Application of the Rotating Cylinder Electrode in Molten LiCl-KCl Eutectic Containing Uranium(III)- and Magnesium(II)-Chloride

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Abstract

The application of the rotating cylinder electrode (RCE) to molten LiCl-KCl eutectic mixtures for electroanalytical measurements is presented. This enabled the measurement of the limiting current which was observed to follow a linear trend with the rotational rate raised to 0.64-0.65 power on average, which closely agrees with existing RCE mass-transfer correlations. This is the first publication of electroanalytical RCE measurements in LiCl-KCl eutectic based molten salt mixtures, to our knowledge. These measurements were made in mixtures of molten LiCl-KCl eutectic containing UCl₃ and MgCl₂. Kinetic parameters were calculated for Mg²⁺ in LiCl-KCl eutectic. The exchange current density (i_o) of Mg²⁺ deposition varied with mole fraction (x) according to $i_o(\text{A cm}^{-2}) = 1.64x^{0.689}$. The parameters from RCE measurements were also applied in an electrochemical co-deposition model entitled DREP to detect and predict the deposition rate of U and Mg. DREP succeeded in detecting the co-deposition of U and Mg, even when Mg constituted less than 0.5 wt% of the deposit.

1. Introduction

Many electroanalytical studies have been performed in molten LiCl-KCl eutectic salt containing a wide range of different metal chlorides (MCl_x) as electrochemically active species. These studies are particularly relevant to the study and optimization of used nuclear fuel (UNF) electrorefining, which can be used to separate uranium from transuranic elements, fission products, and cladding hulls. The molten LiCl-KCl- MCl_x electrochemical studies have almost exclusively been limited to stationary electrode studies. However, rotating electrodes will likely lead to improved processing throughput and consistency of the uranium deposits. In lab-scale experiments, the control of hydrodynamics via a rotating electrode can provide a stable diffusion layer, mask natural convection effects, and allow for more direct observation of kinetic parameters (i.e. exchange current density and transfer coefficient) by facilitating more rapid mass transfer. Despite the potential advantages of rotating electrodes during processing, significant challenges have limited experimentation with rotating electrodes in molten salts. Limited studies have been reported on the application of the Rotating Disk (RDE) and Rotating Ring-Disk Electrodes (RRDE) to molten LiCl-KCl [1–3] and cryolite-based melts [4]. However, this has required the fabrication of a complex electrode with multiple insulator-electrode interfaces or the positioning of the electrode exactly at the molten salt surface. A rotating cylinder electrode (RCE) can have a simpler design and require less exact placement. Additionally, the RCE can provide high rates of convective mass transfer in the turbulent regime (i.e. $1000 < Re < 100,000$), as demonstrated in aqueous solutions [5]. The RCE has been employed extensively in aqueous solutions [6–8] and has also been applied in cryolite-based melts [9,10], but no reported RCE studies could be found on eutectic LiCl-KCl.

The paper presents the initial application of the RCE in molten LiCl-KCl eutectic to provide rapid, controllable mass-transfer which enabled the quantitative evaluation of exchange current density (i_0) and mass transfer coefficients (h) for U^{3+} and Mg^{2+} ions and to assess DREP, a cathodic deposition model. UCl_3 and $MgCl_2$ were used as analytes to simulate a UNF electrorefiner salt, in which U^{3+} and Pu^{3+} are primary ions of interest both of which could potentially deposit at the cathode. $MgCl_2$ is a good

surrogate for PuCl_3 due to the proximity of their standard apparent reduction potentials, as previously demonstrated at stationary electrodes [11]. Four $\text{LiCl-KCl-UCl}_3\text{-MgCl}_2$ mixtures were analyzed using the RCE.

Until recently, exchange current density has received little attention in eutectic LiCl-KCl molten salts. The exchange current density of U^{3+}/U redox reaction has been determined at stationary electrodes using linear polarization, Tafel methods and electrochemical impedance spectroscopy [12–17]. No measurements of the exchange current density of Mg^{2+}/Mg couple in molten LiCl-KCl eutectic have been identified. Mass transfer coefficients at a rotating cylinder have not been measured yet for U^{3+} and Mg^{2+} ions. This work seeks to determine the exchange current density and mass transfer coefficient of each ion and their behavior by varying rotational rate and concentration.

Both the exchange current density and mass transfer coefficient are important parameters for simulating and understanding the behavior of ions during the UNF electrorefining process. Feedback on the cathodic deposition process is particularly valuable to ensure product purity and to verify declared activities by a domestic regulator or the international atomic energy agency (IAEA). DREP is derived to use parameters, such as exchange current density and the mass transfer coefficient, with observed potential and current of the UNF electrorefining operation to determine the number of metals depositing and their individual deposition rates. The derivation of DREP has been presented elsewhere [18], but has yet to be compared to experimental results. DREP's key assumptions are a stable, well-defined diffusion layer and constant bulk concentration of each analyte over the duration of each current step cycle. The assessment of DREP, in light of this RCE experimental work, can help gauge its current performance and guide its future development.

2. Experimental Details

The electrochemical cell used is illustrated in Figure 1 and is similar to the cell used in [19] with three exceptions. First, an alumina crucible (AdValue Technology, Part No. AL-2100, 4 cm dia., 9.5 cm

height) was used instead of a stainless steel (SS) crucible. Second, the reference electrode (RE) was made out of a mullite tube (Ceramic Solutions, 7 mm OD, 5 mm ID), 1 mm silver wire (99.9%, Alfa-Aesar) and 5 mol% AgCl (99.997% Premion®, Alfa-Aesar) in LiCl-KCl eutectic (99.99%, SAFC Hitech, 44 wt% LiCl). Lastly, the working electrode (WE) was a RCE which was made by attaching a bare 7.6 cm long, 2 mm diameter tungsten rod to a rotator (Autolab RDE-2) using a custom-made stainless steel coupler with a diameter of 6.35 mm and length of 22.9 mm. One end was machined to mate with the rotator. On the other end, a hole was machined to be slightly larger than the 2 mm tungsten rod with set screws on the side to secure the tungsten rod. The RCE was held in place by two clamps on a ring-stand. The orientation of the RCE was verified to be vertical using a level. The immersed depth of the WE was estimated by observing the salt adhering to the WE upon removal.

