Voltammetric Analysis of Mixtures of Molten Eutectic LiCl-KCl Containing LaCl₃ and ThCl₄ for Concentration and Diffusion Coefficient Measurement

Zhong-hang Wang^{a,b,c}, Devin Rappleye^a, and Michael F. Simpson^{*a}

^a Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, USA

^b National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

Abstract

Several electrochemical techniques, including cyclic voltammetry (CV), chronopotentiometry-open circuit potential (CP-OCP), chronoamperometry (CA) and normal pulse voltammetry (NPV) were applied to the eutectic LiCl-KCl melt containing LaCl₃ and ThCl₄ at 773K. The dependence of diffusion coefficient of La(III) on concentration of LaCl₃ was investigated by using CV, CP and CA. As the concentration of LaCl₃ increases, the $D_{\text{La(III)}}$ value obtained from CV gradually decreases, while the values derived from CA and CP exhibit a dome-shaped variation trend. In the LiCl-KCl-LaCl₃-ThCl₄ system, the diffusion coefficients of La(III) and Th(IV) are both approximately constant regardless of changes in the composition of LaCl₃ and ThCl₄. Concentration correlations were developed for LaCl₃ and ThCl₄ using the normalized CV peak

* Corresponding author. Tel.: +1 (801) 581-4013;

Email address: michael.simpson@utah.edu (M.F. Simpson).

heights in addition to the diffusion-limited relationships for CV, CA and NPV. NPV was found to be superior for the concentration prediction over the range studied in this work.

Keywords: molten salt; voltammetry; nuclear fuel reprocessing; electrorefining

1. Introduction

Pyroprocessing is a technology that has been developed for application to reprocessing spent nuclear fuel [1, 2]. In the pyrochemical process, the electrorefiner (ER) is a key unit operation, in which the spent fuel is anodically dissolved in molten chloride salts, and pure U metal is recovered on a steel cathode [3, 4]. In comparison with other reprocessing methods, pyroprocessing offers several advantages, including compact space requirements, inability to produce material attractive for proliferation, simple waste processing, compatibility with fast reactor fuel recycle, and reduced criticality risk. During the process, the composition of the molten salt bath continuously changes, which presents problems with respect to both process control and safeguards. Implementation of international safeguards protocol is complicated by the hold-up of actinides in the ER, which needs to be constantly monitored to safeguard against proliferation. A desirable feature in a pyroprocessing system would be real-time concentration monitoring of the salt in ER. Conventional techniques for analyzing the salt rely upon sampling and destructive analysis and are, thus, not suitable for real time monitoring. New innovative techniques involving potentiometric and spectroscopic sensors have been proposed for this function, but each has serious technical hurdles to implementation based on materials properties and remote operability [5, 6].

Alternatively, the monitoring method should be designed based on approaches that are compatible with the remote operating environment, high radiation field, high temperature, and inert gas atmosphere. Because the ER is already an electrochemical environment compatible

1
2
3
4 with all of these conditions, electroanalytical techniques utilizing electrode probes are logical
5
6 choices for in situ quantitative measurements of ER salt composition [7]. A number of specific
7
8 voltammetry methods such as cyclic voltammetry [8], normal pulse voltammetry [9], and
9
10 repeating chronoamperometry [10], have been proposed and studied as alternatives for real-time
11
12 monitoring of electrorefiner salt composition. Under conditions of limited concentration ranges,
13
14 each of these methods have exhibited a linear response to solute concentrations [8]. However
15
16 significant loss in responsiveness at high concentration is often observed and has not been
17
18 studied in great deal [8]. Also, the studies published to date have predominately tested simple
19
20 ternary salts (LiCl-KCl plus one additional actinide or lanthanide chloride) and, thus, have
21
22 neglected consideration of potential interferences and other matrix effects for multi-component
23
24 salts.
25
26
27
28
29
30

31 In this paper, we address the challenges involved with making such concentration
32
33 measurements with both an actinide and rare earth element are present in the chlorides melt. In
34
35 this study, we have limited study to LiCl-KCl-ThCl₄-LaCl₃ with the anticipation that the findings
36
37 will inform the further development of the technique for multi-actinide and multi-lanthanide
38
39 mixtures. This study is a part of a larger investigation of quaternary salts featuring two
40
41 actinide/lanthanide ions that both reduce/oxidize within the electric potential window available
42
43 for molten LiCl-KCl. The relatively large difference in standard potentials is representative of
44
45 uranium or thorium in the presence of rare earths. Molten salt electrolyte used for processing
46
47 spent nuclear fuel will include a wide range of lanthanides and actinides. Our larger study is
48
49 aimed at understanding the impact of reduction potential separation on the feasibility of real time
50
51 analysis using voltammetry. In this study of LaCl₃-ThCl₄, a redox potential difference on the
52
53 high end of the spectrum has been investigated. In theory, this should be the easiest multi-
54
55
56
57
58
59
60
61
62
63
64
65

component system to analyze via voltammetry. Fundamental electrochemical process mechanisms were studied, diffusion coefficients were calculated, and different approaches for calculating concentration were attempted and compared to actual values.

2. Experimental

2.1. Chemicals/Materials

Salt mixtures were prepared by weighing out known masses of anhydrous lithium chloride/potassium chloride eutectic beads (SAFC-Hitech, 99.99%), anhydrous lanthanum chloride (Alfa Aesar, 99.99% (REO)), and thorium chloride (Fisher Scientific, purified). The thorium chloride had absorbed water during storage and required purification prior to use. The purification process is described in detail below. Thorium metal (International Bio Analytical Industries, Inc., Part No. T-1002-50) was obtained in the form of chips for use as a counter electrode in voltammetry tests. For preparation of reference electrodes, silver chloride (Strem Chemicals, 99.9%) was obtained in a brown glass bottle and was stored in a dark paper box to protect it from light-induced degradation. After receipt, all chemicals were stored and handled in a dry atmosphere argon glovebox (Innovative Technologies, PureLab HE 4) typically maintained with H_2O and O_2 concentrations of less than 1 ppm.

