Investigation of the Effects of Uranium(III)-Chloride Concentration on Voltammetry in Molten LiCl-KCl Eutectic with a Glass Sealed Tungsten Electrode

Devin Rappleye^{a, c*}, Kevin Teaford^b and Michael F. Simpson^a

^aDepartment of Metallurgical Engineering, University of Utah, 135 S 1460 E Rm 412, Salt Lake City, UT 84112-0102, USA (michael.simpson@utah.edu)

^bDepartment of Chemistry, University of Utah, 315 S 1400 E Rm 2020, Salt Lake City, UT 84112, USA (kteaford@chem.utah.edu)

^cPresent Affiliation: Lawrence Livermore National Laboratory, P.O. Box 808 L-350, Livermore, CA 94551-0808

*Corresponding Author, rappleye1@llnl.gov, 925-422-0315

Abstract

One of the major sources of error for electroanalytical measurements in high-temperature molten salts is from the measurement of the working electrode (WE) area. A glass sealed working electrode (GSWE) was developed in order to set the exposed area of tungsten and reduce the error associated with WE area. The insulating property of the glass while in contact with molten salt was verified by observing the independence of electrochemical signals with adjustments in the WE position. The integrity of the glass coating was also confirmed by observing the stability of electrochemical signals ($\pm 1.9\%$) over several hours. Cyclic voltammetry (CV) and normal pulse voltammetry (NPV) were applied at 10 different concentrations of UCl_3 . Above 0.17 mol dm^{-3} UCl_3 , the electrochemical signals from CV and NPV deviate significantly from linearity with concentration, but in opposite directions. A shift from reversible to quasi-reversible behavior and migration are theorized to cause the non-linearity for CV and NPV, respectively. A model is proposed to account for migration in NPV resulting in a significant error reduction in the electrochemical concentration measurement.

Keywords: electrodeposition; uranium; molten salt; cyclic voltammetry; normal pulse voltammetry

1. Introduction

Voltammetry can be an accurate, in situ technique to measure the concentration of ions in high-temperature, molten salts, such as eutectic LiCl-KCl which is used for the electrorefining of used nuclear fuel (UNF) [1], the electrolysis of lithium, magnesium, or titanium [2], and the recycling of rare-earths [3]. However, one of the greatest challenges in making accurate concentration measurement with voltammetry is determining the surface area of the working electrode (WE). In many publications, the method of measuring the surface area of the WE is not discussed in detail or explicitly stated which results in an unknown uncertainty of the measured WE surface area. However, some researchers have discussed their WE immersion depth measurements in detail.

The most common and simple method is to observe a frozen salt layer or residue on a WE after exposure to the molten salt. The length of the salt layer on the WE is used with the diameter of the WE to calculate the area of the electrode-salt interface [4]. The simplicity of this method results in less accurate WE surface area due to surface tension effects (i.e. wetting, etc.) and observational errors. In most cases, electrochemical measurements in molten LiCl-KCl eutectic are performed in an opaque furnace preventing the visual confirmation of the WE surface area in the salt. However, a transparent furnace can be built and the WE immersion depth in the salt can be visually measured in the salt using a cathetometer [5]. However, visibility will be further reduced when applying voltammetry on an actual UNF electrorefiner in a hot cell. Visual confirmation of the WE area may not be practical due to the number of layers around the molten salt and the interference of additional processing equipment.

One possible way to avoid the visual confirmation of the WE area is to use a differential area rather than an absolute surface area [6,7]. This method performs an electrochemical technique at different increments of immersion depth. These increments can be made or measured precisely using a vertical position translator. The differential current with respect to the differential area can be related to concentration without the need to determine the absolute WE area. The precision of this method results in

a greater design complexity and longer turnaround time on concentration measurements due to the requirement to measure signals at multiple WE immersion depths.

Some researchers have used insulating material, such as alumina [8–10], boron nitride [11], or borosilicate [12,13] to fix the WE area at a known value. However, none of these studies indicate whether the WE was simply sheathed, cemented, fused or affixed to the insulator by some other means, except one [12] in which the word “sheathed” is used. In other publications [8–10,13], the word “encased” is used. If the WE was simply sheathed, this would allow molten salt to creep up the thin gap between insulator and the WE, possibly augmenting the fixed area of the WE. Similar creepage could occur due to imperfect seals created by binding the insulator to the WE with cement or some other paste. Fusing the insulator to the WE should result in a leak-proof seal creating a truly fixed WE area. A WE with a well-defined fixed surface area created by an inert insulating coating would simplify the construction of an electroanalytical probe without sacrificing accuracy. This probe could be used to detect impurities, monitor ions of interest, and provide feedback for process control and optimization in high-temperature molten salts.

To this end, a glass sealed working electrode (GSWE) was developed and tested in eutectic LiCl-KCl containing UCl_3 . The demonstration and validation of the GSWE involved 3 sets of tests: (1) immersion, (2) stability, and (3) concentration correlation. The first test was designed to confirm the insulating properties of the glass in contact with molten salt while fused to an electrode by observing the behavior of CV peaks at various immersion depths. The immersion depth was incremented by a vertical position translator (Velmex Inc., Part No. XN10-0012-M02-71). The second test was intended to identify whether significant degradation of the quartz coating on the GSWE occurs over time by monitoring the CV peak heights and shapes over a prolonged period of time. The purpose of the third set of tests was two-fold: (1) to characterize the CV and NPV response over a range of U^{3+} concentrations and (2) to test the stability of the glass coating at higher concentrations.

2. Experimental Details

2.1. Development of the Working Electrode

The WE was developed by using a quartz-based #1 grading glass (GS-10, Transition Glass Products Ltd., 84.8% SiO₂ 10.0% Bi₂O₃ 4.7% Al₂O₃ 0.45% BaO 0.01% Fe₂O₃) to coat a tungsten rod. The tungsten must be high grade, clean and polished without any pitting, corrosion or foreign matter attached. The easiest seals are achieved with a tungsten rod having a diameter between 0.76 mm (.030 in) and 2.03 mm (.080 in). In this case, tungsten rods (99.95%, Alfa-Aesar) 30 cm in length and 1.5 mm in diameter were used. When coating the tungsten, it is very important to use flame of hydrogen and oxygen. The flame is set fairly sharp and the tungsten is washed with the flame. When the tungsten reaches the necessary temperature, the tungsten surface will begin to pool and appear wet. At this point, the #1 cane (grading glass) is drawn across the rod with both the cane and tungsten in the flame to the desired length. It is important to emphasize that the tungsten surface must be pooling to properly fuse the glass and tungsten. In all cases, the glass was fused to the tungsten rod starting approximately 1 cm from one end of the rod and ending 5-7.5 cm closer to the other end. A tungsten rod with a glass coating fused to it is referred to as a glass **sealed** working electrode (GSWE).