Four mixtures of molten LiCl-KCl eutectic were prepared by adding varying amounts of UCl_3 (synthesized from depleted U and dry HCl gas) and MgCl_2 (99.99%, Ultra-Dry, Alfa-Aesar) into a crucible contain eutectic LiCl-KCl, while at room temperature. The mixtures were heated to a temperature of $773 \text{ K} \pm 2 \text{ K}$, as measured by a thermocouple (Omega, KQXL) placed next to the RCE. The thermocouple was removed during electrochemical measurements. The concentration of UCl_3 and MgCl_2 in each mixture were measured using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and are reported in Table 1. Linear sweep voltammetry (LSV) was used at scan rates ranging from 5 to 50 mV s^{-1} to determine the limiting current for the reduction of U^{3+} and Mg^{2+} ions at rotation rates ranging from 25 to 500 RPM ($\pm 0.5 \text{ RPM}$). Chronopotentiometry (CP) was used to simulate the operation of a UNF electrorefiner which typically runs in galvanostatic mode. Between each test, an anodic potential was applied to strip the deposited metals after which the cell was left open until a steady potential was observed.

3. Results

Important properties of each analyte (i.e. U^{3+} and Mg^{2+}) are the standard reduction potential (E^o), number of electrons exchanged (n), mass-transfer coefficient (h), standard rate constant (k^o), transfer coefficient (α), and the activity coefficient (γ). In this work, apparent standard reduction potential or formal potential, $E^{o'}$, was used in place of E^o , and γ was set to one. $E^{o'}$ values determined elsewhere [11] for U^{3+}/U and Mg^{2+}/Mg redox couple were used in this analysis. Since both ions undergo single step reduction to the metallic state [11], the valance states of 3 and 2 were used as n values for U and Mg, respectively. This leaves h , k^o , and α as crucial properties to be determined using an RCE.

3.1. Mass-Transfer Coefficients

In order to determine the values of h , measurements of the mass-transfer limiting current needed to be made. This was accomplished by running LSV at various rotational and scan rates. When LSV is performed under non-static or hydrodynamic conditions created by the rotation of an electrode, it ideally will take on the shape of a sharp rise followed by a plateau. The current plateaus in a hydrodynamic linear sweep voltammogram (HD-LSV) are due to the complete depletion of an electroactive ion at the electrode surface and should be independent of time if a constant diffusion layer thickness is assumed. The plateau in HD-LSV is called the limiting current (I_L), given by the following expression.

$$I_L = nFAhC_b^{ox} \quad (1)$$

The dependence of the mass-transfer coefficient on the rotational rate of a RCE is captured in many mass transfer correlations, as has been reviewed extensively[6–8]. The most common relation used is the Eisenburg equation.

$$h = 0.0791U^{0.7}d^{-0.3}\nu^{-0.344}D^{0.644} \quad (2)$$

U represents the rotational velocity ($U = \pi d\omega$), D is the diffusion coefficient, d is the diameter of the electrode, ν is the kinematic viscosity of the molten salt ($\nu = \mu/\rho$), μ is the dynamic viscosity, ρ is the density and ω is the rotational rate.

Two main challenges complicated the determination of the limiting current. One was the initial transient behavior of the diffusion layer (δ). The other was growth of the WE surface area due to metal deposits. Both of these challenges are illustrated in Figure 2. At a very low scan rate, 5 mV/s, the U^{3+} reduction peak is almost imperceptible and the limiting current for U^{3+} is quickly achieved. As the scan rate increases the peaks grow, but eventually settle to the limiting current value with the exception of 10 and 15 mV/s for Mg^{2+} and 25 mV/s for U^{3+} . In the case of 10 and 15 mV/s, the deposited metals begin to significantly increase the surface area before the Mg^{2+} limiting current can be reached. For 25 mV/s, the U^{3+} reduction peak is so large that it does not decay to the limiting current before Mg^{2+} reduction commences. Thus, the limiting current for the rotational rate of the RCE was measured by repeating LSV at multiple scan rates and identifying the settings at which the current plateaus at the same value to avoid inflation of the limiting current due to a transient diffusion layer (δ) and/or WE area growth.

In order to evaluate the mass transfer dynamics, a dimensionless analysis was performed using the Sherwood ($Sh = hd/D$), Reynolds ($Re = Ud/\nu$) and Schmidt ($Sc = \nu/D$) numbers. Due to insufficient data, the viscosity and density of the molten salt was assumed to be that of pure LiCl-KCl and the RCE surface was assumed to be smooth. Under these assumptions, Re was calculated to be 7 to 77 using rotational rates from 50 to 500 RPM, a dynamic viscosity of 2.2×10^{-3} Pa s [20,21], and a density of 1.62 g cm⁻³ [22]. Sc was calculated to be 1250 for U^{3+} and 780 for Mg^{2+} using diffusion coefficients of 1.09 and 1.74×10^{-5} cm² s⁻¹ for U^{3+} and Mg^{2+} , respectively [11]. Lastly, Sh was calculated using the following equation:

$$Sh = \frac{I_L d}{n F A D C_b^{ox}} \quad (3)$$

It would be expected for Sh to be constant with Re between 7 and 77 because the flow around an RCE is laminar below an Re of 200. In the laminar flow regime, the flow is anticipated to be tangential to the electrode offering little or no enhancement of mass flow to the electrode [6–8,23]. However, when Sh numbers are plotted versus the Re for mix no. 1, as shown in Figure 3, both U and Mg deposition rates

appears constant below $Re = 20$, but then increase monotonically. This is similar to the results of Cornet and Kappesser [23], but the transition from constant to increasing Sh occurs at $Re = 200$ and Sh was equal to 37 in the constant regime. Burgman and Sides [9,10] also experienced increasing Sh at Re values less than 200 in cyrolite-based molten salts. Their $Sh/Sc^{0.356}$ values (1-2) are comparable to those calculated in this work (0.5-3.3) over a similar range of Re values (40-100). This may be due to uncertainty in the viscosities of molten salts. The value for eutectic LiCl-KCl is not well-established in the literature. Additionally, the surface roughness from metal deposits (U and Mg) can enhance mass transfer [6–8]. This effect is unaccounted for in the calculated Re values. Hence, it is assumed that surface roughness is inducing turbulence at Re values below 200 because mass transfer is clearly enhanced with increasing rotational rate despite the low values calculated for Re .