The melt of LiCl-KCl-LaCl_3 was prepared by directly adding a predetermined amount of LaCl_3 powder into the LiCl-KCl eutectic beads followed by heating the mixture to 500°C in an auto electro-melt furnace (Kerr, No. 35224).

The thorium chloride was dried at $100\text{-}110^\circ\text{C}$ for multiple days in a muffle furnace (MTI Corporation, 1100X) located in the argon atmosphere glove box. Based on thermodynamic

properties, it was predicted that some of the thorium chloride would convert to thorium oxide (ThO_2) during the drying process. The dried mixture of thorium chloride and thorium oxide was then mixed with eutectic LiCl-KCl and heated to 500°C . After cooling down, the salt ingot was removed from the crucible, and the gray layer of ThO_2 at the bottom was cut off to leave only the white salt (LiCl-KCl-ThCl_4). This salt mixture was then crushed and saved for future use.

The content of ThCl_4 in the purified LiCl-KCl-ThCl_4 was determined as follows. The salt was dissolved in high purity water for half a day, to ensure all the ThO_2 be collected at the bottom of the sample tube, then some of the liquid solution was collected and diluted using nano-pure water and HNO_3 . The solution was kept for one day after being shaken for 15min, and was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Model No. 20.05.2009).

The melt of $\text{LiCl-KCl-LaCl}_3\text{-ThCl}_4$ was prepared from anhydrous LiCl-KCl eutectic beads, anhydrous LaCl_3 powder, and the concentrated LiCl-KCl-ThCl_4 mixture previously described. The predetermined amount of LiCl-KCl , LaCl_3 and LiCl-KCl-ThCl_4 were mixed and heated in the electro-melt furnace. After being kept at 500°C for more than 5 hours, the melt was left to cool down to room temperature naturally to ensure that all the ThO_2 introduced from the concentrated LiCl-KCl-ThCl_4 salt would settle to the bottom of the crucible. Then the melt was reheated to 500°C , and CV tests were performed in a potential range of $-2.6\sim 1.1\text{V}$ (vs. Ag/AgCl (5mol.%)) to check whether there was ThO_2 remaining in the eutectic salt. The above-described procedures were repeated until the baseline in the cyclic voltammogram was close to zero, and no obvious peaks associated with ThO_2 were observed.

2.2. Experimental apparatus and procedure

All the experimental tests were carried out by heating the alumina crucible (AdValue Technology, Part No. AL-2100) containing the salt mixtures in a Kerr Electro-Melt Furnace. The furnace was placed in an argon atmosphere glovebox with the content of oxygen and moisture both be controlled to be less than 1 ppm. Electrodes were inserted into the salt from above through an opening in the top of the furnace. A polished tungsten rod ($d=2$ mm, 99.99%, Alfa Aesar) was used as the working electrode. The same kind of electrode was used as the counter electrode for tests in the LiCl-KCl-LaCl₃ system. For the LiCl-KCl-LaCl₃-ThCl₄ system, a stainless steel basket (7 mm in diameter, 10 mm in height) containing the thorium metal chips was used as the counter electrode. The reference electrode (RE) was fabricated by inserting a silver wire ($d=1$ mm, 99.99%, Alfa Aesar) into a mixture of LiCl-KCl-AgCl (5 mol.%), contained in a Pyrex tube (10 mm in OD, 177.8mm in long, Sigma Aldrich). The upper end of the Pyrex tube was sealed by a tapered cylindrical silicon stopper, through which the Ag wire was held vertically suspended. The electrodes were connected to electrical feedthroughs on the glove box which were connected to an Autolab potentiostat (PGSTAT302N) and a Gamry potentiostat (Gamry Instruments, Interface 1000) respectively controlled by Nova software (Version 1.11) and Gamry Instruments Framework (Version 6.25) run on a Windows PC laptop. After the temperature of the salt stabilized at 500 °C, as measured directly in the salt with an internal thermocouple (Omega, Part No. KQXL-116G-12), the electrodes (WE, RE and CE) were connected to the Autolab potentiostat. CV and CA cleaning were applied sequentially and repeatedly, till the responding CV and CA signals were smooth, and without any singularity. Then the electrodes were switched to the Gamry potentiostat, and the ohmic resistance between the reference electrode and the working electrode was measured using the electrochemical

impedance spectroscopy (EIS) method. Multiple potentials (close to but more positive than the reduction potential observed from the cyclic voltammogram) were applied to the system, and the corresponding resistances were determined automatically by the Gamry Instruments Framework. Then the electrodes were re-connected to the Autolab potentiostat, and a series of voltammetry experiments were performed. Samples of the salt were taken after each experiment to verify the composition via analysis using an ICP-OES instrument.

3. Results and Discussion

3.1. Study of LiCl-KCl-LaCl₃

Fig. 1 shows the cyclic voltammograms (CVs) obtained on an inert tungsten electrode ($A=0.534\text{ cm}^2$) in pure LiCl-KCl melt and in the LiCl-KCl-LaCl₃ ($6.39\times10^{-5}\text{ mol/cm}^3$) melt at 773 K. The result is consistent with other reports found in the literature [11-13]. The solvent decomposition reactions occur at about -2.60 V (vs. Ag/AgCl (5 mol %), the same below) for Li⁺ electrodeposition and +1.05 V for Cl⁻ oxidation. When LaCl₃ is present in the salt, a cathodic peak A occurs at -2.24 V. Its steep rise and slow decay is characteristic of the formation of a new insoluble phase. And the corresponding anodic peak A' found at -2.12V, has the expected characteristics for a stripping peak. The sharp decay of A' is due to the depletion of the metal deposited during the forward scan. The shapes of peaks A and A' suggest that the reduction of La(III) ions into La metal is a one-step process, and that the dissolved La has only one stable electroactive oxidation state in the large electrochemical window of the molten LiCl-KCl eutectic, as has been observed by other researchers [11, 12, 14].

