Estimation of Key Physical Properties for LaCl_3 in Molten Eutectic LiCl-KCl by Fitting Cyclic
Voltammetry Data to a BET-based Electrode Reaction Kinetics Model

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Abstract:

Understanding the electrochemical properties of rare earth elements is important for developing efficient techniques for separating rare earth elements from actinides recovered during the electrodeposition process. In this study the cyclic voltammetry for lanthanum in molten LiCl-KCl eutectic was recorded at 773 K for different scan rates and different bulk concentrations. A model accounting for mass transport, kinetics and adsorption was applied to analyze the experimental data via performing a nonlinear least squares fit. The results of the simulation are compared against the results of a conventional analysis of the cyclic voltammograms and against the existing literature. At the scan rates used, the reduction/oxidation process is quasi-reversible. The values of diffusivities derived from

simulation were larger than the ones derived commonly using equations for diffusion-limited processes. However, those equations were derived based on an assumption of reversibility. This simulation-based approach may provide a more accurate option for analyzing systems that do not exhibit reversibility.

Keywords: Cyclic Voltammetry, Rare earth, Quasi-reversible, Model, Adsorption.

Introduction:

Pyroprocessing of spent nuclear fuel is a promising technology for recycling spent nuclear fuel that is currently being studied by the United States, Republic of Korea, and other nations for potential application to treating and possibly recycling used commercial nuclear fuel [1-3]. The process has many advantages such as integrated waste processing and waste form production, compact space requirements, suitability for processing short-cooled fuel, compatibility with metallic fast reactor fuel, and some non-proliferation advantages. The main step in pyroprocessing is electrowinning where actinides and active fission products such as rare earth elements are oxidized and dissolved into a molten chloride salt (LiCl-KCl eutectic). Actinides such as U and Pu are subsequently recovered onto the cathode leaving rare earth chlorides in the electrolyte. The gradual accumulation of fission products makes the deposition potentials of rare earth elements and uranium get closer to each other. Therefore, rare earth elements may co-deposit with actinides. This issue can have deleterious consequences especially when

the separated uranium is needed for nuclear fuel fabrication because some rare earth elements have a large neutron capture cross section. Therefore, it is quite necessary to develop a fundamental understanding of the electrochemical properties of not only actinide elements, but also rare earth elements. Understanding these properties will allow for an effective separation of actinides from rare earth elements during the electrodeposition process and for molten salt recycling. Therefore, it is not surprising that the study of thermodynamic and transport properties of these elements in molten salt under the operating conditions of electrochemical separation has been the subject of several investigations over the past two decades [4-9].

Lanthanum, which exists in the form of La (III) cations in the melt, is a rare earth element and a fission product. Therefore, its electrochemical properties have also recently been examined by several studies [5, 10, 11]. Liu et al. [5] studied the cyclic voltammogram (CV) obtained on a W electrode) at 723K with a LaCl_3 concentration of $9.74 \times 10^{-5} \text{ mol/cm}^3$. The authors found that the La (III) reduction takes place at about -2.11 V (vs. Ag/AgCl (1 wt% AgCl) in a single soluble-insoluble electrochemical step La(III)/La(0) . Vandarkuzhali and coworkers [10] examined the electrochemical behavior of lanthanum at an inert tungsten electrode and reactive aluminum electrode in LiCl–KCl eutectic melt in the temperature range 698–798 K using transient electrochemical techniques. Their study concluded that the reduction of La(III) to La(0) at the tungsten electrode takes place in a single step, shows quasi-reversible behavior for scan rates between 25 and 150 mV s^{-1} . The overwhelming majority of these studies were made at low concentrations. But in a commercial pyroprocessing facility, concentrations can increase well beyond the levels which have been studied thus far [12]. Therefore, and to enable efficient

electrochemical separation of lanthanum under such conditions an accurate characterization of the physical properties of lanthanides that are relevant to electrochemical processing is necessary. Rather than using a conventional, analytical approach to determining these properties, the present study looks to utilize an integrated model which accounts for the mass transport, the kinetics of the reaction and adsorption effects. By adopting this approach, physical properties such as the diffusion coefficient and the apparent reduction potential can be extracted by fitting the model to experimentally measured cyclic voltammograms .

