2</td>
<td>-114</td>
</tr>
<tr>
<td>Average</td>
<td>-130</td>
</tr>
</tbody>
</table>

The final metal to be discussed, tungsten, proved to be the most promising alternative anode material investigated. Neither the electrochemical characteristics indicated by Table 9, nor the lack of passivation behavior observed in the polarization plot of Figure 22 strongly suggests tungsten's nobility or ability to passivate at anodic potentials. With a few small exceptions at +100 and 400mV vs Hastelloy B the oxidation rate rises, similar to molybdenum, at roughly an order of magnitude per 600mV. The exceptional characteristic of tungsten was observed after removing it from the salt after polarization. While all previously discussed materials were coated in oxidized corrosion products and salt after they were subjected to polarization testing tungsten appeared clean with no visual degradation. The remarkably unaffected surface after polarization testing is shown in Figure 23.

Figure 23: Tungsten electrode after potentiodynamic polarization to +1.5V in LiCl–2wt% Li₂O at 700°C. Note the clean, polished like finished of the anode subjected to highly oxidizing conditions.
Based on an analysis of the above polarization studies SS 316, Inconel 718 and tungsten were chosen for further investigation. It was desirable to further characterize the three classifications of materials investigated; iron based alloys, high nickel content alloys, and pure metals. SS 316 was chosen due to extensive knowledge and use of the metal as the cathode in the current electrolytic reduction process. Building off such knowledge would result in reduced costs and complications associated with introducing new materials to the process. Inconel 718, was chosen due to suggestions from previous research [42-44], in addition to the observed noble potential and stable passivation behavior. Tungsten was specifically chosen because of its lack of degradation during polarization. Since, the potential required for the reduction of UO₂ is well beyond the transpassive breakdown potential for all materials investigated, tungsten was considered to have superior corrosion characteristics as it showed no sign of degradation after being subject to >100mA/cm² of current density in the electrolyte.

4.5 Electrochemical Impedance Spectroscopy

EIS was employed as a second in situ procedure used to evaluate the surface interactions between the three candidate materials and the molten LiCl-Li₂O electrolyte. Due to the complex nature of EIS, and the extreme experimental conditions only a brief discussion of the following data will be presented as it pertains to corroborate alternative experimental data.
**Figure 24:** The Bode plot for Inconel 718 in LiCl-2wt%Li$_2$O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. The impedance shows a continuous increase at lower frequencies, while the phase shift appears to stabilize below 0.1Hz.

**Figure 25:** The Nyquist plot for Inconel 718 in LiCl-2wt%Li$_2$O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. The electrochemical system is suggested to be more stable at lower frequencies compared to the other systems investigated subsequently.
The EIS results for Inconel 718, shown in Figures 24 and 25, suggest stability of the surface interactions in the molten salt electrolyte. The curve trends are smooth down to low frequencies, indicative of stable processes. When compared with the EIS data for the other candidate materials, the magnitude of the impedance is significantly larger. In addition, the Bode plot shows increased impedance below 0.1Hz while the phase shift remains constant. The EIS spectra are generally indicative of mixed control.

**Figure 26:** The Bode plot for SS 316 in LiCl-2wt%Li$_2$O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. A decrease in impedance at lower frequencies shows a tendency to corrode.
Figure 27: The Nyquist plot for SS 316 in LiCl-2wt%Li₂O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. The electrochemical system is suggested to be quasi-stable at lower frequencies.

The EIS results for SS 316 are shown in Figures 26 and 27. Similar to the Inconel 718 EIS plots seen earlier, the Nyquist plot for SS 316 appears to be stable at low frequencies; however, the impedance is observed to decrease at the lowest frequencies. The magnitude of the impedance is seen to be less than half that of Inconel 718 at a given frequency.
Figure 28: The Bode plot for W in LiCl-2wt%Li$_2$O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. A rapid increase in impedance from 0.1Hz to 0.01Hz is indicative of superior corrosion resistance.