The above conclusion was also supported by the chronopotentiometry-open circuit potential (CP-OCP) measurement. The chronopotentiogram in Fig. 2 was recorded with a charging current

of -40 mA in LiCl-KCl-LaCl₃ (6.39x10⁻⁵ mol/cm³) melt at 773K. Immediately following the CP, a current of zero was imposed to the system, and the OCP was recorded and was plotted as an inset of Fig. 2. In the chronopotentiogram, only one potential plateau at ca. -2.21V is observed, indicating that the deposition of La(III) ions into La metal is a one-step process. After this plateau, the potential decreases rapidly to reach a limiting value corresponding to the deposition of lithium ions when the charging current is maintained for times longer than the transition time. In the OCP curve, again, there is only one potential plateau, and the equilibrium potential for La(III)/La was determined to be -2.18V.

In order to evaluate the reversibility of the La(III)/La reaction, the cyclic voltammetric measurements were carried out for 3.29x10⁻⁵ mol/cm³ LaCl₃ in LiCl-KCl melt with scan rates ranging from 0.02 to 1.0 V/s on a tungsten rod electrode at 773K, and some of them were plotted in Fig. 3. It was observed that with an increase of scan rate, the reduction peak potential (E_{pc}) shifted to slightly more negative value and the reduction peak current (i_{pc}) increased in succession. This indicates that a charge transfer step may be included in the overall electrode reaction control [11]. Thus, to avoid an experimental artifact from the contribution of electrolyte resistance, the potential was compensated by the ohmic drop, as described in Eq. (1).

$$E = E_m - i \cdot R_e \quad (1)$$

where E and E_m are corrected potential and measured potential, respectively, i is current, and R_e is the resistance between the reference electrode and the working electrode. R_e was determined to be 0.4026 Ω by using the EIS method, which is almost the same value as measured by Tang et al. [11].

After potential correction, the peak potential and current for La(III) reduction were respectively plotted as a function of the logarithm of the scan rate ($\log(v)$) and the square root of

scan rate ($v^{0.5}$), as shown in Figs. 4 and 5. The plots in Figs. 4 and 5 both show obvious bending with the increase of scan rate, indicating that the reduction of La(III) transforms from reversible to quasi-reversible or irreversible between 0.1-0.2 V/s, most likely at 0.15 V/s. The above conclusion has also been confirmed by other researchers [11, 13].

The zero-intercept linear plot shown in Fig. 5 suggests that the reduction of La(III) to La metal is under diffusion control of La(III) ions to the surface of working electrode when the scan rate is lower than 0.15 V/s, and the Berzins-Delahay Equation (Eq. (2)) can be used to quantitatively describe the relationship between the peak current and the scan rate [15].

$$j_p = i_p/A = -0.6105 \left(\frac{nF}{RT} \right)^{1/2} nFD^{1/2}C^*v^{1/2} = k_1 \cdot v^{1/2} \quad (2)$$

where j_p , i_p , A , n , F , R , T , D , C^* , and v are peak current density (A/cm^2), peak current (A), area of working electrode (cm^2), n is the electron transfer number, Faraday constant (96485 C/mol), gas universal constant (8.314 J/mol-K), Kelvin temperature (K), diffusion coefficient (cm^2/s) of La(III) ion (cm^2/s), bulk concentration of La(III) ion (mol/cm^3) and the scan rate (V/s), respectively.

To investigate the dependence of $D_{La(III)}$ as determined from this equation on the concentration of $LaCl_3$, cyclic voltammograms were recorded in LiCl-KCl melt with various concentration of $LaCl_3$. For each concentration, the Berzins-Delahay Equation was verified through the linearity of the plot of the current density of the cathodic peak (j_{pc}) vs. $v^{1/2}$, as shown in Fig. 6 for $LaCl_3$ concentration of $6.39 \times 10^{-5} mol/cm^3$. The reduction peaks were used rather than the oxidation peaks, which were found to be affected by the stop potentials. Depending on the scan rate employed, different stop potentials were used. Thus, the anodic current density peaks were not linear functions of the square root of the scan rate. Using the slope of each regressed line, the diffusion coefficient was calculated according to Eq. 2. The fits are shown in

Fig. 7, and the calculated diffusion coefficients are listed in Table 1. Note that even though reversibility was only confirmed up to about 150 mV/s, scan rates up to 250 mV/s were used for fitting the diffusion coefficients. This was done, because it was difficult to obtain sharp reduction peaks at very low scan rates using the larger concentrations. Each fit was forced through the origin, and the higher scan rates do not appear to affect the slope of each line.

The CP's with various charging currents were also recorded on a tungsten electrode in LiCl-KCl melt containing $6.39 \times 10^{-5} \text{ mol/cm}^3$ LaCl_3 at 773K and were plotted in Fig. 8. The transition time (τ) for each CP was determined using the method shown in Fig. 2. The linearity of charging current I vs. $\tau^{-1/2}$ was examined and was plotted in Fig. 9, along with results for other concentrations of LaCl_3 .

