Electrochemical behaviour of LaCl₃ at tungsten and aluminium cathodes in LiCl–KCl eutectic melt

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1. Introduction

Pyrochemical reprocessing based on molten salt electrorefining is considered as the most suitable method for separation of actinides from the spent metallic fuels irradiated to high burn-up. In this process flow sheet, uranium is recovered onto a solid steel cathode by electrorefining and uranium, plutonium and minor actinides are recovered together on liquid cadmium cathode leaving behind the fission products in the molten salt and in the anode residue [1–3]. Similar stabilities of actinide and lanthanide chlorides and those of their intermetallic compounds with cadmium make it difficult to separate actinides from lanthanides when cadmium is used as the cathode. Many molten metals (Cd, Bi, Zn, Sn, Ga, and Al) were studied in the fluoride media by extracting the actinides from molten fluoride salts into molten metal solvent based on the technique of reductive extraction in view of actinide–lanthanide separation [4–8]. It is reported in literature that among the molten metal solvents studied aluminium shows better selectivity for actinides than lanthanides [9]. Hence it is envisaged that use of aluminium as cathode may prove to be more efficient way for An–Ln separation during the electrorefining process [10]. In order to have a better understanding of the electrorefining process using solid aluminium as cathode, it is necessary to have complete knowledge of the thermochemical properties of the actinide and lanthanide chlorides and their electrochemical behaviour on inert and aluminium cathodes. In this paper, we have chosen to study the behaviour of lanthanum at tungsten, inert electrode and solid aluminium reactive electrode in LiCl–KCl eutectic melt. Fundamental studies on the mechanism of electrode reaction and thermochemical data are not much reported on tungsten and aluminium electrodes over wide temperature range. Fusselman et al. have reported standard electrode potential data for Y, La, Ce, Pr and Gd in molten LiCl–KCl in the temperature range 673–723 K by equilibrium potential measurements [11]. The electroreduction of lanthanum trichloride at 773 K on a tungsten electrode in LiCl–KCl and LiCl–KCl–NaCl eutectic was reported by Lantelme et al. [12]. Castrillejo et al. studied the electrochemical behaviour of lanthanum and yttrium ions in LiCl–KCl eutectic at 773 K and in an equimolar mixture of CaCl₂–NaCl at 823 K on tungsten electrode [13]. They had studied the reaction mechanism, nucleation phenomena and the transport parameters of the electroactive species using cyclic voltammetry, chronopotentiometry and chronocoulometry. Masset et al. had studied the electrochemical reduction of lanthanum and neodymium chlorides at a tungsten working electrode in LiCl–KCl melt using cyclic voltammetry and chronopotentiometry [14]. They had derived the thermochemical data from their measurements. Taxil et al. have reported the reduction behaviour of lanthanide ions (Ce, Gd, Sm and Nd) on molybdenum electrode and co-reduction of lanthanide ions along with aluminium ions on tantalum electrode in LiF–CaF₂ melt [15,16]. Researchers at ITU have reported electrorefining experiments using solid aluminium as electrode for separation of An–Ln [17–20]. Castrillejo et al. have studied the behaviour of Er and Pr on Al electrode in LiCl–KCl melt [21,22]. But there is no report to our knowledge on complete elucidation of the reaction of La on...
aluminium electrode. The purpose of our investigation is to study the electrochemical behaviour of lanthanum chloride in LiCl–KCl eutectic in the temperature range 698–798 K at an inert electrode and aluminium electrode using transient electrochemical techniques and derive the thermochemical properties.

2. Experimental

2.1. Chemicals

Anhydrous lithium chloride (AR grade, M/s. Chempure Private Ltd, India), anhydrous potassium chloride (AR grade, M/s. Ranbaxy Fine Chemicals, India) and LaCl3 (Alfa Aesar 99.99%) were used for the preparation of the electrolyte. High purity aluminium wire (Alfa Aesar 99.99%) was used for preparing the aluminium working electrode.

2.2. Preparation of the electrolyte salt

LiCl–KCl eutectic mixture was pre-dried under vacuum for 120 h at 420 K. The salt mixture was purified by passing chlorine gas at 723 K and melting under chlorine atmosphere in a set up discussed elsewhere [23]. Addition of LaCl3 to the purified salt was done at 723 K in a high purity argon atmosphere glove box. The concentration of lanthanum in the LiCl–KCl eutectic was measured by dissolving a sample in 0.1 M HNO3 and analyzing by AAS.

2.3. Electrochemical apparatus and electrodes

A three electrode cell assembly was used for all the electrochemical measurements and the cell is described elsewhere [24]. 1.5 mm diameter tungsten and Al wires were used as working electrodes. The area of working electrode was calculated from the depth of immersion of the electrode in the melt. 1 mm diameter tantalum wire coiled at one end was used as the counter electrode. Both the working and the counter electrodes were insulated by using 1.5 mm bore alumina sleeves. The reference electrode was Ag/0.1 mol% AgCl in LiCl–KCl eutectic taken in a pyrex glass tube. A kanthal wire wound resistance furnace was used for heating the cell and the temperature was controlled by a PID controller with an accuracy ±1 K. The temperature of the melt was monitored by a chromal–alumel thermocouple kept in an alumina sleeve. Cyclic voltammograms, square wave voltammograms, chronopotentiograms, open circuit potential measurements and impedance spectrum were obtained using AUTOLAB PGSTAT30 from M/s Eco Chemie, Netherlands equipped with IF 030 interface. The voltammograms were processed using GPES 4.9 software and the impedance spectrum was processed using FRA 4.9 software.

