Measurement and Analysis of Exchange Current Density for U/U^{3+} Reaction in LiCl-KCl Eutectic Salt via Various Electrochemical Techniques

Dalsung Yoon and Supathorn Phongikaroon

Abstract

Electrochemical impedance spectroscopy (EIS), linear polarization (LP), Tafel and cyclic voltammetry (CV) were performed to investigate the exchange current density (i_0) of U/U^{3+} reaction in LiCl-KCl eutectic salt under different UCl_3 concentrations (0.5 wt% - 4 wt%) and temperature conditions (723 K – 798 K). The EIS spectra were measured by applying minimum overpotential from equilibrium potential and fitted to the proposed equivalent circuit. From the EIS experiments, the calculated values of i_0 were ranging from 0.0054 A cm^{-2} to 0.102 A cm^{-2} . For the LP and Tafel methods, i_0 values were determined from the linear fitting at small and large overpotential ranges of the current-potential curves. The measurement for i_0 via CV was done analogously to the LP method. All i_0 values have the linear trend with the change of concentration and temperature; however, these values measured by LP, Tafel, and CV methods are greatly influenced by the change in electrode surface area. Overall, i_0 agreed within 33% relative error range with the EIS method being the most consistent and accurate in comparison to reported literature values. Dimensionless analysis was done on the EIS data sets providing insightful correlations for prediction of i_0 under various experimental conditions.

1. Introduction

Studies on pyroprocessing technology have been stimulated in several countries including the United State, Russia, France, Japan, South Korea, and India. [1-2]. The main purpose of this advanced technology is not only to treat the irradiated nuclear fuel, but to reduce volume of the nuclear waste, recycle actinides, and close the fast reactor fuel cycle [2]. Therefore, increasing interests in the development of pyroprocessing technology with variety applications are expected. However, compared to the aqueous reprocessing methods such as PUREX, pyroprocessing is performed with discrete steps [3]. The products and wastes from each process container are handled as a discrete package and transported between the process steps [2-3]. This may result in accumulations of special nuclear materials (SNM) in the process or unaccounted loss of SNM; therefore, pyroprocessing facility needs to be adequately safeguarded for guarantee of non-proliferation of SNM. Also, International Atomic Energy Agency (IAEA) in charge of international safeguards has emphasized the development of technology for nuclear material accountability in pyroprocessing applications [3].

In pyroprocessing, the most important process to safeguards is an electrefiner (ER) where uranium and minor actinides are separated on electrode surface while rare earth fission products are accumulated in LiCl-KCl eutectic salt [4]. Therefore, in order to develop ER safeguards, several researchers have studied various electrochemical methods to quantify uranium and actinide materials in LiCl-KCl molten eutectic salt systems in near-real time [5-7]. Kim et al. in 2014 [5] employed cyclic voltammetry (CV) and chronoamperometry (CA) to develop a real-time monitoring system for pyroprocessing. They found a good linearity of current and the passed charges with concentration of NdCl_3 solutes up to 9 wt % in LiCl-KCl salt. Tylka and co-workers [6-7] concluded that CV was a good tool for real-time quantitative

analysis, and U and Pu concentrations were precisely quantified up to approximately 2 wt%. In addition to the experimental efforts, computational models for ER have been actively developed in order to predict the material distribution in the system [8-11]. Zhang [8-9] developed kinetic models for the ER which could be applied to identify the kinetic features of materials flow in the system. Rappleye et al. [10-11] developed various simulation techniques to monitor the solid product on cathode electrode and predict U and Pu concentrations in the ER.

For the advancement of the safeguard technologies, it is necessary to build fundamental database for SNM, which will enhance kinetic models and the real-time monitoring technologies [12]. Particularly, uranium is the most abundant element in reprocessing paths; thus, the assessment of fundamental features must be accurately done. For the pyroprocessing applications, kinetic, thermodynamic, and electrochemical properties of uranium should be necessarily known in LiCl-KCl salt and documented with different conditions. Despite numerous studies on kinetic, thermodynamic, and electrochemical features in LiCl-KCl eutectic salt [13-17], an exchange current density (i_0) of uranium has not been fully explored and understood. The i_0 is a criterion of the reaction rate on the electrode, which plays a significant role in electrochemical equations and expressions; hence, the measurement and collection of i_0 for U^{3+}/U reaction in LiCl-KCl are extremely crucial for developing the kinetic models and near-real time monitoring system for pyroprocessing technology.

In 2009, Choi et al. [18] reported their measured i_0 of uranium (approximately 3.3 wt% UCl_3 in LiCl-KCl) via a linear polarization (LP) method and these values range from 0.0202 A cm^{-2} to 0.0584 A cm^{-2} and, varied with respect to the electrode material. Ghosh et al. [19] used Tafel plot and determined the value of i_0 at 8 ± 2 mA cm^{-2} . Rose and co-investigators [20] calculated the i_0 of uranium (5 wt % of UCl_3 in LiCl-KCl) by using pre-Tafel region data,

1
2
3
4 69 ranging from $69.5 \pm 9 \text{ mA cm}^{-2}$ to $220 \pm 32 \text{ mA cm}^{-2}$. The most recent data sets were reported by
5
6
7 70 Lim and co-workers in late 2015 [21] providing the measured values via both LP and Tafel
8
9 71 methods in LiCl-KCl-1wt% UCl_3 . The results from both techniques indicated a good agreement
10
11 72 with various scan rate between 0.005 V s^{-1} and 0.1 V s^{-1} and the values of i_0 were reported to be
12
13 73 $18.5 \pm 0.37 \text{ mA cm}^{-2}$ at 773 K. To the best of our knowledge, only these values are available
14
15
16 74 from the literature survey, which are not sufficient to understand the nature of U/U^{3+} reaction in
17
18
19 75 LiCl-KCl salt system. Furthermore, these literatures used different scales of electrochemical cell,
20
21 76 electrodes, and solute concentrations; therefore, resulting data values were scattered and an entire
22
23
24 77 trend of i_0 according to various temperatures and concentrations was difficult to fully
25
26 78 comprehend.