The glassblowing process exposed the tungsten rod to very high-temperatures which resulted in severe oxidation, as shown in Figure 1. The yellowish green layer in the top image of Figure 1 is indicative of tungsten (VI) oxide [14]. **The oxide layer is key to enable chemical bonding between the glass and metal creating a hermetic seal [15]. On the exposed tungsten portion of the rod, the oxide layer was removed by polishing it** with 2000-grit SiC paper until the surface was smooth and lustrous. After polishing, the diameter of the **GSWE** was verified to still be 1.5 mm using calipers. The length of the tungsten exposed beyond the glass coating was measured digitally and using calipers. The digital measurement used a photograph of the **GSWE** aligned with a square ruler and Plot Digitizer 2.6.6 [16]. The ruler was used as the axes to correlate pixels to distance. The distance was then calculated by marking the end of the tungsten rod and the tungsten-quartz interface. The exposed tungsten length was

12.8 mm for **GSWE** A and 12.2 mm for **GSWE** B. The respective estimated errors of the measured diameter and length measurements are 0.01 and 0.1 mm resulting in less than 1.5% error in the WE area.

2.2. Electrochemical Cell

GSWE A and B were used in all experiments in the arrangement photographed and illustrated in Figure 2. This setup was contained in an argon atmosphere glovebox (Inert Technology Inc., PL-HE-4GB-2500) with H₂O and O₂ content below 0.5 ppm. The salt mixtures were heated in a Kerr Electro-melt furnace (Model No. 35224) to 500°C ±2°C. The interior of the furnace consisted of a graphite crucible in contact with a heating element. A 6-cm diameter alumina (99.6%) crucible (AdValue Technology, Part No. AL-2250) was inserted into the furnace to act as a liner in case of cracking in the primary crucible containing the molten salt. The primary crucible was a 316 stainless steel (SS) tube (1.5 in/3.8 cm OD, 3 in/7.6 cm long) and disc welded together. A 5-cm diameter hole was drilled into the lid of the furnace. Two SS plates (Sharpe Products, Part No. 9445) were machined to have identical port holes that aligned precisely preventing the tilting and swaying of electrodes. The two plates sandwiched the furnace lid and were attached using all-thread and nuts. Alumina tubes (McMaster-Carr) that fit snug in the holes were cemented in place on the top plate. A pseudo-reference electrode (RE) was used and made of a 1 mm diameter W wire (99.95%, Alfa-Aesar) sheathed in an alumina tube (1.6 mm ID, 3.2 mm OD) until about 1-2 cm above the salt. The WE was rinsed in 3N HCl, polished by 2000-grit silicon carbide paper and anodically cleaned before conducting electrochemical tests. The WE was also sheathed in an alumina tube (3.2 mm ID, 4.7 mm OD) above the salt. The alumina sheaths of the WE and RE were bound together with two other alumina tubes (4.7 mm OD) and Viton O-rings (McMaster-Carr) in a circular arrangement. The alumina tubes electrically isolated the WE and RE and spaced the electrodes apart from each other. Two types of counter electrode (CE) were used. One CE was a stainless steel rod and basket containing U metal sheets (International Bio-Analytical Industries Inc.). The U metal sheets came with a black layer that flaked off easily. The black layer was supposedly an oxide layer and was polished in the glovebox until the surface was silvery-gray. Another CE was the primary SS crucible with a SS rod attached as a

lead. U metal from SS basket was electrotransported to the SS crucible wall. This CE was used to verify that U metal in SS basket was a sufficiently large CE.

2.3. Measurement Methods

Anhydrous UCl_3 was synthesized from depleted U metal by first converting it to a hydride with hydrogen gas, then exposing the hydride to dry HCl gas resulting in a dark red powder [17]. UCl_3 was added to eutectic LiCl-KCl (99.99% anhydrous, SAFC Hitech) salt with U metal present to form mixtures of various compositions. Some additions of UCl_3 were made while the salt was still molten by using a custom made borosilicate funnel which was fed through a port in the lid until it was 1-2 cm above the salt surface. The salt was then gently mixed by hand with a flat-end, SS stir rod for approximately 1 minute after the additions. Cyclic voltammetry was then performed every 5 minutes until a stable, consistent response was observed. The actual concentration of UCl_3 in each eutectic LiCl-KCl mixture was determined by sampling of the salt followed by analysis via ICP-AES and listed in Table 1 for each mixture. Table 1 lists the concentration in two units for reference, but molar concentration is used throughout the paper. Each mixture was analyzed electrochemically using cyclic voltammetry (CV) and normal pulse voltammetry (NPV) using a potentiostat (Autolab PGSTAT302N). CV was performed at scan rates ranging from 50-250 mV s^{-1} . At least 4 cycles were recorded at each scan rate to ensure repeatability. NPV was performed with a pulse time (t_p) of 0.3 s, an interval time (t_i) of 15 s and a step potential of 10 mV. The potential range for the pulse potential (E_p) in NPV was at least ± 0.1 V from the equilibrium potential of U^{3+}/U redox potential. The base potential (E_b) was 0.2-0.3 V more negative than the $\text{U}^{4+}/\text{U}^{3+}$ equilibrium potential. Only relative potential values can be reported due to the use of a pseudo-RE.

3. Results and Discussion

3.1. Selection of Insulator

A ceramic such as alumina or boron nitride is difficult to seal to a metal substrate. A ceramic cement would not create a leak-tight seal. Even if a good seal was formed at room temperature, cracks could form in the cement or other adhesives when heated to temperature. Furthermore, cyclic voltammetry (CV) measurements were unintentionally made with the alumina sheath on the RE in contact with the molten salt in close proximity to the WE (3-5 mm). Upon recognition of this error the alumina was removed resulting in different peak heights and peak shapes, as shown in Figure 3, indicating some possible interaction between alumina and the salt. No glass was in contact with the molten salt during these measurements. In Figure 3, the U^{3+} reduction (negative current) peak has an additional wave before the peak when the alumina tube was in contact with the molten salt and the peak height is 3.2% lower.

