Electroanalytical Measurements of Binary-Analyte Mixtures in Molten LiCl-KCl Eutectic: Uranium(III)- and Magnesium(II)-Chloride

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Abstract

The electrochemical behavior of MgCl_2 in molten LiCl-KCl eutectic was investigated to evaluate its suitability as a surrogate for PuCl_3 in studies related to the electrorefining of used nuclear fuel. The reduction of Mg^{2+} was found to be electrochemically reversible up to 300 mV s^{-1} at 773 K. The diffusion coefficient for Mg^{2+} was calculated to be 1.74 and $2.17 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ with and without U^{3+} present, respectively, at 773 K using cyclic voltammetry (CV). Upon comparison to literature data, the diffusion coefficient of Mg^{2+} differs by only 8.8% (with U^{3+} present) from that of Pu^{3+} and the difference in peak potentials was only 79 mV. Binary-analyte mixtures of UCl_3 and MgCl_2 in eutectic LiCl-KCl were further investigated using CV, normal pulse voltammetry (NPV), chronoamperometry (CA) and open-circuit potential (OCP) measurements for the purpose of comparing each technique's accuracy in measuring U^{3+} and Mg^{2+} concentrations. Of all the techniques tested, NPV resulted in the lowest error which was, on average, 11.4% and 9.81% for U^{3+} and Mg^{2+} , respectively.

1. Introduction

Recently, quaternary molten salt mixtures have been examined to elucidate and resolve some of the challenges associated with using electroanalytical techniques to measure the concentration of key elements in a used nuclear fuel (UNF) electrorefiner [1–5]. These salt mixtures were comprised of a matrix salt, eutectic LiCl-KCl, and two analytes. These studies identified signal overlap, interaction of deposited metals and working electrode (WE) area growth as key issues associated with a binary-analyte mixture. Semi-differentiation of cyclic voltammetry (CV) measurements was used to reduce the interference of a background current from another analyte [2,5]. The deposition of alloying metals has been found to affect the potentials at which the more active metal deposits and to create additional signals. However, the inclusion of these signals in the correlation of current to concentration has had a minimal effect on accuracy [3–5]. Square wave voltammetry was identified to be suitable for only low concentrations (<0.1 wt% Pu) due to metal deposition augmenting the WE area, but normal pulse voltammetry (NPV) was found to be suitable at higher concentrations [1].

The improvement of the application of electroanalytical techniques to multi-analyte molten salt mixtures would enable accurate, in situ, real-time concentration measurements. Such measurements are beneficial for process monitoring, optimization and control, as well as for international safeguards and nuclear material accountancy. Two of the most important elements to monitor in a UNF electrorefiner are uranium (U) and plutonium (Pu). Only two of the studies mentioned actually performed electroanalytical measurements on binary-analyte mixtures containing U and Pu [1,2]. In these studies, the Pu content was limited to low concentrations (<1.67 wt% Pu) and/or a narrow range (1.28-1.44 wt% Pu). This is understandable, because PuCl_3 is difficult to obtain and handle. Due to the limited work on and availability of PuCl_3 , establishing an electrochemical surrogate for Pu would be valuable to increase the understanding of the challenges specifically associated with LiCl-KCl- UCl_3 - PuCl_3 mixtures. MgCl_2 was selected to act and be evaluated as a surrogate for PuCl_3 .

Only three studies on the electrochemical behavior of magnesium in LiCl-KCl eutectic have been identified [6–8]. All three studies found Mg^{2+} ions to reduce in a single-step to Mg^0 with no other stable valence state within the potential window of eutectic LiCl-KCl. The first study found the reduction of Mg^{2+} to be reversible up to 2 V/s at 400°C [6]. The second study does not comment on the reversibility of Mg^{2+} reduction, but it does use the Berzins-Delahay equation to determine diffusion coefficients which implicitly assumes reversibility [7]. The last study concludes that Mg^{2+} reduction is reversible until 300 mV/s from 723 to 908 K [8]. Due to the discrepancy in the boundary of reversible behavior and limited data in the literature, the behavior of MgCl_2 is reinvestigated in this paper.

Several studies have been performed on uranium in LiCl-KCl eutectic [9–15]. They have found that uranium has two stable valence states, +3 and +4, within the potential window of LiCl-KCl eutectic. Uranium reduces from the +4 to +3 in a single step, likewise for the oxidation from +3 to +4. A single-step mechanism has also been observed for the transitions from the +3 ionic state to deposited metal. An additional pair of oxidation and reduction peaks with a large spacing between them was reported as well. This pair of peaks was located between the U^{3+}/U^0 reduction peak and the $\text{U}^{3+}/\text{U}^{4+}$ oxidation peak and has been attributed to adsorption/desorption [10,16]. Most of these studies have found the reduction of U^{3+} to U^0 metal to be reversible up to 200 mV/s at 773 K, except for one [14] which reported it as irreversible due to decreasing peak potentials with increasing scan rate. This shift in peak potential was reported to be more significant at higher concentrations. It also appears that charge transfer may begin to limit the reduction of U^{3+} at high concentrations, thereby reducing the scan rate below which reversibility is maintained [17]. This paper extends the knowledge of uranium electrochemical behavior in eutectic LiCl-KCl to mixtures containing MgCl_2 .

In addition to examining the electrochemical behavior of Mg and U in eutectic LiCl-KCl, the paper seeks to evaluate electrochemical techniques suitable for in situ, real-time concentration measurements. The techniques investigated include cyclic voltammetry (CV), chronamperometry (CA), open-circuit potential (OCP) measurements and normal pulse voltammetry (NPV). Chronopotentiometry (CP) was

excluded due to difficulty in determining transition times and the partial current to attribute to each ion. Previous work on U and Pu in LiCl-KCl eutectic only examined one or two techniques [1,2]. Also, the use of MgCl₂ enabled a broad range of concentrations to be evaluated in this work. The accuracy of each technique was determined by comparing the concentration determined from electroanalytical measurements to inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements of concentration.