27
28
29 79 In this work, the exchange current density values of U/U^{3+} reaction were examined in
30
31
32 80 LiCl-KCl eutectic salt. For the confidence of the data, four different electrochemical methods—
33
34 81 LP, Tafel plot, electrochemical impedance spectroscopy (EIS), and CV—were performed, and
35
36
37 82 their results of the i_0 values were compared. In addition, the properties were determined at
38
39 83 different concentrations from 0.5 wt% to 4 wt% at temperatures ranging from 723 K to 798 K for
40
41 84 evaluating concentration and temperature effects on the i_0 of U/U^{3+} reaction. Based on the results,
42
43
44 85 dimensional analyses were done to provide an estimation of the i_0 of U/U^{3+} couple in the
45
46 86 concentration and temperature ranges. By providing a full integrated data on i_0 for U/U^{3+} in LiCl-
47
48
49 87 KCl, this current study will help to understand U/U^{3+} behaviors in LiCl-KCl salt system and
50
51 88 develop technologies for real-time material accountability in the ER.

52 53 54 89 55 56 57 90 **2. Experimental**

All sample preparations and electrochemical measurements were carried out in a glove box system (Innovative Technologies, Figure 1(a)) in which oxygen and water level were controlled under 5 ppm. For melting and maintaining electrolyte at desired temperatures, Muffle furnace (Thermo Scientific) was purchased and remodeled for the electrochemical applications as shown in Figure 1(b). LiCl-KCl- UCl_3 salts were loaded into an Inconel® crucible (Inconel 601 alloy, nickel-chromium-iron alloy from Alfa Aesar), which was placed in a secondary alumina crucible inside of the furnace as shown in Figure 1(c). Then, the salt was melted at desired temperatures, and an electrode assembly (see Figure 1(d)) including cathode, anode, reference, and the sheathed thermocouple was lowered into the molten salt from the top of furnace. The schematic setup of electrochemical cell inside of the furnace is illustrated in Figure 2. The salt temperature was monitored by using the inserted thermocouple and maintained within one degree deviation from the desired temperature. Once the electrochemical cell and electrodes were prepared, electrochemical measurements were performed using a VSP-300 potentiostat/galvanostat from Biologic Science Instrument.

Using a precision balance (Mettler Toledo, $< 1 \mu\text{g}$), anhydrous lithium chloride (LiCl, 99.995%, Alfa Aesar) and potassium chloride (KCl, 99.95%, Alfa Aesar) were weighed and mixed to prepare a LiCl-KCl (58.2:42.8 in mol%) eutectic salt. Once pure LiCl-KCl eutectic salt was prepared in the Inconel crucible, a certain amount of 73 wt% uranium chloride (UCl_3 , provided by Idaho National Laboratory (INL)) was added to make a desired concentrations (0.5 wt%, 1 wt%, 2 wt%, and 4 wt% of UCl_3 in LiCl-KCl eutectic salt). While each experiment was carried out, the salt sample was taken from the electrolyte bath and quantitatively analyzed by an Agilent 7900 inductively coupled plasma-mass spectrometry (ICP-MS), as shown in Figure 1(e). The small pieces of salt sample were dissolved into 2 wt% HNO_3 acid and diluted into the

concentration ranging from $10 \mu\text{g L}^{-1}$ to $20 \mu\text{g L}^{-1}$ in preparation prior ICP-MS analyses. The analyzed concentrations for the experimental sets are summarized in Table 1.

A tungsten rod (2 mm in diameter from Alfa Aesar) was used as the working electrode. The geometric surface area was determined by measuring length of the working electrode submerged into the salt via a digital caliper (± 0.04 mm). By obtaining nearly the same CV curves at the beginning and ending of each experiment, it was assumed that the surface area has no significant effect in the measurement. Definitely, there was a possibility that the effect might be coming from a possible layer of salt built up on to the submerged working electrode; however, this was not being observed and considered minimal in this study. The electrode surface area on each experimental run is also listed in Table 1. For maintaining the salt electrolytes at the same concentration during the electrochemical measurements, a uranium metal was used as a counter electrode. The depleted uranium plates were (provided by INL) were first chopped and loaded into a molybdenum anode basket. Silver-silver chloride (Ag/AgCl) was used as the reference electrode. Silver wire (1 mm in diameter, Alfa Aesar) was contacted with LiCl-KCl-1 mol% AgCl (Alfa Aesar, 99.998%) in a 7 mm diameter Pyrex® tube (Research glass). At the tip of the Pyrex tube, the thickness of the wall was made extremely thin allowing ionic conduction between the solution and electrolyte. Between electrochemical measurements, the working electrode was anodically cleaned at -0.45 V (vs. Ag/AgCl reference), and polished by fine sand paper in case of necessity. The K type thermocouple was sheathed into the Pyrex tubing and the top of the sheath was blocked with Teflon tape to prevent heat loss.