Experimental Setup:

Chemicals/Materials

Salt mixtures were prepared by weighing out known masses of anhydrous lithium chloride/potassium chloride (LiCl-KCl) eutectic beads (SAFC-Hitech, 99.99%) and anhydrous lanthanum chloride (Alfa Aesar, 99.99%). For preparation of reference electrodes, silver chloride (Strem Chemicals, 99.9%) was mixed with LiCl-KCl at a concentration of 5 mol% in Pyrex NMR tubes (10 mm in OD, 177.8mm in long, Sigma Aldrich). The reference electrode (RE) was fabricated by inserting a silver wire (d=1 mm, 99.99%, Alfa Aesar) into the mixture of LiCl-KCl-AgCl (5 mol%), contained in a Pyrex NMR tube. The upper end of the Pyrex tube was sealed by a trapezoidal rubber stopper, through which the Ag wire was held vertically suspended. Polished tungsten rods (d=2mm, 99.99%, Sigma Aldrich) were used as both the working and counter electrode. After receipt, all chemicals were stored and handled in a dry atmosphere argon glove box (Innovative Technologies, PureLab HE 4) typically maintained with H₂O and O₂ concentrations of less than 1 ppm.

Experimental apparatus and procedure

All the experiments were carried out by heating an alumina crucible (AdValue Technology, Part No. AL-2100) containing the salt mixtures in a Kerr Electro-melt Furnace (Model No. 35224).

The furnace was operated in the argon atmosphere glovebox. Electrodes were inserted into the salt from above through an opening in the top of the furnace. The electrodes were connected to electrical feedthroughs on the glove box, which were connected to an Autolab potentiostat (PGSTAT302N) controlled by Nova software 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), a series of voltammetry experiments were performed using the potentiostat. Samples of the salt were taken after each experiment to verify the composition via analysis using an ICP-OES instrument (Spectro Genesis, Model No. 20.05.2009).

Results and Discussion:

For the experiments that were analyzed by simulation in this paper, the temperature was held at 773 K and the cyclic voltammograms were recorded at three different concentrations of the metal chloride (LaCl_3). At each concentration, cyclic voltammograms were recorded using five scan rates ranging from 100 to 500 mV/s. The experimentally recorded cyclic voltammograms at concentrations of 0.97, 2.68, and 6.38 wt% LaCl_3 (corresponding to 64, 177, and 427 mM respectively) are shown below in Figures 1, 2, and 3 for scan rates of 100, 200, 300, 400 and 500 mV/s.

Figure 1. Three cyclic voltammograms recorded for LaCl_3 in the LiCl-KCl molten salt at 773K for five different scan rates at concentration 0.97 wt% ($6.397 \times 10^{-5} \text{ mol/cm}^3$).

Figure 2. Three cyclic voltammograms recorded for LaCl_3 in the LiCl-KCl molten salt at 773K for five different scan rates at concentration 2.68 wt% ($1.77 \times 10^{-4} \text{ mol/cm}^3$).

Figure 3. Three cyclic voltammograms recorded for LaCl_3 in the LiCl-KCl molten salt at 773K for five different scan rates at concentration 6.38 wt% ($4.27 \times 10^{-4} \text{ mol/cm}^3$).

The electrolyte resistance between the working electrode and reference electrode was empirically determined to be 0.4026 ohm. This value can be used to correct the potentials for the IR drop. Figure 4 shows a comparison between uncorrected and corrected CV plots for 1 wt% LaCl_3 and a scan rate of 0.5 V/s.

Figure 4. Comparison of CV plots with and without IR correction applied (1 wt% LaCl_3 , 500 mV/s).

Both for the conventional and the model-based analysis approaches, only the reduction peak is used. From Figure 4, it is evident that the IR correction has relatively little effect on the shape and magnitude of the reduction peak. Thus, we decided to forego performing this correction on all of the data, rather using the original uncorrected data.

