4.1 Introduction

As discussed earlier, in the electrorefining process, liquid cadmium cathode is used to recover the trans-uranium metals. The activities of Pu and MA are reduced at the cadmium cathode and they co-deposit along with small amounts of U [1, 2]. The product will contain small amounts of rare earth metals also [3, 4]. Cd is considered to be a typical liquid metal cathode since the activities of Pu and MAs in the Cd phase are very small. Cd has a low melting point and sufficiently low boiling point. This property enables the distillation of Cd for the recovery of the actinides [5, 6]. Therefore, several studies were conducted on electrorefining using cadmium cathode and recovery of the actinides by distilling off cadmium [7]. The distribution behavior of actinides and lanthanides between the LiCl-KCl eutectic melt and liquid Cd were studied by equilibrium measurements to evaluate the thermodynamic properties for these elements with cadmium [8-12]. The activities of these elements in the liquid Cd phase and separation factors of actinide elements from rare earth elements were evaluated from the studies. However, the reduction behaviour of actinide and rare earth chlorides at the interface between the LiCl-KCl eutectic melt and liquid Cd are not much studied.

In the present work we had investigated the electrochemical behavior of LaCl₃, NdCl₃ and UCl₃ on liquid cadmium pool cathode using cyclic voltammetry. The Gibbs energy formation of the intermetallics, LaCd₁₁ and NdCd₁₁ were estimated from the open circuit potential measurement on Cd film electrode.

The reduction behaviour of UCl₃ in LiCl-KCl eutectic melt was studied on cadmium electrode in the temperature range 698-798 K using cyclic voltammetry. Gibbs
energy formation of UCd₁₁ and the activity coefficient of uranium in the solvent rich region were computed from molten salt galvanic cell emf method.

4.2 Literature survey

Many studies have been reported on the reduction behaviour of lanthanides on cadmium cathode. Castrillejo et al. had investigated the electrochemical behaviour of some rare earths ions (Ce, La, Pr, Gd, Er, Ho) and Y in the LiCl–KCl eutectic at various reactive electrodes, namely, liquid Cd and Bi and solid Al electrodes. They had obtained the redox potentials for the rare earth metals and yttrium on these cathodes [13, 14]. They had derived the thermodynamic properties of their intermetallics using open circuit potential measurement. Shirai et al. had studied the reaction of LaCl₃ on cadmium film cathode in LiCl-KCl-LaCl₃-CdCl₂ melt by cyclic voltammetry. They had evaluated the Gibbs energy formation of the five intermetallic compounds of the La-Cd system using open circuit chronopotentiometry [15]. The work of Castrillejo et al. and Caravaca et al. had been compiled in the project report PYROREP [16]. The electrochemical behaviour of uranium on W electrode, lanthanides (La, Ce, Pr, Nd ) and Y on W, Cd, Bi and Al electrodes has been reported in the study. The standard reduction potentials of lanthanides on cadmium electrode were estimated from the cyclic voltammograms. The Gibbs energy formation of the various intermetallics of lanthanides with cadmium was estimated from the open circuit potential measurements. The activity coefficients of lanthanides in cadmium and other thermodynamic properties were evaluated from the electrochemical studies. Shibata et al. had studied the Ce-Cd system using electrochemical techniques. They had derived the Gibbs energy formation of six intermetallic compounds of the system [17]. Other than PYROREP [16], we have not come across any study on the behavior of NdCl₃ on cadmium cathode in LiCl-KCl melt.
There have been many studies on the recovery of uranium, plutonium and minor actinides on liquid cadmium cathode at laboratory scale and engineering scale [18-20]. However, there are not many reports on the electrode reaction of the actinides on liquid cadmium pool cathode. Shirai et al. had studied the reduction behaviour of PuCl₃ on cadmium cathode in LiCl-KCl melt by cyclic voltammetry and open circuit potentiometry [21]. They had derived the Gibbs energy formation of the intermetallics of Pu-Cd system. Iizuka et al. had studied the behaviour of Pu and Am in liquid Cd cathode and evaluated their redox potentials on Cd cathode [22]. To our knowledge, the reaction mechanism of uranium chloride on liquid cadmium electrode has been reported by Shirai et al. alone [23]. They had studied the reduction behaviour of UCl₃ on cadmium cathode in LiCl-KCl melt using cyclic voltammetry and had observed underpotential deposition of uranium on cadmium due to formation of the intermetallic, UCd₁₁.