2. Experimental Details

The electrochemical cell used is illustrated in Figure 1 and is similar to the cell used in [17] with a few exceptions. First, an alumina crucible (AdValue Technology, Part No. AL-2100) was used as the primary crucible instead of a stainless steel crucible. Also, the counter electrode (CE) was either U metal sheets (International Bio-Analytical Industries Inc.) or a Mg rod (Alfa-Aesar, 6.35 mm diameter, 25.4 mm height) in a stainless steel (SS) basket. The Mg rod was only used in LiCl-KCl-MgCl₂ mixtures. 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. CV, CA, OCP and NPV measurements were all made at 773 K ± 2 K. A total of 29 mixtures were tested using electroanalytical techniques, 26 of which were binary-analyte mixtures. The weight fractions were converted to molar concentration by assuming ideal mixing which introduces minimal error (<1.5%) at less than 10 wt% UCl₃ [18].

$$\frac{1}{\rho_{mix}} = \sum_i \frac{w_i}{\rho_i}$$

w is weight fraction, ρ is density, i represents eutectic LiCl-KCl, MgCl₂, or UCl₃. The density values used for eutectic LiCl-KCl, UCl₃, and MgCl₂ are 1.62 [19], 5.20 [20], and 2.21 g/cm³ [21], respectively.

The working electrode (WE) was a bare tungsten rod (Alfa-Aesar, 2 mm diameter, 30 cm height). The WE was attached to a vertical translator (Velmex Inc., Part No. XN10-0012-M02-71) using two

custom-machined aluminum arms. In each arm, two holes were machined to align precisely with each other. An alumina tube (McMaster-Carr, 3.175 mm ID, ~5 cm long) was inserted through the holes in each arm and secured with set screws to electrically isolate the WE from the aluminum. The WE was fixed in place at the top and bottom of the alumina tube using Viton O-rings (McMaster-Carr). A gap between the alumina tube and one of the O-rings also served as an indicator that the WE did not move with the vertical translator arms.

The vertical translator was used to determine in situ the immersion depth of the WE. The WE was immersed to an arbitrary depth (typically ~1 cm) into the salt. Then the depth of the WE was adjusted using the vertical translator with a precision of ± 0.0025 mm. The U^{3+} reduction peak value and change in WE depth from the initial position was recorded at each position. The plot of the U^{3+} reduction peak current versus the change in immersion depth was plotted, as shown in Figure 2. The y-intercept in this plot corresponds to a zero peak current which would occur when the electrode is completely removed. Thus, the y-intercept represents the change in the WE depth from its initial position required to completely remove the WE. In other words, the absolute value of the y-intercept is the initial depth of the WE. In the case of mixture no. 19, the initial position was 2.817 cm and removed 1.3 cm from the salt resulting in the final immersion depth of 1.517 cm at which the electrochemical tests were performed. The WE depth determined for each mixture is given in Table 2. In some cases, UCl_3 (synthesized from depleted U metal) and/or $MgCl_2$ (99.99% anhydrous, Alfa-Aesar) were added to the LiCl-KCl eutectic (99.99% anhydrous, SAFC Hitech) mixtures using a Pyrex funnel so that the concentration could be varied without disturbing the electrodes and solidifying the salt. Thus, some immersion depths are assigned to multiple mixtures in Table 2 because the WE remained in the same position for each mixture.

3. Results

3.1. Electrochemistry of $MgCl_2$ in LiCl-KCl Eutectic

A complete CV scan of the LiCl-KCl-MgCl₂ system is displayed in Figure 3. The upper limit of the electrochemical window is indicated by the upward rise in the current on left side of the plot corresponding to tungsten dissolution and/or chlorine evolution. The current is flat until about -1.95 V at which point a prominent cathodic peak is formed. Due to the sharp shape of the accompanying anodic peak at -1.85 V and previous analysis [8], this pair of peaks are presumed to be Mg(II)/Mg redox couple. An additional pair of sharp peaks appear before Li deposition which corresponds to the underpotential deposition of lithium on magnesium due to alloying. An additional small pair of peaks proceed and follow the Mg(II)/Mg reduction and oxidation peaks, respectively, possibly due to reduction/oxidation of a monolayer of magnesium. This was not found in previous studies [6–8], but those studies were performed at much higher concentrations (0.8-1.8 wt%) which may have removed this effect or not been evident due to larger current signals.

CV measurements made under electrochemically reversible conditions have two key characteristics: (1) linearity of peak current with the square root of scan rate and (2) constant peak potential with scan rate. The peak current and potential can be calculated by the following equations [11,22]:

$$I_p = 0.6105AC_{M^{n+}}\sqrt{\frac{n^3F^3}{RT}D_{M^{n+}}\nu} \quad (1)$$

$$E_p = E^{o'} + \frac{RT}{nF}[\ln(x_{M^{n+}}) - 0.8540] \quad (2)$$

where I is current, E is potential, the subscript p represents peak, A is the surface area of the WE, C is concentration, n is number of electrons exchanged, F is Faraday's constant, T is temperature, D is the diffusion coefficient, ν is scan rate, $E^{o'}$ is the standard apparent (or formal) reduction potential, x is mole fraction, and M^{n+} represent an arbitrary metal ion. Figures 4 and 5 verify the applicability of (1) and (2) for MgCl₂ in eutectic LiCl-KCl up to 300 mV s⁻¹ by demonstrating a stable peak potential and linearity of peak current with square root of scan rate. The peak potentials were adjusted for ohmic (or IR) drop due

