CHAPTER 5

Electrochemical behavior of La-, Nd- and U-trivalent ions in LiCl-KCl eutectic melt on solid aluminium electrode

5.1 Introduction

The thermodynamic stabilities of the intermetallic compounds formed between the actinides and lanthanides with cadmium are similar. When the concentration of the lanthanides in the electrolyte becomes very high during the electrorefining process, selective deposition of actinides on cadmium cathode without the contamination of lanthanides becomes impossible. Many molten metals (Cd, Bi, Zn, Sn, Ga and Al) have been studied as solvents by extracting the actinides from molten fluoride salts based on the technique of reductive extraction for effecting the actinide-lanthanide separation [1-3]. It is reported in literature that among the molten metal solvents studied aluminium shows better selectivity for actinides than lanthanides, as is also expected from the data on thermodynamic stabilities of the intermetallic compounds of lanthanides and actinides [4]. As mentioned earlier in Chapter 1, there is interest in exploring the suitability of solid aluminium cathode for efficient recovery of actinides over lanthanides in the electrorefining process [5-7]. Investigations are being carried out on elements pertaining to the electrorefining process, to understand the electrode reaction, kinetics, derive the standard potentials and activities of these elements on Al electrode in order to evaluate the efficiency of the electrode [8-10]. In this chapter we have reported a detailed elucidation on the redox behavior of LaCl₃, NdCl₃ and UCl₃ on solid aluminium electrode. The thermodynamic properties of the La-Al, Nd-Al and U-Al systems were estimated from the open circuit potential measurement.
5.2 Literature survey

The pyrochemical separation technique is being developed at ITU, Karlsruhe, Germany, for selectively reducing the actinides on solid aluminium cathode using molten LiCl-KCl melt [11-13]. Cassayre et al. investigated the feasibility of carrying out electrorefining of alloy fuel (U-Zr and U-Pu-Zr) using solid aluminium cathode instead of liquid cadmium cathode [11]. They selectively deposited the actinides, while the lanthanides remained in the salt. Serp et al. had determined the An/Ln separation efficiency on simulated spent alloy fuel using aluminium cathode [6, 12]. Soucek et al. had investigated the selective reduction of uranium, plutonium and minor actinides on aluminium cathode from simulated An-Ln-Zr alloy fuel followed by their recovery from An-Al alloy through chlorination route [13-15].

Fundamental studies on the reaction of lanthanide and actinide chlorides at the aluminium electrode, their redox mechanism and standard electrode potential for alloy formation have been reported in the literature. Studies related to the electrochemical behavior of some of the lanthanides on aluminium electrode have been carried out extensively by Castrillejo et al. [8, 16-19]. They had obtained the redox potentials for the rare earth metals (La, Ce, Pr, Gd, Er, Ho, Tm) and yttrium on Al electrode. The work of Castrillejo et al. and Caravaca et al. on the redox behavior of lanthanides on various cathodes has been compiled in the project report PYROREP as mentioned in chapter 4 [20]. The underpotential reduction of lanthanides on Al electrode has been studied by cyclic voltammetry. The Gibbs energy of formation of the various intermetallics of lanthanides with aluminium was estimated from the open circuit potential measurement. Taxil et al. have reported the reduction behaviour of lanthanide ions (Ce, Gd, Sm and Nd) on molybdenum electrode and co-reduction of lanthanides and aluminium on the tantalum electrode using LiF-CaF₂-AlCl₃-LnCl₃ melt [21-22]. They had investigated the alloy
formed by galvanostatic electrolysis at potentials less cathodic than that required for metal formation.

Studies related to the electrochemical behavior of some of the actinides on aluminium electrode have been carried out at ITU. Cassayre et al. had studied the redox behavior of UCl$_3$ on Al electrode [10, 11]. Underpotential reduction of uranium on aluminium takes place with formation of the intermetallics, UAl$_4$ and UAl$_3$. Mendes et al. [23] had investigated the reduction behavior of Pu(III) ions and Soucek et al. [24] had investigated that of Np(III) ions on aluminium electrode using cyclic voltammetry. The formation and thermochemical properties of the AnAl$_n$ alloys were evaluated by open circuit potentiometry in their study. Cordoba et al. had studied the reduction behavior of AmCl$_3$ on liquid aluminium cathode and estimated the activity coefficient of Am on aluminium [25].

Other than these studies, there aren’t many reports on the electrochemical behaviour of lanthanides and actinides on aluminium electrode to our knowledge. Though the behavior of LaCl$_3$ and UCl$_3$ are reported, the studies have not been carried out over a range of temperature. Also, the electrode behavior of NdCl$_3$ on Al has not been carried out in detail. In order to have a better understanding of the reaction of lanthanides and actinides at the solid aluminium cathode, we had investigated the electrochemical behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ on solid aluminium electrode using cyclic voltammetry and open circuit potentiometry. The reduction potentials of La(III), Nd(III) and U(III) ions on Al electrode were estimated and the formation of La$_3$Al$_{11}$, Nd$_3$Al$_{11}$ and UAl$_n$ alloys were studied. The details are discussed in the chapter.