Figure 29: The Nyquist plot for W in LiCl-2wt%Li$_2$O at 700°C against a Hastelloy B reference with a Hastelloy B counter electrode. The magnitude of the impedance is very small, and the electrochemical system is suggested unstable at lower frequencies, and suffers from Warburg diffusion.
Bode and Nyquist plots obtained for tungsten are shown in Figures 28 and 29. These figures display seemingly conflicting data trends. The Bode plot shows very small impedance, with a sharp rise below 0.1Hz. The small magnitude is indicative of a low energy threshold for surface reactions. An additional point of complication is noted in the lower frequency region of the Nyquist plot. The erratic nature of these data points is common for unstable, non-equilibrium surface interactions at low frequencies. The trend of trailing off at a 45° angle is characteristic of Warburg diffusion. This is logical because the solution resistance to ionic mobility in the electrolyte becomes comparable to surface interactions when the impedance of the electrochemical system is so small, <10 Ω [45, 46].

4.6 Effect of Li$_2$O in Electrolyte on Corrosion Behavior

During the actual electrolytic reduction of UO$_2$ the oxide concentration in the salt will inevitably change due to the incomplete and imperfect evolution of O$_2$ at the anode. The composition change will also change the redox potential of the salt, making it necessary to evaluate the candidate materials at a variety of oxide concentrations. In order to investigate the change in redox potential on electrode stability potentiodynamic polarizations were run at 0, 2, and 8wt% Li$_2$O. As in previous experiments potentials were swept from -400mV to +1.5V at a scan rate of 1mV/s. In the case of pure LiCl the current density was found to rise rapidly, and as a result these polarizations were halted prior to completion.
Figure 30: Potentiodynamic polarization scans of Inconel 718 measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode in LiCl with 0, 2 and 8wt% Li$_2$O at 700°C.

The effect of varying the concentration of Li$_2$O between 0, 2 and 8wt% had a large effect on Inconel 718, as can be seen in Figure 30. In pure LiCl, the $E_{corr}$ value is significantly more active then with the inclusion of Li$_2$O. The cathodic polarization resulted in two orders of magnitude less current density then with Li$_2$O, however under anodic polarization the current density rapidly surpassed the alternatives. The difference between 2 and 8wt% Li$_2$O provides insight into the surface film formation under anodic polarization. Both concentrations passivated at the same potential, ~50mV, and show roughly the same transpassive potential, ~1.25V. The consistency of these potentials suggests that the surface oxides formed in the two electrolytes are the same. The higher oxide concentration shows multiple regions of increased current density compared to 2wt%, likely due to the increase in O$^2-$ cation mobility in the electrolyte. The increase in ion mobility reduces the solution resistance of the electrochemical system, resulting in an increased current density for a given potential.
Figure 31: Potentiodynamic polarization scans of Inconel 718 measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode in LiCl–2wt% Li$_2$O at 700°C.

SS 316 showed similar results to varying Li$_2$O concentration in the LiCl. The plot shown in Figure 31 shows a more active $E_{corr}$ potential in pure LiCl, with a large reduction in cathodic current density, and a rapid rise in current density under anodic polarization. Both Inconel 718 and SS 316, show an increased $E_{corr}$ with an increase in oxide concentration in the salt. The anodic current density recorded for SS 316 is consistently greater for 8wt% Li$_2$O which again can be attributed to increased O$^{2-}$ mobility in the electrolyte resulting in decreased solution resistance.
Figure 32: Potentiodynamic polarization scans of W measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode in LiCl–2wt% Li₂O at 700°C.

Varying the Li₂O concentration had a very different influence on W polarization compared to the alloys investigated. In the absence of Li₂O, the metal exhibited similar trends in corrosion behavior but with much reduced anodic and cathodic current densities. This is likely due to both anodic and cathodic current densities’ dependence on oxide concentration. Without the inclusion of O²⁻ ions in the solution, the ion mobility is relatively low resulting in a large solution resistance. This trend follows into the anodic polarization; with an order of magnitude less current density recorded up to +0.9V. The current density recorded is also slightly less on average for 8wt% Li₂O compared to 2wt%. This is a non-intuitive result and suggests an alternative mechanism for anodic oxidation of tungsten compared to the alloys Inconel 718 and SS 316. There is also a difference in the potential at which current density peaks take place between 2% and 8%. This is the first evidence for an alternative oxidation pathway for tungsten at higher oxide concentration.
4.7 Post-polarization Microscopy

In order to simulate the highly oxidizing environment that would be encountered in the electrolytic reduction of UO₂ the three materials chosen for further analysis, Inconel 718, SS 316 and W, were potentiostatically polarized to +2.5V vs SS316 for 10 min in Li₂O at 700°C. After polarization the micrographs of the anodes were taken using an FESEM, to investigate the morphological changes undergone by the candidate anode materials, and obtain a qualitative view of the corrosion that would take place during the reduction process.