to the uncompensated resistance (R_u) in the circuit. The R_u was measured using the current-interrupt method at the Mg^{2+} reduction peak potential. The black line in Figure 4 represents the linear regression of the peak heights versus the square root of scan rate from 0 to 300 $mV s^{-1}$ and has a slope of $-0.0743 A V^{-0.5} s^{0.5}$. This slope coupled with WE surface area ($0.64 cm^2$) and the concentration ($0.0392 mol L^{-1}$) enable the calculation of the diffusion coefficient using (1) which resulted in $2.16 \times 10^{-5} cm^2 s^{-1}$ with a 99.5% confidence interval (CI) of $3.88 \times 10^{-7} cm^2 s^{-1}$. This compares well to the literature values of 2.42 [6], 1.26 [7], $1.57 [8] \times 10^{-5} cm^2 s^{-1}$. The horizontal line in Figure 5 is the average value ($-1.994 V$) of the IR-adjusted peak potentials from 0-300 $mV s^{-1}$ which was used with (2) to calculate the standard apparent reduction potential ($E^{o'}$). The resulting value of $-2.816 \pm 0.010 V$ vs Cl^-/Cl_2 ($-1.746 V$ vs $Ag/AgCl[5 mol\%]$) is between the reported values of $-2.850 [8]$ and $-2.796 [23]$ and matches open-circuit potential measurements between a Mg rod in a SS basket (see section 3.6).

3.2. $MgCl_2$ as a surrogate for $PuCl_3$

In order to evaluate the accuracy with which the UCl_3 - $MgCl_2$ - $LiCl$ - KCl mixtures approximate the behavior of the UCl_3 - $PuCl_3$ - $LiCl$ - KCl mixtures, the reduction peaks from CV measurements in each mixture under similar conditions were compared in Figure 6. The data for CV measurements of UCl_3 and $PuCl_3$ in eutectic $LiCl$ - KCl in Figure 6 were digitized [24] from Figure 6 of the publication by Tylka et al. [2] at Argonne National Laboratory (ANL). Mixture no. 4 contained comparable molar quantities of U^{3+} . However, an area was not specified for the ANL data and a pseudo-RE was used. Therefore, in order to get an accurate comparison of the Mg^{2+} and Pu^{3+} reduction peaks, the U^{3+} reduction peak current from mixture no. 4 was normalized to height of the U^{3+} reduction peak in the ANL data. Furthermore, the U^{3+} reduction peak potential was set to zero to match the potential of ANL's pseudo-RE.

The two sets of reduction peaks in Figure 6 have a similar shape and magnitude. The peak for Mg^{2+} reduction is slightly smaller, broader and more negative than the Pu^{3+} reduction peak. The peak current of Mg^{2+} reduction is 1.15 mA less negative than Pu^{3+} reduction despite Mg^{2+} having a higher

molar quantity than Pu^{3+} . This is due to the dependence of peak height on n and D , as shown in (1). The lower number of electrons exchanged in the deposition of Mg^{2+} causes the lower and broader peak. A concentration closer to 0.53 mol% MgCl_2 would be required to produce similar peak heights based on the diffusion coefficients of $1.60 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [2] and $2.16 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Pu^{3+} and Mg^{2+} , respectively. The peak potentials for Mg^{2+} and Pu^{3+} differ by 79 mV. Hence, the separation of peaks in each series is similar. Furthermore, the CV measurement in $\text{UCl}_3\text{-MgCl}_2\text{-LiCl-KCl}$ mixture contains no additional features (i.e. peaks or waves) and captures all the features from measurements on the $\text{UCl}_3\text{-PuCl}_3\text{-LiCl-KCl}$ mixture.

3.3. Cyclic Voltammetry of $\text{UCl}_3\text{-MgCl}_2\text{-LiCl-KCl}$

CV measurements of $\text{UCl}_3\text{-MgCl}_2\text{-LiCl-KCl}$ mixtures reveal fairly ideal (i.e. additive) behavior of the measured current, as shown in Figure 7. No additional peaks are created when Mg^{2+} reduces onto U metal. This was expected due to the lack of interaction of U and Mg metal based on their phase diagram [25]. Furthermore, the electrochemical behavior of uranium appears unaltered. The peak pairs A/A', B/B' and C/C' have all been observed previously in eutectic LiCl-KCl mixtures containing uranium ions [9–15]. Peak A and A' have been attributed to redox couple of U^{3+} and U^{4+} . The phenomena behind the B/B' pair of peaks is less certain, but has been attributed to adsorption/desorption. C and C' peaks are caused by the reduction of U^{3+} and oxidation of U metal. Lastly, the D/D' pair of peaks align with peaks previously observed in the $\text{MgCl}_2\text{-LiCl-KCl}$ mixtures. Thus peaks D and D' are ascribed to the Mg^{2+}/Mg redox couple.

As can be seen in Figure 7, the Mg^{2+} reduction peaks sits on the tail of the U^{3+} reduction peak. The height of this tail is dependent on the concentration of U^{3+} . Thus, in order to obtain an accurate peak current for Mg, the residual U^{3+} reduction current needs to be subtracted out. This was done two ways: (1) subtraction of the current at the base of the Mg^{2+} reduction peak and (2) semi-differentiation of the current

with respect to time (i.e. $d^{1/2}I/dt^{1/2}$). The first and second methods are referred to as base subtraction and semi-differentiation, respectively.

Using the base subtraction method, the actual Mg^{2+} reduction peak current density was determined and regressed linearly with respect to the square root of scan rate (i.e. $\sqrt{v}$) up to 300 mV s^{-1} . The U^{3+} reduction peak was similarly regressed up to 200 mV s^{-1} . The regressed slopes, or normalized peak currents, are plotted in Figure 8 versus the concentration of their respective ion. A linear correlation is observed between normalized peak current and concentration for both U^{3+} and Mg^{2+} , although there is some degree of scatter.