5.3. Experimental

5.3.1. Chemicals
High purity aluminium wire and sheets (Alfa Aesar 99.99 %) were used for preparing the aluminium working electrode. The purity of other chemicals used in the study is same as those described in Chapter 3 and 4.

5.3.2. Preparation of the electrolyte salt

Purification of LiCl-KCl salt mixture was carried out as described earlier in Chapter 2. Preparation of LiCl-KCl-LaCl₃, LiCl-KCl-NdCl₃ and LiCl-KCl-UCl₃ electrolytes was discussed earlier in Chapter 2.

5.3.3. Electrochemical apparatus and electrodes

A 1.5 mm diameter Al wire was used as working electrode for the cyclic voltammetry and open circuit potentiometry studies. The working electrode was sheathed with an alumina sleeve exposing 40 mm of the wire and the area of the working electrode was calculated from the depth of immersion. A 5mm thick aluminium sheet was used as working electrode for potentiostatic deposition of the alloys. The reference electrode and the counter electrodes are the same as described in Chapter 2. The cell assembly, experimental procedure and instrumentation are the same as discussed in Chapter 2.

5.4 Results and discussion

5.4.1 Electrochemical reduction behaviour of LaCl₃ & NdCl₃ on solid Al electrode

5.4.1.1. Analysis of the cyclic voltammograms

Cyclic voltammograms obtained on W and Al electrodes in pure LiCl-KCl melt are compared with that obtained with the melt containing LaCl₃ on Al electrode in Fig.5.1. The electroactive domain of pure LiCl-KCl on aluminium electrode 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 oxidation of
Fig. 5.1 Electroactive domain of pure LiCl-KCl on aluminium electrode as compared to that on a W electrode.

Fig. 5.2 Cyclic voltammograms obtained on the tungsten and aluminium electrodes for LiCl-KCl-NdCl₃ melt.
the Al metal. Fig. 5.2 shows the cyclic voltammograms obtained at 698 K on the tungsten and aluminium electrodes at 25 mVs⁻¹ for LiCl-KCl-NdCl₃ melt. It was observed that the reduction of the rare earth chlorides on Al occurs at a less cathodic potential than that on inert W electrode. Only a single redox couple was observed similar to the RE-Cd system. The redox potentials shift by ~ 600 mV towards the positive direction. The reduction takes place in a single step with three electron transfer on the aluminium electrode forming their respective intermetallic compound during the cathodic cycle and dissolution of the alloy during the anodic cycle. Fig. 5.3 and Fig. 5.4 show the phase diagrams of the La-Al and Nd-Al systems respectively [26, 27]. Lanthanum and neodymium form various intermetallic compounds with aluminium. Based on the reported phase diagrams, the probable reaction on the aluminium rich side could be the formation of the intermetallic rich in aluminium, namely, Al₁₁RE₃.

\[
3\text{RE}^{3+} + 11\text{Al} + 9\text{e}^- \leftrightarrow \text{Al}_{11}\text{RE}_3
\]  

(5.1)

where RE³⁺ here refers to La/Nd ions. Similar observations have been made by other authors earlier in case of lanthanum, cerium, praseodymium and erbium [16-18]. Further, the formation of Al₁₁RE₃ has been supported by the XRD pattern and SEM-EDX analysis of the electrodeposits, details of which has been discussed in section 5.4.1.4.

Fig. 5.5 and Fig. 5.6 show the cyclic voltammograms of LaCl₃ and NdCl₃ in LiCl-KCl melt at 748 K on solid aluminium cathode at various scan rates respectively. The voltammograms show a single reduction wave and its corresponding oxidation wave in the electrochemical domain. The shape of the voltammogram resembles closely that of a soluble-soluble reversible system. It may be observed that the cathodic and anodic peaks for the formation and dissolution of alloy do not vary significantly between sweep rates 10-100 mVs⁻¹. In the cathodic cycle, the magnitude of \( E_{p,c} - E_{p,c/2} \) agrees with the
Fig. 5.3 Al-La phase diagram

Fig. 5.4 Al-Nd phase diagram
Fig. 5.5 Cyclic voltammograms for $7.54 \times 10^{-5}$ mol cm$^{-3}$ LaCl$_3$ in LiCl-KCl melt on Al electrode at various scan rates. Electrode area: 0.347 cm$^2$. Temperature: 723K.

Fig. 5.6 Cyclic voltammogram for LiCl-KCl-NdCl$_3$ melt at Al electrode at 748 K; Concentration of NdCl$_3$: $6.66 \times 10^{-5}$ mol cm$^{-3}$. Inset: Cyclic voltammograms at different scan rates.
criteria for soluble-soluble reversible system (Eq. 3.1) yielding the value of n close to 3. The reduction may be presumed to be close to reversibility at low scan rates and show Nernstian behavior. However, it may not be appropriate to estimate the half wave potentials from the cathodic and anodic peak potentials as was adopted for RE-Cd system using the relation (Eq. 4.2). Eq 4.2 is applicable for soluble-soluble species undergoing reversible exchange. It may not be applicable in this case, since the rate of diffusion of RE(III) ions in salt phase is not comparable to the rate of diffusion of RE in solid aluminium phase. Further, when the concentration of RE exceeds its solubility, precipitation of the solid phase, Al11RE3 occurs and the electrode surface loses its homogeneity. Hence, we consider it is more appropriate to derive the apparent standard potentials of La/Nd on aluminium electrode using the Nernst equation.