3. Results and discussion

3.1. Reduction behaviour on inert W electrode

3.1.1. Analysis of the cyclic voltammograms

Fig. 1 shows the cyclic voltammogram obtained at the W working electrode in a molten salt of LaCl3 (1.64 × 10⁻⁴ mol cm⁻³) in LiCl–KCl eutectic melt at 773 K. Reduction of LaCl3 was found to take place in a single step. The cathodic peak, Ic and the associated anodic peak, Ia are characteristic of a soluble-insoluble exchange. Peak Ic lies close to −1.95 V and this potential is in agreement with that reported by Plameck and co-workers [25] for La(III)/La couple. Hence peak Ic in Fig. 1 corresponds to the reduction of La(III) to La and the corresponding anodic peak Ia to the dissolution of La metal that had been deposited during the cathodic sweep.

Fig. 1. A comparison of the cyclic voltammogram for pure LiCl–KCl melt and LiCl–KCl–LaCl3 melt. Working electrode: tungsten, apparent electrode area: 0.301 cm². Temperature: 773 K; scan rate: 0.11 V s⁻¹.

We had investigated the dependence of peak potential and peak current on the polarization rates for the reduction process. Cyclic voltammograms recorded in a molten salt of LaCl3 (7.54 × 10⁻⁵ mol cm⁻³) in LiCl–KCl eutectic melt at 798 K at different scan rates are shown in Fig. 2. Table 1 shows the cathodic peak analysis at various scan rates and temperatures. The following equation gives the relationship among the peak potential, the half peak potential and the number of electrons transferred for a reversible electrochemical reaction involving insoluble species [26]:

\[ E_p - E_{p/2} = -\frac{0.77RT}{nF} \]

It was observed that the magnitude of \( E_p - E_{p/2} \) increased with increasing scan rates and is much larger than that expected for a reversible process. The value of n estimated using Eq. (1) is much less than the expected value 3. The cathodic peak current was plotted against square root of scan rate. Linear dependence of peak current, \( I_{pc} \), on the square root of scan rate, \( v^{1/2} \) was observed for low scan rates only, namely in the scan range 25 ≤ v ≤ 150 mV s⁻¹ as seen in Fig. 3. These observations suggest that the reduction is not controlled by diffusion of La₃⁺ ions alone.

Fig. 2. Cyclic voltammogram for 7.54 × 10⁻⁵ mol cm⁻³ LaCl3 in LiCl–KCl melt for a tungsten electrode at various scan rates. Apparent electrode area: 0.347 cm². Temperature: 798 K. Inset: variation of peak potential with logarithm of sweep rate.
It was observed that the cathodic peak potential shifted to more cathodic values at higher scan rates as seen in the inset in Fig. 2. However, we did not observe a gradual shift in the peak potentials within the scan interval studied. The value of $\alpha n_F$ calculated using the following relation which is applicable for an irreversible process is shown in Table 1 [27]

$$E_P - E_{P/2} = -1.857 \frac{RT}{\alpha n_F}$$

(2)

The value of $\alpha n_F$ was obtained from the slope of the plot of $E_p$ vs. log $v$ for scan rates 75, 150 and 200 mV s$^{-1}$ at 798 K and found to be 1.77. A detailed analysis on the reversibility of the reduction process is done in Section 3.1.4.

We had observed a linear dependence of the cathodic peak current on the square root of scan rate in the scan range $25 \leq v \leq 150$ mV s$^{-1}$ for all the temperatures studied. Later in this section we have discussed about the convoluted curves and their logarithmic analysis indicating the reduction process being diffusion-controlled at low polarization rates. Also we have verified the validation of Sand’s equation for a diffusion-controlled process from the chronopotentiograms. Hence, we think it is more appropriate to use the Berzins–Delahay equation for a diffusion-controlled process with formation of an insoluble product for calculation of the diffusion coefficient in this case as has been adopted by many authors earlier [30]. The diffusion coefficient of La(III) ion was calculated from the slope of the plot, $i_{pc}$ vs. $v^{1/2}$, in the scan range $25 \leq v \leq 150$ mV s$^{-1}$ using the Berzins–Delahay equation given below [31]

$$i_{pc} = 0.61(nF)^{3/2}(RT)^{-1/2}AD_{La(II)}^{1/2}C_{La(II)}^{0}v^{1/2}$$

(4)

where ‘$n$’ is the charge transfer coefficient and $n_F$ is the number of electrons transferred in the rate determining step. It may be noted that the values obtained are not consistent and the values do not have any significance for scan rates between 25 and 150 mV s$^{-1}$. Hence we consider use of Eq. (3) might be a better method of estimating the charge transfer coefficient since it incorporates the variation of cathodic peak potential for a range of scan rates [28,29].

$$\Delta E_P = \frac{2.303RT}{2\alpha n_F}$$

(3)

Fig. 3. Plot of current density vs. square root of scan rate for LiCl–KCl–LaCl₃. Concentration of LaCl₃: $7.54 \times 10^{-3}$ mol cm$^{-3}$. Temperature: 798 K.
where $i_{pc}$ is the cathodic peak current (A), $n$ the number of electron transferred, $F$ Faraday’s constant, $R$ the universal gas constant (8.314) mol−1 K−1, $T$ the absolute temperature, $A$ the electrode area (cm²), $c_{La(II)}$ the bulk concentration of LaCl₃ (mol cm⁻³), $D_{La(II)}$ the diffusion coefficient (cm² s⁻¹) and $v$ the potential sweep rate (V s⁻¹). The diffusion coefficients of La(III) in 7.54 × 10⁻⁵ mol cm⁻³ LaCl₃ in LiCl–KCl in the temperature range 698–798 K are reported in Table 2. The diffusion coefficient values at 723 K reported by Castillejo et al. [13] and Masset et al. [14] are also listed in the table and the values are in agreement with that of ours.