This increase in mass transfer limitations with rotational rate was evident in all mixtures at Re values above 20, as shown in Figure 4. The logarithm of the Sh and Re values are plotted and regressed in Figure 4. If the mass transfer correlation is assumed to have following form:

$$Sh = aRe^b Sc^c \quad (4)$$

then the slope of each series is equal to b and the y-intercept represents the logarithm of aSc^c . A power regression of the y-intercepts and Sc values yielded $c = 0.307$. This agrees well with the common assignment of $1/3$ to c . However, the regression of two data points is not reliable, hence; c is assumed to be $1/3$ in this work. If all four series for U and Mg are regressed together, then overall $a = 0.296$ and $b = 0.656$ for U and $a = 0.299$ and $b = 0.634$ for Mg. The mass transfer correlation constants for U and Mg compare well to each other and are within the range of constants determined in literature. For comparison, four mass-transfer correlations as determined by Cornet and Kappesser ($a = 0.126$, $b = 0.640$, $c = 0.333$) [23], Eisenberg et al. ($a = 0.079$, $b = 0.700$, $c = 0.356$) [5], Nassar et al. ($a = 1.58$, $b = 0.725$, $c = 0.330$) [24], and Robinson and Gabe ($a = 0.169$, $b = 0.660$, $c = 0.330$) [25] are also plotted in Figure 4.

Ideally, the Re values should be higher and cover a broader range. Unfortunately, due to the instability of the RCE, the rotational rate could not exceed 500 RPM without significant vibration. Therefore, the Re number was limited to 77 in this setup. The stability of the RCE at or below 500 RPM was verified by video recording of the salt surface with the RCE revolving. The RCE was observed to rotate about a central axis. No whipping was observed, and the salt surface appeared flat.

Despite the low rotational rate and narrow range, it is evident from Figures 3 and 4 that the limiting current (i.e. mass transfer) is increasing with rotational rate. Overall, this increase follows similar trends (i.e. comparable b values) to those in the literature. However, there is a large degree of variation between mixtures, as shown in Figure 4. To quantify the degree of variation, the mass-transfer coefficient was calculated for U^{3+} and Mg^{2+} ions at 250 RPM using a and b values calculated from the slope and intercept of each series in Figure 4 in equation (4). The resulting values for the mass-transfer coefficient are displayed in Table 2 along with the diffusion layer thickness ($\delta = D/h$). There is a high degree of variability in the mass-transfer coefficient between mixtures as indicated by a standard deviation (σ) that is half of the average value.

3.2. Kinetic Parameters

The kinetic parameters of ions in eutectic LiCl-KCl were measured by using an approximation of the Butler-Volmer equation at low overpotentials (η) which uses the first two terms of the Taylor series expansion for an exponential function (i.e. $e^x \approx 1 + x$) and the assumption that the bulk and surface concentrations of ions are equal (i.e. negligible concentration overpotential). The approximation yields the following form of the Butler-Volmer equation which is linear with overpotential [26,27]:

$$I = i_o A \frac{nF}{RT} \eta = i_o A \frac{nF}{RT} (E - E_{eq}) \quad (5)$$

$$i_o = nFk^o (x_b^{ox})^{(1-\alpha)} (x_b^{red})^\alpha \quad (6)$$

where i_0 is the exchange current density and the superscript *red* represents the reduced species. This approximation deviates from the Butler-Volmer and Current-Overpotential equations by 1% or less for $\eta = 16.5$ mV, if $n = 2$, $T = 773$ K and $\alpha = 0.5$. Because no alloy forms between Mg and U metal [28], the activity of the reduced species was set to 1.

The exchange current density was determined by regression of the slope for each HD-LSV in every RCE mixture from a few millivolts after the commencement of reduction up to 16.5 mV in the negative direction for U and Mg, respectively, as shown in Figure 5 for Mg^{2+} reduction. The slope for each mixture was taken for multiple HD-LSVs at various scan rates and rotational rates to ensure that neither diffusion nor convection was affecting the slope of the reduction curve in the region described. The slopes were divided by the area and nF/RT to obtain exchange current density and are plotted in Figure 6 for Mg. The lines in Figure 6 represent the average over the scan rates and rotational rates where the exchange current densities were observed to be stable. The average exchange current density values for Mg^{2+} reduction in each RCE mixture are plotted in Figure 7. According to (6), the exchange current density should relate to mole fraction by a power law. The exchange current densities were plotted versus the mole fraction and regressed to yield a power law, as displayed in Figure 7. As a result of this regression, k^0 and α were found to be $0.850 \times 10^{-5} \text{ mol s}^{-1} \text{ cm}^{-2}$ and 0.311 on the mole fraction basis, respectively, for Mg^{2+} reduction. On the molar concentration basis, k^0 becomes 0.0976 cm s^{-1} . There was significant noise in the HD-LSV measurements made on mixture no. 4, hence the large variance in exchange current density values in Figures 6 and 7. Attempts were made to remove this noise, but the source could not be determined.