Glass can be fused to tungsten to create a complete seal that can withstand the thermal cycling of the electrode from room temperature to the molten salt temperature. Borosilicate glass was considered because its coefficient of linear thermal expansion ($3.3 \times 10^{-6} \text{ K}^{-1}$) [18] is similar to that of tungsten ($4.5 \times 10^{-6} \text{ K}^{-1}$) [19], but its low maximum service temperature (763-773 K) would limit its application. Quartz was targeted, but its thermal expansion coefficient ($0.53 \times 10^{-6} \text{ K}^{-1}$) [20] differed too greatly from tungsten's coefficient which could possibly lead to cracking due to thermal stresses while heating. Therefore, the #1 grading glass, previously described, was used in this work to ensure a good seal and compatible thermal expansion coefficients ($1.05 \times 10^{-6} \text{ K}^{-1}$). Furthermore, its strain point (898 K) is 115 K higher than that of borosilicate glass (783 K) which represents the absolute maximum limit of serviceability for brief durations. This glass appeared to be durable with no visible signs of cracking or deformation after being heated gradually ($25\text{-}35 \text{ K h}^{-1}$) from room temperature to 773 K four times.

3.2. Electrochemical Behavior of UCl_3

The cyclic voltammogram displayed in Figure 4 was recorded after the glass coating had been in contact with the molten salt for more than 13 h and is characteristic of CV measurements made with the **GSWE**. Its features are consistent with CVs reported in the literature [4,9,13,21–25] which were measured without a glass coating. These previous studies have identified the prominent pair of peaks at

approximately 0 V in Figure 4 as the reduction of U^{3+} and oxidation of U metal. The sharp anodic peak and steep rise of the cathodic peak is characteristic of metal stripping and multiple electron transfer in a single step. The pair of peaks at 1.2 V is identified in the literature as the oxidation of U^{3+} and the reduction of U^{4+} . These broader peaks are characteristic of a single electron transfer reaction with a soluble reactant and product (soluble-soluble). A pair of peaks with a large spacing between them is also present in the cyclic voltammogram in Figure 4, but due to their small size, the peaks are difficult to see. It has been speculated that these peak are either the adsorption of uranium ions or the formation of a metal monolayer [21,22].

3.3. Immersion Tests

The initial test performed after heating the electrochemical cell to 773 K at 25-35 K h⁻¹ was the incremental immersion test. In this test, the position of the GSWE was adjusted using the vertical position translator. After adjustment, the surface tension on the WE was allowed to settle for two or more minutes, and then a CV measurement was made. The U^{3+} reduction peak heights at each position of GSWE A for mixture nos. 1, 5, and 9 are plotted in Figure 5. As can be seen, there is a clear region where the peak height is linearly dependent on immersion depth followed by a region where peak height is independent of immersion depth. The latter region indicates that the glass coating is indeed insulating the tungsten rod. The position of the glass-tungsten interface was determined by fitting the linearly dependent peak heights (dotted lines) in Figure 5 and calculating the point at which the linear fit intercepted the average of the independent peak heights (dashed lines). This intersection was consistent at each concentration of UCl_3 and differed by a maximum of 2.1 mm from the expected depth. It should be noted that calculation of the expected depth has been observed to be ± 2 mm due to surface tension effects [26]. No noticeable difference was observed in the features of the CV measurements with and without the glass in contact with the exception of the U^{3+} oxidation peaks above 0.150 mol dm⁻³ UCl_3 which will be discussed later.

3.4. Stability Tests

An initial stability test was performed on mixture no. 1 using GSWE B. Figure 6 displays the temporal behavior of the U^{3+} reduction peak current for an 11-hour test with boxed letters indicating key events during the test. The time of the events are indicated by vertical, black, dashed lines. The duration of some events are indicated by brackets at the top of the graph. Initially (event A), the GSWE is anodically cleaned by scanning the potential in the positive direction until tungsten dissolution. Immediately afterward (beginning of event B), the immersion depth of the GSWE is incrementally moved upward out of the salt. As can be seen, the current rises slightly, then starts to drop significantly when the glass coating is removed from the salt. Then the GSWE was incrementally moved downward, resulting in the subsequent rise in the peak current. Once a clear plateau was established, the immersion depth of the GSWE was no longer adjusted (end of event B).

After fixing the vertical position of the GSWE (beginning of event E), a slight rise above the stable peak height value is observed in Figure 6 followed by a slight decay. This decay was erroneously supposed to be due to the accumulation of a passivating layer on the GSWE surface, essentially blocking a small fraction of the GSWE. Thus the GSWE was anodically cleaned again by scanning up to the tungsten dissolution potential (event C). After cleaning, the peak current values in Figure 6 returned to the values recorded after event A. Because the magnitude of current decreased after cleaning, it appears that a passivating layer was not formed. However, the monitoring of the peak heights at a fixed position revealed that some time is required for the conditions in the salt near the WE to equilibrate after scanning the potential to the dissolution of tungsten at the WE. This may be due to the oxidation of some U^{3+} to U^{4+} near the WE while the tungsten rod is being anodically cleaned. Applying a potential more negative than the U^{3+}/U^{4+} equilibrium potential or stirring the salt may expedite the return to pre-cleaning conditions at the tungsten-salt interface.

After 1.5 h, the peak current in Figure 6 settled to a stable ($\pm 1.9\%$) value indicated by the solid, gray line which represents the peak current averaged over the period of high stability (event D). It also appears that the peak current was settling to the same stable value before the second anodic cleaning of

the GSWE. This stable value was maintained for 4 h. Unfortunately, at the 10 h and 20 min mark, the computer controlling the potentiostat went to sleep (event F) and cyclic voltammograms were no longer recorded. The experimental system was unmonitored at this point. After 3 h, the computer was turned back on and CV measurements were recorded again. The peak current was 2.5% more negative than the stable value, but was less negative than the most negative (minimum) peak value recorded at the 3 h and 50 min mark. This slight increase may have been caused by the absence of CV measurements conditioning the GSWE over the past 3 hours.

To test the repeatability of the GSWE-salt interface, GSWE B was removed from the salt then reinserted to the same position at the 13 h and 30 min mark (event G). After waiting 5 min, 4 cycles of CVs were run. The peak current recorded was in excellent agreement (0.3% error) with the previous peak height recorded. This indicates that the removal and replacement of the GSWE from the molten salt will not compromise the precision of the measurements. Thus the GSWE could be suspended above the salt in the hot zone when not recording measurements, potentially prolong its life by limiting its exposure in the molten salt bath.