As seen in Figure 33, Inconel 718 underwent severe morphological degradation during the polarization in molten LiCl. The corrosion appears to be fairly uniform, oxidizing and dissociating the surface material relatively evenly. The crack observed in Figure 33 (C) suggests intergranular corrosion cracking (ICC) as the chief degradation mechanism. This would agree well with the large amount of material, seen in Figure 33 (A), which was stripped off the electrode.

Figure 33: Electron micrographs of Inconel 718 subjected to potentiostatic polarization at +2.5V vs SS316 in LiCl–2wt% Li₂O at 700°C. A) FESEM image at 60 x magnification B) FESEM image at 520 x magnification C) FESEM image at 3500 x magnification.
Figure 34: Electron micrographs of stainless steel alloy 316 subjected to potentiostatic polarization at +2.5V vs SS316 in LiCl–2wt% Li₂O at 700°C. A) FESEM image at 60 x magnification B) FESEM image at 503 x magnification C) FESEM image at 9030 x magnification.

SS 316 suffered less corrosion from anodic polarization in the electrolyte. The large chunk dissociated from the right side of Figure 34 (A) contrasted by the less affected region surrounding it displays a highly selective oxidation tenancy for SS 316. Specific regions of the electrode were severely oxidized while others were barely seen to be damaged. This is shown again in Figure 34 (B&C) were larger regions of up to 100 μm² show no obvious degradation, yet smaller cracks appear to be severely affected. These observations again suggest ICC as the leading degradation pathway for oxidation of SS 316 in the molten electrolyte.

Figure 35: Electron micrographs of tungsten subjected to potentiostatic polarization at +2.5V vs SS316 in LiCl–2wt% Li₂O at 700°C. A) FESEM image at 110 x magnification B) FESEM image at 350 x magnification C) FESEM image at 1300 x magnification.

Tungsten’s post-polarization morphology, is shown in Figures 35 (A-C). When compared to Figures 33 and 34, the metal’s superiority to act as an anode for the reduction of UO₂ is obvious. The
macroscopic surface of the material is almost unscathed by the anodic polarization. There is no large scale degradation, and no residual LiCl crystals remaining on the surface. The linear pattern observed in Figure 35(B) is the result of the pre-exposure polishing. The 600 grit sandpaper used during polishing has an average particle size of ~15μm, meaning that after ten minutes at +2.5V in the electrolyte less than 15μm of material was dissociated from the surface. The observation of this pattern after polarization is a remarkable portrayal of tungsten’s inert nature under anodic polarization in molten LiCl-2wt% Li₂O. It should be emphasized that even under polarization to +1.5V, platinum did not maintain such obvious structure as seen in Figure 35. This fact alone is proof of tungsten’s ability to act as an alternative anode for the reduction of UO₂

4.8 Oxidation of Tungsten as a Function of Li₂O Concentration

After examining the microstructure of the three candidate materials; only tungsten proved to sustain an acceptable amount of degradation after being subjected to potentiostatic polarization. Considering this, a further investigation was undertaken to study the effect of electrolyte composition to evaluate the ability of tungsten to operate in a variety of electrolyte solutions that could be encountered in the commercial reduction of UO₂. Two different experiments were undertaken; (I) anodic potentiodynamic polarizations were conducted in electrolytes containing 0 to 8%, and (II) potentiostatic polarizations at 2.5V in electrolytes containing 0, 2, 4 and 6wt% Li₂O. The results obtained from the potentiodynamic polarizations are provided in Figure 36.
Figure 36: Potentiodynamic polarization scans of W measured against a Hastelloy B reference electrode using a Hastelloy B counter electrode in LiCl with varying [Li_2O] in 1wt% increments.

The results shown in Figure 36 show a general trend for the effect of increasing oxide concentration in the salt, however due to the nature of the experiments and associated variance, several outliers are observed. Contrasting the observation of section 4.6, the trend seen in Figure 36 is an increase in the activity of the sample, as well as an increase in current density at a given potential. The likely cause of this difference is the lack of cathodic polarization in the polarizations in Figure 36. During cathodic polarization Li^+ attack is damaging to the electrode surface, and increases the activity of materials. At different oxide concentrations a trend of increased potential for rises in current density is observed. The deviation from a consistent trend likely arises from the experimental variations and inconsistencies associated with these experiments. Again, it should be noted that due to the highly dynamic environment encountered in molten chloride salts even duplicate polarizations in the same melt have been proven to produce significantly different results. Establishing a general trend is all that
can be reported without extensive investigation of these effects in order to reduce the statistical errors associated with repeat experiments.

