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Experimental and Simulation Study of the Electrode Reaction Mechanism of La^{3+} in LiCl-KCl Eutectic Molten Salt

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Nuclear energy increasingly represents an important option for generating largely clean CO_2 -free electricity. The present investigation addressed the electrochemical reduction of La^{3+} , a rare earth element, in LiCl - KCl eutectic molten salt in the temperature range 450–550°C using transient techniques such as cyclic voltammetry (CV) and square-wave voltammetry (SWV). Simulation of the CV data suggested a reaction mechanism in which lanthanum reduction occurred in a single three-electron step ($\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}^0$). The rate constant, k^0 was determined to be 5.7×10^{-3} , 14.6×10^{-3} and 31.7×10^{-3} cm/s and the Matsuda et al.¹ dimensionless parameter Λ was 0.82, 1.52 and 2.89 for temperatures of 450, 500 and 550°C, respectively and therefore it was concluded that the was process quasi-reversible.

Pyroelectrochemical processes based on molten chloride or fluoride electrolyte systems have over the past decade received renewed interest for the reprocessing of irradiated nuclear fuel. The renewed interest owes its origin to several potential advantages of the pyroelectrochemical approach with respect to hydrometallurgical reprocessing.² Lanthanum is also an important rare earth element to be refined from its minerals for “green” products, e.g., hybrid vehicle batteries as LaNiH .

Several authors have studied the electrode reaction of lanthanum in LiCl-KCl eutectic molten salt at different temperatures.^{3–9} Overall, it is reported that the electrode reaction $\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}^0$ is a reversible reaction up to about 1.0 V/s scan rate. Fusselman et al.³ reported the standard electrode potential for the reaction at 450°C to be -3.1462 V vs. Cl_2/Cl^- with a number of electrons exchanged, n , equal to 2.5 from a linear fit. Kuznetsov et al.⁸ reported -3.108 V vs. Cl_2/Cl^- for the same temperature. Moreover, significant discrepancies were found on the value of the electrode potentials at different temperatures from a limited quantitative analysis. The aim of the present study therefore is to probe the reaction mechanism for the electrode reaction of lanthanum using cyclic voltammetry and square-wave voltammetry with a comprehensive data analysis and simulation of the CV data to extract their thermodynamic and electrokinetics properties using DigiElch.

Experimental

High purity LiCl (Aldrich, 99%) and KCl (Merck, 99.999%) were used to prepare the eutectic melt (59% mol LiCl and 41% mol KCl). The working electrode (WE) was a 1 mm diameter tungsten wire (W), the bottom-end rounded off to simulate a hemicylinder and was polished with 4000 grit SiC paper, rinsed with diluted nitric acid and distilled water and dried for least 1 h at 80°C. The counter electrode (CE) was a 3 mm diameter \times 400 mm glassy carbon rod (SIGRADUR G) encased in an alumina tube of 6 mm OD. The Ag/AgCl reference electrode was prepared with 0.75 mol kg^{-1} AgCl and 1 mm diameter silver wire embedded in 6mm OD \times 4 ID \times 300 mm quartz tubing sealed with the high temperature epoxy resin. The eutectic melt was weighed into a glassy carbon crucible (SIGRADUR G, GAZ 12; 50 mm OD \times 85 mm H) in a nitrogen filled (<1 ppm oxygen and water) glove box. The electrochemical reactor evacuated to about 0.2 mbar and dehydration of the salt was undertaken by heating under vacuum at about 300°C for 72 hours. The reactor was kept under

an inert atmosphere with argon 5.0 ($\geq 99.999\%$ purity) gas during the test work. An AUTOLAB potentiostat PGSTAT302N from Eco Chimie was used with its Nova 1.6 and GPES 4.9 software packages.

Results and Discussion

Cyclic voltammetry of lanthanum.— In this publication the simulation of the CV data is obtained not only to determine the rate of the electrochemical reaction, k^0 but also the parameter Λ from the classical paper by Matsuda et al.¹ to then assess the mechanism and reversibility/irreversibility of the electrochemical reaction of lanthanum. The parameter Λ is superimposed on the analysis of the CV data in terms of ΔE_{pp} , mV vs. $\log_{10} \nu$ plot in which ΔE_{pp} is the difference between the anodic and cathodic peak potentials and ν is the scan rate. The value of the parameter Λ indicates the limits of reversible/irreversible reactions.