Additional stability tests were performed occasionally with GSWE A after additions of UCl_3 to ensure that the glass coating was not being degraded. The results of these stability tests are displayed in Figure 7. The numbers in parenthesis correlate to the mixture number in Table 2. For comparative purposes, the x-axis in this plot displays the duration of the stability test, rather than the exposure time to the molten salt. Since UCl_3 was added while the salt was molten, there were two purposes to the stability tests: (1) to ensure the integrity of the glass coating and (2) to determine when the mixture has equilibrated after the addition of UCl_3 and stirring. These tests were performed within 15-30 min of the addition of UCl_3 . The gentle rise at begin of the stability tests in mixture no. 3, 4, and 10 is assumed to be the equilibration of thermal and concentration gradients in the salt mixture after adding cold UCl_3 powder. Mixture no. 8 may have reached equilibrium more quickly due to better initial mixing since stirring after each addition was done by hand and may have been inconsistent. The system was considered to be

stabilized when the peak current stopped climbing. At this point, the peak current was averaged over at least an hour and compared to all U^{3+} reduction peaks recorded. After stabilizing, the peak current measured agreed within $\pm 1.58\%$, 1.67% , 1.53% and 1.03% of the average for mixture nos. 3, 4, 8, and 10 respectively.

3.5. Concentration Tests

3.5.1. Cyclic Voltammetry

In Figure 8, the U^{3+} reduction peaks recorded in CV at each concentration are plotted from 50 to 200 $mV\ s^{-1}$ which has been identified in the literature to be the limit of electrochemical reversibility for U^{3+} reduction [22–25]. When an electrodeposition reaction is reversible, the Berzins-Delahay reaction is applicable to CV reduction peak [27]:

$$I_p = 0.6105 \sqrt{D \frac{n^3 F^3}{RT} \nu AC} \quad (1)$$

where n is the number of electrons transferred, F is Faraday's constant, R is the universal gas constant, T is temperature, D is the diffusion coefficient, ν is the scan rate and C is concentration. Thus at each concentration, the peak current of U^{3+} reduction was regressed with respect to square root of scan rate as shown in Figure 8. The slopes, called normalized peak currents, from Figure 8 are plotted versus UCl_3 concentration in Figure 9. The black line in the plot represents the linear trend regressed from 0 to $0.123\ mol\ dm^{-3}\ UCl_3$. The normalized peak current begins to depart significantly ($>5\%$) from that trend after the $0.170\ mol\ dm^{-3}\ UCl_3$ data point. Possible explanations for this departure at higher concentrations could be diffusion layer growth, transition from planar to radial diffusion, counter electrode limitations, migration, transition from reversible to quasi-reversible behavior, or concentration dependence of the diffusion coefficient.

It was observed that as UCl_3 concentration increased, the width of the U^{3+} reduction peak increased. This could be at least partially due to increasing ohmic (IR) drop (i.e. uncompensated

resistance). Regardless of the cause of this broadening, more time is required to reach the peak. During this time, U^{3+} is actively reducing at the electrode. This increased duration of reduction may cause a gradual increase in the diffusion layer thickness due to depletion of ions. However, this phenomenon is accounted for in the CV theory and diffusion layer thickness is not expected to increase with concentration.

Next, a possible transition from semi-infinite planar to radial diffusion was considered. Based upon the diameter (d) of the WE (0.15 cm) and the diffusion coefficient of U^{3+} , the relative effect of radial diffusion is less than 5% when $4D\tau/d^2 \leq 3 \times 10^{-3}$ [27] where $\tau = RT/(nFv)$ for potential sweep methods [28,29]. The diffusion coefficient of U^{3+} calculated from the linear regression in Figure 9 is $1.09 \pm 0.0056 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Thus, the scan rate, v , needs be greater than 14 mV s^{-1} in order for peak current recorded with a cylindrical electrode to agree within 5% or less of a planar electrode. Furthermore, upon examination of the expressions for radial and planar diffusion [30], it is clear that radial diffusion would cause an increase in the absolute value of the current.

The CE limitation was also eliminated from consideration by using the SS crucible as the CE as described earlier in the experimental details. This effectively quadrupled the CE area and the magnitude of the current only increased by 0.3% which is within experimental error. Migration was also considered, but when a positively charged ion is being reduced, migration increases the magnitude of the current as well [29,31]. However, there is evidence from spectroscopic studies that UCl_3 forms a $[UCl_x]^{(x-3)-}$ complex in molten LiCl-KCl eutectic where x has ranged from 5 to 7 [32–36]. The extent or strength of this complexation is questioned by some authors because electromotive force measurements of the U^{3+}/U redox couple are in good agreement with thermodynamic calculations [37–39]. If this complex is maintained in the presences of an applied electric field and migrates in this form then the migration of the negatively charged complex could reduce the magnitude of the current as observed in Figure 9. Further investigation of the migration behavior of U^{3+} in eutectic LiCl-KCl is needed and theoretical CV models accounting for migration may need to be developed.

Tylka et al. [7] suggested that the bend in the uranium peak current at higher concentrations is due to a change in the diffusion coefficient. This is a plausible theory, but it should be validated via measurement of diffusion coefficients using a non-electrochemical approach. That is a non-trivial endeavor, however, and the resources for such a measurement were not available to us.

Based on our observation, the most likely explanation for the curvature in Figure 9 is the onset and increase in charge transfer limitations. The rate of diffusion is dependent on the gradient between bulk and surface concentrations. As the bulk concentration increases, the limiting diffusional flux of U^{3+} is also increased. However, charge transfer is dependent on surface concentration. The reduction of ions at the WE surface decreases the surface concentration to zero, if diffusion limited, or some smaller value. Consequently, charge transfer rate may stay the same or increases to lesser degree because the surface concentration is increased at a slower rate than the concentration gradient near the WE. Eventually, the rate of charge transfer (i.e. reaction kinetics) could begin to have some control on the current density, rather than diffusion exclusively, as assumed in (1).

Matsuda and Ayabe [40] formalized the theory and characterized the shape of CV peaks under the mixed control of diffusion and charge transfer calling this condition quasi-reversibility. In their theory, the current is governed by a function, ψ , the shape of which is dependent on the transfer coefficient (α) and the parameter, Λ . The derived current is given by:

$$I = nFA \sqrt{D \frac{nF}{RT}} \nu C \psi(E) \quad (2)$$

where E is electrode potential and becomes the following equation at the peak:

$$I_p = 0.447A \sqrt{D \frac{n^3 F^3}{RT}} \nu CK(\Lambda, \alpha) \quad (3)$$

K is a tabulated function. The shape of the ψ -function is independent of scan rate at Λ -values greater than 15 below which the peak broadens and decreases in height until $10^{-2(1+\alpha)}$. This peak broadening and

shortening is indicative of quasi-reversible behavior (i.e. mixed diffusion and charge transfer control).