5.4.1.2. Apparent standard potentials of RE(III)/RE(Al) system in LiCl-KCl melt

The equilibrium potential of the redox system RE(III)/RE(Al) is given by the following expression:

$$E_{RE(III)/RE(Al)}^{eq} = E_{RE(III)/RE(0)}^{0} + \frac{RT}{3F} \ln \frac{a_{RE(III)}}{a_{RE(Al)}}$$  \hspace{1cm} (5.2)

where $E_{RE(III)/RE(0)}^{0}$ is the standard potential of RE(III)/RE(0) in LiCl-KCl melt. $a_{RE(III)}$ and $a_{RE(Al)}$ are the activities of RECl3 in salt and that of RE metal in aluminium respectively.

Introducing the expression for apparent standard potential, $E_{RE(III)/RE(0)}^{*}$ given in Eq. 5.3,

$$E_{RE(III)/RE(0)}^{*} = E_{RE(III)/RE(0)}^{0} + \frac{RT}{3F} \ln \gamma_{RE(III)}$$  \hspace{1cm} (5.3)

Eq. 5.2 is rearranged as

$$E_{RE(III)/RE(Al)}^{eq} = E_{RE(III)/RE(0)}^{*} + \frac{RT}{3F} \ln X_{RE(III)} - \frac{RT}{3F} \ln a_{RE(Al)}$$  \hspace{1cm} (5.4)

The apparent standard potential for reduction of RECl3 on Al electrode is given as [11]
$$E_{RE(III)/RE(Al)}^* = E_{RE(III)/RE(0)}^* - \frac{RT}{3F} \ln a_{RE(Al)}$$  
(5.5)

Eq. 5.2 is rewritten as

$$E_{RE(III)/RE(Al)}^{eq} = E_{RE(III)/RE(Al)}^* + \frac{RT}{3F} \ln X_{RE(III)}$$  
(5.6)

The equilibrium potential, $E_{RE(III)/RE(Al)}^{eq}$, was obtained graphically as shown in Fig. 5.6, for cyclic voltammograms obtained at 25 mVs$^{-1}$. The apparent standard potentials for reduction of LaCl$_3$ and NdCl$_3$ on Al electrode were determined using Eq. 5.6 and the results are listed in Table 1 and Table 2 respectively. The values are compared with those reported by Serp et al. [28]. A difference of about 70 mV and 110 mV for $E_{La(III)/La(Al)}^*$ and $E_{Nd(III)/Nd(Al)}^*$ respectively, was observed between our value and the reported value. It may be noted that the value of apparent standard potentials for reduction of LaCl$_3$ and NdCl$_3$ on Al electrode reported by Serp et al. were practically the same which is not so in our case.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$E_{La(III)/La(Al)}^<em>$ vs. Ag/Ag$^+$, V$^</em>$</th>
<th>$E_{La(III)/La(Al)}^*$ vs. Cl$_2$/Cl$^-$, V</th>
<th>This Study</th>
<th>Serp et al. [28]</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>-1.329</td>
<td>-2.564</td>
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</tr>
<tr>
<td>798</td>
<td>-1.230</td>
<td>-2.465</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Potentials obtained vs. Ag/Ag$^+$ ($X_{AgCl} = 0.001$) rescaled to Ag/Ag$^+$ ($X_{AgCl} = 0.0031$) reference electrode
Table 5.2 Apparent standard potential (± 0.002 V) for Nd(III)/Nd(Al) estimated from cyclic voltammogram on Al electrode, \( \chi_{NdCl_3} = 0.00224 \).

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( E^*_{Nd(III)/Nd(Al)} ) vs. Ag/Ag(^+), V</th>
<th>( E^*_{Nd(III)/Nd(Al)} ) vs. Cl(_2/Cl^-), V</th>
</tr>
</thead>
<tbody>
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<td>698</td>
<td>-1.283</td>
<td>-2.517</td>
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<tr>
<td>723</td>
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<td>-2.496</td>
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<tr>
<td>748</td>
<td>-1.230</td>
<td>-2.475</td>
</tr>
<tr>
<td>798</td>
<td>-1.178</td>
<td>-2.432</td>
</tr>
</tbody>
</table>

5.4.1.3 Open-circuit chronopotentiometry

Open circuit potential transients were obtained using LiCl-KCl-LaCl\(_3\) and LiCl-KCl-NdCl\(_3\) melt by polarizing the aluminium electrode at different cathodic potentials in the range -1.5 to -1.8 V. Fig. 5.7 shows the open circuit potential transient curves obtained on the aluminium electrode using LiCl-KCl-LaCl\(_3\) at 723 and 753 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 the figure. From our earlier inference from the cyclic voltammograms, the intermetallic formed is Al\(_{11}\)La\(_3\) and the potential plateau is due to coexistence of Al\(_{11}\)La\(_3\) and Al. The potential measured with respect to Ag/ 0.1 mol % AgCl in LiCl-KCl reference electrode was rescaled with reference to that of the La(III)/La electrode, which was obtained earlier as discussed in Chapter 4. Replicate measurements were made to estimate the standard deviation of the measured emf. Fig. 5.8 shows the open-circuit chronopotentiograms obtained with a solution of NdCl\(_3\) in LiCl-KCl at Al electrode for a cathodic polarization of -1.8 V for various durations. A significantly distinct plateau was observed at \(~ -1.4\ V\) vs. Ag/Ag(I) (\( \chi_{AgCl} = 0.0031 \)) reference electrode in all the transients, the same potential about which a peak was
Fig. 5.7 OCP transient curve for LiCl-KCl-LaCl₃ melt on Al electrode at different temperatures. Cathodic polarization: -1.8 V vs. (Ag/Ag⁺, X_{AgCl} = 0.001) reference electrode.