3. Results and Discussion

For the measurements of i_0 for U/U^{3+} reaction, four electrochemical techniques including EIS, LP, Tafel, and CV were explored in the salt samples listed in Table 1 at the temperature of 723 K, 748 K, 773 K, and 798 K. Prior to the measurements, the equilibrium potential of U/U^{3+} was measured at the temperature range through an open circuit potential (OCP). The U metals were first deposited on the working electrode by applying negative potential at -1.6 V versus Ag/AgCl reference and then OCPs were obtained. The resulting equilibrium potentials are summarized in Table 2. The results of i_0 measurement from each technique are shown and discussed in Sections 3.1 to 3.3, and the comparison and further discussion are done in Section 3.4.

3.1 Electrochemical impedance spectroscopy (EIS)

EIS is a technique to measure the cell/electrode impedance as a function of the frequency [22]. This is useful to understand the electrode process with respect to contributions from diffusion, kinetics, double layer, and reactions [23]. Especially, from the charge transfer resistance at the electrode, the exchange current density of the ion transfer can be calculated. For a proper measurement of i_0 , the EIS measurements should be performed at an equilibrium potential of U/U^{3+} . However, a tungsten rod was used as the working electrode in the present work, so that the electron transfer does not occur at the equilibrium potential. Therefore, minimum overpotential must be applied to the working electrode forcing U reduction to the tungsten electrode. Then, a charge transfer feature can be measured via impedance spectra. This minimum overpotential method was used in previous study [12], in which i_0 for Ce/Ce^{3+} in LiCl-KCl was successfully determined at different concentrations and temperatures. Figure 3 illustrates a procedure for finding minimum overpotential for U/U^{3+} reaction for UCl_3 -0.5 salt at

748 K. While the impedance infinitely increased at the equilibrium potential, a semicircle associated with double-layer capacitance at the electrode started showing with increasing the overpotential. At -1.499 V versus the Ag/AgCl reference electrode, a diffusion related impedance (Warburg impedance) was being observed at a low frequency, on which the Warburg slope is very steep due to the difficulty of the diffusion at the minimum overpotential. If the overpotential was further increased, the phase angle of Warburg impedance would become smaller (see Figure 3(a)). For the verification of the stable charge transfer kinetic at the minimum overpotential, different potential amplitudes were applied ranging from 5 mV to 10 mV, and the impedance spectra displayed a good agreement (as shown in Figure 3(b)).

All EIS measurements used the frequency ranging from 50 kHz to 0.1 Hz, and the obtained impedance spectra were fitted to an equivalent circuit as indicated in Figure 4. The R_s is the solution resistance and R_{ct} is the charge transfer resistance which occurs on the electrode surface. The double-layer capacitance was expressed as the constant phase element (CPE_1) and the diffusion related impedance was represented with CPE_2 and Warburg impedance (W) in parallel. Resistance and capacitance, diffusion impedance, or its combinations can be represented by the CPE which is expressed as [24]

$$Z_{CPE} = \frac{1}{\zeta(j\omega)^\phi} \quad (1)$$

where ζ is the constant in $F\ cm^{-2}\ s^{\phi-1}$, ϕ is the number constant between -1 and 1, and ω is the frequency. The obtained impedance spectra were first analyzed through randomize and simplex method in Z-fit software (Bio-Logic), then each component of the equivalent circuit was manually adjusted. Figure 5 illustrates the measured and fitted impedance spectra in the complex plane for all four samples under the different temperature conditions. Small current values were

applied during the EIS measurement ($< 3 \text{ mA cm}^{-2}$), so that the surface area change by uranium deposition is expected to be negligible. However, due to the small current density being passed, the working electrode might not be fully covered by U metal. Future studies would be required to develop a methodology in confirming and maximizing the effective surface area of the EIS method. From the results of curve fitting, charge transfer resistances (R_{ct}) were measured, which could be employed to calculate the value of i_0 and rate constant (k^0 , cm s^{-1}) for U^{3+}/U by using the following relationship as [22]

$$R_{ct} = \frac{RT}{nFi_0} \quad (2)$$

where R is the universal gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K), F is the Faraday constant (C mol^{-1}), and n is the number of electrons transferred. Figures 6(a) and 6(b) show plots of the calculated i_0 values versus temperature and concentration (UCl_3 mole fraction), respectively. The EIS experiments were repeated three to four times with the same experimental conditions to confirm the reproducibility of the results, and the variations of the value are represented as the standard deviations (error bars). The values of i_0 for U/U^{3+} reaction are ranging from 0.0054 A cm^{-2} to 0.102 A cm^{-2} under different concentration and temperature conditions. The values were almost linearly proportional to an increase in the concentration and temperature, slight deviations were observed when the UCl_3 concentration is over 4 wt% in LiCl-KCl .