The semi-differentiation method removes the baseline because the current decays by time to the negative $1/2$ power (i.e. $t^{-1/2}$), as shown in Figure 9. The current before the semi-differentiated Mg^{2+} reduction peak is nearly zero ($<10 \text{ mA}$). The semi-differentiation was performed using Autolab NOVA 1.11.2 software. In some cases, noise was present in the original current measurements. Semi-differentiation would amplify the noise present in these cases and Savitzky-Golay smoothing [26] was thus applied. The semi-differentiated peak height (e_p) is given by the following expression under reversible conditions for a soluble-insoluble reaction [2].

$$e_p = \frac{n^2 F^2 A v \sqrt{D_{M^{n+}}}}{2RT} C_{M^{n+}} \quad (3)$$

Thus, e_p is linear with both scan rate and concentration. The linearity with scan rate was verified for both U^{3+} and Mg^{2+} SD reduction peaks up to 200 and 300 mV s^{-1} , respectively, in all mixtures. Figure 10 displays the regressed slope with respect to scan rate versus concentration for both U and Mg. There is a high degree of scatter and linearity is only maintained at low concentrations ($<0.01 \text{ mol L}^{-1}$).

3.4. Normal Pulse Voltammetry

Normal pulse voltammetry (NPV) records the current at the end of a potential pulse (i.e. pulse current) and then relaxes to a base potential between pulses. The pulses are successively incremented to a

more negative potential. If selected properly and held sufficiently long, the base potential can strip the metal deposited during the pulse and renew the diffusion layer. However, this renewal of the WE surface and diffusion layer can create longer turnaround times. For example, an NPV of $\text{UCl}_3\text{-MgCl}_2\text{-LiCl-KCl}$ mixture can take more than 20 min, but a CV measurement can take less than a minute.

NPV was applied to mixture nos. 1-18. A pulse time (t_p) of 0.25 s, base potential (E_b) of -0.75 V vs Ag/AgCl (5 mol%) and step potential (ΔE) of 5 mV were used in each mixture tested. An interval time (t_i) of 5 s was used initially for mixture nos. 1-5, but this was found to be insufficient for complete renewal as concentration increased. For mixture nos. 6 and 7, interval times of 10 and 12 s were used, respectively. Eventually, it was found that 15 s was sufficiently long, even at the highest concentrations. Thus, an interval time of 15 s was used for all remaining mixtures (mix nos. 8-18). This resulted in the base potential being held for 4.75, 9.75, 11.75 and 14.75 s depending on the interval time used.

The NPV measurement for mixture no. 14 is shown in Figure 11. The pulse current begins to rise at -1.55 V indicating the deposition of U metal. Eventually, the pulse current reaches a plateau indicating that the deposition of U metal is limited by diffusion. The height of this plateau is called the diffusional current. At -1.85 V, the pulse current rises again indicating that Mg metal is depositing as well. Eventually, Mg metal is also limited by diffusion and a second plateau is formed. The difference between the second and first plateau heights is the Mg diffusional current. Under semi-infinite linear diffusion control (i.e. the plateau region), the diffusional current is proportional to concentration, as quantified in the following equation [27].

$$I_d = nFAC_{M^{n+}} \sqrt{\frac{D_{M^{n+}}}{\pi t_p}} \quad (4)$$

In mixture nos. 1-4, no clear plateaus were formed for Mg, likely due to the short interval time. For these mixtures, the diffusional current was determined by differentiating the pulse current with respect to the potential (i. e. dI/dE), as done by Iizuka et. al [1]. As shown in Figure 12, this forms two peaks, one

for U and another for Mg. These peaks are formed by the rise and subsequent flattening of pulse current. Typically, the differentiated pulse current returns to zero after both peaks. The areas of these peaks are equivalent to the observed diffusional currents. However, in mixture nos. 1-4, the differentiated current does not return to zero after the Mg peak, but steadily rises. This non-zero baseline is presumed to be a growing WE area, because the base potential is not being held long enough for complete renewal. Thus, by fitting the Mg peak with a linear baseline, as shown in Figure 12, the WE area growth effect should be minimized and a more accurate diffusional current can be determined. This peak baseline adjustment was done for mixture nos. 1-4 to determine Mg diffusional current.

The U and Mg diffusional current densities for mixture nos. 1-18 are plotted versus their respective concentrations in Figure 13. A linear trend is maintained over the range of concentrations tested for both U^{3+} and Mg^{2+} . The diffusional current density is also less scattered than the normalized peak current in CV. Thus, NPV appears to be a promising technique to measure concentration, but may require longer turnaround times (15-30 min).

3.5. Chronoamperometry

Chronoamperometry (CA) is similar to NPV, but only requires a single step to a potential where the current is controlled by semi-infinite linear diffusion (i.e. independent of potential). The current response for a potential step into the region of semi-infinite linear diffusion control is characterized by the following equation [28]:

$$I = nFAC_{M^{n+}} \sqrt{\frac{D_{M^{n+}}}{\pi t}} \quad (5)$$

where t is the time elapsed from the initiation of the potential pulse. CA was applied to mixture nos. 1-18. CA was applied in a repeating manner. A potential was applied to induce Mg^{2+} and/or U^{3+} reduction for two seconds and then a potential approximately 100 mV more negative than the U^{4+}/U^{3+} redox couple was applied for 20 s. The process was repeated multiple times. The applied potentials were from the CV peak

potential of U^{3+} or Mg^{2+} reduction up to 100 mV more negative in 10 mV increments. For example, if the U^{3+} and Mg^{2+} reduction peak potential is -1.6 V and -2.0 V, respectively, then CA would be applied from -1.6 up to -1.7 V and from -2.0 up to -2.1 V. The CA process was repeatedly applied until the current response from different applied potentials overlapped, as shown in Figure 14. These overlapping current responses were used in analysis because they were under semi-infinite diffusion control and (5) is applicable. This was done for both U and Mg deposition. Overlap of current response at applied potentials more negative than the Mg^{2+} reduction peak was not obtained in mixture nos. 6 and 8 due to rapid WE area growth. CA responses in these mixtures were excluded from further analysis.