Semi-integral of the cyclic voltammetric data gives the convoluted curves, a form resembling a steady-state voltammetric curve [32,33]:

$$m^* = \frac{2}{\sqrt{\pi}} \int_0^t \frac{i(t)}{\sqrt{t-t'}} dt$$

where $i(t)$ is the current measured at the time $t$ of the $i(t)$ transients. A potential plateau, $m^*$, occurs in the region of cathodic potentials which indicates that the rate transfer is limited by diffusion. The forward and backward waves are more or less superimposed as seen in Fig. 4. The hysteresis could be attributed to the non-reversibility of the electrode process or the existence of nucleation overpotential or possibly a combination of both. For a reversible charge transfer process the convoluted curve should obey the following relationship [34]

$$E = E^0_{La(II)/La(0)} + \frac{RT}{nF} \ln \frac{q_{LaCl}}{a_{La(0)}} + \frac{RT}{nF} \ln \left( \frac{m^* - m}{m^*} \right)$$

where $E^0_{La(II)/La(0)}$ is the standard potential of the La(III)/La(0) redox couple, $q_{LaCl}$ and $a_{La(0)}$ are the activities of LaCl₃ and pure lanthanum metal, respectively, $m$ is the semi-integral of the current density and $m^*$ the cathodic limiting value of the functions. The plot of $E$ vs. $\ln((m^* - m)/m^*)$ should yield a straight line with slope corresponding to three electron transfer. The convoluted curves obtained at various scan rates appeared similar. However, we observed that the plot $E$ vs. $\ln((m^* - m)/m^*)$ corresponding to the convoluted curves obtained at 25 mV s⁻¹ and 50 mV s⁻¹ alone yielded slope close to that corresponding to three electron transfer. According to the theory of convolution [35], the diffusion coefficient of La(II) can be obtained using Eq. (7):

$$m^* = -nFAC_{La(II)}[i/ETB]^{1/2}$$

$m^*$ was obtained from cyclic voltammograms at 25 mV s⁻¹ graphically [36]. The diffusion coefficients calculated from the convoluted curve at 25 mV s⁻¹ for various temperatures is also given in Table 2.

3.1.2. Analysis of the chronopotentiograms

Fig. 5 shows the chronopotentiograms at various current densities for LiCl–KCl melt containing 7.54 × 10⁻⁵ mol cm⁻³ LaCl₃ at 798 K at the W electrode. There is only one plateau corresponding to the reduction of the La(III) to La(0) as observed in the cyclic voltammograms. The Sand’s relation for reversible process was used for calculating the diffusion coefficient of the La(III) ion [37]:

$$i_{pc} = \frac{0.5nFp_0^1/2}{\pi^{1/2} D_{La(III)}}$$

where $i$ is the current density (A cm⁻²) and $t_c$ is the transition time (s). The product $i_{pc}t_c^{1/2}$ remained almost constant in the current density range investigated as seen in the inset of Fig. 5. The value of diffusion coefficient of the La(III) ion calculated from the chronopotentiograms are also given in Table 2.

3.1.3. Analysis of the square wave voltammograms

Fig. 6 shows the square wave voltammograms of 7.54 × 10⁻⁵ mol cm⁻³ LaCl₃ in LiCl–KCl melt at 793 K at 8 Hz. It was observed that only a single redox species is present in the potential range studied. The width $W_{1/2}$ of the peak at half its height depends on the number of electrons transferred, $n$ and temperature by the following equation [38,39]

$$W_{1/2} = 3.5 \frac{RT}{nF}$$

This equation is valid for a perfectly Gaussian peak. But it may be observed from Fig. 6, that the peak is asymmetric due to nucleation phenomena. Limited fitting was done considering only the left part of the voltammogram. The value of $n$ using the above relation for the Gaussian fit was evaluated to be 2.93 ± 0.08. This substantiate our earlier findings from cyclic voltammetry and chronopotentiometry that the La(III) ion reduces to La metal in a single step.

3.1.4. Kinetic study of the electrode reaction – reversibility study

Though there was no indication of large overpotential from the cyclic voltammograms and convoluted curves such as cross over in the cathodic branch, the cathodic peak potential was found to shift cathodically with increasing scan rates and the peak potential difference $E_p - E_{pc}$ increased with increasing scan rates. It is
Table 2
Diffusion coefficient of La(III) ion in LiCl–KCl melt at different temperatures. Concentration of LaCl$_3$: $7.54 \times 10^{-5}$ mol cm$^{-3}$. $D$ (×10$^5$ cm$^2$ s$^{-1}$).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>698</th>
<th>723</th>
<th>748</th>
<th>798</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic voltammetry</td>
<td>0.74 ± 0.05</td>
<td>0.91 ± 0.10</td>
<td>1.31 ± 0.07</td>
<td>1.52 ± 0.07</td>
</tr>
<tr>
<td>Convolution</td>
<td>1.02 ± 0.05</td>
<td>1.16 ± 0.06</td>
<td>1.38 ± 0.07</td>
<td>1.79 ± 0.09</td>
</tr>
<tr>
<td>Chronopotentiometry (using Sand’s equation for reversible system)</td>
<td>1.52 ± 0.07</td>
<td>–</td>
<td>2.75 ± 0.13</td>
<td>3.2 ± 0.35</td>
</tr>
<tr>
<td>(Literature value)</td>
<td>1.17 [13]</td>
<td>0.8 [14]</td>
<td>1.76 [12]</td>
<td></td>
</tr>
</tbody>
</table>