The exchange current densities and kinetic parameters for magnesium compare well to other similar studies. The exchange current density of magnesium in this study is on the same magnitude as values reported for the deposition of uranium and rare-earths from eutectic LiCl-KCl containing dilute amounts of the metal-chloride at 773 K [15,16,29,30]. No studies were found on the kinetic parameters of magnesium in molten LiCl-KCl eutectic, but some values were reported in other molten salts. In a pure

MgCl₂ melt on a liquid Mg electrode, an exchange current density of 2.15 A cm⁻² was determined at 998 K for the rate-determining step in magnesium deposition using electrochemical impedance spectroscopy (EIS) [31]. The pure MgCl₂ would correspond to a k^o of 1.11×10^{-5} mol s⁻¹ cm⁻² since the MgCl₂ concentration is 100 mol%. Similarly, the exchange current density of magnesium deposition was measured to be 2.56 A cm⁻² at 938 K and 33.3 mol% MgCl₂ in the binary melt of MgCl₂-NaCl on a liquid Mg electrode using EIS [32]. An exchange current density of 0.75 A cm⁻² was reported in MgCl₂-KCl at 1028 K at 80 mol% KCl which compares to 0.54 A cm⁻² calculated at 20 mol% MgCl₂ and 773 K using the k^o and α determined in this study [33].

These studies [31–33] all used an Mg electrode, but an inert, tungsten electrode was used in this study. Exchange current density can be highly dependent on electrode material. A study of exchange current density of magnesium using a tungsten electrode could not be found. However, the exchange current density of magnesium of 2.3 A cm⁻² was determined at 998 K using an inert, molybdenum electrode in a MgCl₂(78 mol%)-MgF₂ melt which is similar to the value report for the Mg electrode at the same temperature [34]. Accounting for the fact that the measurements in this study occurred at a lower temperature, our lower exchange current densities of magnesium determined in this study appear reasonable in comparison to the other studies.

Unfortunately, the spacing of the uranium concentrations in the various mixtures (see Table 1) and the resulting exchange current densities (11 mA cm⁻² for mix nos. 1 and 2 and 27 mA cm⁻² for mix nos. 3 and 4) resulted in essentially two data points which resulted in poor regression statistics and unreliable k^o and α values. However, when compared to previous studies, the exchange current density values determined in this study are comparable to other studies, as shown in Figure 8. A similar treatment of the U³⁺ reduction peaks in cyclic voltammograms by Cumberland and Yim [14] yielded an k^o of 0.38×10^{-5} mol s⁻¹ cm⁻², assuming that α is equal to 0.5 based on same formulation used in (5) and (6). Lim et al. [16] investigated the exchange current density of uranium using Tafel plots and linear polarization (LP) which is the linearization technique employed in this work. The Tafel plots yielded an $\alpha = 0.22$ -0.23, but

their plot of exchange current density is linear with concentration which would be indicative of an $\alpha \approx 0$ according to (6). A more recent and thorough study by Yoon and Phongikaroon [17] of the uranium exchange current density revealed a linear trend with concentration using both LP and electrochemical impedance spectroscopy (EIS) to determine the values. Their linear regression of i_o and mole fraction resulted in a slope of 12.047 A cm^{-2} which compares to the slope of 16.168 A cm^{-2} determined in this work. Additionally, their Tafel analysis at 0.5 wt% UCl_3 revealed an $\alpha = 0.015\text{-}0.04$ which would be more consistent with the observed trends of exchange current density with concentration in this work and the two previously cited works [16,17]. However, caution should be applied to values determined from a Tafel analysis of U^{3+} reduction because of uranium's facile kinetics in molten LiCl-KCl eutectic. Tafel relationships require high overpotentials in the absence of mass-transfer effects which is easily accomplished in kinetically sluggish systems, but may not be achievable in U^{3+}/U system.

3.3. DREP Assessment with RCE data

Several models of electrorefining in molten LiCl-KCl eutectic already exist [27,35–44], but these models are forward progressing simulations that use the initial concentrations of each phase (i.e. anode, cathode, salt) of the electrorefiner to predict the cathode deposit. DREP's novelty is that it does not require complete information about the compositions of each phase (i.e., anode, electrolyte, and cathode) in the electrorefiner which may be difficult to obtain. Rather, it uses the cell current and electrode potential to determine if more than one ion is reacting at an electrode and to calculate the concentration and deposition rates of the electroactive ions. Any one of those results would be valuable to an operator or an inspector who is interested in verifying the expected or declared electrochemical separation route of nuclear material when processing used nuclear fuel (UNF).

DREP's derivation and sensitivity to input parameters is discussed in detail elsewhere [18]. Only a brief synopsis is provided here. DREP merges several key electrochemical relations (Current-

Overpotential equation, Fick's law, Nernst equation and Faraday's law) into one simplified equation, as shown:

$$I_{j,k} = \frac{n_j F k_j^o A \{ C_{tot} \exp[(1-\alpha_j) n_j f (E_k - E_j^o)] - \gamma_j^{ox} C_{b,j}^{ox} \exp[-\alpha_j n_j f (E_k - E_j^o)] \}}{k_j^o \gamma_j^{ox} \exp[-\alpha_j n_j f (E_k - E_j^o)] / h_j + C_{tot}} \quad (7)$$

where $f = F/RT$, F is Faraday's constant, R is the universal gas constant, T is temperature, A is the surface area of the WE, α is the transfer coefficient, n is the number of electrons exchanged, E is the measured potential, E^o is the standard reduction potential, γ is the activity coefficient, C is concentration, h is the mass transfer coefficient, and k_j^o is the standard rate constant. The subscripts j , k , b and tot signify the species (i.e. uranium or magnesium), the current (or potential) step, the bulk of the mixture, and the total mixture, respectively. The superscript ox indicates the oxidized state. The expression in (7) was derived elsewhere [18] and was modified slightly to better match IUPAC convention [45]. Therefore the previous expression was multiplied by negative one so that negative current indicated a cathodic current. Furthermore, the α term in the previous expression was actually β which is $(1-\alpha)$ in most conventions. At zero current or equilibrium, (7) reduces to the Nernst equation, assuming unit activity for deposited metal:

$$E_{eq} = E^o + \frac{RT}{nF} \ln \left(\gamma_j^{ox} \frac{C_{tot}^{ox}}{C_{tot}} \right) = E^{o'} + \frac{RT}{nF} \ln(x^{ox}) \quad (8)$$

where the activity coefficient can be combined with the E^o to form the apparent standard reduction potential ($E^{o'}$), and the concentration of the oxidized metal divided by the total concentration of the mixture (i.e. molar density) is the mole fraction (x). This demonstrates the theoretical soundness of the expression derived in (7)