The zero-intercept linear fits again support the conclusion that the reduction process is governed by mass transfer of La(III) ions from the bulk to the surface of working electrode. The Sand Equation [16] (Eq. 3) is, thus, applicable for the CP data [16]. And the diffusion coefficients for La(III) calculated using this method are also included in Table 1.

$$j = i/A = \frac{nFD^{1/2}C^*\pi^{1/2}}{2} \cdot \tau^{-1/2} = k_2 \cdot \tau^{-1/2} \quad (3)$$

where j , i , A , n , F , D , C^* , and τ are driving current density (A/cm^2), driving current (A), working electrode surface area (cm^2), electron transfer number, Faraday constant, diffusion coefficient of La(III) ion (cm^2/s), bulk concentration of La(III) ion (mol/cm^3), and transition time (s), respectively.

Sampled-current voltammetry was carried out by applying a series of step potentials to the system and recording the perspective current-time response, followed by examining the dependence of current response on applied potentials at sampled time of 0.75 s, as shown in Fig 10.

Region A involves potentials where La(III) ions can be reduced to La metal, while not so effectively that the surface concentration of La(III) ions is zero. In region B, as step potentials move to more negative values, the same currents are obtained, indicating that the step potentials are in the mass-transfer-limited region, and the surface concentration of La(III) ion is always kept at zero. In region C, current starts to increase as the step potential continues to grow more negative, and this is probably due to the deposition of lithium ions on the electrode.

In the mass-transfer-limited region, the Cottrell Equation [16], derived for mass transfer controlled electrochemical process, is applicable to the deposition of La(III) ions.

$$j(t) = i(t)/A = \frac{nFD^{1/2}C^*}{\pi^{1/2}} \cdot t^{-1/2} = k_3 \cdot t^{-1/2} \quad (4)$$

where $j(t)$, $i(t)$, A , n , F , D , C^* , and t are response current density (A/cm^2) at time t , response current (A) at time t , working electrode area (cm^2), electron transfer number, Faraday constant, diffusion coefficient of La(III) ion (cm^2/s), bulk concentration of La(III) ion (mol/cm^3), and time (s), respectively.

The k_3 values from Eq. 4 for various concentrations of $LaCl_3$ were correlated from the $j(t)$ vs. $t^{-1/2}$ plots shown in Fig. 11. And diffusion coefficients for La(III) ions were then calculated and listed in Table 1.

All diffusion coefficients calculated from the methods (CV, CA, and CP) investigated are presented in Table 1 and Fig. 12, along with some literature values [8, 11-13, 17].

Table 1. Diffusion coefficient of La(III) ion in LiCl-KCl melt at 773K

LaCl ₃ Conc. 10 ⁻⁴ mol/cm ³	10 ⁵ D, cm ² /s		
	CV	CP	CA
0.639	0.98±0.05	1.63±0.06	2.05±0.05

1.772	0.56±0.03	2.42±0.14	2.50±0.03
2.760	0.54±0.03	2.01±0.01	2.48±0.05
4.267	0.53±0.02	1.82±0.02	2.45±0.05

When using the CV method, $D_{\text{La(III)}}$ gradually drops with increasing concentration of LaCl_3 . The values can be regarded reasonable, considering that diffusion coefficients calculated using the same strategy were always in the same order of $10^{-6} \text{ cm}^2/\text{s}$ [18]. When the CP or CA method was used, a maximum in the $D_{\text{La(III)}}$ value was observed as a function of concentration, is in good agreement with the variation in a report by Sridharan et al. [8] in addition to other references [11-13, 17] whose data are included in Fig. 12 with a symbol of a hollow circle.

3.2. Study of $\text{LiCl-KCl-LaCl}_3\text{-ThCl}_4$

To understand how electrochemically active species may interact with each other in molten eutectic LiCl-KCl , a series of voltammetry measurements were made with $\text{LiCl-KCl-LaCl}_3\text{-ThCl}_4$ mixtures. A representative CV for the $\text{LiCl-KCl-LaCl}_3\text{-ThCl}_4$ system is shown in Fig. 13. Due to the significant difference in the standard potentials [19], there was no overlap of reduction peaks for Th(IV)/Th (peak A) and La(III)/La (peak B). Different from the system with only LaCl_3 , in the $\text{LaCl}_3\text{-ThCl}_4$ system Th(IV) ions first deposit on tungsten electrode as the potential is linearly decreased, making the working electrode surface partly be covered with Th metal by the time La(III) starts to deposit. Underpotential deposition (UPD) of La(III) ions tended to occur on Th metal, as evidenced by a tiny shoulder that appeared on the positive side of peak B (the area circled by dash line in Fig. 13). This is believed to be due to formation of a Th-La alloy. Fortunately, in most scans for this study, the shoulder was negligible in comparison

1
2
3
4 with the prominent peak B. Thus the UPD of La(III) on Th metal was ignored in this study. For
5
6 broader application of voltammetry to electroanalytical chemistry of molten salts used for
7
8 nuclear fuel processing, such underpotential peaks may have significant affect on the analysis.
9
10 This is an important effect that is being investigated in our study of several different
11
12 actinide/lanthanide pairs.
13
14

15
16 Fig. 14 presents the CP-OCP curve recorded on a tungsten electrode in a LiCl-KCl-LaCl₃
17
18 (6.67x10⁻⁵ mol/cm³)-ThCl₄ (2.99x10⁻⁵ mol/cm³) melt at 773 K. The chronopotentiogram was
19
20 recorded with a charging current of -40 mA. Two obvious potential plateaus were observed,
21
22 corresponding to the deposition of Th(IV) ions at ca. -1.72 V and La(III) ions at ca. -2.20 V,
23
24 respectively. This is in good agreement with those from the cyclic voltammogram shown in Fig.
25
26 13 and is consistent with other reports found in the literature [11, 18, 20]. Two corresponding
27
28 potential plateaus appeared in the potential profile when the OCP was measured afterward, as
29
30 shown in the inset of Fig. 14, and the equilibrium redox potentials for Th(IV)/Th and La(III)/La
31
32 redox were determined to be -1.65 and -2.18 V, respectively. Thus, the presence of ThCl₄ in the
33
34 salt did not affect the equilibrium potential for La(III)/La.
35
36
37
38
39
40