necessary to evaluate the kinetic parameter – the heterogenous rate constant, $k_s$, of the electrode reaction in order to determine the scan rates at which the reduction showed reversible, quasi-reversible and irreversible behaviour. Electrochemical impedance spectroscopy is a suitable method for the estimation of heterogenous rate constant. The electrochemical impedance spectrum was recorded at 798 K for $7.54 \times 10^{-5}$ mol cm$^{-3}$ LaCl$_3$ in LiCl–KCl melt at the rest potential – 0.25 V in the frequency range 1 Hz to 1 MHz with an applied amplitude of 10 mV on the W working electrode. The impedance data between 100 Hz to 50 kHz were fitted into an equivalent circuit containing a general diffusion related element, known as Warburg impedance ($W$), a resistor element ($R_1$), corresponding to the electrolyte resistance, another resistor element ($R_2$) corresponding to the charge transfer resistance and the diffuse double layer capacitance ($C$). This circuit, called the Randles cell was used to simulate the impedance data [40]. The measured and simulated impedance data are shown in Fig. 7. It is observed that the complex impedance diagram consists of two parts, one a capacitance loop in the higher frequency region which corresponds to the electrochemical charge transfer at the electrode/electrolyte interface and a straight line with a slope of about 45$^\circ$ in the lower frequency attributed to the diffusion of the La(III) ions. The resistance of the molten salt was found to be 0.72 $\Omega$. The charge transfer resistance, Warburg impedance and the capacitance values were 0.78 $\Omega$, 0.016 and 20.77 $\mu$F, respectively. The conceived Randles cell is able to simulate the measured data fairly well. The charge transfer resistance, $R_{CT}$ at the rest potential is given by the following equation [40]:

$$R_{CT} = \frac{RT}{nF\lambda_0} = \frac{RT}{n^2F^2k_sC_{La(III)}^{1-\alpha}}$$

![Fig. 6. Square wave voltammograms for $7.54 \times 10^{-5}$ mol cm$^{-3}$ LaCl$_3$ in LiCl–KCl melt at 793 K. Working electrode: tungsten. Apparent electrode area: 0.347 cm$^2$. Frequency: 8 Hz.](image)

![Fig. 7. Complex impedance spectra for $7.54 \times 10^{-5}$ mol cm$^{-3}$ LaCl$_3$ in LiCl–KCl melt at 793 K for a working electrode at rest potential (–0.25 V vs. Ag/Ag). (a) Nyquist plot; (b and c) Bode plots; (d) corresponding equivalent circuit.](image)
where \( j_0 \) is the exchange current density. This expression allows us to calculate rate constant of charge transfer. The value of the rate constant \( k_r \) was estimated to be \( 5.05 \times 10^{-6} \) cm s\(^{-1}\).

It may be noted that the value of \( k_r \) depends largely on the value of \( \alpha \). The value of \( \alpha \) used was that obtained from the slope of the plot of \( E_p \) vs. \( \log \nu \) for scan rates 75, 150 and 200 mVs\(^{-1}\) according to Eq. (3). In order to verify the value of the rate constant obtained from impedance spectrum, an alternative approach was adopted for the estimation of the kinetic parameters from the convoluted curves [13,30]. The following relationship is valid in the case of a quasi-reversible exchange with formation of an insoluble product.

\[
E = E^0 + 2.3 \frac{RT}{nF} \log k_r + 2.3 \frac{RT}{nF} \log B
\]

\[
B = \frac{(m - m')D^{-1/2} + nFA \exp[(nF/RT)E - E^0]}{I}
\]

where \( k_r \) and \( \alpha \) are the charge-transfer rate constant and the transfer coefficient, respectively. \( E^0 \) is the standard potential of the \( \text{La(III)}/\text{La(0)} \) system, \( A \) is the surface area of the electrode, \( m \) the convoluted current and \( m' \) its limiting value. Plot of \( E \) vs. \( \log B \) were obtained for polarization rates 75, 100, 125 and 150 mVs\(^{-1}\) using values of \( m \) from 10% to 90% of \( m' \) and they were found to be linear. The value of apparent standard potential calculated in the following section was used for \( E^0 \). The transfer coefficient, \( \alpha \), was obtained from the slope and the charge-transfer rate constant, \( k_r \), was obtained from the intercept. The results are shown in Table 3 and the average value of \( \alpha \) and \( k_r \) were found to be \( 0.71 \pm 0.05 \) and \( 4.1 \pm 0.6 \times 10^{-6} \) cm s\(^{-1}\) respectively. The value of \( k_r \) is found to be close to the value obtained from the impedance spectrum. However we did not observe a linear trend for the plots of \( E \) vs. \( \log B \) for scan rates 25 and 50 mVs\(^{-1}\).