The species current in (7) is dependent on potential and concentration. If non-faradaic processes are negligible, the cell current is then given by:

$$I = \sum_j I_{j,k}(E_k, C_{b,j}^{ox}) \quad (9)$$

where the current for each species, j , and at each current step, k , is given by (7) and dependent on the concentration and the electrode potential. The potential of the electrode can be easily and instantaneously measured. The concentration of each species is the remaining unknown. In the case of uranium and magnesium co-deposition, two concentrations are unknown which can be determined if two current steps are applied to the cell and the WE potential is measured. These current steps need to be short enough that the bulk concentration is constant over both steps, but long enough that double-layer charging and other transient effects are negligible. The current steps and potential measurements create the needed system of equations to solve for the concentration and deposition rates.

A UNF electrorefiner typically operates under controlled current. Thus, chronopotentiometry (CP) was applied to simulate electrorefining. A cycle of constant current steps were applied to the electrochemical cell while rotating the RCE at 250 RPM. First, the cell current was set for 10 seconds (13 seconds for mixture RCE2, cycle A) to an “operational” current where U and Mg would co-deposit. The operational current was selected by examining the HD-LSV curves. Next, the cell current was set to zero for one second and then set to 5 mA for another second. Then, the cell current was returned to the operational current. This cycle was repeated twice so that the operating current step was applied three times, and the one-second open-circuit and 5 mA steps were applied twice. At the end of the third operating current step, the RCE was raised out of the salt, while the cell was set to the operational current. The WE area, total time held at the operational current, the value of the operational current, and the measured potentials at the end of each current step are given in Table 3. The letters A and B represent the first and second cycle of the current steps.

The potential was sampled at the end of each step to avoid interference from possible transient effects. For example, the measured WE potential during the current cycle for mixture RCE2 is given in Figure 7. In the first step of cycle A, there are transient effects and the potential response looks like a static CP measurement. However, after a couple seconds, the potential settles out to a steady value unlike static CP measurements, which continue to decrease until Li deposition occurs. On the last operational

step, a sharp decrease in the potential marks the removal of the WE from the cell. The open-circuit and 5 mA steps are used in DREP to solve for concentrations of UCl_3 and MgCl_2 . These concentrations are then used in (7) to predict the deposition rate of U and Mg at the operational current.

There are two sets of model parameters: species properties (e.g. diffusion coefficient, etc.) and cell settings/measurements. The cell current settings and measured WE potentials used in DREP are listed in Table 3. The species properties have all been determined in previous sections or gathered from other references. They are summarized in Table 4. If no source appears next to a value, then it was determined in this work.

DREP predicts three things with only the information provided in Tables 3 and 4. First, DREP determines if one or more metal ions are being reduced at the WE. Second, it solves the concentration of each depositing metal ion in the bulk electrolyte using the two low current steps (i.e. open-circuit and 5 mA). Lastly, it uses the calculated concentrations and (7) to predict the deposition rate at the operational step settings. DREP succeeds in all mixtures and cycles to identify that more than one metal ion is depositing at the WE. The results of DREP concentration calculations are given in Table 5. For mixture nos. 1 and 2, the concentrations calculated by DREP agree fairly well with ICP-MS measured values. However, for mixture nos. 3 and 4, negative concentrations are calculated and the solutions drastically disagree with ICP-MS values. Essentially, DREP does not converge to physically possible solutions for the concentration of the ions, except in mixture no. 3 (cycle B) which is quite inaccurate.

Deposition rates were also calculated by DREP. To gauge the accuracy of the predicted deposition rates, the deposited metal on the WE was dissolved in a known volume of 10 vol% nitric acid and the U, Mg, Li, K content was measured using ICP-MS. Inevitably, some salt adhered to the metal deposits. The amount of adhering salt was calculated based off of the Li and K content in the following manner:

$$m_{\text{salt}} = \frac{6.107m_{\text{Li}} + 1.907m_{\text{K}}}{1 - w_{\text{MgCl}_2} - w_{\text{UCl}_3}} \quad (10)$$

where m is the mass, w is the weight fraction and the subscripts indicate the species. The coefficients in the numerator were calculated based on the ratio of molecular weights of the metal chloride to the metal (i.e. MCl_x/M). The weight fractions of UCl_3 and $MgCl_2$ were given in Table 1. The amount of U and Mg contained in the adhering salt was calculated by multiplying the weight fraction of U and Mg in the salt mixture (see Table 1) and the calculated amount of adhering salt. This amount was subtracted from the measured U and Mg content in the dissolution to determine the amount of U and Mg metal deposited. Key values in calculating the adhering salt are provided in Table 6.

DREP's deposition rates were multiplied by the summed total duration of the operational steps (see Table 3) and were compared to the amount of U and Mg metal deposits calculated from ICP-MS measurements. It is important to note that the third operational step did not last 10 seconds because of the early removal. However, the time of removal was marked clearly by a sharp drop in the potential. The early removal is accounted for in the deposition times listed in Table 3. Because the predicted deposition rates are dependent on the concentration calculations in DREP, a similar trend was found in the deposition rates. Mixtures no. 1 and 2 were reasonably close while mixture nos. 3 and 4 were quite inaccurate or diverged to negative values.