The current response from CA was sampled at 0.25s for both potential ranges (i.e. 0-0.1 V more negative than the U^{3+} and Mg^{2+} reduction peak). The sampled current was assumed to be additive. Thus, the sampled U^{3+} reduction current was subtracted from the total sampled current at potentials more negative than the Mg^{2+} reduction potential to obtain the sampled Mg^{2+} reduction current. The trend of the U and Mg sampled current with their respective ion concentration is displayed in Figure 15. As in NPV, linearity is maintained over the tested range of concentrations, although the correlation is not as strong.

3.6. Open-Circuit Potential

Thus far, the methods that have been presented involve the correlation between concentration and current. Potential is another measurable signal that can be correlated to concentration. This relationship is given by the Nernst equation, shown below.

$$E = E^o + \frac{RT}{nF} \ln(\gamma_{M^{n+}} x_{M^{n+}}) \quad (6)$$

This version of the Nernst equation assumes an activity of 1 for the deposited metal. The $\ln(\gamma_{M^{n+}})$ term is frequently grouped with E^o to constitute the formal or standard apparent reduction potential ($E^{o'}$). If the activity coefficient (γ) is constant over the concentration range and the ion exhibits Nernstian

behavior, then the open-circuit potential (OCP) will be proportional to the natural logarithm of the mole fraction (x).

The OCP for the U^{3+}/U couple was measured using the CE (i.e. U metal in SS basket) as the WE in a two-electrode cell setup with the RE. This resulted in highly stable potentials with variations below 0.015 mV s^{-1} . The Mg^{2+}/Mg couple's OCP was measured by pre-depositing U and Mg onto the WE at a fixed current and then setting the cell current to zero, except when $MgCl_2$ was the only analyte, in which case a Mg rod in a SS basket was used to measure the OCP. As shown in Figure 16, two plateaus are formed during deposition and OCP measurement. The a and a' plateaus correlate to the deposition of U^{3+} and OCP of U^{3+}/U , respectively. Likewise, the b and b' plateaus correlate to the deposition of Mg^{2+} and OCP of Mg^{2+}/Mg , respectively. The b' plateau was not completely flat; therefore, the inflection point of the plateau was used to determine the OCP of the Mg^{2+}/Mg couple.

The OCP for each couple is plotted against mole fraction in Figure 17. The single-analyte mixtures (nos. 27-29) are also included and indicated by the solid markers. The OCP measurements were converted to the Cl^-/Cl_2 RE scale using data from Yang and Hudson [29]. The regressed slopes of the U^{3+}/U and Mg^{2+}/Mg OCP data are $0.0204 \text{ V} \pm 0.0047 \text{ V}$ and $0.0330 \text{ V} \pm 0.0091 \text{ V}$. The estimated error is based on the 99.5% confidence interval (CI). This results in the calculated electrons exchanged and $E^{o'}$ in Table 3 using the slopes and intercepts, respectively, in Figure 17 and (6). In Figure 17, the single-analyte OCP measurement for U^{3+}/U agrees very well with the binary analyte measurements. Also, in Table 3, the calculated $E^{o'}$ value for U falls in the range of literature values. However, for Mg^{2+}/Mg , the single-analyte measurements are considerably more negative and the $E^{o'}$ value is outside of the range of literature values.

3.7. Concentration Measurements

In order to calculate the concentration from electrochemical measurements, the diffusion coefficient (D) and $E^{o'}$ need to be known. $E^{o'}$ was calculated for U and Mg in the previous section and

values in Table 3 are used with (6) to calculate the mole fraction of U^{3+} and Mg^{2+} in each mixture. The diffusion coefficients can be calculated for CV, NPV and CA measurements by using the slopes in Figures 8, 13, and 15 with (1), (4), and (5), respectively. The calculated diffusion coefficients (D) are reported in Table 4 with literature values for comparison. D values for CA and NPV are in good agreement with each other, but are significantly higher than the CV D values. The D for Mg^{2+} determined by using CV is in good agreement with the literature, but the CV value for U^{3+} is slightly lower.

The concentration was calculated for each binary-analyte mixture by using the measured OCP from each mixture, then n and $E^{o'}$ values from Table 3 in (6) or the peak current (CV), diffusional current (NPV), or sampled current (CA) from each mixture and the diffusion coefficients from Table 4 in (2), (4), or (5), respectively. The error of the concentration determined from electroanalytical measurements was determined relative to the ICP-AES measured concentration. The distribution of this relative error is plotted in Figure 18. The 2nd and 3rd quartiles are represented by the gray and white boxes. The bars (or whiskers) on the end represent the minimum and maximum values. The average is indicated by the black line with “x” markers. As can be seen, CV and NPV have the lowest median values. On average, CV error is 14.8% for U^{3+} and 10.6% for Mg^{2+} and NPV error is 11.4% for U^{3+} and 9.81% for Mg^{2+} .

4. Discussion

4.1. Cyclic Voltammetry

The base subtraction method employed to determine the Mg^{2+} reduction peak current may introduce some error depending on the behavior of U^{3+} reduction current after the commencement of the Mg^{2+} reduction peak. The U^{3+} current could continue to decay, if diffusion continues to control the current. It could also flatten out, if natural convection begins to control the current. Lastly, it could increase, if sufficient U has deposited to cause the WE area increase. By keeping the scan rate sufficiently fast, the last option can be eliminated.