In order to avoid the errors encountered in the potentiodynamic investigation of tungsten oxidation with varying Li$_2$O concentration, potentiostatic polarizations were recorded with 2wt% increments. It was also noticed that due to the longer polarization times at the given potential, potentiostatic polarizations produced cleaner results with larger discrepancies between oxide concentrations. The current densities recorded during these polarizations are shown in Figure 37, and the subsequent microscopy studies of the various samples are shown in Figures 38 through 42.

**Figure 37:** The current as a function of time recorded during the potentiostatic polarization of W vs SS 316 at +2.5 V in LiCl at 0, 2, 4 and 6 wt% Li$_2$O.

The currents recorded during potentiostatic polarizations at various Li$_2$O concentrations show an interesting relationship between oxidation rate and oxide concentration of the salt. The measured current increases with increasing Li$_2$O concentrations from 0wt% Li$_2$O to 4wt% Li$_2$O and then drops
significantly in experiments conducted using 6wt% Li₂O with a noticeable rise in between the two at 4%.

This fact is noted as evidence of a shift in oxidation mechanism as the oxide concentration is increased.

**Figure 38**: Images of tungsten subjected to anodic polarization at +2.5 V vs SS 316 for 600 seconds in pure LiCl at 700°C. (A) Digital camera image (B) FESEM image at 60 x magnification (C) FESEM image at 500 x magnification (D) FESEM image at 3,000 x magnification (E) FESEM image at 11,000 x magnification.

After polarization in pure LiCl the morphology of the tungsten anode showed a salt coat formation, visible in Figure 38 (A), however after being washed and imaged with the FESEM minimal degradation was observed. The corrosion that was apparent was found along with scratch patterns remaining on the surface from polishing. At high magnification small cracks are apparent in the metal, but no significant loss of material was observed. Thus, it is suggested that these cracks do not penetrate deeply. The oxidation rate, observed as the current in Figure 37, was very low and extremely stable. This is expected for a single compound electrolyte as it is indicative of a constant surface oxidation reaction.
Figure 39: Images of tungsten subjected to anodic polarization at +2.5 V vs SS 316 for 600 seconds in LiCl2wt% Li2O at 700°C. (A) Digital camera image (B) FESEM image at 60 x magnification (C) FESEM image at 400 x magnification (D) FESEM image at 3,500 x magnification (E) FESEM image at 11,000 x magnification.

Table 7: Elemental composition of W surface after polarization in 2%Li2O obtained from EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>W M</td>
<td>100</td>
</tr>
</tbody>
</table>

With the inclusion of 2wt% Li2O in the electrolyte, there was almost no observable corrosion damage to the tungsten anode, as shown in Figure 39. The tungsten shows almost a mirror surface upon removal from the salt. At low and high magnification no corrosion in the form of bulk material loss or pitting was observed. For a further comparison, Figure 40 shows micrographs of a fresh tungsten wire. The small dark regions, and the polishing streaks observed on the polarized wire in Figure 39 are also present in Figure 40. In addition, EDX recorded tungsten as the only chemical constituent after polarization. This proves the truly minimal degradation to the tungsten anode during anodic polarization.
Figure 40: Tungsten wire subjected to the standard polishing practice, prior to exposure to molten LiCl.

Figure 41: Images of tungsten subjected to anodic polarization at +2.5 V vs SS 316 for 600 seconds in LiCl–4wt% Li2O at 700°C. (A) Digital camera image (B) FESEM image at 60 x magnification (C) FESEM image at 254 x magnification (D) FESEM image at 3,500 x magnification (E) FESEM image at 11,000 x magnification. Image (D) and (E) are from the locations indicated by the D and E in image C.

Table 8: Elemental composition of W surface after polarization in 4%Li2O obtained from EDS.