According to the phase diagram of the uranium-cadmium system, UCd₁₁ is the only intermetallic compound and it decomposes peritectically to liquid + α U beyond 746 K [24, 25]. Martin et al. [24] have constructed the phase diagram of the U-Cd system. They had studied the U-Cd system by thermal, metallographic, X-ray and sampling techniques. They had identified a single intermetallic compound, UCd₁₁ which melts peritectically at 746 K to form α-uranium and melt containing 2.5 wt % uranium in the cadmium rich region. A unique feature of the U-Cd system was the retrograde solubility of uranium in the temperature region 746-873 K. Shirai et al. [23] have reported the appearance of a peak in cyclic voltammograms recorded at temperatures above 746 K and had attributed the peak to UCd₁₁ which is not consistent with the phase diagram. Also there is disagreement in value of the Gibbs energy of formation of the intermetallic, UCd₁₁, reported by Shirai et al. using cyclic voltammetry and those reported by Johnson et al. [25] by molten salt emf measurement and Veleckis et al. [26] using vapour pressure
measurement. To understand the anomalous behavior of U on cadmium cathode, we have studied the reduction behavior of uranium in liquid cadmium cathode using cyclic voltammetry and open circuit potential measurement in LiCl-KCl melt. The U-Cd system was also studied in the cadmium rich region by galvanic cell emf method in the temperature range 653 to 764 K.

4.3. Experimental

4.3.1. Chemicals

Anhydrous lithium chloride (AR grade, M/s. Chempure Private Ltd, India), anhydrous potassium chloride (AR grade, M/s. Ranbaxy Fine Chemicals, India), LaCl₃ (Alfa Aesar 99.99 %), NdCl₃ (Alfa Aesar 99.99 %) and anhydrous cadmium chloride (M/s. Merck, Germany 99%) were used for the studies. High purity cadmium metal shots (Alfa Aesar 99.99%) were used for preparing the cadmium working electrode. Uranium metal of nuclear grade obtained from BARC, Mumbai was used for making uranium metal electrode, for preparation of UCl₃ and uranium-cadmium alloys.

4.3.2. Preparation of the electrolyte salt

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

4.3.3. Electrochemical apparatus and electrodes

4.3.3.1. Cyclic voltammetry

A three electrode cell assembly was used for all the electrochemical measurements. The schematic of the electrochemical cell and the electrode assembly were as discussed in Chapter 2. The reference electrode consisting of a silver wire (2 mm dia) dipped in 0.31 mol % AgCl-LiCl-KCl mixture contained in a pyrex glass tube was used for all the measurements. All the potentials reported in this chapter are with respect to this
reference electrode unless otherwise specified. Different working electrodes were used for the studies: (a) 1.5 mm diameter tungsten wire, (b) cadmium pool electrode, (c) cadmium film electrode. The tungsten working electrode was sheathed with an alumina sleeve exposing 40 mm of the wire and the area of working electrode was calculated from the depth of immersion. The cadmium pool electrode was prepared by placing cadmium granules in an alumina crucible which was in turn placed in an SS 430 holder assembly. The crucible was immersed in molten LiCl-KCl to melt cadmium. A 1mm diameter tungsten wire covered with an alumina sheath was immersed in the cadmium melt through the SS assembly and this served as the lead wire. Photograph of the electrode assembly used for liquid cadmium cathode is shown in Fig. 4.1. The Cd film electrode were prepared in-situ by electrodepositing Cd on a W wire of 1.5 mm in diameter as working electrode from melt containing LiCl–KCl–CdCl₂–UCl₃. The electrodeposition was carried out at about -1 V vs. reference electrode for a period of 300 s. A tantalum wire of 1mm in diameter, coiled at one end was used as the counter electrode. The instrumentation, assembling of cell and other experimental procedures are the same as described in Chapter 2.