The effect of the residual U current on the Mg peak will be most pronounced at high UCl_3 concentrations due to the formation of larger peaks with broader tails and at high scan rates due to the limited time allowed for the U current to decay before the formation of the Mg peak. Mix no. 25 has one of the highest concentrations of UCl_3 . For the analysis of Mg^{2+} reduction peaks, the scan rate was limited to 300 mV s^{-1} or less. Thus, Figure 19 portrays one of the worst-case scenarios for possible error introduced using the base subtraction method. As shown by the dashed line in Figure 19, the base subtraction method assumes a flat baseline or natural convection control. However, if diffusion continues to control the current, then the decay would continue, as shown by the grey, dotted line. The difference between the peak heights based on these two baselines is 8.9%.

SD peaks do not appear to be a reliable way to correlate concentration to current in this system due to the scatter and curvature in Figure 10. This may be the actual behavior of the ions which is convoluted in measured current, but revealed upon filtering out background with semi-differentiation. However, this may be an artifact of the amplified noise and/or smoothing process. SD peaks could possibly be used, if the noise in the measured current is minimized. Minimal noise was present in semi-differentiated Gd^{3+} and La^{3+} reduction peaks which required no smoothing [5]. This may be due to the use of a thin Pyrex membrane for the RE, as opposed to the 1 mm thick mullite membrane used in this work.

4.2. Normal Pulse Voltammetry and Chronoamperometry

As noted, CA resulted in significantly weaker correlations to concentration and, therefore, was less accurate. This may be due to a decreased ratio between relaxation and reduction time. In NPV the ions were reduced for 0.25 s and then the cell relaxed for 4.75-14.75 s yielding relaxation-to-reduction ratios from 19 to 59. In CA, reduction occurred for 2 s and relaxation for 20 s—a ratio of only 10. This decreased ratio may have resulted in inconsistent renewal of the diffusion layer and/or WE surface. Nonetheless, if CA can be properly tuned, it could be coupled with NPV to reduce turnaround time while maintaining similar accuracy. NPV could be used to identify the two appropriate potentials to apply for

U^{3+} and Mg^{2+} reduction. Then CA could be repeatedly applied at each of the potentials for 0.25 s with a 15-60 s relaxation period in between reduction.

4.3. Open-Circuit Potentials

Based on Figure 17 and Table 3, it appears that the OCP for U^{3+}/U is unaffected by presence of $MgCl_2$, but the OCP for Mg^{2+}/Mg is affected by the presence of UCl_3 . This may be due to the interaction of U^{3+} and Mg^{2+} ions or U and Mg metal deposits. However, the increase in OCP in the presence of UCl_3 is mostly likely due to the procedure employed. The single-analyte mixtures allowed the OCP to be measured using pure metal as the WE. However, in binary-analyte mixtures, a pure Mg rod could not be used to measure the OCP of Mg^{2+}/Mg because U^{3+} would immediately corrode the rod drastically altering the salt mixture composition. Hence, U and Mg were co-deposited on to a W rod in an attempt to measure the OCP of Mg^{2+}/Mg .

Because uranium is present in the pre-deposited metal and the salt, the Mg^{2+}/Mg current is not truly zero; rather it is equivalent to and opposite of the uranium current. If Mg is present on the WE, then the WE potential is much more negative than U^{3+}/U equilibrium potential creating a reducing current for U. Since the Mg current is equal and opposite of that generated by U, then Mg is oxidizing at a rate that would create a cell current of zero which requires a potential more positive than the Mg^{2+}/Mg equilibrium potential. Thus, the OCP for Mg^{2+}/Mg is skewed in binary-analyte mixtures. However, the $E^{o'}$ values for mixture nos. 28 and 29 are respectively -2.850 and -2.817 V vs. Cl^-/Cl_2 which is in better agreement with the literature values in Table 3. This demonstrates the need to further refine the OCP measurement for the more active ion(s). The selection criteria for identifying the potential plateau value may need to be reconsidered. For example, the commencement of the plateau may be better because more of the WE is covered by Mg at that point. Ultimately, isolating the ion of interest by a selective membrane [30] may be necessary for an accurate OCP measurement of the more active ion(s).

4.4. Diffusion Coefficient of U^{3+}

The low D value for U^{3+} in Table 4 may be due to the recent observation that the increase in CV peak height magnitude diminishes as the concentration of U^{3+} increases above 2 wt% U^{3+} (2.9 wt% UCl_3 , 0.14 mol L^{-1}) [2,17]. This effect may not have been perceptible in Figure 8 due to the limited concentration range ($<5 \text{ wt\% } UCl_3$) and the scatter in the data. If only concentrations less than 2.9 wt% UCl_3 are used, then a diffusion coefficient of $1.09 \pm 0.023 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is calculated which agrees with the value from [17] within 0.035%. However, in order to evaluate and compare each electroanalytical method over the entire concentration range tested, the diffusion coefficient of $0.917 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was used to correlate the concentration to CV peak height.

4.5. Concentration Measurements

Due to the exponential relationship between concentration and potential, there was a wide distribution of errors for OCP measurements in Figure 18, particularly in the case of Mg^{2+} . This is mostly likely caused by shifts in the reference potentials. These experiments took place over the course of months and three REs were used. Efforts were made to construct each electrode identically. However, by comparing the upper (chlorine evolution/tungsten dissolution) and lower (lithium deposition) limits of the electrochemical window, it was observed that there was a shift in potentials between each reference. This shift was quantified by aligning the upper and lower limits and taken into account when developing the correlations in Figure 17. However, this shift could have been slightly undercompensated or overcompensated. Furthermore, the thermal cycling and prolonged use of the REs likely resulted in a gradual change in $AgCl$ composition. Thermal gradients can lead to the deposition of silver [31] and condensation of vaporized salts on the wall of the mullite tube. This can cause shifts in the potential despite using the same RE. Hence, the development of a highly stable RE for molten salt mixtures is vital to the use of OCP as a real-time, in situ concentration monitor.