According to Matsuda and Ayabe the following criteria is applicable for an electrochemical process [27].

For reversible (Nernstian) process:

\[
\frac{k_r}{(DnF/RT)^{1/2}} \geq 15
\]

For quasi-reversible process:

\[
10^{-2(1+\alpha)} < \frac{k_r}{(DnF/RT)^{1/2}} < 15
\]

Totally irreversible process:

\[
\frac{k_r}{(DnF/RT)^{1/2}} \leq 10^{-2(1+\alpha)}
\]

The following observations were made for \( 7.54 \times 10^{-5} \) mol cm\(^{-3}\) \( \text{LaCl}_3 \) in LiCl–KCl melt at 798 K at various scan rates using the value of 0.71 for \( \alpha \) and 4.1 \times 10^{-6} \) cm s\(^{-1}\) for \( k_r \) as obtained from the convoluted curves:

\[
\begin{align*}
k_r &< 5.31 \times 10^{-6} \text{ for scan rate 250 mVs}^{-1}, \\
k_r &< 4.75 \times 10^{-6} \text{ for scan rate 175 mVs}^{-1}, \\
3.9 \times 10^{-6} &< k_r < 0.16 \text{ for scan rate 150 mVs}^{-1}, \\
3.36 \times 10^{-6} &< k_r < 0.13 \text{ for scan rate 100 mVs}^{-1}, \\
2.91 \times 10^{-6} &< k_r < 0.12 \text{ for scan rate 75 mVs}^{-1}.
\end{align*}
\]

Hence it may be concluded that the reduction of \( \text{La(III)} \) ion on \( \text{W} \) electrode shows quasi-reversible behaviour for scan rates up to 150 mVs\(^{-1}\) and irreversible behaviour for scan rates higher than this. The reduction of \( \text{La(III)} \) ion is predominantly controlled by charge transfer for scan rates higher than 75 mVs\(^{-1}\).

### 3.1.5. Apparent standard potential of \( \text{La(III)}/\text{La(0)} \) system in LiCl–KCl melt

As stated in Section 3.1.1 the convoluted curves obtained at 25 mVs\(^{-1}\) obeyed Eq. (6) for a reversible charge transfer process. Eq. (6) may be used for deriving the apparent standard potential of the \( \text{La(III)}/\text{La} \) redox couple as follows.

The apparent standard potential \( E^0 \) for the redox couple \( \text{La(III)}/\text{La} \) is defined as

\[
E^0_{\text{La(III)/La(0)}} = E^0_{\text{La(III)/La(0)}} + \frac{RT}{nF} \ln \gamma_{\text{LaCl}_3}
\]

where \( \gamma_{\text{LaCl}_3} = \frac{a_{\text{LaCl}_3}}{X_{\text{LaCl}_3}} \) is the activity coefficient of \( \text{LaCl}_3 \). Eq. (6) may be rewritten as

\[
E = E^0_{\text{La(III)/La(0)}} + \frac{RT}{nF} \ln X_{\text{LaCl}_3} + \frac{RT}{nF} \ln \left( \frac{m - m'}{m'} \right)
\]

The voltammograms recorded at 25 mVs\(^{-1}\) were considered, as diffusion predominates at this scan rate. The apparent standard potential was deduced from the convoluted curves using Eq. (14). Plots of the electrode potential versus \( \ln([m - m']/m') \) were linear as seen in Fig. 8 and the number of electron transfer computed from the slope of the plot was close to three. This substantiates our earlier contention that the reduction is predominantly controlled by diffusion of \( \text{La(III)} \) ions at low polarization rates. The apparent standard potential was obtained from the intercept as per Eq. (14) after substituting the concentration of \( \text{LaCl}_3 \) in terms of mole fraction.

The apparent standard potential thus obtained versus the \( \text{Ag/AgCl} \) (0.1 mol%) was converted to the scale of \( \text{Cl}_2/\text{Cl}^- \) reference electrode. Assuming unit activity of the pure metal and unit activity coefficient for \( \text{AgCl} \) at low concentration of \( \text{AgCl} \) as reported by Flenas and Ingraham [41], the potential of the \( \text{Ag/AgCl} \) reference electrode is defined as

\[
E_{\text{AgCl}} = E^0_{\text{AgCl}} - \frac{RT}{nF} \ln X_{\text{AgCl}}
\]
The value of $E^0_{\text{AgCl}}$ relative to the $\text{Cl}_2/\text{Cl}^-$ is given by Fusselman et al. [11]

$$E^0_{\text{AgCl}} = -1.0910 + 0.0002924 \times T(K)$$  (16)

The potentials $E^0_{\text{AgCl}}$ vs. $\text{Cl}_2/\text{Cl}^-$ and $E_{(0.1 \text{ mol}\% \text{AgCl})}$ vs. $\text{Cl}_2/\text{Cl}^-$ at various temperatures were evaluated using Eqs. (16) and (15) respectively. The apparent standard potentials of $\text{La(III)}/\text{La(0)}$ vs. $\text{Cl}_2/\text{Cl}^-$ reference electrode at different temperatures were thus evaluated and are shown in Table 4.