4.3.3.2. Galvanic cell emf measurement

The electromotive force of the following galvanic cell was measured in the temperature range 653 to 764 K.

\[
U(s)/UCl_3 \text{ in } LiCl - KCl_{eut} (l) / \{UCd_{11}\} + \{Cd\}
\]

(4.1)

The uranium metal electrode was tied on to a Ta strip using 1mm Ta wire. The Ta strip was welded to 1.5 mm Ta wire and the wire was sheathed in an alumina sleeve. The Ta wire served the as lead electrode. The alloy electrode was prepared by taking stoichiometric amounts of uranium metal and cadmium shots in an alumina crucible which was placed in an SS 430 assembly similar to that used for cadmium pool cathode.
The crucible was immersed in molten LiCl-KCl to melt the cadmium. The reaction was allowed to proceed for completion by equilibrating for several hours. A 1mm diameter tungsten wire covered with an alumina sheath was immersed in the alloy melt and this served as the lead wire. Alternately, the alloy was also prepared by electrotransport of uranium from uranium electrode to a liquid cadmium electrode in a cell containing LiCl-KCl-UCl₃ electrolyte. Assembling of the cell and positioning of the set-up in the furnace are the same as described in Chapter 2. The cell was heated to the desired temperature and the emf values were allowed to stabilize for several hours. The emf of the cell was measured using a high impedance electrometer, Agilent 34970A and the data were acquired using a Data Logger.

Fig. 4.1 Photograph of the electrode assembly for liquid cadmium cathode.
4.4 Results and discussion

4.4.1 Reduction behaviour of LaCl₃ and NdCl₃ at the Cd electrode

4.4.1.1 Cyclic voltammetry

Fig. 4.2 compares the cyclic voltammogram recorded for molten LiCl-KCl on tungsten inert electrode with that on liquid cadmium pool electrode. It may be observed that the electrochemical window of the LiCl-KCl melt is limited by the dissolution of Cd at ~ -0.5 V in the anodic side and under-potential deposition of lithium on cadmium surface forming Li-Cd alloy (~ -1.6V) on the cathodic side, when cadmium was used as the cathode. Behavior of LaCl₃ and NdCl₃ on cadmium pool and film electrodes were studied in LiCl-KCl melt at various temperatures using cyclic voltammetry. Fig. 4.3a and Fig. 4.3b show the cyclic voltammograms of LaCl₃ and NdCl₃ in LiCl-KCl melt at 748 K on liquid cadmium pool cathode, respectively. Reduction of LaCl₃ and NdCl₃ on these electrodes takes place at much positive potential than on the W electrode. The behavior is attributed to the reduced activity of La and Nd on Cd surface due to formation of the intermetallic compounds of La-Cd and
Fig. 4.2 Cyclic voltammograms for LiCl-KCl melt on W and Cd pool cathodes.
Temperature: 698 K; Area: 0.314 cm$^2$ (W) and 0.21 cm$^2$ (Cd)

Fig. 4.3a Cyclic voltammograms for LaCl$_3$ in LiCl-KCl melt at cadmium pool electrode.
Polarization rate: 10 mVs$^{-1}$; Concentration of LaCl$_3$: 6.66 x 10$^{-5}$ mol cm$^{-3}$. 
Nd-Cd systems. Thus underpotential deposition of lanthanum and neodymium occur on cadmium electrode. The reduction of La(III) and Nd(III) ions on Cd surface takes place in a single step with three electron transfer. It may be recalled that reduction of Nd(III) ion to Nd metal takes place in two steps on W electrode with the formation of Nd(II) ion as the intermediate which was discussed in Chapter 3, whereas the reduction of Nd(III) ion takes place in a single step with three electron transfer on cadmium electrode forming intermetallic compound during the cathodic cycle and dissolution of the alloy during the anodic cycle.