<table>
<thead>
<tr>
<th>Figure 42 (D)</th>
<th>Element</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl K</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td>W M</td>
<td>68.5</td>
<td></td>
</tr>
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</table>

<table>
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<tr>
<th>Figure 42 (E)</th>
<th>Element</th>
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<tbody>
<tr>
<td>Cl K</td>
<td>73.05</td>
<td></td>
</tr>
<tr>
<td>W M</td>
<td>26.95</td>
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</table>

At 4wt% Li2O surface oxidation as a result of polarization becomes apparent, as can be seen in Figure 41. The anode is brown in color upon removal from the salt, and displays regions of an oxide formation when imaged with the FESEM. At this concentration of Li2O, the oxide film appears to be thick, brittle and incomplete, covering approximately 60% of the material. Figures 41 (D) and (E) show
the two different regions observed on the sample at higher magnification, with their locations indicated on a larger scale in 41 (C). Figure 41 (D) shows a very similar morphology to that of the sample polarized in 2wt% Li$_2$O, however 41 (E) shows a cracked pattern. This film formation is the first visual confirmation of an alternative oxidation pathway for the tungsten anode with an increase in Li$_2$O concentration above 2wt%, proposed earlier in section 4.6. The elemental composition data obtained from EDS, shown in Table 8, suggests that not only does the film formation of Figure 42 (E) consist of mostly chlorine, but chlorine is also seen on the bulk metal in Figure 42 (D). This is further evidence of a different oxidation product formation, because there was no chlorine detected on the surface of the anode polarized in the 2wt% Li$_2$O.

Figure 42: Images of tungsten subjected to anodic polarization at +2.5 V vs SS 316 in LiCl–6wt% Li$_2$O at 700°C. (A) Digital camera image (B) FESEM image at 80 x magnification (C) FESEM image at 250 x magnification (D) FESEM image at 450 x magnification (E) FESEM image at 3,000 x magnification. The (A) and (B) in Figure 43 (D) indicate separate points were EDS measured from.
Table 9: Elemental composition of W surface after polarization in 6%Li₂O obtained from EDS with indications of (A) and (B) for their respective locations in Figure 43 (D).

<table>
<thead>
<tr>
<th>Figure 43 (A)</th>
<th>Element</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td></td>
<td>O K</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>Cl K</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>W M</td>
<td>37.2</td>
</tr>
<tr>
<td>Figure 43 Film (B)</td>
<td>O K</td>
<td>33.23</td>
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<tr>
<td></td>
<td>Cl K</td>
<td>55.2</td>
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<tr>
<td></td>
<td>W M</td>
<td>11.57</td>
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</table>

Figure 42 shows the tungsten anode after potentiostatic polarization in LiCl-6wt% Li₂O. At this oxide concentration, large amounts of salt accumulate on the anode during polarization. After rinsing, the surface film is observed to fully cover the anode. This full encapsulation of the surface film gives rise to the structural integrity of the LiCl crystal seen on the surface in Figure 42 (A). The micrographs in Figures 42 (B-E) show an interesting mixture of an even surface film, and larger clumps of oxidation products. The EDS data collected from this sample shows the first detection of oxygen on any of the three samples. These data further support that there are different chemical complexes formed on the surface during the oxidation of tungsten correlated to the concentration of Li₂O in the salt.

The observation of this level of degradation of the anode is deemed unacceptable for the reliability of an electrode in a commercial application. With this amount of film formation and corrosion product buildup on the surface, the electrochemical properties of the metal are no longer predictable or stable. It is thus noted that should tungsten be considered as an alternative anode material for the reduction of UO₂, that the oxide content of the salt melt be monitored and controlled to ensure consistent electrode behavior.
4.9 Raman Spectroscopy

Raman spectroscopy was employed to characterize the chemistry of the corrosion products formed on the anode surface during polarization. The Raman spectroscopy results shown in this section facilitate the only analysis of the chemical makeup of the electrode surfaces in this research.

The first Raman spectrum to be discussed is that obtained from platinum after polarization in the molten salt electrolyte. As shown in Figure 43, the Raman spectrum for polarized platinum shows three distinct features at 533, 565 and 599 cm\(^{-1}\).

![Raman Spectrum of Pt](image)

**Figure 43:** Raman spectrum of Pt after potentiodynamic polarization to +1.5V in LiCl-2wt% Li\(_2\)O at 700\(^\circ\)C.