Fig. 5.8 OCP transient curve for LiCl-KCl-NdCl₃ melt on Al electrode for different duration. Cathodic polarization: -1.8 V vs. (Ag/Ag⁺) reference electrode. Inset: OCP transient curve at 723 K. Cathodic polarization: -1.8 V for 600 s.
observed in the cyclic voltammograms. The potential shown in Fig. 5.8 is rescaled with respect to Nd(III)/Nd(0) electrode. A plateau ~ 0.6 V vs. Nd(III)/Nd(0) electrode may be seen in the figure. The equilibrium potential of the Nd(III)/Nd(0) couple was obtained earlier as described in chapter 3. Similar to the La-Al system, only one intermetallic was observed for the Nd-Al system under our experimental condition. The plateau corresponds to the coexistence of the phases $\text{Al}_{11}\text{Nd}_3$ and Al.

The potentials of the plateaus obtained for the La-Al and Nd-Al systems were rescaled to the potentials of the rare earth metal electrode correspond to the emf of the cell represented as:

$$RE\,(s) / RECl_3\,_{\text{in}} \, LiCl - KCl_{\text{out}}\,(l) / (\text{Al}_{11/3}RE) + (\text{Al})$$

(5.7)

The Gibbs energy of formation of the intermetallics, $\text{Al}_{11}\text{La}_3$ and $\text{Al}_{11}\text{Nd}_3$ were estimated from the emf values at different temperatures. Table 5.3 shows the values of the Gibbs energy of formation of the intermetallic, $\text{Al}_{11}\text{La}_3$. Our values are in good agreement with those reported by Castrillejo et al. [8] measured using the same technique. Sommer et al. [29] had measured the enthalpy of formation of aluminium-lanthanum alloys by solution calorimetry. They had reported the enthalpy of formation of $\text{Al}_{11}\text{La}_3$ at 1513 K to be $-41 \pm 2.5$ kJ mol$^{-1}$atom$^{-1}$. Borzone et al. had reported the enthalpy of formation of $\text{Al}_{11}\text{La}_3$ at 298 K to be $-41 \pm 2.0$ kJ mol$^{-1}$atom$^{-1}$ measured by direct calorimetry [30]. In the present work, we had derived the enthalpy of formation of $\text{Al}_{11}\text{La}_3$ from the slope of the plot of $\Delta G/T$ vs. $1/T$ in the temperature range 710-773 K. The heat capacity contribution ($\Delta C_p$) is considered negligible. The enthalpy of formation of $\text{Al}_{11}\text{La}_3$ at the mid temperature, namely, 742 K was found to be $-42.92 \pm 1.5$ kJ mol$^{-1}$atom$^{-1}$ which is within the experimental uncertainty reported by calorimetric method.
Fig. 5.9 Enlarged view of the aluminium rich region of Al-La phase diagram.

The Gibbs energy of formation of the intermetallic Al$_{11}$Nd$_3$ at different temperatures were estimated from the emf values and are shown in Table 5.4. Gschneider et al. have given an extensive review of the thermodynamic properties of the rare earth alloys [31]. Our values are compared with those obtained by Kober et al. by emf measurement taken from the review. The values are fairly in good agreement with those of Kober et al. within the uncertainties. The emf value and Gibbs energy formation of Nd$_3$Al$_{11}$ estimated from OCP measurement reported in “PYROREP” [20] are higher than those of ours. This difference arises from the difference in the equilibrium potentials of Nd(III)/Nd(0) obtained in our study and that reported in “PYROREP”.

The activities of the La and Nd in aluminium were calculated from Eq. 5.8 and the values are given in Table 5.5 and Table 5.6 for La-Al and Nd-Al systems respectively.
\[ \text{emf} = -\frac{RT}{3F} \ln a_{\text{RE(Al)}} \]  

(5.8)

The excess Gibbs energy of RE in aluminium, \( \Delta G_{\text{RE}}^\alpha \) was evaluated using Eq. 5.9

\[
\Delta G_{\text{RE}}^\alpha = RT \ln \gamma_{\text{RE(Al)}} = -3F\Delta E - RT \ln X_{\text{RE(Al)}}
\]

(5.9)