Conventional analysis of the experimental data:

The measured potential for a metal in equilibrium with its oxidized state is determined via the Nernst equation:

$$E_{La(III)/La(0)}^{eq} (vs. Ag/Ag^+) = E_{La(III)/La(0)}^0 + \frac{RT}{nF} \ln \left(\frac{a_{La(III)}}{a_{La(0)}} \right) \quad (1)$$

where $E_{La(III)/La(0)}^0$ is the standard potential at a hypothetical supercooled liquid reference state of unit mole fraction and unit activity, $a_{La(III)}$ and $a_{La(0)}$ are the activities of La^{3+} ions and of metallic La , respectively. The apparent standard potential, $E_{La(III)/La(0)}^{*0}$ of the La redox couple is given by:

$$E_{La(III)/La(0)}^{*0} = E_{La(III)/La(0)}^0 + \frac{RT}{nF} \ln \gamma_{La(III)} \quad (2)$$

From a standard analysis of the recorded cyclic voltammogram for a reversible insoluble/soluble system, the apparent potential (vs. Ag/Ag^+) can be obtained from the cathodic peak by applying the equation [13]:

$$E_{p,c}(vs. Ag/Ag^+) = E_{La^{3+}/La}^{*0} + \frac{RT}{nF} \ln(X_{La(III)}) - 0.854 \frac{RT}{nF} \quad (3)$$

Next, and by using unit activity for the pure metals, the apparent potential for the *La* redox couple measured against the Cl_2/Cl^- reference electrode may be expressed as:

$$E_{La(III)/La(0)}^{*0} (vs. Cl_2/Cl^-) = E_{La(III)/La(0)}^{*0} (vs. Ag/Ag^+) + E_{Ag^+}^0 + \frac{RT}{F} \ln X_{Ag^+} \quad (4)$$

Based on extrapolation to infinite dilution of the data of Yang and Hudson [14] at low AgCl concentrations in LiCl/KCl (a reference electrode with 0.05 mole fraction was used in this work), the following equation was obtained for the potential of E_{AgCl}^0 relative to the Cl_2/Cl^- reference couple[15]:

$$E_{Ag/Ag^+}^0 = -1.0910 + 0.0002924 \times T (K) \quad (5)$$

The apparent Gibbs free energy of the reaction in the salt was calculated from the equation:

$$\Delta G_{LaCl_3}^{*0} = -n F E_{La(III)/La(0)}^{*0} \quad (6)$$

The activity coefficient of $LaCl_3$ in LiCl–KCl eutectic melts was determined from the difference between the Gibbs free energy of formation derived from the electrochemical measurements and the Gibbs free energy of formation for pure compounds in the super-cooled state, according to the equation:

$$2.303RT \log \gamma_{LaCl_3} = \Delta G_{LaCl_3}^{*0} - \Delta G_{LaCl_3(SC)}^0 \quad (7)$$

where $\Delta G_{LaCl_3(SC)}^0$ is the Gibbs free energy of formation from reaction of the pure compounds in the supercooled state. In our analysis, we used a cubic spline interpolation to determine the value of the supercooled state $\Delta G_{LaCl_3(SC)}^0$ at 773 K from the values reported by Pesic et al. [16]. We found this value to be -880.8584 kJ/mol.

Analytic equations describing the shape of cyclic voltammograms as a function of the diffusion coefficient, electrode area, temperature, concentration, and scan rate for electrode processes which are at equilibrium were developed by Randles [17] and Sevcik [18]. However, these equations do not describe electrode processes that yield an insoluble product. For this type of reaction, Berzins and Delahay developed an equation [19]:

$$i_p = 0.6105AC \sqrt{\frac{n^3 F^3 D \nu}{RT}} \quad (8)$$

The problem is that this equation assumes a reversible process, while reports from the literature indicate that La(III)/La transitions are quasi-reversible in eutectic LiCl-KCl. In a separate paper, Wang et. al. presented CV data for scan rates ranging from 20 to 1000 mV/s that shows convincingly that the process is only reversible at scan rates slower than 150 mV/s [20]. They calculated D using equation (8) for data limited to no higher than 150 mV/s. The results are included in Table 1 along with the apparent potential of the La (III)/La redox couple, the apparent Gibbs energy of formation for LaCl₃, and the calculated range of activity coefficients. The results for the redox potential, the apparent Gibbs free energy and the activity coefficient at each concentration level were calculated for each scan rate and then their average and standard deviation were reported in Table 1 below.