The apparent standard potentials were also obtained from the chronopotentiograms as discussed below. The potential–time relation of the chronopotentiometric curve for a reversible redox couple with the formation of an insoluble metallic deposit is given by the equation [17]

$$E(t) = E^0_{\text{La(III)/La(0)}} + \frac{RT}{nF} \ln(a_{\text{LaCl}_3}) + \frac{RT}{nF} \ln \left( \frac{t^{1/2} - t_1^{1/2}}{t^{1/2} - t_2^{1/2}} \right)$$  (17)

Introducing the relation for apparent standard potential from Eq. (13), Eq. (17) may be rewritten as

$$E(t) = E^0_{\text{La(III)/La(0)}} + \frac{RT}{nF} \ln(X_{\text{LaCl}_3}) + \frac{RT}{nF} \ln \left( \frac{t^{1/2} - t_1^{1/2}}{t^{1/2} - t_2^{1/2}} \right)$$  (18)

The plots of cathodic potential of the chronopotentiograms versus $\ln(t^{1/2} - t_1^{1/2}/t^{1/2} - t_2^{1/2})$ were also found to be linear. The apparent standard potential was obtained from the intercept. The apparent standard potential obtained for temperatures 748 and 798 K are shown in Table 4.

3.2. Electrochemical reduction behaviour on solid aluminium electrode

3.2.1. Analysis of the cyclic voltammograms

The electroactive domain of pure LiCl–KCl on aluminium electrode is shown in Fig. 9 which is significantly smaller than that on the W electrode. The cathodic limit is shifted to a lesser value due to the formation of Al–Li alloy. The anodic limit is imposed by the oxidation of the Al metal. Fig. 10 compares the cyclic voltammograms obtained at 723 K on tungsten and aluminium electrodes at 100 mV s$^{-1}$. Reduction of La(III) on Al occurs at a less cathodic potential than the reduction on inert W electrode. This is due to formation of La–Al alloy. Only a single redox system was observed in the scan rates examined.

![Fig. 9. Electroactive domain of pure LiCl–KCl on aluminium electrode as compared to that on a W electrode.](image)

![Fig. 10. Cyclic voltammograms for LaCl$_3$ in LiCl–KCl melt at a tungsten and aluminium electrodes. Polarization rate: 100 mV s$^{-1}$; temperature: 723 K. Concentration of LaCl$_3$: 7.54 × 10$^{-5}$ mol cm$^{-3}$.](image)

Based on the reported phase diagram [42] shown in Fig. 11, the probable reaction on the aluminium rich side could be the formation of the compound richest in aluminium, namely, $\text{Al}_{11}\text{La}_3$:

$$3\text{La(III)} + 11\text{Al} + 9\text{e}^- \rightleftharpoons \text{Al}_{11}\text{La}_3$$  (19)

Similar observations have been made in case of praseodymium and erbium by previous authors [21,22]. Also later in Section 3.4, it is proved by XRD and SEM–EDX analysis that the redox species correspond to La(III)/Al$_{11}$La$_3$.

Fig. 12 shows cyclic voltammograms recorded at various scan rates in the LiCl–KCl–LaCl$_3$ melt on the Al electrode. The voltammograms show a single reduction wave and its corresponding oxidation wave. The shape of the voltammogram resembles closely that of a soluble–soluble reversible system. The redox couple is associated to the reduction of La(III) ions into La metal (dissolved in Al) in a single step and to the re-oxidation of La metal to La(III), with the exchange of three electrons. Though the peak potential shift in the cathodic direction at higher scan rates, the magnitude of $E_{pc} - E_{pa/2}$ does agree with the condition for soluble–soluble couple (≈ −2.2RT/nF) at very low scan rates and the reduction may be presumed close to reversibility at low scan rates and show Nernstian behaviour.

![Fig. 11. Al–La phase diagram [42].](image)
Table 4

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(E^0_{\text{La(III)/La(0)}}) vs. Cl(_2)/Cl(^-) (V)</th>
<th>(\Delta G^\circ_{\text{LaCl}_3} (\text{kJ mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>(-3.152 (-3.146))*</td>
<td>(-912.5)</td>
</tr>
<tr>
<td>748</td>
<td>(-3.138)</td>
<td>(-908.3)</td>
</tr>
<tr>
<td>773</td>
<td>(-3.140)</td>
<td>(-909.1)</td>
</tr>
<tr>
<td>798</td>
<td>(-3.116)</td>
<td>(-902.1)</td>
</tr>
</tbody>
</table>

*Fusselman et al. [11].

\[ E^0_{\text{La(III)/La(0)}} = E^0_{\text{La(III)/La(Al)}} + \frac{RT}{3F} \ln \frac{a_{\text{La(III)}}}{a_{\text{La(Al)}}} \]  

(20)

where \(E^0_{\text{La(III)/La(0)}}\) is the standard potential of La(III)/La(0) in LiCl–KCl melt, \(a_{\text{La(III)}}\) and \(a_{\text{La(Al)}}\) are the activity of LaCl\(_3\) in salt and that of La in aluminium respectively. Introducing the expression for apparent standard potential, \(E^0_{\text{La(III)/La(Al)}}\) from Eq. (13), Eq. (20) is rearranged as

\[ E^\circ_{\text{La(III)/La(Al)}} = E^0_{\text{La(III)/La(0)}} + \frac{RT}{3F} \ln X_{\text{La(III)}} - \frac{RT}{nF} \ln a_{\text{La(Al)}} \]  

(21)

where \(X_{\text{La(Al)}}\) is the mole fraction of lanthanum in aluminium. The apparent standard potential for reduction of LaCl\(_3\) on Al electrode is given as [10]

\[ E^0_{\text{La(III)/La(Al)}} = E^0_{\text{La(III)/La(0)}} - \frac{RT}{nF} \ln a_{\text{La(Al)}} \]  

(22)

Eq. (21) is rewritten as

\[ E^\circ_{\text{La(III)/La(Al)}} = E^0_{\text{La(III)/La(Al)}} + \frac{RT}{3F} \ln X_{\text{La(III)}} \]  

(23)

The equilibrium potential was obtained graphically as shown in Fig. 13. Using Eq. (23) the apparent standard potentials on Al electrode were determined and the results are listed in Table 5. The Gibbs energy formation of Al\(_3\)La\(_3\) intermetallic compound was calculated from the standard electrode potentials of lanthanum on tungsten and aluminium electrodes and is shown in Table 6.