An enlarged view [32] of the aluminium rich region of the La-Al phase diagram is shown in Fig. 5.9. The solid solubility of La in aluminium is reported to be negligible as seen in the figure. Since we did not find any solubility data for La in aluminium, the solubility was taken from the liquidus curve of the phase diagram shown in Fig. 5.9. The solubility of La in aluminium at 823 K from the phase diagram was \( X_{\text{La(Al)}} = 1 \times 10^{-5} \) which was used for calculation of the excess Gibbs energy. The values of the excess Gibbs energy of La in aluminium, \( \Delta G_{\text{La}}^\alpha \) and activity coefficients of lanthanum in solid aluminium calculated using Eq. 5.9 are shown in Table 5.5. The low activity coefficient values show the strong interaction of lanthanum in aluminium. Similarly, the solubility of Nd in solid Al is negligible as reported in literature [33]. Considering the behavior of rare earth elements to be similar, the solubility value was considered as \( X_{\text{Nd(Al)}} = 1 \times 10^{-5} \). The values of the excess Gibbs energy of Nd in aluminium, \( \Delta G_{\text{Nd}}^\alpha \) and activity coefficients of neodymium in solid aluminium calculated using Eq. 5.9 are shown in Table 5.6.
Table 5.3 Gibbs energy of formation of La$_3$Al$_{11}$ estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>emf (±0.002) V</th>
<th>$\Delta_f G_{La_3Al_{11}}$, kJ mol$^{-1}$</th>
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<td>753</td>
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<td>-177.8</td>
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<td></td>
<td>0.616 [20]</td>
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Table 5.4 Gibbs energy of formation of Nd$_3$Al$_{11}$ estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>emf (±0.002) V</th>
<th>$\Delta_f G_{Nd_3Al_{11}}$, kJ mol$^{-1}$</th>
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<tr>
<td>748</td>
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<td>-166.5</td>
</tr>
<tr>
<td>773</td>
<td>0.567</td>
<td>-164.2</td>
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Table 5.5 Thermodynamic properties of La-Al intermetallic compound estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$\log a_{La(Al)}$</th>
<th>$\Delta G^\gamma_{La}$ kJ mol$^{-1}$</th>
<th>$\log \gamma_{La(Al)}$</th>
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Table 5.6 Thermodynamic properties of Nd-Al intermetallic compound estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>log $a_{Nd(Al)}$</th>
<th>$\Delta G^{\infty}_{Nd}$ (kJ mol$^{-1}$)</th>
<th>log $\gamma_{Nd(Al)}$</th>
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<tr>
<td>773</td>
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<td>-90.2</td>
<td>-6.1</td>
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5.4.1.4 Potentiostatic electrolysis

To confirm the underpotential deposition of La/Nd on aluminium surface and examine the alloy formed at the equilibrium potential measured in OCP measurements, potentiostatic electrolysis was carried out on an aluminium sheet using the LiCl-KCl-LaCl$_3$ and LiCl-KCl-NdCl$_3$ melts respectively. The aluminium sheet electrode was polarized at -1.5 V vs. Ag/AgCl reference electrode at 773 K for 4 hrs. The salt adhering to the cathode deposit was scarped and the sheet was washed with ethylene glycol. Fig. 5.10 shows the SEM micrographs and the corresponding EDX analysis of the cathode deposit for LiCl-KCl-LaCl$_3$ melt. The SEM-EDX analysis reveals the formation of the intermetallic Al$_{11}$La$_3$. Fig. 5.11 shows the XRD pattern for electrodeposition of lanthanum on aluminium electrode at -1.5V for 6 hrs at 798 K. The XRD pattern also shows the formation of the intermetallic Al$_{11}$La$_3$. Fig. 5.12 shows the SEM micrograph and the corresponding EDX analysis of the cathode deposit for LiCl-KCl-NdCl$_3$ melt indicating underpotential deposition of Nd on aluminium surface. The XRD analysis of the sample confirms the formation of the intermetallic Al$_{11}$Nd$_3$ as seen in Fig. 5.13.
Fig. 5.10 (a) Cross-sectional SEM image of La-Al film formed by potentiostatic electrolysis at 773 K. Cathodic polarization: $-1.5 \text{ V} \text{ vs. } (\text{Ag/Ag}^+, X_{\text{AgCl}} = 0.001)$ reference electrode (b) corresponding EDX analysis confirming the formation of $\text{Al}_{11}\text{La}_3$

Fig. 5.11 XRD pattern of La–Al film formed by potentiostatic electrolysis at 798 K for cathodic polarization of $-1.5 \text{ V} \text{ vs. } (\text{Ag/Ag}^+, X_{\text{AgCl}} = 0.001)$ reference electrode for 6 hrs.
Fig. 5.12 (a) Cross-sectional SEM image of Nd–Al film formed by potentiostatic electrolysis at -1.5 V vs. (Ag/Ag⁺) reference electrode at 773 K and (b) corresponding EDX analysis confirming the formation of Al₁₁Nd₃.