The higher error of CA can be explained by the earlier discussion of an insufficient relaxation period. CV and NPV can be further improved by reducing the error in the WE surface area measurement

and allowing more settling time between measurements. The extrapolation of y-intercept from measured data, as demonstrated in Figure 2, may have introduced significant error. For example, the standard error on the y-intercept in Figure 2 was 0.9 mm which results in 99.5% CI of 4.5 mm on the y-intercept. The possible error in the WE area is evidenced by the U^{3+} and Mg^{2+} reduction peak heights in mixture nos. 5-8 and 20-25, respectively, in which the concentration of U^{3+} and Mg^{2+} ions was varied, but the WE was fixed at the same position and undisturbed. The reduction peak heights from mixture nos. 5-8 and 20-25 are plotted for U^{3+} and Mg^{2+} , respectively, in Figure 20. The trend of peak heights is more strongly correlated with concentration except at the highest concentration point for U^{3+} , but this is expected due to reasons discussed in section 4.4 and is excluded from the regression. Using the regressions and only the data in Figure 20, the average relative error drops to 3.6% and 3.4% for U^{3+} and Mg^{2+} concentrations, respectively, with a maximum of 7.3% for both ions. The error in the WE surface area measurement can be reduced by using the differential area technique [15] or fixing the area of the WE with a compatible insulator [17] and precisely measuring the area a priori. As mentioned, the relaxation period for NPV was initially too short. Prolonging this period resulted in more clear and stable plateaus. A consistent and sufficient relaxation period should improve NPV. If necessary, rotating the WE between pulses may also help to more completely renew the diffusion layer.

4.6. Data Comparison

Other studies [2,14,17] have performed CV measurements over a similar range of UCl_3 concentrations, but with only UCl_3 as an analyte in LiCl-KCl eutectic. The normalized CV peak current from this study is plotted with the other studies in Figure 21. Although there is more variance in this data, it is scattered around a similar trend. This further affirms that the presence of $MgCl_2$ at the concentration levels in this study had a minimal effect on the electrochemistry of UCl_3 .

5. Conclusions

The reduction of Mg^{2+} was found to be electrochemically reversible in eutectic LiCl-KCl up to 300 mV s^{-1} at 773 K. MgCl_2 was established as a good electrochemical surrogate for PuCl_3 which is needed for experimental study of used nuclear fuel electrorefiner salts outside of nuclear facilities. The surrogacy of MgCl_2 also enabled a broad range of concentrations to be tested. CV, NPV, CA and OCP measurements were applied to 26 binary-analyte mixtures. Diffusion coefficients and apparent standard reduction potentials were calculated from the aggregate data and then used to predict the concentration from each mixture. On average, NPV resulted in the lowest error and OCP yielded the highest error. The presence of MgCl_2 did not significantly affect the electrochemical measurements of UCl_3 . However, the presence of UCl_3 interfered with the electrochemical signals of MgCl_2 . In NPV and CA, the current from UCl_3 could simply be subtracted from total current at potentials inducing the diffusion-limited reduction of Mg^{2+} . CV was more complicated due to the decaying tail of the U^{3+} reduction peak. Semi-differentiation was used to establish zero baselines, but resulted in peak heights with a non-linear dependence on concentration and higher degree of variance. The subtraction of the U^{3+} reduction current at the base of Mg^{2+} reduction was found to yield a better correlation of Mg^{2+} peak currents to concentration. The accuracy of the electroanalytical measurements of concentration can be improved by more precise measurement or control of the WE area, longer relaxation periods between measurements and the development of a more stable reference electrode.

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Figure 1: Illustration of electrochemical cell

Table 1: ICP-AES measured concentration of UCl_3 and MgCl_2 in each mixture

			Binary-Analyte Mixtures						Single-Analyte Mixtures		
Mix No.	UCl_3 (wt%)	MgCl_2 (wt%)	Mix No.	UCl_3 (wt%)	MgCl_2 (wt%)	Mix No.	UCl_3 (wt%)	MgCl_2 (wt%)	Mix No.	UCl_3 (wt%)	MgCl_2 (wt%)
1	1.07%	0.23%	10	4.06%	0.74%	19	2.23%	0.40%	27		1.17%*
2	0.68%	0.27%	11	4.14%	0.98%	20	2.44%	0.25%	28		0.23%
3	0.79%	0.51%	12	4.09%	1.30%	21	3.56%	0.23%	29	0.99%	
4	0.61%	0.70%	13	1.57%	1.23%	22	4.29%	0.25%			*ICP-MS
5	1.51%	0.23%	14	2.78%	1.29%	23	4.24%	0.51%			
6	2.57%	0.25%	15	3.39%	1.26%	24	4.59%	0.80%			
7	3.42%	0.25%	16	1.92%	0.50%	25	4.42%	1.31%			
8	4.45%	0.24%	17	2.68%	0.72%	26	3.12%	1.01%			
9	4.10%	0.50%	18	3.45%	0.87%						

Figure 2: Immersion depth determination using the change in WE immersion depth (Δh) for mixture no. 19 (2.23 wt% UCl_3 , 0.40 wt% MgCl_2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = Mg Rod in SS basket)

Table 2: Immersion depth of WE in each mixture

Mix No.	Depth (mm)	Mix No.	Depth (mm)	Mix No.	Depth (mm)	Mix No.	Depth (mm)
1-4	12.37	13-15	12.7	19	15.17	27	13.00*
5-8	12.46	16-17	13.17	20-25	15.66	28	9.71
9-12	11.15	18	11.14	26	14.82	29	12.8

*Based on adhered salt measurement

Figure 3: Cyclic voltamogram of MgCl_2 (0.23 wt%) in LiCl-KCl eutectic at 300 mV/s (WE = 2 mm W rod, CE = Mg Rod in SS basket, Area = 0.64 cm^2 , $T = 773 \text{ K}$)