Fig. 4.4 and Fig. 4.5 show the phase diagrams of the La-Cd system and Nd-Cd systems respectively [27, 28]. Lanthanum and neodymium form various intermetallic compounds with cadmium. However we have observed only one redox peak predominantly for both the electrodes. It may be envisaged from the phase diagram and also from the extent of potential shift towards the anodic direction that the substrate rich intermetallic is formed in both the cases. The electrode reaction for the reduction of La(III) and Nd(III) ions on Cd electrode is given by,

\[ \text{RE(III)} + 11\text{Cd} + 3e \rightarrow \text{RECd}_{11} \]  

(4.2)

Formation of \( \text{RECd}_{11} \) has been reported for other lanthanides in the literature [14, 15, 29]. Further, the fact that the compounds formed are \( \text{LaCd}_{11} \) and \( \text{NdCd}_{11} \) has been supported by the XRD pattern of the electrodeposits, details of which will be discussed in section 4.4.1.5.
Fig. 4.3b Cyclic voltammograms for NdCl$_3$ in LiCl-KCl melt at cadmium pool electrode. Polarization rate: 10 mVs$^{-1}$; Concentration of NdCl$_3$: $6.66 \times 10^{-5}$ mol cm$^{-3}$.

Fig. 4.4 Cd-La phase diagram [27].
4.4.1.2 Estimation of apparent standard potential for RE(III)/RE(Cd) from cyclic voltammograms

Fig. 4.6 compares the cyclic voltammograms recorded for a solution of NdCl$_3$ in LiCl-KCl at 723 K on cadmium pool and cadmium film electrodes and the inset of Fig. 4.6 shows the cyclic voltammogram on cadmium film electrode at different scan rates at 698 K. Fig. 4.7 shows the cyclic voltammograms recorded for a solution of LaCl$_3$ in LiCl-KCl at 748 K on cadmium film electrode at different scan rates. The reduction peak and the oxidation peak currents appeared at much positive potentials than those on tungsten inert electrode. On the cadmium pool electrode, the cathodic and anodic peaks are similar to those for soluble-soluble reversible system. The cathodic peak potentials do not shift appreciably.
Fig. 4.6 Comparison of cyclic voltammograms for LiCl-KCl-NdCl₃ melt at Cd pool and film electrode; Polarization rate: 10 mVs⁻¹; Concentration of NdCl₃: 6.66 x 10⁻⁵ mol cm⁻³. Inset: Cyclic voltammograms at Cd film electrode at different scan rates; Temperature: 698 K.

Fig. 4.7 Cyclic voltammograms for LaCl₃ in LiCl-KCl at cadmium film electrode at different scan rates. Temperature: 748 K.
with increase in the polarization rates. The magnitude of \( E_{pc} - E_{pc/2} \) is in agreement with the one expected for soluble-soluble couple (Eq. 4.3) for a three electron transfer [30]. Thus, the reduction is presumed to show Nernstian behavior.

\[
E_p - E_{p/2} = -2.2 \frac{RT}{nF}
\]  

(4.3)

Assuming that the concentration of RE(III) ions is very less than that required for exceeding saturation, we have used the voltammetric curves to derive the half wave potential, using Eq. (4.4) for a soluble-soluble reversible system. For soluble-soluble species, the half wave potential, \( E_{1/2} \), is related to the standard potential and apparent standard potential by the following relation [21, 31, 32]

\[
E_{1/2} = \left( E_p^c + E_p^d \right)/2
\]  

(4.4)

Where

\[
E_{1/2} = E^0_{RE(III)/RE(Cd)} + \frac{RT}{3F} \ln \frac{\sqrt{D_{RE(Cd)}}}{\gamma_{RE(III)}} + \frac{RT}{3F} \ln \left( \frac{\gamma_{RE(III)}}{\gamma_{RE(Cd)}} \right)
\]  

(4.5)

And the apparent standard potential is described as

\[
E^*_{RE(III)/RE(Cd)} = E^0_{RE(III)/RE(Cd)} + \frac{RT}{3F} \ln \left( \frac{\gamma_{RE(III)}}{\gamma_{RE(Cd)}} \right)
\]  

(4.6)