Fig. 5.13 XRD pattern of Nd–Al film formed by potentiostatic electrolysis at -1.5 V vs. (Ag/Ag⁺) reference electrode for 5 hrs at 773 K.
5.4.2 Electrochemical reduction behaviour of UCl$_3$ on solid aluminium electrode

5.4.2.1 Analysis of the cyclic voltammograms

The reduction behavior of UCl$_3$ on aluminium electrode was studied from the cyclic voltammograms obtained at different switching potentials and at different polarization rates. Fig. 5.14 shows the cyclic voltammograms obtained for LiCl-KCl-UCl$_3$ melt on W and Al electrodes at 723 K. The reduction behavior of UCl$_3$ on W surface was discussed in detail in chapter 3 and we had observed that the peak for the reduction of U(III) ion to U metal appeared $\sim$ -1.45 V. From the peak positions, we attribute peak II$_c$ in Fig. 5.14 to the reduction of U(III) ion to U metal and peak I$_c$ at $\sim$ -1.1 V to the underpotential reduction of U(III) ions on the Al surface forming U-Al alloy. It may be observed from the figure that the reduction peak potential for U(III)/U(0) shifted by $\sim$ 350 mV towards the positive direction on the aluminium electrode. Fig. 5.15 shows the cyclic voltammogram obtained for LiCl-KCl-UCl$_3$ melt on Al at 698 K and the inset to those at 723 and 743 K. It may be observed that the redox potentials for U(III)/U(Al) couple is very close to that of the Al electrode. The re-oxidation peak for the U(Al) alloy was not well resolved for all the cyclic voltammograms recorded. This occurred because the re-oxidation peak for the U(Al) alloy was masked by the unlimited current for the dissolution of Al in the anodic cycle. Cyclic voltammograms obtained at low polarization rates alone showed the peaks for formation and dissolution of the U-Al alloy. The nature of the voltammograms was very much dependent on the scan rates and switching potentials. The peak for reduction of Al(III)/Al largely affected the peak position of U(III))/U(Al) couple. The shift in peak potentials with scan rates and the shape of the voltammograms show that the redox couple does not show reversible behavior. Though the peaks for formation and dissolution of the U-Al alloy were not similar to those obtained in the case of the lanthanides, the underpotential reduction of U(III) ion is
revealed from the cyclic voltammograms. The reaction for the reduction of U(III) ions on Al electrode is given as

\[
\text{U(III) + nAl + 3 \overline{e} \leftrightarrow UAl}_n \tag{5.10}
\]

Our observation is very much similar to the observations made by Cassayre et al. [10-11]. Similar studies carried out by Mendes et al. and Soucek et al. for PuCl$_3$ and NpCl$_3$, respectively on aluminium electrode showed reduction peak \( \sim -1.2 \) V and re-oxidation peak \( \sim -0.95 \) V. They had reported that the re-oxidation of An-Al$_n$ alloy was well distinguished from the oxidation of pure Al electrode in contrast to the U-Al alloy [23, 24]. Fig. 5.16 shows the phase diagram of the U-Al system [33]. Though uranium forms three intermetallic compounds with aluminium, only a single redox peak was observed for alloy formation. The formation of U-Al has been investigated further by open circuit potential measurements and potentiostatic electrolysis discussed in the following sections.
Fig. 5.14 Cyclic voltammograms obtained on the tungsten and aluminium electrodes for LiCl-KCl-UCl$_3$ melt at 723 K.

Fig. 5.15 Cyclic voltammograms obtained on the aluminium electrode for LiCl-KCl-NdCl$_3$ melt at different temperatures.
5.4.2.2 Open-circuit chronopotentiometry

Open circuit potential transients were obtained using LiCl-KCl-UCl$_3$ melt by polarizing the aluminium electrode at different cathodic potentials. Fig. 5.17 shows the open circuit potential transient curves obtained on the aluminium electrode at 723 K for cathodic polarization at -1.3 V. The plateau for the equilibrium between the U-Al alloy and Al is very close to the rest potential of the aluminium electrode. It is presumed that the plateau for the equilibrium between the U-Al alloy and Al lies between -1.05 and -1V where a change in slope was observed as seen in Fig. 5.17. However Cassayre et al. [10] have reported that the potential for the UAIm alloy and the rest potential for Al were
Fig. 5.17 Open circuit potential transient curve for UCl₃ in LiCl-KCl melt on Al electrode at different temperatures. Cathodic polarization: -1.3 V vs. (Ag/Ag⁺) reference electrode practically identical. They had considered the rest potential of the Al electrode for estimating the emf and Gibbs energy of formation of the alloy UAlₙ. One possible reason why they had not observed the change in slope could be due to the long time period of their OCP transient and this could have resulted in poor resolution of the potentials. Inset of Fig. 5.17 shows the open circuit transient obtained for a cathodic polarization of -1.6 V at 823 K. A plateau corresponding to U(III)/U(0) couple is observed ~ -1.35 V. The difference between the potentials of plateau 1 and 2 corresponds to the Gibbs energy of formation of the U-Al alloy. Table 5.7 shows the difference in the potentials of the two plateaus and the Gibbs energy of formation of the intermetallic UAlₙ. The Standard Gibbs energy of formation of the intermetallics, UAl₄, UAl₃ and UAl₂ reported by Chiotti et al. from emf measurement are given by the Eq. 5.11, 5.12 and 5.13 respectively [35].