3.2 Linear polarization (LP) and Tafel methods

LP and Tafel methods are derived from the Butler-Volmer equation which describes the charge transfer kinetics when there is a reaction on the electrode. With an assumption of no mass-transfer effects, the equation is expressed as [22]

$$i = i_0 \left[\exp\left(\frac{\alpha n F}{RT} \eta\right) - \exp\left(-\frac{(1 - \alpha) n F}{RT} \eta\right) \right] \quad (3)$$

where i is the current density (A cm^{-2}), α is the charge transfer coefficient of U^{3+}/U , and η is the overpotential (V) applied to the working electrode. In case of very small overpotential, an exponential term (that is, $\exp(X)$) can be approximated as $1+X$ by Maclaurin series. Thus, Eq. (3) can be simplified to

$$i = i_0 \left(\frac{n F}{RT} \right) \eta \quad (4)$$

representing that the current is linearly proportional to the overpotential in the narrow potential range (typically $\eta < 10$ mV). From the slope of i - η curve, the value of i_0 can be easily calculated by using Eq. (4). When the η is sufficiently large, Eq. (3) can be re-expressed as

$$\ln(i) = \ln(i_0) + \frac{\alpha n F}{RT} \eta \quad (5)$$

Therefore, at a large overpotential region in the Tafel plot, the i_0 value can be measured by fitting the linear Tafel region and obtaining the i_0 at y-intercept on a plot of $\ln(i)$ versus η .

For both LP and Tafel measurements, the potential was swept from -350 mV to 250 mV based on the equilibrium potentials. By scanning in the negative potential with a slow scan rate, the U metal was coated on the electrode. Then, the transient values were explored between the deposited U and the bulk UCl_3 at small overpotential and large overpotential values for LP and Tafel methods, respectively. Figure 7(a) shows an example of current-potential curve in UCl_3 -0.5 salt. The slopes were obtained in the overpotential ranging from -5 mV to 5mV at the

different temperatures, which were employed to calculate i_0 of U/U^{3+} . As mentioned above, Eq. (3) is valid with no diffusion effect; thus, very slow scan rate should be applied for the proper exploration of the charge transfer kinetics. However, at extremely slow scan rates ($< 3 \text{ mV s}^{-1}$), the electrode surface area continued increasing due to the uranium deposition on the electrode. Therefore, LP method was examined with the different scan rates ranging 3 mV s^{-1} to 100 mV s^{-1} . Figure 7(b) illustrates Tafel curves in UCl_3 -0.5 salt at the same temperature range. Here, the linear Tafel regions can be observed at the overpotential from -100 mV to -230 mV , which are fitted to measure the value of i_0 . Unfortunately, the linear Tafel region cannot be acquired at the concentration higher than 1 wt% UCl_3 as shown in Figure 7 (c). This issue is mainly owing to the vigorous U deposition with the high bulk concentrations. Therefore, Tafel plot method was only applied with the scan rates of 3 mV s^{-1} , 5 mV s^{-1} , and 7 mV s^{-1} in UCl_3 -0.5 salt for determining the i_0 of U/U^{3+} pair.

Figure 8 shows the measured values of i_0 by LP method under different scan rates. For UCl_3 -0.5 and UCl_3 -1.0 (Figures 8(a) and 8(b), respectively), the i_0 values rapidly decrease when the scan rates increase from 3 mV s^{-1} to 15 mV s^{-1} while they increase sharply at the scan rate faster than 20 mV s^{-1} . This result signifies that the diffusion limits caused by an increase in the scan rate dominantly affects the kinetic measurements. In contrary, steady decreases can be observed with increasing the scan rate in UCl_3 -2.0 and UCl_3 -4.0 salts as shown in Figures 8(c) and 8(d), respectively. The latter results indicate that the variation of the electrode surface area may contribute an effect on the resulting i_0 due to the U deposition. Therefore, having these challenges, the measured i_0 values appear dispersed at various scan rates. Figure 9 shows all measured i_0 values from LP and Tafel methods. In general, the i_0 values of U/U^{3+} follow the linear relationship with temperature. While the relative errors from the averaged i_0 were less than

10% for both UCl_3 -0.5 and UCl_3 -1.0, these errors went up to 24% in UCl_3 -4.0 salt due to the aforementioned challenges. The effect of the surface area changes becomes problematic on the LP and Tafel measurements. Tafel curves were measured in UCl_3 -0.5 salt, and the i_0 calculated from y-intercept was varying for the scan rates of 3 mV s^{-1} to 7 mV s^{-1} (see the inset graph in Figure 9). Tafel results also show a linear trend with the temperature and agree with the LP result within 20% of relative error range.

3.3 Cyclic voltammetry (CV)

CV is powerful and the most widely practiced among the electrochemical methods [22]. The CV method is analogous to the LP measurement because CV observes current based on the potential change. Only difference from the LP method is that CV is a reversal method executed by higher scan rates. As mentioned in Section 3.2, the results from LP method show the agreement within 24% relative error range under the different scan rates. Therefore, CV curves at both 50 mV s^{-1} and 100 mV s^{-1} were used, and the charge transfer resistance in very small overpotential region was obtained to estimate the values of i_0 for U/U^{3+} . It should be mentioned that this selected scan rate was not considered fast in the CV application; however, this method was being explored to compare with LP method and to assess the applicability for the estimation of i_0 . Figure 10 shows an example of CV curve at 50 mV s^{-1} scan rate in UCl_3 -0.5 salt at 748 K. The potential where the deposited U starts to be oxidized (indicated by red circle in Figure 10) can be found, and the slope from current-potential curve within 10 mV overpotential can be measured, which is the charge transfer resistance. Then, the value of i_0 for U/U^{3+} reaction would be calculated by using Eq. (4). Figure 11 reveals that the value increases when both the concentration and temperature increase; however, it was difficult to observe the linearity from

these results. The discrepancy of CV data would be due to the fact that CV was a technique based on the diffusion limitation, so that the kinetics could be difficult to observe. However, CV method possesses the advantage of the rapid data acquisition through an instant scan rate; hence, this technique would be useful in development of the near-real time technique for the material detection and accountability in the ER system.