Figure 4: Trend of Mg^{2+} reduction peak current with the square root of scan rate (v) for mix no. 28 (0.23 wt% MgCl_2 , $T = 773 \text{ K}$, WE = 2 mm W rod, Area = 0.64 cm^2 , CE = Mg Rod in SS basket)

Figure 5: Trend of the IR-adjusted ($R_u = 0.37 \Omega$) Mg^{2+} reduction peak potential with the logarithm of scan rate (v) for mix no. 28 (0.23 wt% MgCl_2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = Mg Rod in SS basket)

Figure 6: Comparison of U^{3+} and Pu^{3+} reduction peaks measured by ANL [2] to U^{3+} and Mg^{2+} reduction peaks from mixture no. 4 (50 mV s^{-1} , $T = 773 \text{ K}$)

Figure 7: Cyclic voltammograms of $MgCl_2$ in LiCl-KCl eutectic at 100 mV s^{-1} and 773 K with and without UCl_3 added (WE = 2 mm W rod, CE = U metal in SS basket)

Figure 8: Correlation of CV peaks with U^{3+} and Mg^{2+} concentration at 773 K

Figure 9: Semi-differentiated (SD) current with original current overlay for mix no. 25 at 250 mV s^{-1} (4.42 wt% UCl_3 , 1.31 wt% $MgCl_2$, Area = 1.02 cm^2 , 773 K , WE = 2 mm W rod, CE = U metal in SS basket)

Figure 10: Trend of semi-differentiated (SD) peak current with concentration for U (left) and Mg (right) at 773 K

Figure 11: NPV measurement from mix no. 14 (2.78 wt% UCl_3 , 1.29 wt% $MgCl_2$) with $t_p = 0.25 \text{ s}$, $t_i = 15 \text{ s}$, $E_b = -0.75 \text{ V}$ (Area = 0.83 cm^2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 12: Differentiated NPV measurement with non-zero baseline for Mg peak (0.79 wt% UCl_3 , 0.51 wt% $MgCl_2$, $t_p = 0.25 \text{ s}$, $t_i = 5 \text{ s}$, $E_b = -0.75 \text{ V}$, Area = 0.81 cm^2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 13: U^{3+} and Mg^{2+} diffusional current densities regressed with concentration ($t_p = 0.25 \text{ s}$, $T = 773 \text{ K}$, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 14: Chronoamperograms at varying applied potentials versus an Ag/AgCl(5 mol%) RE in mix no. 12 (4.09 wt% UCl_3 , 1.30 wt% $MgCl_2$, Area = 0.73 cm^2 , $T = 773 \text{ K}$, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 15: Correlation of CA current density sampled at 0.25 s with U^{3+} and Mg^{2+} concentration (T = 773 K, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 16: OCP measurement with pre-deposition of U and Mg (inset) on WE at 0.32 A (area = 1.02 cm²) in mix no. 25 (4.42 wt% UCl_3 , 1.31 wt% $MgCl_2$, T = 773 K, WE = 2 mm W rod)

Figure 17: OCP for the U^{3+}/U and Mg^{2+}/Mg redox couple regressed with respect to mole fraction (T = 773, $E[Ag/AgCl(5 \text{ mol}\%)] = -1.071 \text{ V vs } Cl^-/Cl_2$ [29])

Table 3: Calculated number of electrons exchanged and apparent standard potentials from OCP data in Figure 17

Redox Couple	<i>n</i>	$E^{o'}$ (V vs Cl^-/Cl_2)	Literature Values (V vs Cl^-/Cl_2) at 773 K		
U^{3+}/U ($\pm 99.5\%$ CI)	2.02 (1.58-2.79)	-2.487 (± 0.026)	-2.453 [9]	-2.491 [11]	-2.514 [12]
Mg^{2+}/Mg ($\pm 99.5\%$ CI)	3.26 (2.65-4.22)	-2.783 (± 0.053)	-2.850 [8]	-2.796 [23]	

Table 4: Calculated diffusion coefficients at 773 K with literature values

Ion	Technique	$D (\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \pm 99.5\% \text{ CI}$	Literature Values ($\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) at 773 K			
U^{3+}	CV	0.917 ± 0.0022	0.980 [10]	2.50 [11]	1.43 [12]	1.09 [17]
	NPV	2.22 ± 0.0066				2.36 [17]
	CA	2.53 ± 0.013				
	CV	1.74 ± 0.0037	1.57 [8]	2.42 [6]	1.26* [7]	
Mg^{2+}	NPV	3.92 ± 0.022				
	CA	3.80 ± 0.039			2.27* [7]	

*Interpolated Values

Figure 18: Box-and-whisker plot of the error of the concentration calculated from electroanalytical measurements relative to the ICP-AES measured concentration

Figure 19: Possible Mg^{2+} reduction peak baselines for mix no. 25 at 250 mV s⁻¹ (4.42 wt% UCl_3 , 1.31 wt% $MgCl_2$, Area = 1.02 cm², T = 773 K, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 20: Reduction peak height correlations with concentration for U^{3+} in mixture nos. 5-8 and Mg^{2+} in mixture nos. 20-25 in which the WE position was undisturbed between UCl_3 and $MgCl_2$ additions (T = 773 K, WE = 2 mm W rod, CE = U metal in SS basket)

Figure 21: Comparison of CV measurements of UCl_3 in eutectic LiCl-KCl at 773 K with MgCl_2 present and without MgCl_2 [2,14,17]

Current (A)

U^{3+}/U Open-Circuit Potential (V vs Cl/Cl_2)

Absolute Value of Relative Error

Three-Electrode Probe

Electrochemical Techniques

Concentration Measurements

Most to Least Accurate
Relative to ICP-MS:

Normal Pulse Voltammetry

Cyclic Voltammetry

Chronoamperometry

Open-Circuit Potential

Electrochemical
Measurement Accuracy
Improvement:

WE Surface Area

Optimization of Wait Times