Hence we get,

\[
E^*_{RE(III)/RE(Cd)} = E_{1/2} + \frac{RT}{3F} \ln \frac{\sqrt{D_{RE(III)}}}{\sqrt{D_{RE(Cd)}}}
\]  

(4.7)

where \( E^0_{RE(III)/RE(Cd)} \) and \( E^*_{RE(III)/RE(Cd)} \) are the standard potential and apparent standard potential of the RE(III)/RE(Cd) redox couple. The apparent standard potentials, \( E^*_{La(III)/La(Cd)} \) and \( E^*_{Nd(III)/Nd(Cd)} \) were obtained from the cyclic voltammograms using Eq. 4.4 and Eq.4.7. Since cadmium is a liquid at the temperature of study, it is assumed that the diffusion coefficient of RE in the salt phase and cadmium phase are identical. Similar
assumption has been made by other authors earlier [14, 15, 23]. The potentials thus obtained versus the reference electrode, Ag/AgCl (X_{AgCl} = 0.0031), were converted to the scale of Cl_2/Cl^- reference electrode using the relation given by Yang and Hudson (Eq. 3.21 and Eq. 3.22) discussed in chapter 3. The values of apparent standard potentials, $E_{La(III)/La(Cd)}^*$ and $E_{Nd(III)/Nd(Cd)}^*$ are shown in Table 1 and 2 respectively. The apparent standard potentials obtained from this study are compared to those reported in the project report PYROREP in the Tables [16]. The present data of NdCl_3 on cadmium electrode are comparable to those of PYROREP but those for LaCl_3 differ from those of PYROREP by about 30 mV.

The difference between the cadmium pool electrode and film electrode is that the amount of Cd in the film electrode is limited. So the deposited metal exceeds its solubility in Cd and the electrode loses its homogeneity. Appearance of separate solid phase makes the voltammograms on cadmium film electrode less accurate for estimating the half wave potential than those obtained from cadmium pool electrode. It may be observed in Fig. 4.6 that the onset potential for the reduction on film electrode is more cathodic than that on pool electrode. The half wave potentials on Cd film electrode are shifted cathodically by ~ 30 mV. Hence we have estimated the apparent standard potentials from the cyclic voltammograms recorded on cadmium pool electrode.

4.4.1.3 Open-circuit chronopotentiometry

Open-circuit potential measurements were recorded after depositing the RE on cadmium film electrode by polarizing the electrode at -1.7 V using LiCl-KCl-RECl_3 melt. Fig.4.8 shows the open circuit potential transient curve on the cadmium film cathode.
Table 4.1 Apparent standard potentials (± 0.002 V) for La(III)/La(Cd) estimated from cyclic voltammogram on Cd pool electrode, $X_{LaCl_3} = 0.00224$. 

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$E^{\circ}_{La(III)/La(Cd)}$ vs. Ag/Ag$^+$, V</th>
<th>$E^{\circ}_{La(III)/La(Cd)}$ vs. Cl$_2$/Cl$^-$, V</th>
<th>$E^{\circ}_{La(III)/La(Cd)}$ vs. Cl$_2$/Cl$^-$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>-1.471</td>
<td>-2.705</td>
<td>-2.730 (693 K)</td>
</tr>
<tr>
<td>723</td>
<td>-1.453</td>
<td>-2.693</td>
<td>-2.728</td>
</tr>
<tr>
<td>748</td>
<td>-1.436</td>
<td>-2.681</td>
<td>-</td>
</tr>
<tr>
<td>773</td>
<td>-1.419</td>
<td>-2.668</td>
<td>-2.707</td>
</tr>
</tbody>
</table>

Table 4.2 Apparent standard potentials (± 0.002 V) for Nd(III)/Nd(Cd) estimated from cyclic voltammogram on Cd pool, $X_{NdCl_3} = 0.00224$. 