The simulation of the electrochemical diffusion-kinetics and adsorption phenomena described in this paper was implemented using the finite difference algorithms developed by Rudolph.^{10,11} The protocol between fast and slow electrode kinetics is related to $k^0 \gg k_{d,i}$ for reversible and $k^0 \ll k_{d,i}$ for irreversible reactions.^{12,13} Furthermore, the transition between reversible, quasi-reversible and irreversible limits can be assessed using the parameter, Λ :¹

$$\Lambda = \frac{k^0}{\sqrt{\frac{nFD\nu}{RT}}} \quad [1]$$

where k^0 is the heterogeneous electron-transfer rate constant, D is the mean of the diffusion coefficient. For β (transfer coefficient, asymmetry parameter) between 0.3 and 0.7, it was shown that for:

$\Lambda \geq 15$ or $k^0 \geq 0.3\nu^{1/2}$ the case follows a reversible reaction (fast electron-transfer),
 $15 > \Lambda \geq 10^{-3}$ or $0.3\nu^{1/2} > k^0 > 2 \times 10^{-5} \nu^{1/2}$ cm s^{-1} the case follows essentially quasi-reversible electron transfer, and
 $\Lambda \leq 10^{-3}$ or $k^0 \leq 2 \times 10^{-5} \nu^{1/2}$ the case follows an irreversible reaction (slow electron-transfer). The potentials versus Ag/AgCl reference electrode were converted to the Cl_2/Cl^- reference electrode using equation 2 where T is in K.¹⁴

$$E_{\text{Ag}/\text{AgCl}} = -1.224 + 2.67 \times 10^{-4} T (\text{V vs. } \text{Cl}_2/\text{Cl}^-) \quad [2]$$

Figure 1 shows the cyclic voltammograms (CV) for $[\text{La}^{3+}]$ at 0.08260 mol/kg and 500 and 550°C. It should be noted that irrespective of concentration and temperature, the horizontal line in