3.4 Data comparison and practical analysis

Figure 12(a) shows the results from the four techniques being explored. The i_0 values from EIS measurements show the most linear trends regarding to the concentration and temperature whereas the values measured by CV method are much scattered and do not have a strong linear correlation with the concentration and temperature. Overall, the results from the four methods are in good agreement within 33% relative difference from their average values. Figure 12 (b) shows i_0 results from this work in comparison to the reported i_0 values. Lim et al. [21] provided the equations of the i_0 as a function of the concentration and temperature. By plotting the equations from the literature, the results reside within the range of i_0 from this study. Particularly, EIS measurements for 1 wt% UCl_3 in the present study agree moderately well with those from Lim and co-workers [21]. However, LP results in this study are significantly influenced by the scan rate, which repudates the conclusion from the study of Lim et al. [21] that the scan rate (5 mV s^{-1} - 100 mV s^{-1}) has no significant effect on the i_0 value. Choi et al. [18] measured i_0 of U/U^{3+} at approximately 3.3 wt% concentration at 773 K and reported that the i_0 value measured with a tungsten electrode was 0.0584 A cm^{-2} which located in the vicinity of i_0 measured in this study.

Because the EIS method provides the most linear trends and agreements with other literature data, the results from EIS measurements have been selected for further analysis without considering the deviations (error bars) of the data. For further understanding of k^0 and α values, the following equation was considered [22]:

$$i_0 = nFk^0 C_{\text{UCl}_3}^{(1-\alpha)} C_{\text{U}}^{\alpha} \quad (6)$$

where C represents the concentration at the interface (mol cm^{-3}). In Figure 6(b), the results show linear relationships between i_0 and the mole fraction of UCl_3 ; therefore, the experimental results imply that either α is zero or C_{UCl_3} is the same to C_{U} at the electrode surface (that is, $C_{\text{UCl}_3} \sim C_{\text{U}}$ at equilibrium condition). In general, the parameter α was incorporated directly into Eq. (2) or Eq. (4) for determining the i_0 values in the EIS, LP, and CV methods, but the Tafel method was the available technique for gaining an insight into this parameter by calculating from the obtaining slope of the overpotential (see Eq. (5)). As indicated earlier that due to the buildup content at high UCl_3 cases, Tafel method did not provide an accurate way of getting i_0 values. Only data sets at 0.5 wt% UCl_3 from the Tafel experiments were available and slopes were obtained to calculate α values, ranging from 0.015 to 0.04, which were slightly less than the value of 0.22 reported by Lim et al. [21]. Ghosh et al. [19] reported extremely low α value of U ($\alpha \sim 0.01$) in LiCl-KCl salt. Although their systems were different, it provided that the system in this study might have small charge transfer coefficient at low concentrations. This general analysis led to the assumption that α values are close to zero; thus, Eq. (6) could be simplified to

$$i_0 = nFk^0 C_{\text{UCl}_3}. \quad (7)$$

Figure 13 plotted the i_0 versus C_{UCl_3} at different temperatures. The k^0 values were calculated from the slopes of the i_0 linear trends at different concentrations and summarized in Table 3.

The linear relationships of i_0 in Figures 6(a) and 6(b) were modeled by using a linear equation, $y = ax + b$ (these fitted values are summarized in Table 4). Here, the equations in Table 4 can be used to determine any desired i_0 . These equations were being extrapolated to estimate the i_0 of U/U^{3+} at the 5 wt% concentration under 723 K and 923 K reported by Rose and co-workers [20]. The calculated results reveal that the values of the i_0 are 0.0739 A cm^{-2} ($C = 5 \text{ wt\%}$ (0.00848 mole fraction) and $T = 723 \text{ K}$) and 0.214 A cm^{-2} ($C = 5 \text{ wt\%}$ (0.00848 mole fraction) and $T = 923 \text{ K}$) agreeing well with the values of i_0 reported by Rose et al. [20]. The projection for i_0 value at 5 wt% UCl_3 can be checked in Figure 12(b) (see a line of orange dot). Although literature i_0 values were being measured under different electrochemical scale and cell configurations, the results are in a good agreement (see Figure 12(b)). Thus, it can be postulated that the effect of system scale and configuration has a weak influence on the i_0 kinetics. In order to confirm this argument, a large number of data collections will be required in different electrochemical environments. Also, the i_0 value reported by Ghosh et al. [19] does not follow the general trends of this work. This discrepancy may be coming from the fact that they used uranium metals as working electrode and observed the anodic polarization by dissolution of the uranium metals in LiCl-KCl.

Based on the EIS data, additional temperature and concentration dependences were further investigated. Here, the temperature relationship of kinetic parameters can typically be expressed by Arrhenius equation, $i_0 = I_0 \exp(-E_a/RT)$, where I_0 is the pre-exponential factor for the Arrhenius equation (that is the maximum value of i_0 at infinite temperature), and E_a is the activation energy for U/U^{3+} reaction (kJ mol^{-1}). Figure 14 shows $\ln(i_0)$ versus $1/T$ for all concentrations. From the slopes and y-intercepts, the I_0 and E_a were tabulated and listed in Table 5. Cumberland and Yim [25] also reported the exchange current density by correlating its values