41 Since the reduction peaks for deposition of Th(IV) and La(III) ions were completely
42
43 separated, they could be respectively analyzed using the same strategy as described in section 3.1.
44
45 For each concentration, the cathodic peak currents for Th(IV)/Th and La(III)/La were determined
46
47 and correlated to $v^{1/2}$ (up to 0.2V/s) using Eq. 2 to yield k_1 . These k_1 's were summarized and
48
49 plotted in Fig. 15 as a function of concentration of LaCl₃ or ThCl₄. Interestingly, it was found
50
51 that k_1 exhibits very good linear relationship with the concentration, apart from some
52
53 singularities. By deduction, the diffusion coefficients of Th(IV) ion and La(III) ion can be
54
55 regarded as constant over the examined composition range. Using the regressed slopes from Fig.
56
57
58
59
60
61
62
63
64
65

15, the diffusion coefficients of Th(IV) and La(III) ions were calculated to be 1.48×10^{-5} and $1.28 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively. These calculated values for the diffusion coefficients for La(III) and Th(IV) ions are in good agreement with those reported in the literature[12, 18, 20]. However, $D_{\text{La(III)}}$ is almost two times of that calculated for LiCl-KCl-LaCl₃ using CV listed in Table 1. This may be due to the fact that the contribution of UPD of La(III) ions on Th metal was ignored. If it had been considered, the measured current would have been smaller, thus resulting in a smaller estimated diffusion coefficient of La(III) ion. Or it could be due to interaction of Th⁴⁺ ions with the La³⁺ ions, resulting in an enhancement in diffusivity. Regardless of the explanation, this result indicates that it can introduce error to use diffusion coefficients measured in simple mixtures to predict behavior in complex mixtures. It appears to be significantly more accurate to estimate diffusion coefficients for ions in the actual salt matrix of interest. Heavy reliance upon diffusion coefficients determined from simple mixtures such as LiCl-KCl-LaCl₃ may introduce much error into modeling of electrochemical processes in molten salts.

In the LiCl-KCl-LaCl₃-ThCl₄ system, sampled-current voltammetry was also carried out using the same strategy described in the previous section. And the sampled-current voltammogram is shown in Fig. 16. When the applied potential is more positive than -1.67 V, only non-faradaic current is observed. In the potential range of -1.67 to -2.10 V, only Th(IV) ions are able to deposit on the W electrode, and more specifically, in the range of -1.72 to -2.10 V, the response current would be independent of the applied potential, indicating that the kinetics of the deposition of Th(IV) ions is in the mass-transfer control region. As the potential moves to a more negative value, La(III) ions would deposit on the working electrode synchronously with Th(IV) ions, resulting in a rapid increase in response current, and eventually the second current plateau would show up when the potential is more negative than -2.30 V.

In the mass-transfer-limited region, the $i \sim t^{-1/2}$ for deposition of Th(IV) ions and La(III) ions could be described using the Cottrell Equation (Eq. 4), and the k_3 's in Eq. 4 were correlated and plotted in Fig. 17 as a function of concentration of LaCl₃ or ThCl₄. Using the regressed slope in Fig. 17, the average diffusion coefficients of Th(IV) and La(III) ions were calculated to be 3.50×10^{-5} and 3.24×10^{-5} cm²/s, respectively, and are listed in Table 2. Similarly, due to the UPD of La(III) ions on the Th metal as well as the enhancement in diffusivity by the Th(IV) ions, the La(III) diffusion coefficient is 30% higher than what was calculated using CA at a similar concentration for the LiCl-KCl-LaCl₃ system reported in Table 1.

Fig. 18 presents the normal pulse voltammograms recorded with various pulse times on a tungsten electrode in LiCl-KCl melt containing 3.19×10^{-5} mol/cm³ ThCl₄ and 3.12×10^{-4} mol/cm³ LaCl₃, with a step potential of -0.01 V and interval time of 10 s.

Similar to the sampled-current voltammogram, two current plateaus are observed in each normal pulse voltammogram, corresponding to the deposition of Th(IV) ions and La(III) ions in mass transfer control. The diffusive currents (i_d) for Th(IV) and La(III) deposition were determined using the method shown in Fig. 18 (inset). And i_d had a relationship to the pulse time τ in the form of the Cottrell Equation [16].

$$j_d = i_d/A = \frac{nFD^{1/2}C^*}{\pi^{1/2}} \cdot \tau^{-1/2} = k_4 \cdot \tau^{-1/2} \quad (5)$$

where j_d , i_d , A , n , F , D , C^* , and τ are diffusive current density (A/cm²), diffusive current (A), working electrode surface area (cm²), electron transfer number, Faraday constant, diffusion coefficient of La(III) or Th(IV) ion (cm²/s), bulk concentration of La(III) or Th(IV) ion (mol/cm³), and pulse time (s), respectively.

For each composition, the k_4 's in Eq. 5 for reduction of Th(IV)/Th and La(III)/La were correlated from the j_d vs. $\tau^{-0.5}$ plots, and were plotted in Fig. 19 as functions of concentrations of

LaCl₃ or ThCl₄. Using the regressed slope in Fig. 19, the diffusion coefficients of Th(IV) and La(III) ions were calculated to be 4.62x10⁻⁵ and 4.37x10⁻⁵ cm²/s, respectively, and were listed in Table 2.