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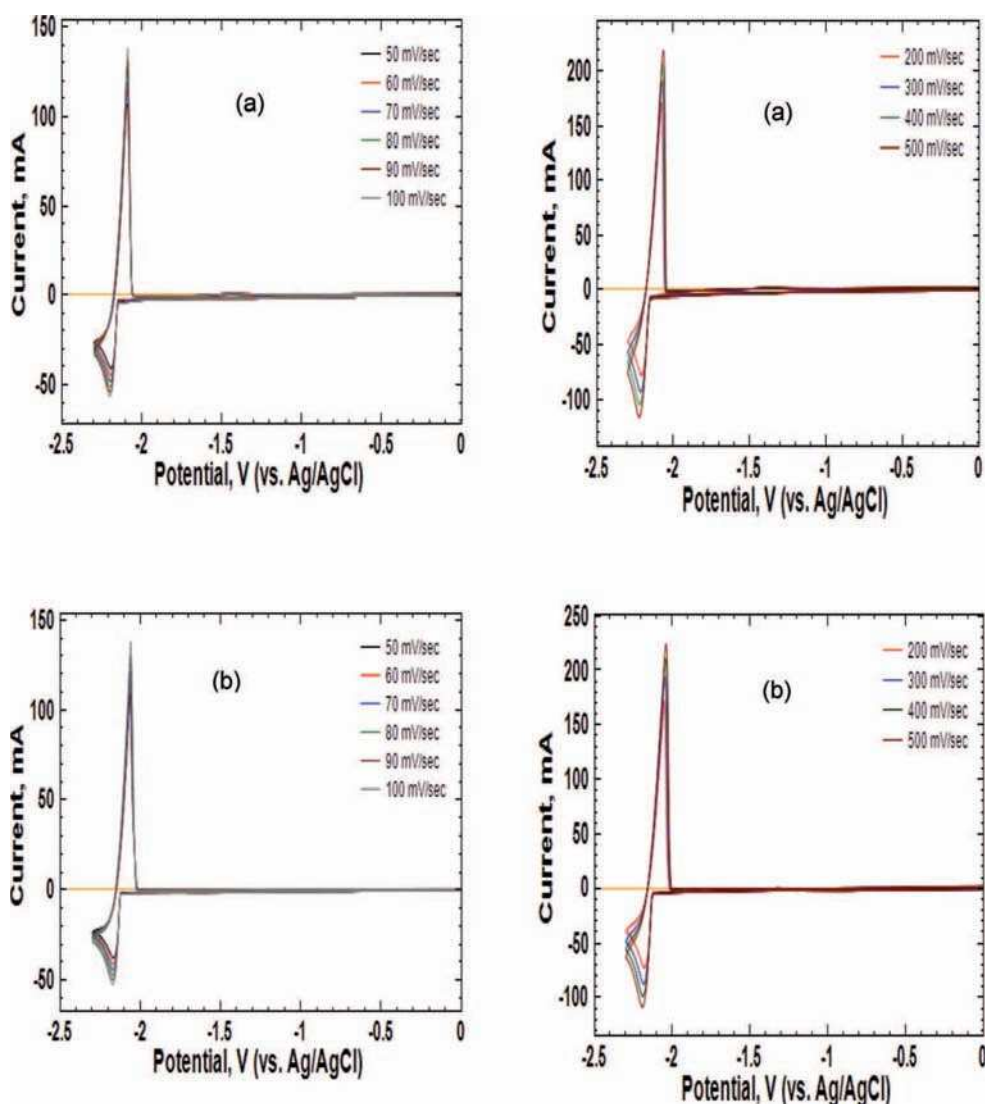


Figure 1. Cyclic voltammograms for the reduction of La^{3+} to La^0 in $\text{LiCl} - \text{KCl}$ eutectic molten salt. WE: W 1 mm dia. Wire; CE - GC rod; REF, Ag/AgCl; $[\text{AgCl}] = 0.75 \text{ mol/kg}$, $[\text{La}] = 0.0826 \text{ mol/kg}$. (a) 500°C and $S = 0.414 \text{ cm}^2$ and (b) 550°C and $S = 0.328 \text{ cm}^2$.

the electrochemical window -not presented and the CV data indicate that the bath appears to be free from oxygen-bound compounds. Figure 1 shows that there is: 1) only one cathodic peak and one anodic peak; 2) a sharp increase in the cathodic current indicated by the arrows probably indicating the preference of nucleation and growth mechanism, e.g. progressive nucleation and quantum chemistry phenomena, and 3) the ratio of the anodic peak to the cathodic peak is greater than one indicating the presence of *adsorption*.¹⁵ Moreover, the weights of the anodic and cathodic areas also indicate that the anodic area is larger than the cathodic area. The sharp increase in the cathodic current and observations 2 and 3 were also reported by Lantelme et al.⁴ who presented single CVs at scan rates of 393, 455 and 566°C and 0.2, 0.5 and $0.2 \text{ V}\cdot\text{sec}^{-1}$, respectively.