In order to evaluate the ability of DREP to predict deposition rates without the propagation of egregious errors in the concentration, the ICP-MS measured concentrations were inputted directly to DREP. The model generated the deposition rates and amounts given in Table 7. In absence of concentration errors, DREP predicts realistic deposition amounts that are within the same order of magnitude as those measured by ICP-MS, with exception of mixture nos. 1 (cycle B) and 3 (cycle A). In the case of mixture no. 1 (cycle A), the relative error is less than 3% for both U and Mg. Most importantly, DREP successfully detected the deposition of Mg in all cases and provided a good estimate of the amount deposited, even when Mg account for less than 0.5% by mass (4.3% on molar basis) of the deposit. This provides confidence that DREP can be used to detect when Pu is being co-deposited onto a

cathode—even at very low rates. However, it cannot yet provide accurate concentration and deposition rate values consistently. Hence, further development of the model is required.

4. Discussion

4.1. Diffusion Layer Behavior

It was noted that the HD-LSV plotted in Figure 2 contained peaks characteristic of static LSV measurements. The peak formation in HD-LSV is theorized to occur because initially the reactants fill the entire diffusion layer. As the potential is scanned in the negative direction, reactants begin to reduce out of solution and onto the electrode. When the reactants are depleted next to the electrode, the reactant are depleted further into the solution causing the diffusion layer to extend further into the solution until the hydrodynamics of the RCE are sufficient to replenish the reactants at the rate of their consumption. In order to mask the peaks in the HD-LSV, the RCE needs to be rotated sufficiently fast that the limiting current exceeds the peak current. This was difficult to achieve in this study, because the ring-stand supporting the RCE would begin to vibrate above 500 RPM. A more sturdy and precisely aligned stand would enable higher rotational rates, which would reduce the interference of peaks and enable the application of the RCE at higher concentrations.

4.2. Mass Transfer Coefficient

As noted, a large variation in mass transfer coefficients was observed across mixtures (see Table 2). The variations may have been due to a number of factors. One such factor may be the WE surface area. The WE area was measured by observing the adhering salt length. It has been observed by the authors that this technique has a variability of ± 2 mm [46]. The high degree of covariance (>1000) and a linear correlation (R^2 of 0.92 for U and 0.98 for Mg) between the mass-transfer coefficient and the exchange current density normalized by concentration (i.e. $i_0/x^{(1-a)}$) from each mixture was observed. Thus, an increase in one of the parameters was accompanied by an increase in the other which would

seem to indicate a systematic error, such as the WE surface measurement. The more accurate method of using a vertical translator to precisely change the immersion depth could not be used with the RCE, because the weight of the RCE exceeded the load limit of the vertical translator [47]. However, an accurate method to controlling the WE surface has since been developed [19]. Furthermore, the large, heavy nature of the RCE made the precise placement of the RCE difficult. A stand specific to the RCE and use of a furnace well would also ease and improve the process of positioning the RCE.

Other experimental variations may also contribute to large variations. The experimental setup described makes no measures to ensure that the reference electrode (RE) and CE do not disrupt the flow of the electrolyte. Thus, variations in the placement of the RE and CE could have caused different flow profiles in each mixture. For example, the CE was asymmetrical. Depending on its orientation, it may have been placed closer to the WE in some mixtures. In this case, the flow disruptions caused by CE would affect the mass transfer coefficient more acutely than in other mixtures. The depth to which the RE was immersed into the molten salt should also be considered. Since the RE is placed close to the WE, a further immersed RE disrupts more of the flow around the WE. In the aqueous study of the RCE [5], special measures were taken to ensure that RE and CE did not disrupt the flow in the cell. The WE and CE were concentric cylinders with the CE as the outer cylinder. The RE was placed outside of the cell and connected using a liquid junction. This could be similarly accomplished in a molten salt cell by centering the WE in a conductive crucible, such as glassy carbon or steel. The conductive crucible would serve as the CE. An external RE may not be feasible, but its effect could be minimized by only slightly immersing it in the molten salt next to the WE or by using a pseudo-RE, which could simply be a wire.

4.3. Exchange Current Density

The exchange current density was demonstrated to be independent of scan and rotational rate at certain values in Figure 5. At high scan rates, the RCE may be polarized too rapidly to allow ions to be replaced by the convection of ions to the RCE, invalidating the assumption of an equal surface and bulk

concentration. Similarly, at too low of rotational rates, there could be inadequate replenishment of ions at the RCE. It should also be noted that nucleation effect could also have affected the exchange current density values. To minimize the influence of nucleation, the first 4-7 millivolts after the commencement of Mg deposition were excluded from the regression of the current-potential curve. At these low scan rates (5-50 mV s⁻¹), the amount of time elapsed over these few millivolts ranges from 0.08 to 1.4 s.

The values of uranium exchange current density used in DREP were taken from the work by Cumberland and Yim because its values are comparable to this and other studies and a non-zero α is used. For example, a study at about 5 wt% U reports an exchange current density of 0.096 A cm⁻² at 773 K which compares to a value of 0.122 A cm⁻² which is calculated using the results from Cumberland and Yim (i.e. $k^o = 0.38 \times 10^{-5}$ mol s⁻¹ cm⁻², $\alpha = 0.5$) [15]. Exchange current density of 0.019 A cm⁻² at 773 K and 1 wt% UCl₃ and 0.058 A cm⁻² at 773 K and about 3.2 wt% UCl₃ are lower than the calculated values of 0.045 and 0.080 A cm⁻², respectively [16]. These are reasonably similar values, particularly since the deposition rates calculated in DREP are mainly dependent on the mass-transfer coefficient for reasons discussed in Section 4.4.

Further motivation for using the Cumberland and Yim relation for exchange current density was the fact that the other data implied an α of zero which also implies that the applied potential does not reduce the free energy barrier for the deposition of uranium or promote the reduction of U³⁺. This does not seem reasonable. When using an α of zero in DREP, (7) becomes the following equation:

$$I_{j,k} = \frac{n_j F k_j^o A \{c_{tot} \exp[n_j f (E_k - E_j^o)] - \gamma_j^{ox} c_{b,j}^{ox}\}}{k_j^o \gamma_j^{ox} / h_j + c_{tot}} \quad (11)$$

This equation indicates that the reduction current for U³⁺ ions is independent of potential which Figure 2 and several voltammetry measurements have illustrated the U³⁺ reduction is increased by applying a more negative potential. When an α of zero was used in DREP, the measured limiting currents could not be obtained because the deposition of uranium was not being increased with increasingly more negative

overpotentials, rather it flattened out at a limiting value dictated by i_o . Further investigation of α and other kinetic parameters is needed. It may be that the trend of exchange current density may appear linear in relation to concentration over the limited range investigated, but curvature could be manifested over a broader range or the assumption of a unit activity coefficient may be distorting the trend. If the α for U^{3+}/U is zero, then the model for uranium would need to be modified to appropriately account for the kinetic limitation.