Table 2. Average diffusion coefficient of La(III) and Th(IV) ions in LiCl-KCl-LaCl₃-ThCl₄ melts at 773K

	Concentration 10 ⁻⁴ mol/cm ³	Diffusion coefficient, 10 ⁻⁵ cm ² /s		
		CV	CA	NPV
La(III)	0.62-3.63	1.28	3.24	4.37
Th(IV)	0.29-1.26	1.48	3.50	4.59

Determination of concentration using voltammetry methods would be a powerful analytical tool if the accuracy could be made comparable to destructive analytical methods. Each of the voltammetric methods (CV, CA, and NPV) used for diffusivity analysis was compared for this purpose. Note that square wave voltammetry (SWV) was also considered for analytical purposes. But previous researchers have shown that it loses sensitivity to changes in composition at relatively high concentrations that are typically encountered in spent nuclear fuel electrorefiners [9]. Thus, it was decided to forego the SWV method. Tests were run in LiCl-KCl melt with 19 sets of different compositions of ThCl₄ and LaCl₃. Peak heights from CVs and correlated diffusion coefficients of La(III) ion and Th(IV) ion obtained from CV, CA and NPV data were used to predict the composition of ThCl₄ and LaCl₃. For each of these analytical techniques, Tests 1-16 were used as training set, and Tests 17-19 were treated as unknowns.

The cathodic CV peak currents for Th(IV)/Th and La(III)/La recorded in Tests 1-19 were normalized by surface area of the working electrode in cm² and square root of scan rate in V/s, and the normalized currents in Tests 1-16 were correlated to concentrations of ThCl₄ and LaCl₃

in mol/cm³, respectively, to form calibration curves. These curves are displayed in Fig. 20 with the regressed linear expressions and the coefficients of determination (R²).

Using the expressions in Fig. 20, the compositions of ThCl₄ and LaCl₃ were predicted for Tests 17-19 and were compared to the ICP measured values in Table 3.

Table 3 Mixture composition prediction using the normalized CV peak heights for mixtures of LiCl-KCl-

ThCl₄-LaCl₃ at 773 K

Test No.	Measured Conc.,		Calculated Conc.,		Relative Deviation,	
	10 ⁻⁴ mol.cm ⁻³		10 ⁻⁴ mol.cm ⁻³		%	
	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃
17	0.417	1.19	0.464	1.26	11.3	5.88
18	0.637	1.79	0.650	1.74	2.04	-2.79
19	0.907	2.50	0.883	2.29	-2.65	-8.40

It can be seen from Table 3 that the concentration prediction using the normalized CV peak height is feasible and acceptable, while the performance is far from outstanding, especially for Test 17. This could be due to several factors. First, cyclic voltammetry has inherent flaws in the quantitative analysis. The results could be easily affected by many factors, including the data recording capability of the instrument, data processing and regression method adopting. Second, as shown in Fig. 13, there is a significant potential difference between the two reduction peaks for Th(IV)/Th (Peak A) and La(III)/La (Peak B). This means that a long period of time elapses before the more negative peak B is reached in the cyclic voltammogram. During this period, metallic Th is continuously formed on the surface of the working electrode, which causes the surface area to grow before the La(III) reduction peak potential is reached. The area growth

would be much more severe when the concentration of ThCl₄ is high, making it erroneous to assume a constant area associated with the La(III)/La reduction peak. Third, the UPD of La(III) ions is much more obvious when the concentration of ThCl₄ is relatively high with respect of LaCl₃. In this study, the effect of UPD has been ignored, potentially causing significant error in data analysis in some cases. Fourth, there may be error in the concentrations determined via ICP-OES.

Alternatively, Eqs. (2), (4) and (5) were used for concentration calculation. Similar to the previous approach depicted in Figs. 15, 17, and 19, Tests 1-16 were included in the training set. But in this approach, the average diffusion coefficients for Th(IV) and La(III) were determined using CV, CA, and NPV. Those diffusion coefficients were plugged into Eqs. (2), (4) and (5), and used to predict concentrations for Tests 17-19. The results and along with the ICP measured values are given in Table 4.

Table 4 Mixture composition prediction using the calculated average diffusion coefficients

	Measured Conc.,		Predicted Conc.,		Relative deviation,		
Test No.	10 ⁻⁴ mol.cm ⁻³		10 ⁻⁴ mol.cm ⁻³		%		Remark
	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃	
17	0.417	1.19	0.444	1.23	6.34	3.90	
18	0.637	1.79	0.635	1.74	-0.31	-2.79	Based on CV
19	0.907	2.50	0.979	2.63	7.94	5.20	
17	0.417	1.19	0.434	1.23	4.08	3.36	
18	0.637	1.79	0.629	1.81	-1.26	1.12	Based on CA
19	0.907	2.50	0.949	2.56	4.63	2.40	
17	0.417	1.19	0.412	1.15	-1.20	-3.36	Based on NPV

	Measured Conc.,		Predicted Conc.,		Relative deviation,		
Test No.	10 ⁻⁴ mol.cm ⁻³		10 ⁻⁴ mol.cm ⁻³		%		Remark
	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃	ThCl ₄	LaCl ₃	
18	0.637	1.79	0.607	1.77	-4.71	-1.12	
19	0.907	2.50	0.894	2.57	-1.43	2.80	

It is evident from Table 4 that the concentration prediction via the diffusion-limited equations are more accurate than those by using the normalized CV peak heights. Specifically, NPV is found to be the best method for concentration prediction for the LaCl₃-ThCl₄ system over the concentration ranges investigated in this work. However, the difficulties in baseline determination for La(III) deposition still exist in some situations, and more work is needed to solve these problems and increase the accuracy and versatility of concentration prediction.