The Λ -value is dependent on scan rate, as shown below and can be varied by adjusting the scan rate.

$$\Lambda = \frac{k^o \gamma_{ox}^{1-\alpha} \gamma_{red}^{\alpha}}{\sqrt{D_{ox}^{1-\alpha} D_{red}^{\alpha} \left(\frac{nF}{RT} v\right)}} \approx \frac{k^o}{\sqrt{D_{ox}^{1-\alpha} D_{red}^{\alpha} \left(\frac{nF}{RT} v\right)}} \quad (4)$$

Thus as the scan rate increases, the Λ -value decreases.

The ψ -function is calculated from the measured U^{3+} reduction current by dividing by the leading terms ($n = 3$, $D = 1.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $T = 773 \text{ K}$, $A = 0.621 \text{ cm}^2$) in (2). This function is plotted in Figure 10 for the lowest (mix no. 1) and the highest (mix no. 10) concentrations of UCl_3 at four different scan rates. Peak broadening may be caused by uncompensated resistance, R_u . Therefore, the potentials reported in Figure 10 have been adjusted for IR drop. As can be seen in Figure 10, the U^{3+} reduction peak shape and height is independent of scan rate in mixture no.1, but the peak becomes more broad and lower as the scan rate increases (Λ -value decreases) in mixture no. 10, indicative of quasi-reversible CV behavior. In fact, the height and the width of the ψ -function in mixture no. 10 at 50 mV s^{-1} is lower and more broad than the ψ -functions in mix no. 1. It is also interesting to note that the minima of the ψ -function reaches -0.609 on average (std. dev. of 0.0054) in mixture no. 1 which corresponds closely with the leading constant of 0.6105 in (1) indicating that (3) simplifies to (1) at the minima when under diffusion control.

The decrease in magnitude of the minima of the ψ -function with increasing scan rate occurred in other high concentration mixtures, but is not directly evident in Figure 8. However, a tilt in the peak height can be observed as the concentration increases. This tilt is observed by noting in Figure 8 that as concentration increases, the peak heights drift further above and below the linear regression at lower and higher scan rates, respectively. A clearer demonstration of the shift in the transitional scan rate is displayed in Figure 11 which includes the peak heights over the full range of scan rates tested (50-250 mV s^{-1}). The solid lines in Figure 11 are the slopes calculated from 0 to 50 mV s^{-1} for each concentration extrapolated to 250 mV s^{-1} . Theoretically, if U^{3+} reduction is reversible up to 200 mV s^{-1} , the slope from

0-50 mV s⁻¹ should be identical to slope from 50-200 mV s⁻¹ and the measured data points in Figure 11 should lie close to the solid lines. However, as concentration increases, the peak heights begin to drift away from solid lines at lower scan rates. This increasing separation between the data points and the solid lines is additional evidence that charge transfer is beginning to influence the shape of the reduction peak because CV peak heights in the quasi-reversible region do not maintain linearity with the square root of scan rate.

From a theoretical standpoint, the limitation of the charge transfer step at higher concentration is unexpected. The parameter, Λ , in (3) was derived to determine if the electrochemical reaction is limited by diffusion (reversible), charge transfer (irreversible) or both (quasi-reversible). If $\Lambda \geq 15$, then the redox reaction is electrochemically reversible. However, Λ is commonly approximated with the expression on the right-hand side of (3) leading to the mistaken conclusion that if k^o and D are constant, then the scan rate at which a CV peak transitions from reversibility to quasi-reversibility is constant with concentration at the same temperature. However, the assumption that activity is equal to concentration is built into the right-hand side of (3). The complete expression in (3) with the γ terms relaxes that assumption for the charge transfer rate, but not for diffusion. Fick's second law is still simplified with the implicit assumption of the equality of activity and concentration. Hence, it becomes conceivable that k^o and D on the right-hand side of (3) could vary with concentration because activity coefficients are essentially embedded into the rate parameters.

Over a broad range of concentrations, the activity coefficient of U³⁺ could vary considerably, resulting in a change in k^o and/or D . A couple of studies [41–43] have investigated the thermodynamic properties of UCl₃ in alkali chloride melts over a range of high (i.e. >0.095 mol dm⁻³ UCl₃) concentrations and they indicate a decreasing activity coefficient with increasing UCl₃. Other studies [4,23,44–46] have evaluated the activity coefficient of UCl₃, but only report a single value, made measurements at a single concentration, and/or studied concentrations less than 0.095 mol dm⁻³ UCl₃. These findings in the literature indicate that the activity coefficients of U³⁺ do vary over the concentration range tested. This

combined with Figures 10 and 11 support the theory that rate of charge transfer becomes more of a limiting factor at higher concentrations. This could be due to the concentration gradient near the WE increasing more rapidly than the WE surface concentration as more UCl_3 is added or due to changes in k^o and/or D with increasing UCl_3 content. Either or both of these explanations could be possible causes.

3.5.2 Normal Pulse Voltammetry

The behavior of the normalized peak current for CV in Figure 9 is particularly perplexing in light of the normal pulse voltammetry (NPV) results. The NPV measurements made at each concentration are plotted in Figure 12. The potential values in this plot are adjusted to align the NPV measurement for convenient comparison. At higher concentrations, the NPV plateau begins to decay at more negative potentials. It becomes visibly discernable above $0.216 \text{ mol dm}^{-3} \text{ UCl}_3$. This decay is believed to be due to cumulative depletion of ions in the diffusion layer, which is caused by the use of a nonpolarographic (i.e. nonrenewing) electrode and the lack of stirring [29,47]. Alternatively, the decay could be due to precipitation of U^{3+} ions near the WE if U^{3+} ions in excess of the solubility limit oxidize into the salt adjacent to the WE. In either case, ions are being depleted near the WE. Because ion depletion decreases the measured pulse current at more extreme potentials, the current value before the decay is used as the plateau or diffusional current. The diffusional current is plotted versus concentration in Figure 13. The diffusional current was linearly regressed versus concentration. The resulting linear trend is plotted as the black, dashed line in Figure 13. The diffusional current departs from linearity as well, but in the opposite direction (more negative) and less drastically.