The present CV data confirm that the La^{3+} and La^0 electrode process involves a one-step three-electron transfer as previously suggested. Moreover, since the ratio of the anodic to cathodic peaks is greater than one, this may indicate not only the presence of adsorption but also that the product is unstable.¹³

The CV data presented in Figure 1 were subject to simulation in order to verify the reaction mechanism and extract the heterogeneous rate constant, k^0 in order to quantitatively assess the electrokinetics of the reaction mechanism. The charge transfer reaction $\text{La}^{*3+} + 3e^- = \text{La}^*$ was supplied to DigiElch as adsorbed species with $\alpha = 0.5$. The equilibrium constant, K^* ; adsorption rate constant, ki^* and the

interaction parameter between adsorbed species, a^* for $\text{La}^{3+} = \text{La}^{3+*}$ at 500°C were equal to $1\text{E-}010$, $1\text{E-}006$ and -2 , respectively. Similarly, K^* , ki^* and a^* for $\text{La} = \text{La}^*$ were 2.75, 900 and 2.75, respectively. The maximum surface coverage, Γ_{max} (mol/cm^2) and the relative surface coverage, θ ($\Gamma/\Gamma_{\text{max}}$), were $1\text{E-}005$ and $1.3\text{E-}011$, respectively. These values slightly change at 450 and 550°C . DigiElch implements the model in such a way that, in equilibrium, the Frumkin isotherm is recovered.