4.4. DREP Results

It is apparent in Table 5 that DREP may not be the best method for determining concentration. This is most likely due to potential drifts and unexpected variations in the mass-transfer coefficients. The possible causes for the large variation in mass transfer coefficients in Table 2 have already been discussed in Section 4.2. The potential of the RE may also have shifted between mixtures, as has been observed in static electrochemical measurements [11]. Between each mixture, the RE was cooled and then reheated with the melt. The thermal cycling and gradients may have caused silver ions to deposit and the reference potential to shift [48]. This shift does not need to be great in order to create major errors in the concentration, as demonstrated by mixture no. 3. In Table 3, the operational potential in cycle B becomes 19 mV less negative than cycle A. Yet, the concentration changes dramatically in Table 5 between the cycles in mixture no. 3. Furthermore, the negative uranium concentrations in Table 5 are due to an overprediction of Mg^{2+} reduction current which may have been caused by a shift in the RE potential. Hence, a highly stable RE may be necessary in order to predict concentrations using DREP.

The deposition rates predicted by DREP in Table 7 were predicted using the ICP-MS measured concentration, which resulted in fairly accurate predictions. Thus, it may be sensible to pair DREP with the concentration measurements of a more accurate electroanalytical technique such as CV or NPV, if a highly stable RE cannot be developed.

The purpose of these experiments was to test the ability of DREP to predict deposition rates when two metal ions were depositing. Because of this, the potential range where the CPs were run was slightly more negative than the Mg^{2+}/Mg equilibrium potential. At this region of the current-potential curve (about -2 V in Figure 2), uranium is at its limiting current. This makes its concentration and deposition rate calculations mostly dependent on the mass transfer coefficient. The mass transfer coefficient does not have as great of an effect on the magnesium predictions because it is not near its limiting current, rather the standard apparent reduction potential becomes more influential. Hence for accurate uranium and magnesium predictions stable, repeatable hydrodynamic conditions and potentials, respectively, are essential.

To illustrate this point, the potential at the operational setting in Table 3 shifts significantly between cycles A and B in mixture nos. 1 and 3. In mixture no. 1, the operational potential shifts more negative in cycle B. As a result, the deposition rate of Mg in Table 7 increases drastically due to its exponential dependence on potential. Similarly, in mixture no. 3, the operational potential shifts more positive resulting in a significant decrease in the predicted Mg deposition rates.

5. Conclusions

Electroanalytical rotating cylinder electrode (RCE) measurements in molten LiCl-KCl eutectic were reported for first time, to our knowledge. These initial measurements were made in four molten LiCl-KCl eutectic mixtures containing UCl_3 and MgCl_2 . The Sherwood number (i.e. limiting current at the RCE) increased with rotational rate raised to 0.64-0.65 power on average, which is in close agreement with existing mass-transfer correlations for the RCE. The determination of limiting currents in linear sweep voltammograms was complicated by peak formation and WE area growth. The peak formation was theorized to occur with the RCE due to the initial transient behavior of the diffusion layer. In order to ensure that the peaks and area growth did not augment the limiting current, multiple scan rates were applied. At properly tuned scan rates, stable limiting currents were observed at various rotational rates.

The calculated mass-transfer coefficients varied considerably between mixtures indicating possible errors in WE area measurements and variations in the hydrodynamics due to variations in the orientation of the CE or depth of the RE. Kinetic parameters were calculated for Mg^{2+} in LiCl-KCl eutectic results in k^o and α of $0.850 \times 10^{-5} \text{ mol s}^{-1} \text{ cm}^{-2}$ and 0.31, respectively, on a mole fraction basis. The cathodic co-deposition model, DREP, accurately predicted the concentration of mixture no. 1, but erred increasingly in subsequent mixtures. The probable cause for the large error in the concentration is shifts in the reference potential due to thermal cycling and gradients. Hence, significant improvement is need in the model and experimental setup. A highly stable RE and repeatable electrode arrangement with minimal flow disruptions are recommended for future RCE studies. Additionally, fundamental understanding of the U^{3+}/U and Mg^{2+}/Mg behavior at the RCE needs more development. This could be accomplished more readily through studies of the individual ions in LiCl-KCl eutectic. Despite these shortcomings, the performance of DREP in predicting deposition rates, based on ICP-MS measured concentration, showed promise for coupling DREP with an electroanalytical technique, such as CV and NPV. Most importantly, DREP successfully detected the co-deposition of U and Mg in all mixtures, even when Mg constituted less than 0.5 wt% of the deposit. It is, thus, a promising method for detecting co-deposition of Pu during U electrorefining when used in conjunction with electroanalytical techniques.

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Figure 1: Illustration of electrochemical cell

Table 1: ICP-MS measured concentration of UCl_3 and MgCl_2 in molten LiCl-KCl eutectic

Mixture No.