![Cyclic voltammogram](image1)

**Fig. 12.** Cyclic voltammogram for 7.54 × 10^{-3} mol cm\(^{-3}\) LaCl\(_3\) in LiCl–KCl melt for an aluminium electrode at various scan rates. Apparent electrode area: 0.347 cm\(^2\). Temperature: 723 K.

![Graphical estimation of equilibrium potential](image2)

**Fig. 13.** Graphical estimation of equilibrium potential from cyclic voltammogram. Concentration of LaCl\(_3\): 7.54 × 10^{-3} mol cm\(^{-3}\); WE: Al; apparent electrode area: 0.347 cm\(^2\). Temperature: 698 K.

Table 5

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(E^\circ_{\text{La(III)/La(Al)}}) vs. AgCl/Ag (V)</th>
<th>(E^0_{\text{La(III)/La(Al)}}) vs. Cl(_2)/Cl(^-) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>(-1.346)</td>
<td>(-2.528)</td>
</tr>
<tr>
<td>723</td>
<td>(-1.333)</td>
<td>(-2.515)</td>
</tr>
<tr>
<td>748</td>
<td>(-1.321)</td>
<td>(-2.509)</td>
</tr>
<tr>
<td>773</td>
<td>(-1.307)</td>
<td>(-2.492)</td>
</tr>
</tbody>
</table>

Table 6

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(\Delta G^\circ_{\text{LaAl}_3} (\text{kJ mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>(-184.4)</td>
</tr>
<tr>
<td>748</td>
<td>(-182.7)</td>
</tr>
<tr>
<td>773</td>
<td>(-180.6)</td>
</tr>
</tbody>
</table>

3.3. Open-circuit chronopotentiometry

In the open-circuit chronopotentiometry, the cathode is polarized for a short period at a high cathodic overpotential and the open-circuit potential of the electrode is measured as a function of time. The potential increases towards anodic direction with the evolution of several plateaus. Each plateau is typical of the equilibrium in the solid state between two intermetallic compounds [43–45]. Initially, potential time transients were obtained on a tungsten electrode by electrodepositing lanthanum for 300 s at a potential of \(-2.1\) V vs. AgCl/Ag reference electrode. It was observed that the potential of the lanthanum-coated tungsten electrode
stabilized at the equilibrium potential of La(III)/La system for a short while and rapidly increased towards anodic direction. This is evidence that there is no compound in the lanthanum–tungsten system.

The potential measured with respect to Ag/0.1 mol% AgCl in LiCl–KCl reference electrode was calibrated with reference to that of a La(III)/La electrode, as obtained above. All the potentials given hereafter are referred to this La(III)/La potential. Then, open-circuit potentiometry was carried out to investigate the formation potential of La–Al alloys. La metal was electrodeposited on Al electrode for a short period (60–300 s). The potential transient curve was monitored by recording the open circuit potential at zero current. Since the deposited La metal reacts with the Al substrate and diffuses into the bulk of the electrode, the electrode potential gradually shifts to more positive values. During this process, potential plateau is observed when a composition of the electrode surface is within a range of two-phase coexisting state. The potential of the plateau referred to the lanthanum electrode is the emf of the cell represented as:

$$\text{La}(0)/\text{La}(III) \text{ in LiCl – KCl/LaAl}_{11/3}$$

Fig. 14 shows the open circuit potential transient curves obtained on the aluminium electrode at 741 and 710 K exhibiting the formation of a solid phase on the aluminium surface. Even though lanthanum forms several intermetallic compounds with aluminium, only one potential plateau was observed as seen in Fig. 14. From our earlier inference from the cyclic voltammograms

as mentioned in Section 3.2.1, the intermetallic formed is Al$_{11}$La$_3$ and the potential plateau is due to coexistence of Al$_{11}$La$_3$ and (Al). Replicate measurements were made to estimate the standard deviation of the measured emf. The Gibbs energies of formation of the intermetallic compound Al$_{11}$La$_3$ was deduced from the emf values at different temperatures and are compared with those reported by Castrillejo et al. [46] in Table 7. Our values are in good agreement with those reported by Castrillejo et al. measured using the same technique. Sommer et al. had measured the enthalpy of formation of aluminium–lanthanum alloys by solution calorimetry [47]. They have reported the enthalpy of formation of Al$_{11}$La$_3$ at 1513 K to be $-41 \pm 2.5 \text{ kJ mol}^{-1} \text{ atom}^{-1}$. Borzone et al. have reported the enthalpy of formation of Al$_{11}$La$_3$ at 298 K to be $-41 \pm 2.0 \text{ kJ mol}^{-1} \text{ atom}^{-1}$ measured by direct calorimetry [48]. In the present work, we have derived the enthalpy of formation of Al$_{11}$La$_3$ from the slope of $\Delta G/\mathcal{T}$ vs. $1/\mathcal{T}$ in the temperature range 710–773 K. The heat capacity contribution is considered negligible. The enthalpy of formation of Al$_{11}$La$_3$ at the mid temperature, namely, 742 K was found to be $-42.92 \pm 1.5 \text{ kJ mol}^{-1} \text{ atom}^{-1}$ which is within the experimental uncertainty reported by calorimetric method.