Figure 2 show the simulation of the experimental CV data shown in Figure 1. It can be noted that the cathodic and anodic peaks are closely matched indicating that the rate of the electrochemical reaction, k^0 , electrode potential, E^0 and diffusion coefficient (D_0) can be extracted from the simulation process. However, a preliminary survey of the diffusion coefficients that appear in the literature for temperatures of 450°C range from $0.72 - 1.47 \times 10^{-5} \text{ cm}^2/\text{s}$.^{4,6,16,17} The average from these values is $1.04 \times 10^{-5} \text{ cm}^2/\text{s}$ which coincides with the result obtained in a report by Fabian et al.¹⁸ and therefore this diffusion coefficient was used for subsequent simulations. Moreover, the diffusion coefficients of 2 and $2.85 (\times 10^{-5} \text{ cm}^2/\text{s})$ at 500 and 550°C , respectively were taken from Fabian et al.¹⁸ since these values were not readily found in the literature.

The fit to the cathodic wave in particular was relatively less effective probably due to the presence of nucleation and growth that cannot be accounted for in the simulation. In relation to nucleation

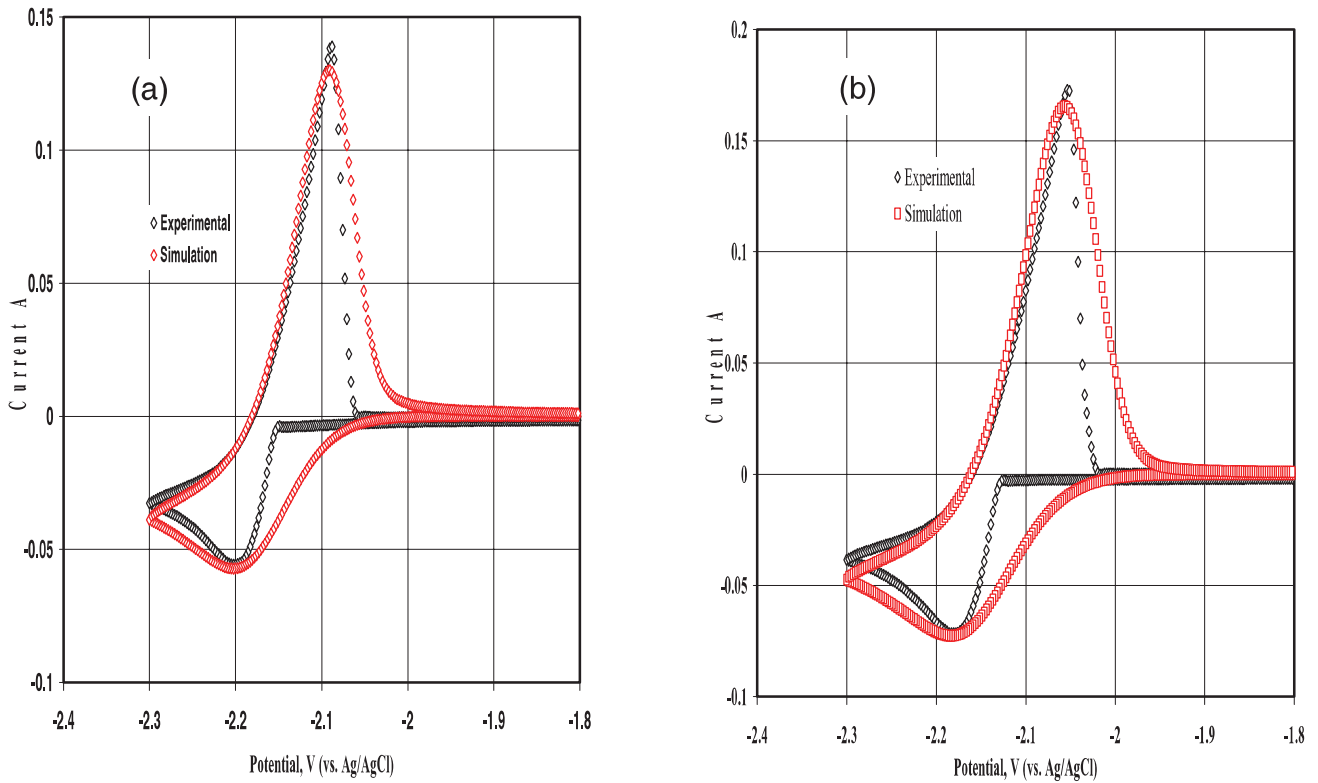


Figure 2. Experimental and simulated CV of La^{3+} at 0.0826 mol/kg (0.132 mol/L) in LiCl – KCl eutectic molten salt. WE: W 1mm dia. wire; CE: - GC rod; REF, Ag/AgCl; [AgCl] = 0.75 mol/kg; (a) 500°C and 100 mV/sec; $k^0 = 0.0146 \text{ cm/s}$; $\Lambda = 1.52$, $\text{Do} = 2.0 \times 10^{-5} \text{ cm}^2/\text{sec}$; $E^0 = -2.190 \text{ V}$ and $S = 0.414 \text{ cm}^2$ and (b) 550°C and 200 mV/sec; $k^0 = 0.0317 \text{ cm/s}$; $\Lambda = 2.89$, $\text{Do} = 2.85 \times 10^{-5} \text{ cm}^2/\text{sec}$; $E^0 = -2.183 \text{ V}$ and $S = 0.328 \text{ cm}^2$.

and growth at electrode surfaces the fundamental questions that need to be addressed are not only the interaction between the metal, La in this case, interacts with the substrate, W, and also the crystallographic misfit between the bulk 3D metal crystal phase and the substrate.¹⁹ This mechanism of initial stages of metal deposition is described by the Volmer-Weber growth mode, Stranski-Krastanov growth mechanism and Frank-van der Merwe growth mode.¹⁹ These issues are

considered beyond the scope of the present communication. Nevertheless, it is believed that the value of k^0 is reasonable since the E^0 derived from this simulation process closely agrees with those derived by Lantelme et al.⁴ at 450°C and Kuznetsov et al.²⁰ at 450, 500 and 550°C as shown in Figure 3.

Table 1 presents the summary of the CV analysis and simulation results and Figure 4 shows the dependence of peak-to-peak potential