The feature at 565 cm\(^{-1}\) is a characteristic vibrational mode of PtO\(_2\) [47]. It is proposed that the spectrum illustrated in Figure 43 is not PtO\(_2\) but a Li\(_2\)PtO\(_3\). The formation of Li\(_2\)PtO\(_3\) has been extensively characterized using cyclic voltammetry and XRD, however no vibrational spectroscopy of the compound has been previously reported. It is suggested that the PtO\(_2\) Raman shift at 514 cm\(^{-1}\) has been altered to 533 cm\(^{-1}\), and the dominance of the 599 cm\(^{-1}\) feature is the characteristic of the vibrational mode of
Li$_2$PtO$_3$. In order to prove the oxides films, presence a 3-D mapping Raman spectrum was taken from an unperturbed rejoin to a region that was polished to bulk Pt. The Spectra taken along this line is shown if Figure 44 (A), and a digital image of the line mapped region is shown in Figure 44 (B).

**Figure 44:** Raman spectrum mapping of a Pt anode after polarization in LiCl to +1.5V. The oxide layer was polished off to a mirror finish at the tip in order to display the disappearance of the oxide spectrum. The scan runs from a full oxide layer starting at 0μm in (A) corresponding to the bottom of (B) to bulk Pt at 450μm in (A) and the top of (B).

Raman spectroscopy was next utilized to analyze the corrosion products formed on tungsten subjected to polarization. First a standard of WO$_3$ was analyzed in order to properly identify characteristic Raman shifts of oxidized tungsten. The standard Raman spectrum for WO$_3$ is shown in Figure 45.
In order to maintain a sufficient oxide film on tungsten, it was necessary to potentiodynamically polarize the samples to +500mV to avoid the destruction of the film through transpassive breakdown. Samples were polarized in LiCl with 2, 4 and 6wt% Li₂O to produce surface films. Samples were not rinsed prior to Raman analysis, but were exposed to atmosphere for roughly five minutes before the spectra were recorded. The Raman spectra from these experiments are shown in Figure 46.

Figure 45: Raman spectrum of a standard of WO₃
Figure 46: Raman spectra of W subjected to potentiodynamic polarization to +500mV in LiCl with 2, 4 and 6wt% Li$_2$O.

The Raman spectra shown in Figure 46 provide the first analytical proof of variations in tungsten oxidation mechanisms due to a change in Li$_2$O concentration when subjected to anodic polarization in molten LiCl. By contrasting Figures 45 and 46, and considering recent publications, several conclusions can be made. First, WO$_3$ has been successfully identified on the anode surface; most notably for the polarization in 2wt% Li$_2$O with the strong features at 95, 714 and 810 wavenumbers. In addition the 340cm$^{-1}$ features has been reported to be characteristic of WCl$_6^{2-}$ [48]. Thus, due to the week intensity of the 340cm$^{-1}$ compared to the characteristic features of WO$_3$, it can be determined that the primary oxidizing agent in the electrolyte is oxygen rather than chlorine.

The most significant feature of Figure 46 is that as the oxide content is increased the features at 76 cm$^{-1}$ and 714 cm$^{-1}$ are suppressed while the feature at 810 becomes more prevalent and shifts to
830cm\(^{-1}\). Identical effects have been reported by Cazzanelli et al. [49] while studding H\(_2\)WO\(_3\) with variable hydrogen content. It was found that as the hydrogen content increased the WO\(_3\) feature at 714cm\(^{-1}\) was suppressed to background while the feature at 810cm\(^{-1}\) became stronger [49]. This is highly analogous to the current study with the substitution of lithium cations in place of hydrogen. With increased oxide content it is believed that there is a shift in oxidation pathway from pure WO\(_3\) formation to that of a Li\(_x\)WO\(_3\) complex. This conclusion is corroborated by the results of polarization, SEM and EDS analyses, which all indicated the occurrence of an alternative degradation mechanism at increasing oxide contents.

After analyzing the potentiodynamically polarized tungsten anodes, Raman spectroscopy was used to evaluate the corrosion products produced during potentiostatic polarization at the potential required for the reduction of UO\(_2\). The highly anodic potential of +2.5V vs SS 316 is well beyond the transpassive potential for tungsten, resulting in a less cohesive oxide film. Because of the less complete encapsulation of the surface film for these samples, spectral mapping across the anode surface was necessary in order to capture a more comprehensive representation of the corrosion products. Raman spectral maps of tungsten subjected to potentiostatic polarization to +2.5 V for 600s in LiCl-2wt% Li\(_2\)O and 6wt% Li\(_2\)O spectra are illustrated in Figures 48 and 49, respectively.
Figure 47: Raman spectrum mapping of a W anode subjected to potentiostatic polarization at +2.5 V vs SS316 for 600 s in LiCl-2wt% Li₂O. The Spectrum shown in (A) derives from the red region in (B) and the location of the red X in (C). (B) is a 3D mapping of a Raman Shift of 839cm⁻¹, while (C) is a digital image of the surface scanned with dots indicating the points at which various spectra were taken.