Chiotti
et al. have given an extensive review of the thermodynamic properties of actinide binary alloys.

\[
\Delta_f G_{\text{UAl}_4}^0 (\text{cal/mole}) = -32140 - 7.52T \ln(T) + 59.07T
\]  
(5.11)

\[
\Delta_f G_{\text{UAl}_3}^0 (\text{cal/mole}) = -26290 - 1.305T \ln(T) + 10.5T
\]  
(5.12)

\[
\Delta_f G_{\text{UAl}_2}^0 (\text{cal/mole}) = -22790 - 2.326T \ln(T) + 18.37T
\]  
(5.13)

The values of the Gibbs energy of formation of the intermetallics, UAl₄, UAl₃ and UAl₂ and their corresponding emf values are given in Table 5.8. It may be observed that the Gibbs energy of formation of the intermetallics, UAl₄ and UAl₃ differ merely by 1 kJ mol⁻¹ and the difference in the corresponding emf is < 10 mV. Taking into consideration of our observation, report by Cassayre et al. [10] and emf values of Chiotti et al. [35] we may conclude that the compound formed about the plateau region on the Al surface corresponds to the intermetallics, UAl₄ and UAl₃. The midpoint of the plateau was considered as the equilibrium potential, \( E_{\text{U(III)/U(IV)}}^{\text{eqbm}} \). Nagarajan et al. had measured the enthalpy of formation of aluminium-uranium alloys by solution calorimetry [36]. They had reported the enthalpy of formation of UAl₄ at 978 K to be -126.5 ± 13.3 kJ mol⁻¹ and that of UAl₃ at 1086 K to be -118.1 ± 8.2 kJ mol⁻¹. In the present work, we have derived the enthalpy of formation of UAlₙ from the slope of the plot of \( \Delta G/T \) vs. 1/T in the temperature range 698 - 823 K. The heat capacity contribution is considered negligible. The enthalpy of formation of UAlₙ at the mid temperature, namely, 748 K was found to be -139.3 ± kJ mol⁻¹ and is in agreement with that of Nagarajan et al. within the uncertainty reported for UAl₄ by the calorimetric method.

The activity of uranium metal in aluminium was calculated from Eq. 5.14 and the excess Gibbs energy of uranium in aluminium, \( \Delta \overline{G}^*_{\text{U}} \) was evaluated using Eq. 5.15.
\[ \text{emf} = -\frac{RT}{3F} \ln a_{U(Al)} \]  
(5.14)

\[ \Delta G_U^{\text{xs}} = RT \ln \gamma_{U(Al)} = -3F \Delta E - RT \ln X_{U(Al)} \]  
(5.15)

The solid solubility of U in aluminium was given as 1.69 atom % at 913 K (eutectic temperature) in literature [35] and this value was used in the estimation of the excess Gibbs energy of uranium in aluminium, \( \Delta G_U^{\text{xs}} \). The activity coefficients of uranium in solid aluminium were calculated using Eq. 5.15. The thermodynamic properties estimated from OCP measurement are shown in Table 5.9. Since the peak potentials for the reduction of U(III)/U(Al) were not reproducible due to the redox peaks for Al(III)/Al, we had estimated the apparent standard potential for reduction of U(III) ion on Al surface from the equilibrium potentials measured by OCP method. The apparent standard potential for reduction of U(III) ion on Al surface, \( E_{U(III)/U(Al)}^{\text{app}} \), was estimated using Eq. 5.6 and the values are shown in Table 5.10.

---

Table 5.7 Gibbs energy of formation of UAl\(_n\) estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>emf (±0.005) V</th>
<th>( \Delta G_{UAl_n} ) kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This study (OCP)</td>
</tr>
<tr>
<td>698</td>
<td>0.367</td>
<td>-106.2</td>
</tr>
<tr>
<td>723</td>
<td>0.363</td>
<td>-105.2</td>
</tr>
<tr>
<td>748</td>
<td>0.360</td>
<td>-104.2</td>
</tr>
<tr>
<td>773</td>
<td>0.356</td>
<td>-103.1</td>
</tr>
</tbody>
</table>
Table 5.8 Gibbs energy formation of UAlₙ from emf measurement [35].

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( \text{U((\alpha)) + 4Al(c) \leftrightarrow UAl}_4(c) )</th>
<th>( \text{U((\alpha)) + 3Al(c) \leftrightarrow UAl}_3(c) )</th>
<th>( \text{U((\alpha)) + 2Al(c) \leftrightarrow UAl}_2(c) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>( \text{emf} ) 0.3654 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -105.79</td>
<td>( \text{emf} ) 0.3593 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -104.02</td>
<td>( \text{emf} ) 0.2978 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -86.21</td>
</tr>
<tr>
<td>723</td>
<td>( \text{emf} ) 0.3647 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -105.57</td>
<td>( \text{emf} ) 0.3590 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -103.94</td>
<td>( \text{emf} ) 0.2975 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -86.13</td>
</tr>
<tr>
<td>748</td>
<td>( \text{emf} ) 0.3639 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -105.37</td>
<td>( \text{emf} ) 0.3588 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -103.87</td>
<td>( \text{emf} ) 0.2973 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -86.05</td>
</tr>
<tr>
<td>773</td>
<td>( \text{emf} ) 0.3634 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -105.19</td>
<td>( \text{emf} ) 0.3686 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -103.81</td>
<td>( \text{emf} ) 0.2970 ( \text{( \Delta \gamma \gamma ) G}_{UAl} \text{kJ mol}^{-1} ) -85.99</td>
</tr>
</tbody>
</table>