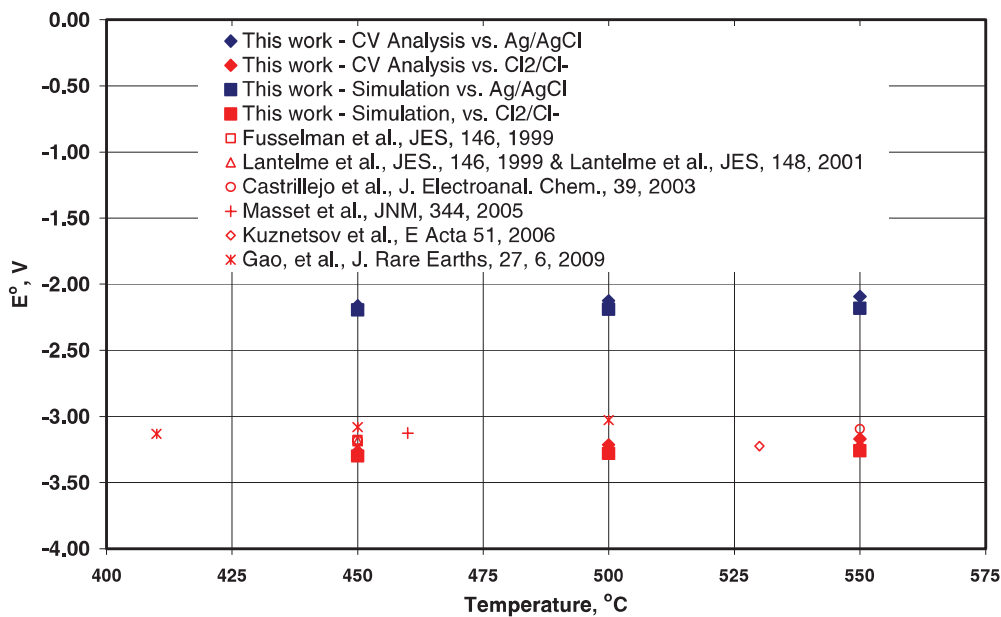


Figure 3. Comparison of Lanthanum Standard Electrode Potentials Derived from CV Analyzes and Simulation. E^0 , V vs. Cl_2/Cl^- for □, △, ○, +, ◇ and * symbols.

Table I. Results of CV Analysis and Simulation for Lanthanum.

T °C	^a E ^o , V (vs. Ag/AgCl)	^a E ^o , V vs. Cl ₂ /Cl ⁻	^c Do cm ² /s	k ^o , cm/s	^b E ^o , V (vs. Ag/AgCl)	^b E ^o , V vs. Cl ₂ /Cl ⁻	Λ
450	-2.163	-3.267	1.0	0.0057	-2.194	-3.298	0.82
500	-2.125	-3.216	2.0	0.0146	-2.190	-3.281	1.52
550	-2.084	-3.161	2.85	0.0317	-2.183	-3.260	2.89

^a CV analysis;^b Simulation,^c Do (× 10⁵)

on scan rate for the reduction of La³⁺ = 0.0826 mol/kg. It can be noted that the value of the electrochemical kinetics, k^o derived from the simulation process is used to obtain the value of the dimensionless parameter Λ. The value of the dimensionless parameter Λ assist us to ascertain the reversibility of the process according to Matsuda et al.¹ Table I shows therefore that the process of La³⁺ + 3e⁻ ↔ La^o is a *quasi-reversible* process. Although previous qualitative studies^{3,4,6,20} have suggested that the reaction is reversible, the present results and their quantitative analysis have unraveled the lanthanum electrode reaction beyond doubt.

Square-wave voltammetry of lanthanum.— Square-wave voltammetry experiments were undertaken to understand the reaction mechanism and the number of electron exchanged of lanthanum in LiCl – KCl eutectic molten salt. The SWV data was obtained at 20 mV (pulse height) amplitude (ΔE_p or E_{sw}) and 5 mV step potential (ΔE_s) and 9, 16, 25, 36, 49 and 64 Hz (scan rate, mV/s: 45, 80, 125, 180, 245 and 320).

Figure 5 shows the typical SWV of lanthanum. It can be seen that the voltammogram indicates asymmetrical Gaussian behavior and the kinetics on the right-side of the vertical line is faster than that on left-side, i.e., less number of points, possibly indicating the effect of

nucleation and growth.^{21,22} It is known that Nernstian systems give a symmetrical bell-shaped curve positioned at the reversible half-wave potential and its full width at half-height (W_{1/2}) for the net current is independent of frequency with cylindrical electrodes.²³

Figure 6 shows the dependence of the net peak current on the square root of the frequency at 500 and 550°C. Linear and polynomial fittings of the data at 500°C gave an R-squared value of 0.9965 and 0.9995, respectively. Similarly, the fitting of the data at 550°C gave 0.9702 and 0.9909 R-squared values for the linear and polynomial fittings, respectively. It can be therefore noted that the dependence of the net current peak on the square root of the frequency is more linear at 500°C than that at 550°C. The small difference on linearity is not fully understood but it is possibly due to quantum chemistry phenomena. In view of these results, the SWV data at 500°C was deconvoluted to work out the full width at half-height (W_{1/2}) and used the equation $W_{1/2} = 3.52RT/2nF$ (R, gas constant; T, temperature, K; n, number of electrons and F, Faraday constant) to calculate the number of electrons exchanged and it was found to be *three*. These results also show that the net current peak of a quasireversible reaction is not a linear function of the square root of the frequency.²⁴ Moreover, in principle, the system may also change from reversible at the lowest frequency to irreversible at the highest frequency.²⁴ In summary, SWV