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$E^{\circ}_{Nd(III)/Nd(Cd)}$ vs. Ag/Ag$^+$, V</th>
<th>$E^{\circ}_{Nd(III)/Nd(Cd)}$ vs. Cl$_2$/Cl$^-$, V</th>
<th>$E^{\circ}_{Nd(III)/Nd(Cd)}$ vs. Cl$_2$/Cl$^-$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>698</td>
<td>-1.499</td>
<td>-2.733</td>
<td>-2.736 (673)</td>
</tr>
<tr>
<td>723</td>
<td>-1.487</td>
<td>-2.726</td>
<td>-2.721</td>
</tr>
<tr>
<td>733</td>
<td>-1.482</td>
<td>-2.723</td>
<td>-</td>
</tr>
<tr>
<td>758</td>
<td>-1.469</td>
<td>-2.716</td>
<td>-</td>
</tr>
<tr>
<td>773</td>
<td>-1.462</td>
<td>-2.711</td>
<td>-2.703</td>
</tr>
</tbody>
</table>

monitored at different temperatures for LiCl-KCl-LaCl$_3$ melt and Fig. 4.9 that for LiCl-KCl-NdCl$_3$ melt. A distinct potential plateau is seen in both the cases. The presence of the plateau indicates that there is equilibrium between two co-existing phases. From the phase diagram and our observations from the cyclic voltammograms, it may be concluded that the plateau corresponds to the coexistence of the phases, RECd$_{11}$ and (Cd). Though...
La and Nd forms various intermetallic compounds with Cd, only one intermetallic is predominantly formed under our experimental condition.

**4.4.1.4 Thermodynamic properties of La-Cd and Nd-Cd systems**

The measurement of equilibrium potential for Nd(III)/Nd(0) redox couple by OCP method was described in section 3.4.6.2.2 in chapter 3. The equilibrium potential of the La(III)/La(0) couple was obtained from the open-circuit chronopotentiograms recorded with a solution of LaCl$_3$ in LiCl-KCl melt at W electrode. The OCP transient curves were obtained by applying a cathodic polarization (-2.1 V) for a period 300 s to deposit La metal on the W surface. The open circuit potential was monitored as a function of time. A potential plateau at ~ -2 V corresponding to the redox couple La(III)/La(0) was observed in the transient which is the equilibrium potential for the redox couple. The potentials of the plateaus that were measured with respect to the reference electrode, Ag/AgCl ($X_{AgCl} = 0.0031$), in LiCl-KCl-RECl$_3$ melt on cadmium film electrode using the OCP method were converted to the equilibrium potentials of the RE(III)/RE(0) couple obtained as described above. The potential of the plateau referred to the rare earth metal electrode is the emf of the cell represented by

$$RE(\text{s})/RECl_3\text{ in LiCl} - KC_{\text{ext}}(l)/\{RECd_{11}\} + \{Cd\}$$  \hspace{1cm} (4.8)

The emf was evaluated for different temperatures for La-Cd and Nd-Cd systems. The Gibbs energy formation of the intermetallics, LaCd$_{11}$ and NdCd$_{11}$ at different temperatures
Fig. 4.8 Open circuit potential transient curve for LaCl$_3$ in LiCl-KCl melt on Cd film electrode. Cathodic polarization: -1.7 V vs. (Ag/Ag$^+$) reference electrode.

Fig. 4.9 Open circuit potential transient curve for NdCl$_3$ in LiCl-KCl melt on Cd film electrode. Cathodic polarization: -1.7 V vs. (Ag/Ag$^+$) reference electrode.
were estimated from the emf values and are shown in Table 3 and Table 4 respectively. The activity of RE in cadmium was calculated from Eq. 4.9 and the values are given in Table 3 and 4.

\[
emf = -\frac{RT}{3F} \ln a_{RE(Cd)}
\]  

(4.9)

The excess Gibbs energy of RE in cadmium, \(\Delta G_{RE(Cd)}^{ex}\) was evaluated using Eq. 4.10 [35-36]

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

(4.10)

The mole fraction of RE in cadmium, \(X_{RE(Cd)}\) was taken from the solubility data reported in the literature [37, 38].