Table 5.9 Thermodynamic properties of U-Al intermetallic compound estimated from OCP measurement on Al electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( \log a_{U(Al)} )</th>
<th>( \Delta \gamma \gamma \gamma \gamma G_{U} \text{kJ mol}^{-1} )</th>
<th>( \log \gamma_{U(Al)} )</th>
</tr>
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<tbody>
<tr>
<td>698</td>
<td>-7.9</td>
<td>-82.5</td>
<td>-6.2</td>
</tr>
<tr>
<td>723</td>
<td>-7.6</td>
<td>-80.6</td>
<td>-5.8</td>
</tr>
<tr>
<td>748</td>
<td>-7.3</td>
<td>-78.8</td>
<td>-5.5</td>
</tr>
<tr>
<td>773</td>
<td>-7.0</td>
<td>-76.9</td>
<td>-5.2</td>
</tr>
</tbody>
</table>

Table 5.10 Apparent standard potential (± 0.005 V) for U(III)/U(Al) estimated from OCP measurement on Al electrode, \( X_{UCl} = 0.00268 \).

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( E_{eqbm}^{*} \text{U(III)/U(Al)} \text{vs. Ag/Ag}^{+}, \text{V} )</th>
<th>( E_{eqbm}^{*} \text{U(III)/U(Al)} \text{vs. Ag/Ag}^{+}, \text{V} )</th>
<th>( E_{eqbm}^{*} \text{U(III)/U(Al)} \text{vs. Cl}_{2}/\text{Cl}^{-}, \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>-1.051</td>
<td>-0.931</td>
<td>-2.165</td>
</tr>
<tr>
<td>723</td>
<td>-1.039</td>
<td>-0.916</td>
<td>-2.155</td>
</tr>
<tr>
<td>748</td>
<td>-1.028</td>
<td>-0.901</td>
<td>-2.145</td>
</tr>
<tr>
<td>798</td>
<td>-1.017</td>
<td>-0.885</td>
<td>-2.135</td>
</tr>
</tbody>
</table>
5.4.2.3 Potentiostatic electrolysis

To examine the underpotential reduction of UCl$_3$ on aluminium surface at the equilibrium potential measured in OCP measurements, potentiostatic electrolysis was carried out using LiCl-KCl-UCl$_3$ melt to electrodeposit uranium on an aluminium sheet. The aluminium sheet electrode was polarized at -1.3 V vs. Ag/AgCl reference electrode at 723 K for over 8 hrs. The adhering salt was scarped and the sheet was washed with ethylene glycol. Fig. 5.18 shows the XRD pattern for electrodeposition of uranium on aluminium electrode. The XRD analysis of the sample showed the presence of UAl$_4$ & UAl$_3$.

Fig. 5.18 XRD pattern of U–Al film formed by potentiostatic electrolysis at -1.3 V vs. (Ag/Ag$^+$) reference electrode for 8 hrs at 723 K.

5.5 Summary

The electrode reaction of the rare earth ion (RE - La, Nd) on solid aluminium electrode was studied by electrochemical methods. The reduction occurred at more
positive potential than that for pure metal formation. It was thermodynamically analysed to be due to lowering of the activity of the rare earth metal in aluminium due to the formation of intermetallic compound $\text{Al}_{11}\text{RE}_3$. The apparent standard electrode potential of $\text{RE}^{(III)}/\text{RE(Al)}$ in the temperature range 698-773 K, was estimated from the cyclic voltammograms. The Gibbs energy of formation of the intermetallics, $\text{Al}_{11}\text{La}_3$ and $\text{Al}_{11}\text{Nd}_3$ were obtained from the open circuit potential measurements similar to the method used for the RE-Cd system. The activity of rare earth metal in aluminium, the excess Gibbs energy and the activity coefficient of rare earth metal in aluminium were estimated from the open circuit potential measurement and are reported by this method for the first time here. SEM-EDX analysis and the XRD pattern of the deposit showed the formation of intermetallic compound $\text{Al}_{11}\text{RE}_3$. The studies reported on Nd-Al system in this work is not reported in open literature earlier.

The redox behavior of $\text{UCI}_3$ on solid aluminium electrode was studied by cyclic voltammetry and open circuit potentiometry. The studies showed the underpotential reduction of $\text{U}^{(III)}$ ion on aluminium electrode at a potential $\sim$ 0.35 V more anodic than pure uranium metal deposition. The cyclic voltammograms did not show well resolved peaks for the formation and dissolution of the U-Al alloy. The OCP transients showed that the equilibrium potential for the U-Al alloy was very close to the rest potential of the aluminium electrode. The apparent standard electrode potentials of $\text{U}^{(III)}/\text{U(Al)}$, activity of uranium in aluminium, the excess Gibbs energy and the activity coefficient of uranium in aluminium were estimated from the open circuit potential measurement and are reported by this method for first time.

XRD pattern of the cathode deposit obtained by polarizing the aluminium electrode at -1.3 V showed the formation of the intermetallic compounds, $\text{UAI}_4$ and $\text{UAI}_3$.

5.6 References