Table 1. Results of the standard CV analysis of recorded experimental data

Concentration (wt%)	E ^{*0} (V) vs. Cl ⁻ /Cl ₂	Apparent Gibbs Free Energy (kJ/mol)	Activity Coefficient	D (cm ² /s) ×10 ⁻⁵
0.97	-3.157±0.01	-913.82±1.74	[4.52-7.77]×10 ⁻³	0.97±0.05
2.68	-3.194±0.014	-924.53±4.05	[0.6 - 2.1]×10 ⁻³	0.56±0.03
6.38	-3.307±0.034	-957.24±9.84	[0.02-0.32]×10 ⁻⁴	0.53±0.02

Description of the BET Model:

The diffusion equation governs both species' concentrations in the solution:

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2} \quad (9)$$

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial x^2} \quad (10)$$

In these equations, c_O and c_R are the concentrations of the oxidized and reduced species, respectively. The domain on which the equations are solved is $0 \leq x \leq L$, where we choose $L = 12\sqrt{DT_{max}}$ (T_{max} is the time needed for one full CV cycle). The product is assumed to have a very low diffusivity ($D_R \sim O(10^{-20})$ cm²/s). In addition, the adsorption on the electrode is described by the BET isotherm originally proposed by Brunauer, Emmett and Teller [21]:

$$\Gamma_R(t) = \frac{\Gamma_s K_1 c_R(0, t)}{(1 - K_d c_R(0, t))(1 + K_1 c_R(0, t) - K_d c_R(0, t))} \quad (11)$$

Here, Γ_s is the maximum surface concentration of the product species, and K_1 and K_d are adsorption equilibrium constants. Unlike the Langmuir adsorption model [22] which only

accommodates one adsorption layer, this model allows for multi-layer adsorption. Finally, the boundary conditions for the diffusion equations at the electrode surface describe the kinetics of the reaction. The boundary conditions sufficiently far from the electrode surface are assumed equal to the bulk concentration values:

$$D_O \frac{\partial c_O}{\partial x} \Big|_{x=0} = c_O(0, t) k_f^o e^{-\frac{\alpha n F}{RT} (E - E_f^o)} - c_R(0, t) k_b^o e^{\frac{(1-\alpha) n F}{RT} (E - E_f^o)} \quad (12)$$

$$D_R \frac{\partial c_R}{\partial x} \Big|_{x=0} = \frac{d\Gamma_R}{dt} - c_O(0, t) k_f^o e^{-\frac{\alpha n F}{RT} (E - E_f^o)} + c_R(0, t) k_b^o e^{\frac{(1-\alpha) n F}{RT} (E - E_f^o)} \quad (13)$$

In the equations, E_f^o is the formal potential, k_f^o and k_b^o are the reaction rates for the forward and backward directions respectively evaluated at the formal potential, F is the Faraday constant, R is the universal gas constant, T is the temperature and α is the charge transfer coefficient. In all our simulations we assumed $k_f^o = k_b^o = k^o$. The initial conditions and the boundary conditions away from the electrode were selected as follows:

$$c_O(x, t = 0) = c_O(L, t) = c_{bulk} \quad ; \quad c_R(x, t = 0) = c_R(L, t) = 0 \quad ; \quad \Gamma_P(t = 0) = 0 \quad (14)$$

In the model, the current was defined as:

$$I = -nFAD_O \frac{\partial c_O}{\partial x} \Big|_{x=0} \quad (15)$$

Application of the BET adsorption model to the experimental data:

Next, we apply the BET-adsorption model to better understand the data. In contrast to equation (2) which assumes the electrode to be completely covered, the model tracks the coverage of the electrode through the BET adsorption model and is therefore more realistic. Furthermore, we fitted the model to the experimental data using a nonlinear least squares

procedure based on the trust region reflective algorithm [23]. Details of the numerical implementation of the model and its validation are discussed elsewhere [24]. In the simulations the temperature is fixed (all simulations and experiments in this study were carried out at 773 K). The maximum surface concentration Γ_s is also presumed to be known and its value was fixed at 10^{-7} mol/cm².