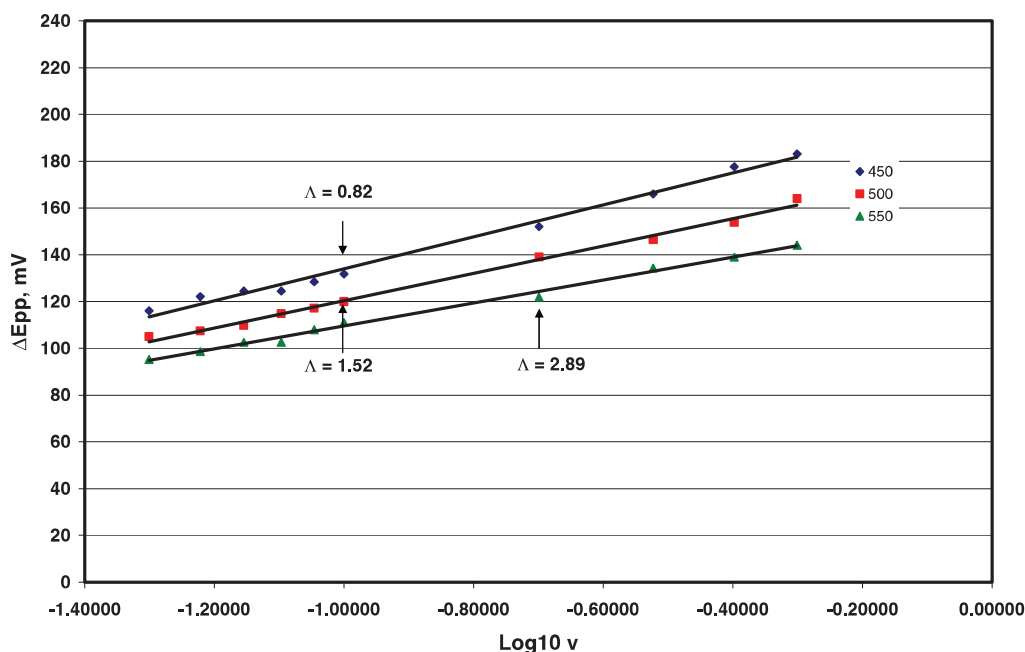


Figure 4. Peak-to-peak potential vs. scan rate for the reduction of La³⁺ = 0.0826 mol/kg to La^o in LiCl – KCl eutectic molten salt. WE: W 1mm dia. wire; CE: - GC rod; REF, Ag/AgCl; [AgCl] = 0.75 mol/kg, α = 0.5. Parameters: 450: E^o = -2.194 V; k^o = 0.0057; D_{La3+} = 1.1 × 10⁻⁵ cm²/sec; S = 0.325 cm². 500: E^o = -2.190 V; k^o = 0.0146; D_{La3+} = 2.0 × 10⁻⁵ S = 0.414 cm². 550: E^o = -2.183 V; k^o = 0.0317; D_{La3+} = 2.85 × 10⁻⁵ cm²/sec; S = 0.328 cm².