At first glance, this deviation could be ascribed to WE area growth. However, the maximum charge passed during a pulse is 0.13 C at $0.362 \text{ mol dm}^{-3} \text{ UCl}_3$, some of which is due to non-faradaic processes (i.e. double layer charging). At the same concentration, the charge passed before reaching the U^{3+} reduction peak in CV ranges from 0.12 C at 200 mV s^{-1} and 0.19 C at 50 mV s^{-1} and yet the peak heights in CV curve downward, rather than upward. Thus, if significant area growth occurs in NPV measurements, it would also occur in CV measurements. Another possibility is radial diffusion, but the

criteria ($Dt/r^2 \leq 3 \times 10^{-3}$) for planar diffusion is met [27]. Alternatively, the upward bend could be migration current that occurs due to potential gradients and contributes more significantly to the current adjacent to the WE at higher analyte concentration. Migration is neglected in most electroanalytical relations because they were derived for dilute analyte concentrations at which migration is negligible. Near the electrode and at non-dilute analyte concentration, the current recorded is given by the summation of the diffusional current (I_d) and migration current (I_m) [29,48]:

$$I = I_d + I_m \quad (5)$$

The diffusional current in NPV is given by [29,49,50]:

$$I_d = \frac{nFA\sqrt{D}C}{\sqrt{\pi t_p}} = aC \quad (6)$$

If mass-transport and the electric field are linear then, the migration current is given by [29]:

$$I_m = \frac{n^2 F^2 ADC}{RT} \frac{\Delta E}{l} = \frac{n^2 F^2 ADC}{RT} \frac{IR_s}{l} = bIC \quad (7)$$

where R_s is the solution resistance and l is the distance between the WE and CE. This results in the following expression for the total current:

$$I = \frac{nFA\sqrt{D}C}{\sqrt{\pi t_p}} / \left(1 - \frac{n^2 F^2 ADC}{RT} \frac{R_s}{l} \right) = \frac{aC}{1-bC} \quad (8)$$

where a and b are constants if the diffusion coefficient does not vary with concentration. Thus when reducing, migration current adds to the magnitude of diffusional current [31,48]. As shown in Figure 13, the measured diffusional current fits (8) very well. Additionally, the diffusion coefficient calculated from a ($D = 1.79 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) is more consistent with the diffusion coefficient calculated from CV at concentrations $\leq 0.123 \text{ mol dm}^{-3} \text{ UCl}_3$ ($D = 1.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) than the diffusion coefficient calculated from a strictly linear fit ($D = 2.36 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) of the data in Figure 13. Additionally, the resistance of the solution calculated from the b coefficient is 6.54Ω assuming a distance of 2 cm between the WE and CE. The estimate of 2 cm is based on the distance from the center of the WE port to the center of the CE port.

The value of 6.54 Ω is on the same magnitude as the resistance calculated (1.72 Ω) based on the estimated distance from CE to WE, the WE area (0.621 cm²) and the specific conductance (1.872 Ω^{-1} cm⁻¹) of molten LiCl-KCl eutectic [51]. The difference may be due to a combination of factors such as the complex geometry of the CE (i.e. uncertain cross-sectional area), the effect of U³⁺ ions on solution resistance and uncertainty in the distance between electrodes. In any case, the parameters calculated from the a and b coefficient are promising evidence for migration.

Another way to evaluate the effect of migration is the transference number ($t_{U^{3+}}$), which is the fraction of the total current carried by the migration of a given ion.

$$t_{U^{3+}} = \frac{i_{m,U^{3+}}}{i} = \frac{|z_{U^{3+}}|u_{U^{3+}}C_{U^{3+}}}{\sum_k |z_k|u_k C_k} \quad (9)$$

The mobility (u) of an ion is given by:

$$u = \frac{|z|FD}{RT} \quad (10)$$

where z is the charge of the ion. The diffusion coefficients of Li⁺, K⁺, Cl⁻ were determined in a molecular dynamics study [52] at the eutectic composition from 638-1007 K and interpolated to be 1.9, 2.4, 2.5 $\times 10^{-5}$ cm² s⁻¹, respectively, at 773 K [53]. The diffusion coefficient for U³⁺ calculated from NPV data is 1.79 $\times 10^{-5}$ cm² s⁻¹. Using these diffusion coefficients, the transference number for U³⁺ is calculated to be 4.2% at 0.362 mol dm⁻³) which suggests a non-negligible portion of the current is carried by U³⁺ ions migrating.

However, as mentioned, there is a possibility that U³⁺ could migrate as the [UCl₆]³⁻ complex in which case migration would actually reduce the current at the WE during the reducing potential pulses. In this case, accumulation of U³⁺ ion near the WE due repeated deposition and stripping of U metal on the WE could be the likely explanation. However, when optimizing the NPV waveform parameters at 0.198 mol dm⁻³ UCl₃, NPV measurements were recorded with a pulse time of 0.3 s and interval times of 10, 15, 20, and 30 s [54]. The difference in the diffusional current at 10 and 30 s was 0.9%. If significant amounts

of ions were accumulating near the WE, it would be expected that the diffusional current would decrease significantly as the interval time is increased because this would allow more time for ions to diffuse away from the WE. However, in order to more conclusively determine that a negligible amount of ions are accumulating next to the WE, NPV measurements are needed at higher concentrations, longer interval times (≥ 60 s), and/or with the rotation of the WE during the stripping of metal deposits.

The contrast in the NPV and CV data further supports the notion that the downward bend in the CV data (see Figure 9) is due to the transition from diffusion to mixed (diffusion and kinetic) control. For example, if the diffusion coefficient decreased, a downward bend would also be reflected in the NPV measurements, because peak height in CV and diffusional current in NPV both depend on the square root of the diffusion coefficient. Indeed, it may be possible that the diffusion coefficient is actually increasing which, as shown in (4), would promote quasi-reversible behavior in CV and an upward bend in Figure 13. Hence, variations in diffusion and activity coefficients cannot be eliminated as possible causes for the non-linear behavior of NPV and CV signals. Regardless, the transition to quasi-reversible behavior at higher concentration provides an explanation that is unique to the CV technique. This can reconcile the discrepancy in the CV and NPV results because the assumption of diffusion control was verified in NPV by the formation of the current plateau and the analysis of CV peaks at higher concentration (see Figures 10 and 11) revealed mixed diffusion and kinetic control. Therefore, the non-linearities in CV and NPV data in Figures 9 and 13 are likely caused by charge transfer limitations and migration, respectively. Migration probably affected CV measurements, but could not be observed due to the additional effect of charge transfer limitations.