To extract the values of the various parameters that would best fit the experimental data we used the least squares fitting procedure to minimize χ^2 with respect to 6 fitting parameters. The parameters which were used in the fitting are the apparent potential E_f , the reaction rate constant k^o , the diffusivity D , the charge transfer coefficient α and the adsorption equilibrium constants K_1 and K_d . Therefore, if we refer to the parameters by a vector

$\mathbf{P} = [E_f, k^o, D, \alpha, K_1, K_d]$ then the Chi-square function to be minimized is:

$$\chi^2(\mathbf{P}) = \|I^{sim}(\mathbf{P}) - I^{exp}(\mathbf{P})\|^2 \quad (16)$$

The nonlinear least squares algorithm searches the six-dimensional parameter space to find the optimum values that minimize the norm. In our application of the least squares fitting and due to the possibility of experimental uncertainties and since the peaks are the most important sources of data in CV experiments, we focused on fitting points around the peaks. Figures 5-7 show the application of the model to the experimental data recorded at 773 K. The optimal values for the recorded parameters of the model determined by the least squares fitting procedure are included in Table 2. The values reported in Table 2 resulted from reporting the

mean and standard deviation of the values of the parameters for each of the five scan rates at each concentration.

Figure 5. Experimental and simulated cyclic voltammograms at 64 mM (0.97 wt%) recorded at five different scan rates at 773 K

Figure 6. Experimental and simulated cyclic voltammograms at 177 mM (2.68 wt%) recorded at five different scan rates at 773 K

Figure 7. Experimental and simulated cyclic voltammograms at 427 mM (6.38 wt%) recorded at five different scan rates at 773 K

Table 2. The values of the model parameters determined from nonlinear least squares fitting

Conc.	E_f (V)	$k^o \times 10^{-3}$	$D \times 10^{-5}$	α	K_1	$K_d \times 10^4$
(wt%)	(vs. Ag/Ag ⁺)	(cm/s)	(cm ² /s)		(cm ³ /mol)	(cm ³ /mol)
0.97	-2.227±0.01	13 ±3	1.86±0.3	0.3±0.01	0.3±0.17	3.26±0.9
2.68	-2.244±0.02	16±1	1.52±0.2	0.3±0.01	0.56±0.06	5.5±3
6.38	-2.285±0.02	6±2	1.47±0.1	0.31±0.03	14±9	9±3

It should be noted that the E_f parameter reported by the simulations is the apparent potential (vs. Ag/Ag⁺). By averaging all five values of the apparent potential for each concentration and then following the procedure in the previous section we can obtain the apparent potentials (vs. Cl_2/Cl^-). These values (vs. Cl_2/Cl^-) are found to be (-3.28±0.01) V, (-3.30±0.02) V, and

(-3.34 ± 0.02) V, at 0.97 wt%, 2.68 wt% and 6.38 wt% respectively. From here we can calculate the apparent Gibbs free energies of formation and then apply equation 7 to obtain the activity coefficients. This analysis yields the activity intervals of $[0.15 - 0.37] \times 10^{-4}$, $[0.04 - 0.23] \times 10^{-4}$, and $[0.16 - 0.4] \times 10^{-5}$ at 0.97 wt%, 2.68 wt%, and 6.38 wt% respectively. As the concentration of La(III) ions in solution increases, we expect this to have an increase in the ionic strength of the solution and ultimately in the activity coefficient. This trend is clearly established in Table 1, and the same trend is observed when examining the simulation results.

From examining the figures we observe that the quality of fits is worse for the high concentration case. The weakness of the model is presumed to stem from its inability to capture the physical processes of nucleation and growth [25]. Nevertheless, and despite the perceived shortcomings of the current model, it is still useful in yielding important thermodynamic properties that may be hard to obtain through a standard analysis.

Next, a comparison of the reduction potentials obtained in this study against the available literature is examined in Table 3.