A digital image of the full area map of the tungsten surface after potentiostatic polarization in LiCl-2wt% Li₂O is shown in Figure 47 (C). The spectrum shown in Figure 47 (A) was selected from the Raman map because it displayed the largest signal intensity at any point on the surface. From this spectrum a Raman shift of 839cm⁻¹ was chosen as the dominant intensity feature. This wavenumber was
then selected, and a regional map of corresponding intensity of this feature across the anode surface is shown in Figure 47 (B). This correlation between the digital image, spectrum and regional intensity allows for a unique qualification of the surface. Specifically, this feature also helps to display that the trends observed at a single location are representative of the whole surface. Considering this, the region of highest intensity of the 839 cm\(^{-1}\) feature, characteristic of WO\(_3\), follows along the axis of the wire anode. This result is not surprising as the anode surface is curved in the azimuthal direction and the signal drops off as the surface drops out of the depth of focus.

The spectrum illustrated in Figure 47 (A) is comparable to the results seen in Figure 46 from potentiodynamic polarization in various oxide concentrations. The ratio of the 839 cm\(^{-1}\) to 714 cm\(^{-1}\) features, and the presence of the feature at 84 cm\(^{-1}\) is similar to that from 4 wt% Li\(_2\)O in Figure 46. In addition the stronger feature at 340 cm\(^{-1}\) is indicative of a larger presence of WCl\(_6\).
Figure 48: Raman spectrum mapping of a W anode subjected to potentiostatic polarization at +2.5 V vs SS316 for 600 s in LiCl-6wt% Li,O. The Spectrum shown in (A) derives from the red region in (B) and the location of the red X in (C). (B) is a 3D mapping of a Raman Shift of 839 cm⁻¹, while (C) is a digital image of the surface scanned with dots indicating the points at which various spectra were taken.

The Raman spectrum map of tungsten subjected to anodic polarization at +2.5V vs SS 316 for 600s in 6wt% Li,O shown in Figure 48 is structured in the same fashion as Figure 49. The larger
blackened regions illustrated in Figure 49 (C) signify a higher degree of corrosion than was observed
from polarization in 2wt% Li₂O, however the relative Raman intensity recorded across the surface is
significantly lower. This result derives from the unstable nature of the oxide film under these conditions;
favoring tungsten ion dissociation over oxide film formation. Again 839 cm⁻¹ has been selected for the
regional intensity map of Figure 49 (B). However, in this case less of a correlation is observed along the
length of the wire. The spectrum shows an increased ratio of 839 to 714 cm⁻¹ signifying the formation of
a more reduced form of W(V). There is no peak at 340 wavenumbers indicating that WCl₆ was not
formed on the surface.
Chapter 5: Conclusions

Pyroprocessing of spent nuclear fuel is highly advantageous over aqueous methods of reprocessing, and is the premier choice for closing the nuclear fuel cycle in the United States. A major incentive for closing the nuclear fuel cycle is the consumption of light water reactor fuel, negating the need for a permanent repository. In order to integrate current stockpiles of light water reactor fuel into such a fuel cycle, the ceramic waste must be reduced to a metallic form. The current process for this reduction is electrolytic reduction in molten LiCl-Li₂O at 700°C. This process currently employs a platinum anode and a stainless steel cathode; however the consumption of the expensive anode has arisen as a major limitation to this process.

This thesis investigated alternative anode materials for the electrolytic reduction of uranium oxide. The basis for experimentation was polarization in the electrolyte used in the reduction process: LiCl-Li₂O at 700°C. Prior to investigating alternative materials, an experimental system had to be developed that could facilitate these experiments. A high temperature electrochemical apparatus housed in an inert atmosphere glove box was designed and constructed specifically for these experiments.