Regardless of the explanation of the data, it is clear that non-ideal behavior is occurring at higher concentration and more work is needed to provide a definitive explanation of U^{3+} electrochemical behavior as concentration increases. This could provide substantial improvements in the accuracy of concentration measurements by electrochemical techniques. For example, if the upward curve in Figure 13 is ignored and a simple linear regression is performed to fit the model in (6), then the 99.5%

confidence interval (CI) on the predicted concentration is $0.036 \text{ mol dm}^{-3}$. On the other hand, if migration is actually occurring and the model in (8) is valid, then the 99.5% CI is $0.0079 \text{ mol dm}^{-3}$ —a dramatic error reduction.

3.6. Limitations

Two limitations to the application of the **GSWE** were elucidated in this study. First, at concentrations greater than $0.150 \text{ mol dm}^{-3} \text{ UCl}_3$, a slight bump on the positive side of U^{3+} oxidation peak began to appear. This became more pronounced as the concentration of UCl_3 increased. It was quite evident at $0.216 \text{ mol dm}^{-3} \text{ UCl}_3$ as shown in Figure 14. The U^{3+} reduction peak appears unaffected. This shape of the CV in the inset of Figure 14 is typical of an electrochemically reversible reaction followed by an irreversible chemical reaction. When an irreversible chemical reaction follows an electrochemical reaction, the peak in the CV after reversal decreases in magnitude more rapidly with scan rate than the peak preceding the chemical reaction. In this case, the U^{4+} reduction (negative) peak will reduce in magnitude more rapidly than the U^{3+} oxidation (positive) peak. Thus, the ratio of the cathodic (U^{4+} reduction) and anodic (U^{3+} oxidation) peak magnitudes would decrease with scan rate. However, no trend was observed. Additionally, the peak ratio (U^{4+} reduction: U^{3+} oxidation) from mixture no. 8 (1.14) is larger than the ratio from mixture no. 2 (1.04), in which no bump was observed, indicating that the reduction peak associated with the bump in Figure 14 may be masked by the U^{4+} reduction peak. The oxidation and reduction of UO_2 occurs at a potential similar to the $\text{U}^{4+}/\text{U}^{3+}$ redox couple [55]. Furthermore, it has been observed that borosilicate glass reacts with UCl_4 [13], which is less stable in LiCl-KCl eutectic than UCl_3 . The following overall reaction is postulated as the possible explanation for the additional peak in Figure 14.

The standard Gibbs free energy of this reaction is 54.0 kJ mol^{-1} resulting in an equilibrium constant of 2.24×10^{-4} [56]. Despite the small equilibrium constant, the reaction is still plausible, especially

considering that high concentrations of UCl_4 would be present at the **GSWE** surface when UCl_3 is oxidized and the highly volatile nature of SiCl_4 (b.p. = 58°C). This volatility would further drive the reaction forward via La Chatelier's Principle by its immediate vaporization and removal from the **GSWE** surface. Shortly after forming UO_2 , the potential of the electrode is scanned to sufficiently positive potentials to oxidize UO_2 creating the bump in Figure 14. Thus the formation of UCl_4 should be avoided, especially at higher concentrations of UCl_3 .

Next, the potential of the **GSWE** should not become more negative than -0.8 V vs. U^{3+} (0.286 mol dm^{-3})/U. While performing CVs on mixture no. 9, the **GSWE** was briefly exposed to extremely negative potentials due to a momentary loss in stability of the pseudo-RE. A pair of peaks appeared at a potential similar to that reported ($0.85\text{ V vs Ca}^{2+}/\text{Ca}$) for the reduction of SiO_2 to Si in LiCl-KCl-CaCl_2 at 773 K [57], as shown in Figure 15. After removing, cleaning, and polishing the **GSWE** A, a small patch of lustrous, metallic material was observed, as photographed in Figure 16. The possibility of uranium was eliminated by scanning **GSWE** A with a Geiger-Mueller counter (Ludlum 26-1), which did not register any counts above background after rinsing **GSWE** A with water. Fortunately, pure silicon is also an insulator. It has a resistivity of $3.78 \times 10^5\ \Omega\text{ cm}$ [58] which is more comparable to silica ($1.27 \times 10^8\ \Omega\text{ cm}$) [18] than tungsten ($1.78 \times 10^{-5}\ \Omega\text{ cm}$) [59] at 500°C . A multimeter (Fluke 115) measured the resistance of the glass coating, the lustrous grey layer and tungsten. The glass and grey layer registered offline on the multimeter—indicating that the glass coating maintained insulating properties despite the possible formation of silicon. When applied to tungsten the multimeter registered a resistance less than $1\ \Omega$. **GSWE** A was only exposed to these extreme conditions briefly, and the immersion tests, stability tests and post-tests inspections (see Figures 5, 7 and 16) indicate that the integrity of the glass coating was not compromised.

3.7. Data Comparison

Further evidence for the integrity of the glass coating over the duration of these tests is gained by comparing the results of this study to previous studies in which a bare tungsten rod was used as the WE.

Two other studies have measured the U^{3+} reduction peak height in CV over a range of concentrations [4,7]. The normalized peak height from each of the other two studies is overlaid with the values from this study in Figure 17. At low concentrations, all three studies are in good agreement, but at higher concentrations the data reported by Hoover et. al [4] departs significantly from Tylka et. al [7] and this study.

4. Future Work

In this study the scan rates were limited ($50\text{-}250\text{ mV s}^{-1}$) and potential measurements were not reliable due to the use of a pseudo-RE. The tungsten wire was used as pseudo-RE because this study aimed to demonstrate a simple, durable 3-electrode probe. The more stable Ag/AgCl RE was not selected due to its thin, fragile glass or ceramic membrane. However, measurements over a broader range of scan rates with a more stable RE could provide a more definitive conclusion on the concentration dependence of the reversible (diffusion-limited) behavior. CV peak height measurement over a broader range and higher resolution of scan rates would identify more precisely at which scan rate linearity with the square root of scan rate is lost. A highly stable reference electrode and reliable solution resistance measurements would facilitate the diagnostics of peak potentials which could provide additional data to corroborate the concentration dependence of the transition from reversibility (diffusion control) to quasi-reversibility (mixed diffusion and charge transfer control). These measurements would allow for a more complete diagnosis of the scan rate required to maintain reversibility as concentration increases. If possible, CV measurements should be made at scan rates low enough to avoid quasi-reversible behavior in order to improve peak height correlations to concentration. However, this may not be possible at higher concentrations due to high deposition currents causing WE area growth before the peak is reached. In this case, models need to be developed to account for the non-linearity in CV peak height with concentration. This will likely require the development of a quasi-reversible model for electrodeposition. The quasi-reversible model developed by Matsuda and Ayabe assumes a soluble product [40]. A model has been developed for migration effects in NPV. However, further improvements and study of migration is needed

for analytes, such as U^{3+} , in molten LiCl-KCl eutectic, as this has received little attention and it may be possible that U^{3+} migrates as an anionic complex.