	UCl ₃ (wt%)		MgCl ₂ (wt%)	
	Targeted	ICP-MS	Targeted	ICP-MS
1	0.40%	0.51%	0.60%	0.53%
2	0.50%	0.48%	0.15%	0.10%
3	1.00%	1.02%	0.30%	0.23%
4	1.00%	0.89%	0.60%	0.74%

Figure 2: Linear sweep voltammograms in mixture no. 1 at 250 RPM (WE = 2 mm W rod, CE = U in SS basket, T = 773 K, Area = 0.78 cm²)

Figure 3: Sherwood (*Sh*) numbers for U³⁺ (left) and Mg²⁺ (right) reduction as a function of the Reynolds (*Re*) number for mix no. 1 at 773 K (WE = 2 mm W rod, CE = U in SS basket)

Figure 4: Sherwood (*Sh*) numbers for $Re \geq 20$ in all mixtures at 773 K (WE = 2 mm W rod, CE = U in SS basket) with mass-transfer correlations from Eisenberg et al. [5], Cornet and Kappesser [23], Nassar et al. [24], and Robinson and Gabe [25]

Table 2: Mass-transfer coefficient and diffusion layer thickness (δ) values calculated at 250 RPM from the slopes in Figure 4

Mixture No.	Uranium				Magnesium				
	UCl ₃ (wt%)	UCl ₃ (mol dm ⁻³)	At 250 RPM		MgCl ₂ (wt%)	MgCl ₂ (mol dm ⁻³)	At 250 RPM		
			<i>h</i> (μm/s)	δ (μm)			<i>h</i> (μm/s)	δ (μm)	
1	0.51%	0.0241	17.5	62.3	0.53%	0.0906	13.1	133	
2	0.48%	0.0227	9.99	109	0.10%	0.0171	26.3	66.2	
3	1.02%	0.0484	23.2	47.0	0.23%	0.0394	46.1	37.7	
4	0.89%	0.0422	37.3	29.2	0.74%	0.1269	46.1	37.7	
Average (±σ)			22.0 ±11.6	61.9 ±34.3	Average (±σ)			32.9 ±16.1	68.6 ±38.8

Figure 5: Current-potential curve (dotted line) from mixture no. 3 at 30 mV s⁻¹ and 250 RPM with low overpotential region fitted (solid line) (Area = 0.74 cm², T = 773 K, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 6: Exchange current densities calculated from the slope of the current-potential curves with varying scan rate (left) at 250 RPM and varying rotational rate (right) at 773 K (WE = 2 mm W rod, CE = U metal in SS basket)

Figure 7: Trend of exchange current density for Mg^{2+}/Mg couple with mole percent at 773 K and 250 RPM (WE = 2 mm W rod, CE = U metal in SS basket)

Figure 8: Values of exchange current density for U^{3+}/U couple compared to literature value by Cumerland and Yim [14], Lim et al. [16], Yoon and Phongikaroon [17]

Figure 9: Current steps applied to mixture no. 2 at 250 RPM (Area = 0.74 cm^2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = U metal in SS basket)

Table 3: Electrochemical cell settings and measurements for each mixture

Mixture No	Area (cm^2)	Time (s)	Current (mA)	Potential [V vs. Ag/AgCl (5 mol%)]		
		Operational	Operational	Operational	Open-Circuit	5 mA
1A	0.78	27.18	20	-1.951	-1.927	-1.923
1B	0.78	27.18	20	-1.963	-1.929	-1.929
2A	0.74	32.16	13	-2.030	-1.971	-1.975
2B	0.74	32.16	13	-2.030	-1.974	-1.975
3A	0.74	29.45	40	-1.990	-1.929	-1.926
3B	0.74	29.45	40	-1.971	-1.928	-1.921
4A	0.85	28.03	120	-2.027	-1.921	-1.918
4B	0.85	28.03	120	-2.003	-1.924	-1.920

Table 4 Species property values used in DREP

Parameters	UCl_3	Source	MgCl_2	Source
$E^{o'}$ [V vs. Ag/AgCl (5 mol%)]	-1.416	[11]	-1.749	[11]
n	3	[11]	2	[11]

k^o (10^{-5} mol s ⁻¹ cm ⁻²)	0.38	[14]	0.85
α	0.5	[14]	0.31
h ($\mu\text{m s}^{-1}$)	22.0		32.9

Table 5 Concentrations calculated by DREP

Mixture No.	Uranium			Magnesium		
	DREP mol dm ⁻³	ICP-MS mol dm ⁻³	Relative Error	DREP mol dm ⁻³	ICP-MS mol dm ⁻³	Relative Error
1A	0.0272	0.0241	13%	0.1031	0.0906	14%
1B	0.0208	0.0241	14%	0.0962	0.0906	6.2%
2A	0.0038	0.0227	83%	0.0486	0.0171	185%
2B	0.0034	0.0227	85%	0.0496	0.0171	190%
3A	-0.0282	0.0484	158%	0.2664	0.0394	576%
3B	16.077	0.0484	33150%	6.7120	0.0394	16920%
4A	-0.1294	0.0422	407%	0.6530	0.1269	414%
4B	-0.2077	0.0422	592%	0.9018	0.1269	610%

Table 6 Input and results for the adhering salt calculations

Mixture No.	Li (mg)	K (mg)	Adhering Salt (mg)
1	0.338	1.40	4.78
2	0.486	2.09	6.99
3	0.597	2.58	8.68
4	0.966	4.23	14.19

Table 7 Comparison of calculated amount of metal deposited calculated from DREP and ICP-MS

Uranium

Magnesium

	Deposition Rate (mg h ⁻¹)	DREP Deposit (mg)	ICP-MS Deposit (mg)	Relative Error	Deposition Rate (mg h ⁻¹)	DREP Deposit (mg)	ICP-MS Deposit (mg)	Relative Error
1A	35.68	0.2694	0.2681	0.48%	1.852	0.0140	0.0136	2.99%
1B	35.68	0.2694	0.2681	0.48%	3.838	0.0290	0.0136	113%
2A	31.79	0.2840	0.2292	23.9%	1.306	0.0117	0.0077	50.8%
2B	31.79	0.2840	0.2292	23.9%	1.289	0.0115	0.0077	48.9%
3A	67.95	0.5559	0.7681	27.6%	1.863	0.0152	0.0035	339%
3B	67.95	0.5559	0.7681	27.6%	0.193	0.0016	0.0035	54.6%
4A	67.77	0.5277	1.5828	66.7%	16.11	0.1254	0.0778	61.2%
4B	67.77	0.5277	1.5828	66.7%	13.50	0.1051	0.0778	35.1%