through a combination of the Arrhenius equation and mole fraction to the power of $(1-\alpha)$ from the computational modeling approach. The values from their study ($\alpha = 0.5$) were ranging from 0.032 A cm⁻² to 0.085 A cm⁻² at the concentrations from 0.5 wt% to 4 wt% and the temperature of 773 K, which agreed well with the results reported in this study. Although the E_a value from their study was at 60.4 kJ mol⁻¹, which is in a similar range with those from this study, their I_0 values were considerably high (382 A cm⁻² to 1030 A cm⁻² at concentrations from 0.5 wt% to 4 wt%) based on the assumption of $\alpha = 0.5$. By using the value of $\alpha = 0$ (as suggested in the current study), the calculated exchange current density values from Cumberland and Yim's correlation [25] were ranging from 0.00091 A cm⁻² to 0.0066 A cm⁻² at 773 K, which were smaller than the current experimental data sets by one order of magnitude. Therefore, an examination of i_0 kinetic data between experimental and computational methods needs to be further investigated, which will bring a significant advancement in understanding kinetic parameters of important elements in the ER system.

The dimensionless relationship between i_0/I_0 and $\exp(-E_a/RT)$ can be plotted (see Figure 15(a)), such that the i_0 can be easily estimated when I_0 and $-E_a$ are known. By exploring the reported E_a and I_0 values from Rose et al. and Lim et al. [20-21], the Furthermore, the concentration dependency of i_0 are being explored in Figure 15(b). The dimensionless quantity of $i_0/i_{0, \max}$ were plotted against mole fraction. Here, $i_{0, \max}$ is the i_0 value at 4 wt% UCl₃ which can be found in Table 3. Thus, i_0 quantity can be estimated by simply knowing $i_{0, \max}$ at 4 wt% UCl₃ condition (reported in the present study). The equations for the dimensionless relationships ($i_0/I_0=1.0046 \exp(-E_a/RT)$ and $i_0/i_{0, \max}=155.2 x$) are shown in Figures 15(a) and 15(b), respectively. The fitted equation of $i_0/I_0=1.0046 \exp(-E_a/RT) \approx \exp(-E_a/RT)$ with the R^2 of 0.997 confirms the Arrhenius behaviors within the system. Data from Rose et al. [20] and Lim et al.

[21] were superimposed on Figure 15(a) showing the same trend and confirming Arrhenius behavior for i_0 kinetics in the system. Overall, the i_0 values for U^{3+}/U in LiCl-KCl system can be easily anticipated by using the provided dimensionless relationships; however, the relationship need to be further validated at higher concentrations from 5 wt% to 10 wt% which is a typical range in ER system.

4. Conclusion

EIS, LP, Tafel, and CV techniques were being explored to fundamentally understand the properties of i_0 of U/U^{3+} in LiCl-KCl eutectic salt. The experiments were carried out in different concentrations ranging from 0.5 wt% UCl_3 to 4wt% UCl_3 and temperature from 723 K to 798 K for looking into the concentration and temperature dependence on i_0 properties. In general, the measured data via the four methods agree within 33% relative error range. The EIS method provided the most reproducible results which are linearly dependent on the concentration and temperature. LP and Tafel methods show large deviations with the different scan rates. The change of electrode surface area due to the uranium deposition affects the i_0 properties at slow scan rate. At a higher scan rate, the i_0 values are strongly influenced by the limiting current. For the CV method, the results were similar to that from LP method, but the data sets did not show the linear relationship with either the concentration or temperature. This low to moderate discrepancy between data from CV and EIS measurements indicates that CV may be used as a rapid data acquisition and analysis providing advantage toward the real time material detection and accountability.

Based on the i_0 data measured via EIS technique, further analyses were performed. The dependences with the concentration and temperature were linearly modeled and the equations

1
2
3
4 374 were summarized in Table 4. These correlations confirm that the reported values from literatures
5
6 375 and those from this study are in an excellent agreement (except the data from Ghosh et al. [19]).
7
8
9 376 Arrhenius temperature relationship was used to fit these data sets, from which the maximum
10
11 377 value of i_0 at infinite temperature and activation energy for U/U^{3+} reaction were obtained. The
12
13 378 dimensionless quantities including i_0/I_0 , $\exp(-E_a/RT)$, and $i_0/i_{0,max}$ were plotted and the linear
14
15 379 relationships were obtained. These dimensionless equations can be utilized to estimate the i_0
16
17 380 properties for U/U^{3+} reaction in various experimental conditions.
18
19
20
21 381

22 23 24 382 **Acknowledgments**

25
26
27 383 This study is being performed using funding received from the DOE Office of Nuclear
28
29 384 Energy's Nuclear Energy University Programs (NEUP) in collaboration with the Ohio State
30
31 385 University (NEUP-13-4908) and the VCU Graduate Fellowship.
32
33
34
35 386

36 37 38 39 387 **Reference**

- 40
41 388 [1] M. F. Simpson, Projected Salt Waste Production from a Commercial Pyroprocessing Facility,
42
43 389 Science and Technology of Nuclear Installations, vol. 2013, Article ID 945858, 8 pages,
44
45 390 2013.
46
47
48
49 391 [2] Pyrochemical Separations in Nuclear Applications, A Status Report, NEA No. 5427 (2004).
50
51
52 392 [3] R. Wigeland, T. Bjornard, B. Castle, The Concept of Goals-Driven Safeguards, INL/EXT-09-
53
54 393 15511 (2009).
55
56
57
58
59
60
61
62
63
64
65