5. Summary

A glass sealed working electrode (GSWE) was developed by fusing a glass coating to a tungsten rod. The insulating properties of the glass coating were verified by incrementing the WE depth until the CV peak height became independent of an increase in immersion depth. The glass coating demonstrated no significant signs of deterioration after 25 hours of exposure to molten LiCl-KCl- UCl_3 . However, if chronically exposed to UCl_4 or highly negative potentials, the glass coating could react with the salt or be reduced introducing oxide ions into the salt and creating pores in the glass coating. The trend of U^{3+} reduction peak height with concentration differed between CV and NPV. In CV, the magnitude of the normalized peak height increased less acutely as concentration increased. In NPV, the opposite occurred for the diffusional current. It is concluded that the U^{3+} reduction peak begins to be under mixed diffusion and charge transfer control (quasi-reversible) between 50-200 $mV\ s^{-1}$ as concentration increases. This mixed control, in turn, attenuates the increase in the normalized peak height with concentration. The diffusional current measured in NPV behaves differently, because it is not dependent on the reversibility of the system. The magnitude of the diffusional current in NPV accelerates its growth as concentration increases, which is suggested to be due to migration effects. If migration is accounted for in NPV, the 99.5% confidence interval on predicted concentrations is 0.0079 $mol\ dm^{-3}$, as opposed to 0.036 $mol\ dm^{-3}$ and 0.065 $mol\ dm^{-3}$ from a linear fit of the diffusional current and peak current, respectively, over all concentrations. The measurements made with a GSWE compare favorably to similar measurements made with bare tungsten as the WE indicating that the glass coating does not significantly affect electrochemical measurements made in molten LiCl-KCl- UCl_3 . The accurately controlled area of the GSWE reduced uncertainty in electroanalytical measurements of U^{3+} concentrations and allowed for more subtle electrochemical behaviors, such as migration, to be identified and characterized.

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Figure 1: Picture of **GSWE** A before (top) and after (bottom) polishing

Figure 2: Picture (left) and illustration (right) of experimental setup

Figure 3: Cyclic voltammograms at 100 mV s⁻¹ in LiCl-KCl(Eutectic)-UCl₃(0.0236 mol dm⁻³) at 773 K with alumina in contact with molten salt (solid, black curve) and after removal (dashed, gray curve) (WE = 1.5 mm W rod, RE = 1 mm W wire, CE = U metal in SS basket, WE Area = 0.46 cm²)

Table 1: Composition of UCl₃ in LiCl-KCl eutectic

Mix No.	1	2	3	4	5	6	7	8	9	10
UCl ₃ (wt%)	0.50% *	0.99%	1.51%	2.21%	2.57%	3.12%	3.53%	4.45%	5.83%	7.31%
UCl ₃ (mol dm ⁻³)	0.0236*	0.0471	0.0719	0.106	0.123	0.150	0.170	0.216	0.286	0.362

*Based on weighed salt amounts

Figure 4: Cyclic Voltammogram at 100 mV s⁻¹ in LiCl-KCl(Eutectic)-UCl₃(0.0236 mol dm⁻³) at 773 K with glass coating on **GSWE** B (Area = 0.593 cm²) in contact with salt for 13.7 h (RE = 1 mm W wire, CE = U metal in SS basket)

Figure 5: Peak height at various immersion levels of the **GSWE** A in the molten salt (dotted lines—linear fits before glass-tungsten(W) interface, dashed lines—average values after glass-W interface)

Figure 6: The peak current for U³⁺ reduction on **GSWE** B over a long-term test with key events marked by boxed letters: (A) 1st CV after initial anodic cleaning, (B) changes in immersion depth, (C) 1st CV after second anodic cleaning, (D) period of high-stability, (E) constant immersion depth, (F) computer goes to sleep, (G) removal and reinsertion of **GSWE** B

Figure 7: Stability tests with **GSWE** A after UCl_3 additions at 100 mV s^{-1} , dashed lines represent the average of the stable peak values and numbers in parenthesis in legend represent mix no.

Figure 8: Peak current versus square root of scan rate (v) at each concentration of UCl_3 with linear regressions (WE = **GSWE** A, $T = 773 \text{ K}$, Area = 0.621 cm^2)

Figure 9: Peak current normalized by the square root of scan rate at each concentration (slopes from Figure 11)

Figure 10: The ψ -function calculated from measured U^{3+} reduction peaks ($\psi = I/(AC\sqrt{Dn^3F^3v/RT})$) at multiple scan rates for mix no. 1 ($0.0236 \text{ mol dm}^{-3}$) and 10 ($0.362 \text{ mol dm}^{-3}$) on the right and left, respectively, with potentials adjusted for IR drop ($R_u = 0.15 \Omega$, WE = **GSWE** A, $T = 773 \text{ K}$, Area = 0.621 cm^2)

Figure 11: Recorded peak heights (data points) with the slope from 0-50 mVs (solid lines) extrapolated to 250 mV s^{-1} for each concentration tested (WE = **GSWE** A, $T = 773 \text{ K}$, Area = 0.621 cm^2)

Figure 12: Normal pulse voltammograms at each concentration of UCl_3 ($t_p = 0.3 \text{ s}$, $t_i = 15 \text{ s}$, 10 mV step , WE = **GSWE** A, Area = 0.621 cm^2 , $T = 773 \text{ K}$)

Figure 13: Diffusional current from NPV at each concentration and fit of data with and without the migration term

Figure 14: Cyclic voltammograms at 100 mV s^{-1} with inset of $\text{U}^{4+}/\text{U}^{3+}$ redox peaks (WE = **GSWE** A, $T = 773 \text{ K}$, Area = 0.621 cm^2)

Figure 15: Cyclic voltammogram at 100 mV s^{-1} , 773 K (WE = **GSWE** A, Area = 0.621 cm^2) in mixture no. 9 at potentials much more negative than U^{3+} reduction peak

Figure 16: Images of **GSWE** A before electrochemical testing (far left), after electrochemical testing (left center), after rinsing with ultrapure water (right center), and after polishing (far right)

Figure 17: U^{3+} reduction peak height normalized by area and square root of scan rate from this study and two other studies [4,7]

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Glass Fused Working Electrode