Table 3. Comparison of the reduction potentials against values from the literature

Study	Temperature (K)	Concentration $\times 10^{-4}$ (mol/cm ³)	$E_{La(III)/La(0)}^{*0}$ (vs. Cl_2/Cl^-) (V)
This work ^(a)	773	1.77	-3.30 ± 0.02
This work ^(b)	773	1.77	-3.185 ± 0.002
Fabian ^(a) [25]	773	1.23	-3.281
Fabian ^(b) [25]	773	1.23	-3.216

Vandarkhuzali [10]	773	0.754	-3.116
Lantelme^(a) [26]	750	1.84	-3.22
Castrillejo [9]	723	0.71	-3.184±0.022
Pesic [16]	783	1.07	-3.064

(a) simulation results (b) standard CV analysis results

It should be pointed out that our simulation is different from the one carried out by Lantelme et al. [26]. In that work, the authors assumed the process to be reversible and applied the Nernst equation at the boundary. This is questionable since several authors have suggested the process may be quasi-reversible [25]. However, our model is more general since it does not assume reversibility and applies the Butler-Volmer equation for the kinetics. In addition, the model we implemented contains four additional parameters which are the rate constant, the charge transfer coefficient and the adsorption equilibrium constants.

From Table 3 it can be seen that both the standard CV analysis and the simulation results are consistent with the literature. The differences in the available literature can be explained by two points. The first is that different investigators use different relationships for converting the measured potential (vs. Ag/Ag⁺) to potentials (vs. Cl₂/Cl⁻). For example, the relationship outlined by Vandarkhuzali [10] yields different results than the one outlined by Pesic [27]. The second reason is that the molten salt composition used by different researchers is often different. Moreover, concentration effects are usually neglected. It is typically safe to neglect concentration effects when the ionic strength is dominated by an inert electrolyte in the medium. In our case, K⁺, Cl⁻, Li⁺, and La³⁺ all contribute to the ionic strength of the solution. La³⁺

may have an important effect on the ionic strength due to its triple valency and variation of concentration may lead to a variation in the ionic strength that cannot be ignored. This variation leads to change in the activity coefficient of LaCl_3 and, thus, affects the outcome of the standard apparent potential. In our study, and by performing a standard CV analysis, the effects of concentration on the formal standard potential are clearly significant.

In addition, and to summarize the results of the simulation-derived and conventional analysis-derived apparent potentials as functions of the scan rate in Figure 8.

Figure 8. The apparent redox potential as a function of the scan rate

Next, we examine the values of the parameter k^o and the parameter Λ :

$$\Lambda = \frac{k^o}{\sqrt{\frac{D n v F}{R T}}} \quad (17)$$

A process is considered quasi-reversible if the parameters k^o and Λ satisfy [28]:

$$(a) \quad 2 \times 10^{-5} \sqrt{v} \leq k^o \leq 0.3 \sqrt{v} \quad \text{and} \quad (b) \quad 10^{-3} \leq \Lambda \leq 15 \quad (18)$$

The values of these parameters are calculated in Table 4 below.

Table 4. Parameters calculated for all concentrations and all scan rates to examine the reversibility

Conc	Parameter	V = 0.1	V = 0.2	V = 0.3	V = 0.4	V = 0.5
wt %		V/s	V/s	V/s	V/s	V/s
All	Lower Limit (eq. 19 a)	6.33×10^{-6}	8.94×10^{-6}	1.10×10^{-5}	1.27×10^{-5}	1.41×10^{-5}
All	Upper Limit (eq. 19 a)	0.095	0.134	0.164	0.190	0.212
0.97	Λ	0.88	1.03	1.55	0.93	0.66
0.97	k^o	0.9×10^{-2}	1.35×10^{-2}	1.35×10^{-2}	1.58×10^{-2}	1.32×10^{-2}
2.68	Λ	3.65	1.62	0.38	0.85	0.76
2.68	k^o	2.69×10^{-2}	1.89×10^{-2}	0.57×10^{-2}	1.44×10^{-2}	1.44×10^{-2}
6.38	Λ	1	0.39	0.38	0.22	0.39
6.38	k^o	7.93×10^{-3}	4.48×10^{-3}	5.43×10^{-3}	3.81×10^{-3}	6.95×10^{-3}

Therefore, we conclude that the process is quasi-reversible [28]. Furthermore, this assessment is consistent with the literature. Investigators in Fabian's study [25] concluded that the process of lanthanum reduction at 773 K in the LiCl-KCl eutectic molten salt was quasi-reversible.

Vandarkhuzali [10] and Pesic [16] also concluded that the process was quasi-reversible.