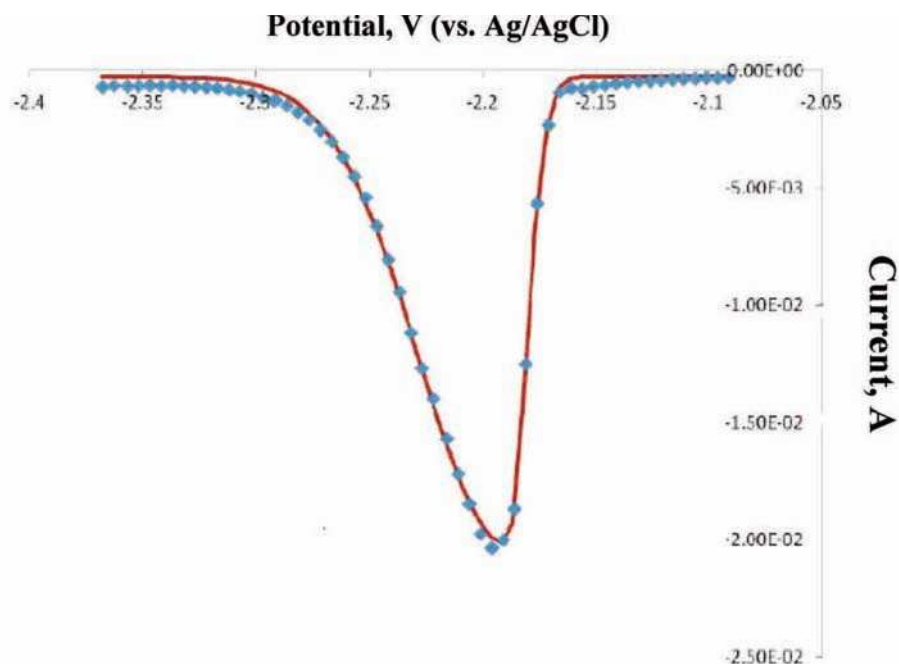


Figure 5. SWV for $\text{La}^{3+} = 0.0408$ mol/kg in LiCl – KCl eutectic molten salt at 25 Hz and 500°C, $E_{\text{sw}} = 20$ mV and $\Delta E_s = 5$ mV. WE: W 1mm dia. wire ($S = 0.72$ cm²); CE: - GC rod; REF, Ag/AgCl; [AgCl] = 0.75 mol/kg.

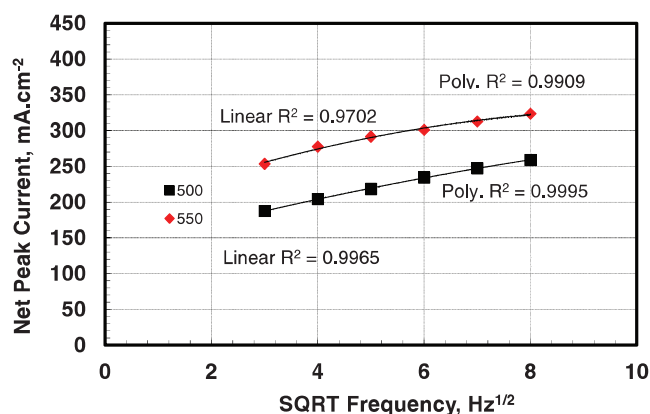


Figure 6. Correlation of Net Peak Current with SQRT Frequency for $\text{La}^{3+} = 0.0408$ mol/kg in LiCl – KCl eutectic molten salt at 500 and 550°C, $E_{\text{sw}} = 20$ mV and $\Delta E_s = 5$ mV WE: W 1mm dia. wire ($S = 0.72$ cm²); CE: - GC rod; REF, Ag/AgCl; [AgCl] = 0.75 mol/kg.

data has also shown that the La^{3+} system in LiCl-KCl eutectic molten salt behaves as a quasireversible electrode reaction.

Conclusions

Lanthanum is fission product that is expected to be present in irradiated fuels and it is an important rare earth element to be refined from their minerals for green technologies, e.g. hybrid vehicle batteries. The experimental CV data was simulated using a three-electron single step reduction process, $\text{La}^{3+} + 3e^- \leftrightarrow \text{La}$. The dimensionless Matsuda et al.¹ parameter Λ were determined to be 0.82, 1.52 and 2.89 for 450, 500 and 550°C, respectively and therefore the lanthanum electrode reaction is quasi-reversible. The dependence of the net current on frequency from SWV analysis also supports this assessment. The electrode potentials derived from the CV analysis closely agrees with those determined by simulation. To the authors' knowledge these quantitative analyzes were conducted for the first time.

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