- [4] J. J. Laidler, J. E. Battles, W. E. Miller, J. P. Ackerman, and E. L. Carls, Development of Pyroprocessing Technology, Progress in Nuclear Energy, 31 (1997) 131-140.
- [5] D-H Kim, S-E Bae , T-H Park, J-Y Kim, C-W Lee, K. Song, Real-time monitoring of metal ion concentration in LiCl–KCl melt using electrochemical techniques,” Microchemical Journal 114 (2014) 261–265.
- [6] M. M. Tylka, J. L. Willit, J. Parkash, and M. A. Williamson, Method Development for Quantitative Analysis of Actinides in Molten Salts, Journal of The Electrochemical Society, 162 (9) (2015) H625-H633.
- [7] M. M. Tylka, J. L. Willit, J. Prakash, and M. A. Williamson, Application of Voltammetry for Quantitative Analysis of Actinides in Molten Salts, Journal of The Electrochemical Society, 162 (12) (2015) H852-H859.
- [8] J. Zhang, Kinetic model for electrorefining, part I: Model development and Validation, Progress in Nuclear Energy, 70 (2014) 279.
- [9] J. Zhang, Kinetic model for electrorefining, part II: Model applications and case studies, Progress in Nuclear Energy 70 (2014) 287-297.
- [10] D. Rappleye, M. Simpson, R. Cumberland, D. McNelis, M-S Yim, Simulated real-time process monitoring of a molten salt electrorefiner, Nuclear Engineering and Design 273 (2014) 75-84.
- [11] D. Rappleye, S-M Jeong, M. Simpson, Application of multivariate analysis techniques to safeguards of the electrochemical treatment of used nuclear fuel, Annals of Nuclear Energy 77 (2015) 265–272.

- [12] D. Yoon and S. Phongikaroon, Electrochemical Properties and Analyses of CeCl_3 in LiCl-KCl Eutectic Salt, *Journal of The Electrochemical Society*, 162(10) (2015) E237-E243.
- [13] P. Masset, D. Bottomley, R. Konings, R. Malmbeck, A. Rodrigues, J. Serp, and J. Glatz, Electrochemistry of Uranium in Molten LiCl-KCl Eutectic, *Journal of the Electrochemical Society*, 152(6) (2005) A1109-A1115.
- [14] S. A. Kuznetsov, H. Hayashi, K. Minato, and M. Gaune-Escard, Electrochemical transient techniques for determination of uranium and rare-earth metal separation coefficients in molten salts, *Electrochimica Acta*, 51 (2006) 2463-2470.
- [15] O. Shirai, H. Yamana, and Y. Arai, Electrochemical behavior of actinides and actinide nitrides in LiCl-KCl eutectic melts, *Journal of Alloys and Compounds*, 408-412 (2006) 1267-1273.
- [16] J.J. Roy, L.F. Grantham, D.L. Grimmer, S.P. Fusselman, C.L. Krueger, T.S. Storvick, T. Inoue, Y. Sakamura, and N. Takahashi, Thermodynamic Properties of U, Np, Pu, and Am in Molten LiCl-KCl Eutectic and Liquid Cadmium, *Journal of the Electrochemical Society*, 143(8) (1996) 2487-2492.
- [17] R. O. Hoover, M. R. Shaltry, S. Martin, K. Sridharan, S. Phongikaroon, Electrochemical studies and analysis of 1-10 wt% UCl_3 concentrations in molten LiCl-KCl eutectic, *Journal of Nuclear Materials*, 452 (2014) 389-396.
- [18] I. Choi, B. E. Serrano, S. X. Li, S. Herrmann and S. Phongikaroon, Paper 9045 presented at Proceedings of Global 2009, Paris, France, Sept. 6-11 (2009).

- [19] S. Ghosh, S. Vandarkuzhali, N. Gogoi, P. Venkatesh, G. Seenivasan, B. Prabhakara Reddy, K. Nagarajan, Anodic dissolution of U, Zr and U–Zr alloy and convolution voltammetry of $Zr^{4+}|Zr^{2+}$ couple in molten LiCl–KCl eutectic, *Electrochimica Acta*, 56 (2011) 8204-8218.
- [20] M. A. Rose, M. A. Williamson, and J. Willit, Determining the Exchange Current Density and Tafel Constant for Uranium in LiCl/KCl Eutectic, *ECS Electrochemistry Letters*, 4(1) (2015) C5-C7.
- [21] K. Hong Lim, S. Park, and J-I Yun, Study on Exchange Current Density and Transfer Coefficient of Uranium in LiCl-KCl Molten Salt, *Journal of The Electrochemical Society*, 162 (14) (2015) E334-E337.
- [22] A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, New York: Wiley (2001).
- [23] Christopher M. A. Brett and Ana M. O. Brett, *Electrochemistry Principles, Methods, and Applications*, Oxford University Press Inc., New York.
- [24] A. Lasia, *Electrochemical Impedance Spectroscopy and Its Applications*, New York: Springer (2014).
- [25] R. M. Cumberland and M-S Yim, A Computational Meta-Analysis of UCl_3 Cyclic Voltammograms in LiCl-KCl Electrolyte, *Journal of The Electrochemical Society*, 161 (4) (2014) D147-D149.