4. Conclusions

The reduction mechanism of La(III) ions on the tungsten electrode in LiCl-KCl melt at 773 K was investigated using cyclic voltammetry (CV) and the CP-OCP method. Reduction of La(III)/La was found to be a one-step reversible process at scan rates up to 0.15 V/s. The dependence of diffusion coefficient of La(III) ($D_{\text{La(III)}}$) on concentration of LaCl₃ in LiCl-KCl melt was investigated by using CV, CP and the chronoamperometry (CA) method. As the concentration of LaCl₃ increases, the $D_{\text{La(III)}}$ obtained from CV gradually decrease, while the ones get from CA and CP go through a maximum when plotted versus concentration.

For mixtures of LiCl-KCl-ThCl₄-LaCl₃, the reduction peaks for La(III)/La and Th(IV)/La on the tungsten electrode in LiCl-KCl melt were completely separated, and diffusion coefficients of La(III) ions and Th(IV) ions were found almost independent of the system composition in

these mixtures. This facilitated the prediction of concentrations of LaCl_3 and ThCl_4 using the normalized peak heights from the cyclic voltammograms in addition to using the theoretical equations for diffusion-limited processes analyzed via CV, CA and NPV. Both CA and NPV based concentration correlations are far superior to the CV normalized peak correlations. Specifically, the NPV correlation exhibited the lowest deviation from the known concentrations. It is believed that this is due to the fact that NPV involves repeated stripping of the electrode to minimize buildup of material and an increase in area of the electrode.

Acknowledgements

Funding from the Department of Energy's Nuclear Energy University program is acknowledged for supporting experimental investigations. Also, the financial support provided by China Scholarship Council (CSC) during a visit of Zhonghang Wang (No. 201404910406) to University of Utah (UU) is acknowledged.

References

- [1] J.J. Laidler, J.E. Battles, W.E. Miller, J.P. Ackerman, E.L. Carls, Development of pyroprocessing technology, *Progress in Nuclear Energy*, 31 (1997) 131-140.
- [2] K.-C. Song, H. Lee, J.-M. Hur, J.-G. Kim, D.-H. Ahn, Y.-Z. Cho, Status of pyroprocessing technology development in Korea, *Nuclear Engineering and Technology*, 42 (2010) 14.
- [3] J.L. Willit, W.E. Miller, J.E. Battles, Electrorefining of uranium and plutonium — A literature review, *Journal of Nuclear Materials*, 195 (1992) 229-249.
- [4] S.X. Li, M.F. Simpson, Anodic Process of Electrorefining Spent Nuclear Fuel in Molten $\text{LiCl-KCl-UCl}_3/\text{Cd}$ System, *Journal of Mineral and Metallurgical Processing*, 22 (2005).
- [5] N.J. Gese, J.-F. Jue, B.E. Serrano, G.L. Fredrickson, Potentiometric Sensor for Real-Time Remote Surveillance of Actinides in Molten Salts, 2012.
- [6] C. Hanson, S. Phongikaroon, J.R. Scott, Temperature effect on laser-induced breakdown spectroscopy spectra of molten and solid salts, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 97 (2014) 79-85.
- [7] 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.

- [8] K. Sridharan, Thermal Properties of LiCl-KCl Molten Salt for Nuclear Waste Separation, in: U.S.D.o. Energy (Ed.), 2012.
- [9] M. Iizuka, T. Inoue, O. Shirai, T. Iwai, Y. Arai, Application of normal pulse voltammetry to on-line monitoring of actinide concentrations in molten salt electrolyte, *Journal of Nuclear Materials*, 297 (2001) 43-51.
- [10] S.E. Bae, D.H. Kim, J.Y. Kim, Y.H. Cho, T.H. Park, J.W. Yeon, K. Song, Concentration Measurement of Actinide and Lanthanide ions in LiCl-KCl Melt by Using Electrochemical Techniques, *Proceedings from the International Pyroprocessing Research Conference* Fontana, 2012.
- [11] H. Tang, B. Pesic, Electrochemical behavior of LaCl_3 and morphology of La deposit on molybdenum substrate in molten LiCl-KCl eutectic salt, *Electrochimica Acta*, 119 (2014) 120-130.
- [12] S. Vandarkuzhali, N. Gogoi, S. Ghosh, B. Prabhakara Reddy, K. Nagarajan, Electrochemical behaviour of LaCl_3 at tungsten and aluminium cathodes in LiCl-KCl eutectic melt, *Electrochimica Acta*, 59 (2012) 245-255.
- [13] F. Gao, C. Wang, L. Liu, J. Guo, S. Chang, L. Chang, R. Li, Y. Ouyang, Electrode process of La(III) in molten LiCl-KCl, *Journal of Rare Earths*, 27 (2009) 986-990.
- [14] Y.-L. Liu, G.-A. Ye, K. Liu, L.-Y. Yuan, Z.-F. Chai, W.-Q. Shi, Electrochemical behavior of La(III) on the zinc-coated W electrode in LiCl-KCl eutectic, *Electrochimica Acta*, 168 (2015) 206-215.
- [15] P. Delahay, *New instrumental methods in electrochemistry: theory, instrumentation, and applications to analytical and physical chemistry.*, Interscience Publishers 1954.
- [16] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley 2000.
- [17] F. Lantelme, Y. Berghoute, Electrochemical Studies of LaCl_3 and GdCl_3 Dissolved in Fused LiCl-KCl, *Journal of The Electrochemical Society*, 146 (1999) 4137-4144.
- [18] G. Pakhui, M. Chandra, S. Ghosh, B.P. Reddy, K. Nagarajan, Electrochemical studies on the reduction behaviour of Th^{4+} in molten LiCl-KCl eutectic, *Electrochimica Acta*, 155 (2015) 372-382.
- [19] J. Zhang, Electrochemistry of actinides and fission products in molten salts—Data review, *Journal of Nuclear Materials*, 447 (2014) 271-284.
- [20] K. Liu, L.-Y. Yuan, Y.-L. Liu, X.-L. Zhao, H. He, G.-A. Ye, Z.-F. Chai, W.-Q. Shi, Electrochemical reactions of the Th^{4+}/Th couple on the tungsten, aluminum and bismuth electrodes in chloride molten salt, *Electrochimica Acta*, 130 (2014) 650-659.