The activity of lanthanum on aluminium was calculated from Eq. (24) and the values are given in Table 7:

$$\text{emf} = -\frac{R\mathcal{T}}{3\mathcal{F}} \ln a_{\text{La(Al)}}$$  (24)
Table 7
Thermodynamic properties of La–Al intermetallic compound calculated from OCP measurement.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>( \Delta G_{Al_{11}La_3} ) (kJ mol(^{-1}))</th>
<th>( \theta_{s}(Al) )</th>
<th>( \Delta C^{\text{ex}}_{\text{La(Al)}} ) (kJ mol(^{-1}))</th>
<th>( \gamma'_{\text{La(Al)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>(-178.0 \pm 0.4 )</td>
<td>(-178.3 \times 10^{-13} )</td>
<td>(-176.9 )</td>
<td>(4.5 \times 10^{-12} )</td>
</tr>
<tr>
<td>740</td>
<td>(-178.1 \pm 0.4 )</td>
<td>(-180.6 )</td>
<td>(-176.6 )</td>
<td>(4.5 \times 10^{-12} )</td>
</tr>
<tr>
<td>710</td>
<td>(-179.5 \pm 0.3 )</td>
<td>(-180.7 )</td>
<td>(-170.1 )</td>
<td>(2.9 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

* Calculated using Eq. (25).

Fig. 17. XRD pattern of a La–Al film formed by potentiostatic electrolysis at \(-1.5\) V vs. Ag/AgCl for 10 hrs at 798 K.

The excess Gibbs energy of La in aluminium, \( \Delta C^{\text{ex}}_{\text{La(Al)}} \), was evaluated using Eq. (25) \cite{49,50}

\[
\Delta C^{\text{ex}}_{\text{La(Al)}} = RT \ln \gamma_{\text{La(Al)}} = -3F \Delta E - RT \ln \chi_{\text{La(Al)}}
\]  

Since the potential plateau correspond to coexistence of Al\(_{11}\)La\(_3\) and Al phases, assuming saturation solubility, the mole fraction of La in aluminium, \( \chi_{\text{La(Al)}} \) correspond to that of La in Al\(_{11}\)La\(_3\). An enlarged view \cite{51} of the aluminium rich region of the La–Al phase diagram is shown in Fig. 15. The solid solubility of La in aluminium is negligible and it may be assumed that the lanthanum formed electrochemically interacts with aluminium and forms Al\(_{11}\)La\(_3\). The activity coefficients of lanthanum in solid aluminium calculated using Eq. (25) is shown in Table 7. The low activity coefficient values show the strong interaction of lanthanum in aluminium.

3.4. Potentiostatic electrolysis

To confirm the underpotential deposition of La on aluminium and examine the alloy formed at the equilibrium potential measured in OCP measurements, potentiostatic electrolysis was carried out at \(-1.5\) V vs. Ag/AgCl reference electrode on an aluminium sheet, for 4h at 773 K. Fig. 16 shows SEM micrographs and EDX analysis of the deposit after washing the salt with ethylene glycol. The SEM–EDX analysis reveals the formation of the intermetallic Al\(_{11}\)La\(_3\). Fig. 17 shows the XRD pattern for electrodeposition of lanthanum on aluminium electrode at \(-1.5\) V for 10 h at 798 K. The XRD pattern also shows the formation of the intermetallic Al\(_{11}\)La\(_3\).

4. Conclusions

Reduction of the La(III) ion to La metal is a single step, three electron transfer process at the tungsten electrode. The reduction shows quasi-reversible behaviour for polarization rates, \(25 \leq v \leq 150 \text{ mV s}^{-1}\) and is predominantly controlled by charge transfer of La(III) ions for scan rates higher than 75 mVs\(^{-1}\). However, logarithmic analysis of the convoluted curves obtained for scan rates 25–50 mVs\(^{-1}\) obeyed the model of reversible exchange. The diffusion coefficient of La(III) ion was calculated in the temperature range 698–798 K. The apparent standard potential of the La(III)/La(0) couple was deduced from the semi-integral of the cyclic voltammograms obtained at 25 mVs\(^{-1}\) and from the chronopotentiograms.

The electrode reaction of La(III)/La couple on solid aluminium electrode was studied by electrochemical methods. The reduction occurred at more positive potential than that on an inert electrode. It was thermodynamically analysed to be due to lowering of the activity of lanthanum in aluminium due to the formation of intermetallic compound Al\(_{11}\)La\(_3\). The apparent standard electrode potential of La(III)/La(Al) was estimated for the temperature range 698–798 K. The Gibbs energy of formation of the intermetallic compound Al\(_{11}\)La\(_3\), activity of lanthanum in aluminium, the excess Gibbs energy and the activity coefficient of lanthanum in aluminium were estimated from the open circuit potential measurement. SEM–EDX analysis and the XRD pattern of the deposit showed the formation of intermetallic compound Al\(_{11}\)La\(_3\).

References