Tables

Table 1 Electrolyte concentration and working electrode surface area for each experimental run

Experimental	Salt prepared	Analyzed salt by	Mole percent	Electrode surface
runs	(wt%)	ICP-MS (wt%)	(mol%)	area (cm ²)
UCl ₃ -0.5	0.5	0.559	0.0828	0.621
UCl ₃ -1.0	1.0	1.06	0.169	0.723
UCl ₃ -2.0	2.0	2.04	0.334	0.471
UCl ₃ -4.0	4.0	4.04	0.664	0.396

Table 2 Equilibrium potential of U/U³⁺ measured via open circuit potential

Salt sample	Equilibrium potential of U/U ³⁺ in LiCl-KCl [V vs. Ag/Ag ⁺ (1 mol %)]			
	723 K	748 K	773 K	798 K
UCl ₃ -0.5	-1.489	-1.477	-1.465	-1.452
UCl ₃ -1.0	-1.470	-1.457	-1.446	-1.433
UCl ₃ -2.0	-1.451	-1.438	-1.425	-1.410
UCl ₃ -4.0	-1.438	-1.424	-1.409	-1.394

Table 3 Summary of k^0 for U/U^{3+} reaction measured by the EIS method

Temperature	k^0	R^2 from plots in
(K)	$\times 10^3 (\text{cm s}^{-1})$	Figure 13
723	1.048	0.993
748	1.230	0.993
773	1.454	0.995
798	1.827	0.996

Table 4 Linear models for concentration and temperature dependence

Equations			R ²
Temperature (T) dependence of i ₀	UCl ₃ -0.5:	$6.752 \times 10^{-5} T - 0.0436$	0.973
	UCl ₃ -1.0:	$1.221 \times 10^{-4} T - 0.0750$	0.987
	UCl ₃ -2.0:	$2.682 \times 10^{-4} T - 0.1678$	0.932
	UCl ₃ -4.0:	$5.494 \times 10^{-4} T - 0.3393$	0.956
Concentration (C) [*] relationship of i ₀	723 K:	8.823 C	0.993
	748 K:	10.274 C	0.993
	773 K:	12.047 C	0.995
	798 K:	15.012 C	0.996

* The concentration is based on mole fraction.

Table 5 The pre-exponential factors and activation energy for U/U³⁺ based on the data from EIS measurements

UCl ₃ -0.5		UCl ₃ -1.0		UCl ₃ -2.0		UCl ₃ -4.0	
I ₀	E _a	I ₀	E _a	I ₀	E _a	I ₀	E _a
[A cm ⁻²]	[kJ mol ⁻¹]	[A cm ⁻²]	[kJ mol ⁻¹]	[A cm ⁻²]	[kJ mol ⁻¹]	[A cm ⁻²]	[kJ mol ⁻¹]
6.5883	-42.468	3.2368	-32.948	9.0449	-35.011	14.595	-33.119

Figures

Figure 1 (a) Glove box system from Innovative Technologies, (b) Muffle furnace from Thermo Scientific, (c) Inconel crucible placed in safety crucible, (d) electrode assembly, and (e) Agilent 7900 ICP-MS instrument.

Figure 2 Schematic drawing for electrochemical setup inside of Muffle furnace.

Figure 3 (a) Nyquist plots measured in $\text{UCl}_3\text{-}0.5$ salt at 748 K. The applied potential was changed from -1.490 V to -1.510V to find the minimum overpotential. (b) Repetition with the applied potential amplitude ranging from 5 mV to 10 mV at -1.499 V.

Figure 4 Equivalent circuit proposed to express the electrochemical cell, comprising solution resistance, charge transfer resistance, and diffusion related impedance.

Figure 5 The measured and fitted impedance spectra in the salt of (a) $\text{UCl}_3\text{-0.5}$, (b) $\text{UCl}_3\text{-1.0}$, (c) $\text{UCl}_3\text{-2.0}$, and (d) $\text{UCl}_3\text{-4.0}$ at temperature ranging from 723 K to 798 K. Applied potential amplitude was 7 mV, and the chi-square goodness of fit (χ^2) was less than 0.003.

Figure 6 (a) plots the i_0 of U/U^{3+} against temperature for different concentrations, and (b) plots the i_0 of U/U^{3+} versus mole fraction of the of UCl_3 for temperature at 723K, 748K, 773K, and 798K.

Figure 7 (a) Current density versus potential at small overpotential region (< 5 mV) in UCl_3 -0.5 salt; (b) Plot of $\log(i_0)$ versus overpotential in UCl_3 -0.5 salt; and (c) Plot of $\log(i_0)$ versus overpotential in UCl_3 -1.0, UCl_3 -2.0, and UCl_3 -4.0 at 748 K. The scan rate was used at 5 mV s^{-1} .

Figure 8 Plots of i_0 results measured by LP methods under different scan rates for (a) UCl_3 -0.5, (b) UCl_3 -1.0, UCl_3 -2.0, and (d) UCl_3 -4.0.

Figure 9 Plots of i_0 values measured via LP and Tafel methods.

Figure 10 Cyclic voltammogram at the scan rate of 50 mV s^{-1} in UCl_3 -0.5 salt at 748 K.

Figure 11 Plots of i_0 by using CV method for U/U^{3+} in UCl_3 -0.5, UCl_3 -1.0, UCl_3 -2.0, and UCl_3 -4.0 salt at the different temperatures with the standard deviations.

Figure 12 (a) The i_0 values measured by the four different methods in the present study, and (b) the reported values of i_0 for U/U^{3+} from different literature studies are being superimposed.

Figure 13 Plots of i_0 measured by EIS versus concentration (mol cm^{-3}) for the different temperatures.

Figure 14 Natural logarithm of i_0 against the inverse temperature.

Figure 15 (a) i_0/I_0 versus $\exp(-E_a/RT)$, and (b) $i_0/i_{0,max}$ versus mole fraction.