Figure Captions

Fig. 1. Comparison of the cyclic voltammograms for pure LiCl-KCl melt and LiCl-KCl-LaCl₃ melt at 773K (LaCl₃ concentration: 6.39×10^{-5} mol/cm³, working electrode area: 0.534 cm², scan rate: 0.1 V/s)

Fig. 2. Lanthanum chronopotentiogram on tungsten electrode in LiCl-KCl-LaCl₃ melt, driving current -40 mA. Inset: OCP for lanthanum on tungsten electrode in LiCl-KCl-LaCl₃ melt (Temperature: 773 K, LaCl₃ concentration: 6.39×10^{-5} mol/cm³, working electrode area: 0.534 cm²)

Fig. 3. Cyclic voltammograms at various scan rates for LiCl-KCl-LaCl₃ melt at 773K (LaCl₃ concentration: 3.29×10^{-5} mol/cm³, working electrode area: 0.283cm²)

Fig. 4. Peak potential of the La(III) reduction peak versus the logarithm of scan rate (Temperature:773K, LaCl₃ concentration: 3.29×10^{-5} mol/cm³, working electrode area: 0.283cm²)

Fig. 5. Peak current as a function of square root of scan rate (Temperature:773K, LaCl₃ concentration: 3.29×10^{-5} mol/cm³, working electrode area: 0.283cm²)

Fig. 6. Peak current density as a function of square root of scan rate (Temperature: 773K, LaCl₃ concentration: 6.39×10^{-5} mol/cm³)

Fig. 7. Verification of the Berzins-Delehay equation for systems with various concentration of LaCl₃

Fig. 8. Lanthanum chronopotentiograms on tungsten electrode in LiCl-KCl-LaCl₃ melt at 773 K (LaCl₃ concentration: 6.39×10^{-5} mol/cm³, Working electrode area: 0.534 cm²)

Fig. 9. Charging current as a function of $\tau^{-1/2}$

Fig. 10. Sampled-current voltammetry in LiCl-KCl-LaCl₃ melt (a) Current-time curves observed in response to the steps. (b) Sampled-current voltammogram. (Temperature: 773K, working electrode area: 0.534cm², LaCl₃ concentration: 6.39x10⁻⁵ mol/cm³)

Fig. 11. Current density as a function of $t^{-1/2}$

Fig.12. Dependence of $D_{La(III)}$ on concentration of LaCl₃ in LiCl-KCl melt at 773K

Fig. 13. Cyclic voltammograms on tungsten electrode in LiCl-KCl melt containing LaCl₃ and ThCl₄ (Temperature: 773K, LaCl₃ concentration: 6.67x10⁻⁵ mol/cm³, ThCl₄ concentration: 2.99x10⁻⁵ mol/cm³, working electrode surface area: 0.471 cm², scan rate: 0.1 V/s)

Fig. 14. Chronopotentiogram on W electrode in LiCl-KCl-LaCl₃-ThCl₄ melt at 773K, driving current -40mA. Inset: OCP on W electrode in LiCl-KCl-LaCl₃-ThCl₄ melt at 773K. (Working electrode area: 0.471cm², LaCl₃ concentration: 6.67x10⁻⁵ mol/cm³, ThCl₄ concentration: 2.99x10⁻⁵ mol/cm³)

Fig. 15. Correlated k_1 in Eq. 2 for LiCl-KCl-ThCl₄-LaCl₃ as a function of concentration of ThCl₄ and LaCl₃ at 773 K.

Fig. 16. Sampled-current voltammogram on W electrode in LiCl-KCl-LaCl₃-ThCl₄ melt (Temperature: 773K, LaCl₃ concentration: 6.67x10⁻⁵ mol/cm³, ThCl₄ concentration: 2.99x10⁻⁵ mol/cm³, working electrode area: 0.471cm²)

Fig. 17. Correlated k_3 in Eq. 4 for LiCl-KCl-ThCl₄-LaCl₃ at 773 K as a function of concentration of ThCl₄ and LaCl₃

Fig. 18. Normal pulse voltammograms with various pulse time in LiCl-KCl-LaCl₃-ThCl₄ melt at 773K. Inset shows determination of diffusion-limited partial currents. Working electrode area: 0.408cm², LaCl₃ concentration: 3.12x10⁻⁴ mol/cm³, ThCl₄ concentration: 3.19x10⁻⁵ mol/cm³, Step potential: 0.01V, Interval time: 10s.

Fig. 19. Correlated k_4 in Eq. 5 for LiCl-KCl-ThCl₄-LaCl₃ at 773 K as a function of concentration of ThCl₄ and LaCl₃

Fig. 20. Concentration correlation with normalized peak current for CV of LiCl-KCl-ThCl₄-LaCl₃ at 773 K

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10a

Figure 10b (revised)

Figure 11

Figure 12 (revised)

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Figure 19

Figure 20