In addition, we find that the diffusivity values determined from the simulation are different from the ones determined through a standard CV analysis, and the simulation values do not fall within the experimental uncertainties. This is an important issue especially considering that the conditions for applying the Berzins-Delahay equation, which assumes reversibility and diffusion

control, do not seem to be satisfied here. This is not surprising in light of the fact that some studies report significantly different values for diffusivity by using different characterization methods such as chronoamperometry and cyclic voltammetry and it is often found that the standard analysis of CV leads to lower values of diffusivity compared to the other characterization methods [10, 29]. The diffusivity from Tables 1 and 2 shows that when the concentration of the metallic ions in the LiCl-KCl molten salt decreases the diffusivity increases. This observation could be explained by molecular level processes. The diffusing lanthanum ions are less likely to suffer collisions when traveling through the molten salt. A major reason for this is the triple valency and the size of the lanthanum ion whose radius is much larger than the radii of K, Li, or Cl.

To enable a more rigorous analysis of the result, we constructed Table 4, which lists the values of diffusivity for the lowest concentration in our study as well as several other recent studies.

Table 5. Comparison of diffusivity values against the available literature

Study	Bulk Conc. (mol/cm ³)	Temperature (K)	Diffusivity (cm ² /s)
This work^(c)	1.77×10 ⁻⁴	773	(1.52±0.2)× 10 ⁻⁵
This work^(b) (CV analysis)	1.77×10 ⁻⁴	773	(0.59±0.02)× 10 ⁻⁵
Lantelme^(c) [30]	0.5×10 ⁻⁴	723	1.47× 10 ⁻⁵
Lantelme^(c) [26]	1.0×10 ⁻⁴	750	(1.76±0.2)× 10 ⁻⁵
Gao et al. [29]	0.770×10 ⁻⁴	773	1.62×10 ^{-5(a)} / 0.67×10 ^{-5(b)}
Fabian et al.^(a) [25]	1.33×10 ⁻⁴	773	2.0 × 10 ⁻⁵

Pesic^(a) [16]	1.1×10^{-4}	763	2.1×10^{-5}
Vandarkhuzali^(a,b) [10]	0.754×10^{-4}	798	3.2×10^{-5} (a) / 1.52×10^{-5} (b)
Masset^(b) [7]	2×10^{-4}	773	0.8×10^{-5}

(a) Chronoamperometry (CP) (b) Cyclic Voltammetry (c) Simulation

The result of the analysis carried out using a standard CV analysis shows reasonable agreement with the literature. This is not surprising because typically either the Berzins-Delahay equation (for CV studies) or the Sand equation (for CP studies) are used to derive these quantities.

However, the application of such equations under the current circumstances is questionable and the conditions for the Berzins-Delahay equation are clearly not satisfied when studying La reduction. The simulation yields a significantly different result.

Finally, the values of α from the simulation (Table 2) are between 0.28-0.34 and appear to show a slight dependence on the concentration.

The parameters k^o , α , and the adsorption equilibrium constants reported from the model are not expected to depend on the concentration. The observed dependence in table 2 is thought to be due to the correlation between the parameters. This issue will require further investigation.

Conclusions:

In this study, the cyclic voltammograms of lanthanum(III) reduction in LiCl-KCl eutectic were recorded at 773 K with scan rates of 0.1 V/s, 0.2 V/s, 0.3 V/s, 0.4 V/s and 0.25 V/s at three bulk concentration values of 0.97 wt%, 2.68 wt%, and 6.38 wt% . Previous studies used the

conventional Berzins-Delahay equation, which is based on assumptions that break down under the circumstances of this study. Therefore, we applied a model accounting for mass transport, kinetics and adsorption to evaluate our experimental data. From applying the model and fitting it to the experimental voltammograms through a nonlinear least squares analysis, we were able to obtain thermodynamic information about the system. The model was able to predict the concentration dependence of the apparent potential. In addition, it was useful in providing valuable information to determine that the process falls in the quasi-reversible regime for the scan rates being used. Finally, the values of diffusivity derived from the model were significantly larger than the values reported through the Berzins-Delahay equation which was shown to be invalid in this situation. We intend to further study this discrepancy using other rare earth chlorides in LiCl-KCl to understand if the model needs to be refined or may in fact be yielding a more accurate value of the diffusion coefficient than is calculated using diffusion-limited reversible transition models.

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