Once a working system had been developed for electrochemical experimentation in molten salt, the initial characterization of a variety of metals and alloys was undertaken though potentiodynamic polarization. Potentiodynamic polarization served as a rough characterization of material nobility and passivation behavior under anodic polarization in the molten electrolyte. This characterization led to the narrowing of the candidate material choices to: a ferrous alloy SS 316, a nickel based superalloy Inconel 718, and elemental tungsten.
After narrowing the candidate materials to three choices, potentiostatic polarization was used to study the stability of the anodes at the anodic potential required for the reduction of UO₂. Tungsten’s superiority in these experiments was dramatic. Microscopic analysis of the alloy materials showed severe oxidation and bulk material loss, while tungsten showed no consequences from oxidation. It was determined that as a result of 600 seconds at the required potential for the reduction of UO₂ less 15μm of material had dissociated from the tungsten surface. A comparison between the anode currently used in industry, platinum, and the proposed alternative anode tungsten is shown in Figures 49 and 50. In these figures platinum is observed to corrode when subjected to anodic polarization to +1.5V while tungsten retains its morphological structure after being subjected to potentiostatic polarization at +2.5V for 600s.

**Figure 49:** Micrographs of platinum subjected to potentiodynamic polarization from -400mV to +1.5V vs Hastelloy B in LiCl-2wt% Li₂O at 700°C.

**Figure 50** Micrographs of tungsten subjected to potentiostatic polarization at +2.5V vs SS 316 for 600s in LiCl-2wt% Li₂O at 700°C.
During these studies, a correlation of tungsten oxidation to the concentration of Li$_2$O was observed. After further investigation, it was found that tungsten oxidation in molten LiCl-Li$_2$O is highly dependent on the concentration of Li$_2$O, and that more degrading surface phenomena occur as the concentration is increased above 4wt%. At 2wt% Li$_2$O the surface degradation and metal dissolution rates are minimal, however as the oxide content was increased to 6wt% bulk material loss and morphological changes due to increased oxidation were observed.

Raman spectroscopy was utilized to determine the chemical composition of the oxidation products formed during polarization. Raman spectroscopy was first used to confirm the presence of a platinum oxide formation on platinum subjected to anodic polarization in molten LiCl-Li$_2$O. This method of spectroscopy was then used to analyze the specific compounds of tungsten oxide that was formed during anodic polarization at various concentrations of Li$_2$O. Spectroscopic analysis concluded that as the concentration of Li$_2$O is increased the oxidation pathway changes from the formation of W(VI) valiency in WO$_3$ to a more reduced from of W(V). It is suggested that this results from the formation of a lithium tungsten oxide complex as the redox potential of the melt becomes more active, however this has yet to be proven.

These studies indicate that tungsten is an adequate anode for the electrolytic reduction of UO$_2$. Tungsten proved superior to alternative materials in virtually all electrochemical and analytical tests performed. It is thus suggested that should tungsten be actively pursued as an alternative anode. In all, tungsten could be a cost effective and functionally viable alternative anode for the electrolytic reduction of uranium dioxide.
Chapter 6: Future Work

Prior to being used as the anode for the reduction of uranium oxide, the oxidation products formed by tungsten under anodic polarization in molten LiCl-Li₂O should be further characterized. The most desirable analytical method is XPS due to its ability to detect lithium. Tungsten, after potentiostatic polarization at +2.5V vs SS 316 at a variety of Li₂O concentrations could be studied using XPS to completely study the compounds formed under these conditions. Additionally, inductively coupled plasma mass spectrometry could be used to study the concentration of tungsten ions in the salt as a function of polarization time. The buildup of tungsten ions from anodic dissociation could lead to undesirable chemical reactions with the spent fuel in the cathode if the concentration increases beyond a minimal amount.

After further characterization of oxidation characteristics of tungsten at laboratory scale, experiments are needed to study the complete reduction circuit behavior of uranium reduction using a tungsten anode. There are a number of potentially critical factors that would need to be investigated once both pure UO₂ and spent nuclear fuel were incorporated. First, the role of dissociated tungsten ions in the reduction of uranium would need to be studied. Subsequently, the role in fission product contamination in the salt would have to be extensively investigated prior to scaling up the process. During the electrolytic reduction of spent fuel at INL it has been reported that iodine and tellurium were observed soluble in the electrolyte and resulted in accelerated oxidation of the platinum anode[50]. These results would need to be addressed prior to full scale reduction processes using a tungsten anode.
References


[36] OMNI-LAB Glovebox System and Accessories