Solubility (La-Cd system), X (mol %)

\[
593-899 \text{ K } \log(X) = 7.350 - 6061/T
\]  

(4.12)

Solubility (Nd-Cd system), X (mol %)

\[
593-803 \text{ K } \log(X) = 6.909 - 5211/T
\]  

(4.13)

The thermodynamic properties for RE-Cd system estimated from OCP measurements are shown in Table 5 and 6. The low activity coefficient values show the strong interaction between the rare earth metal with cadmium. The values of Gibbs energy of formation of LaCd_{11} obtained from the OCP measurement is compared to those reported in literature. Our values are in good agreement with those reported by Johnson et al.[39]. The value of Gibbs energy formation of NdCd_{11} obtained from the OCP measurement is compared to those reported in the project report PYROREP [16] and it may be seen that the values are in agreement. The activity coefficients of the lanthanides in cadmium reported by Sakamura et al. and Johnson et al. are also shown in the table [40, 41]. The activity coefficients of the lanthanides in cadmium are in good agreement with those reported by Sakamura et al.
Table 4.3 Gibbs energy of formation of LaCd$_{11}$ estimated from OCP measurement on Cd film electrode.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>emf (±0.003) V</th>
<th>$\Delta_f G_{LaCd_{11}}, \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This study OCP</td>
</tr>
<tr>
<td>698</td>
<td>0.608</td>
<td>-176.2</td>
</tr>
<tr>
<td>723</td>
<td>0.596</td>
<td>-172.7</td>
</tr>
<tr>
<td>748</td>
<td>0.585</td>
<td>-169.2</td>
</tr>
<tr>
<td>762</td>
<td>0.578</td>
<td>-167.3</td>
</tr>
</tbody>
</table>

Table 4.4 Gibbs energy of formation of NdCd$_{11}$ estimated from OCP measurement on Cd film electrode.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>emf (±0.002) V</th>
<th>$\Delta_f G_{CdCd_{11}}, \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This study OCP</td>
</tr>
<tr>
<td>698</td>
<td>0.531</td>
<td>-153.6</td>
</tr>
<tr>
<td>723</td>
<td>0.529</td>
<td>-153.1</td>
</tr>
<tr>
<td>733</td>
<td>0.527</td>
<td>-152.5</td>
</tr>
<tr>
<td>773</td>
<td>0.521</td>
<td>-150.7</td>
</tr>
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</table>
Table 4.5 Thermodynamic properties of La in Cd estimated from OCP measurement on Cd film electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>log $a_{La(Cd)}$</th>
<th>$\Delta G^{ss}_{La}$ kJ mol$^{-1}$</th>
<th>log $\gamma'_{La(Cd)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>This study (OCP)</td>
</tr>
<tr>
<td>698</td>
<td>-13.2</td>
<td>-131.5</td>
<td>-9.8</td>
</tr>
<tr>
<td>723</td>
<td>-12.5</td>
<td>-130.5</td>
<td>-9.4</td>
</tr>
<tr>
<td>748</td>
<td>-11.8</td>
<td>-129.9</td>
<td>-9.1</td>
</tr>
<tr>
<td>773</td>
<td>-11.5</td>
<td>-129.3</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

Table 4.6 Thermodynamic properties of Nd in Cd estimated from OCP measurement on Cd film electrode

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>log $a_{Nd(Cd)}$</th>
<th>$\Delta G^{ss}_{Nd}$ kJ mol$^{-1}$</th>
<th>log $\gamma'_{Nd(Cd)}$</th>
</tr>
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<td></td>
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<td>This study (OCP)</td>
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<td>-8.8</td>
</tr>
<tr>
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<td>-10.9</td>
<td>-121.6</td>
<td>-8.6</td>
</tr>
<tr>
<td>773</td>
<td>-10.2</td>
<td>-123.6</td>
<td>-8.4</td>
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</tbody>
</table>
4.4.1.5 Electrodeposition

To examine the alloy formed on the cadmium surface, potentiostatic electrolysis was carried out using LiCl-KCl-RECl₃-CdCl₂ melt (RE= La, Nd). A Ta sheet was polarized at -1.55 V vs. Ag/AgCl reference electrode for 5 hours. This potential is slightly cathodic to the potential plateau observed in the OCP measurement for the La-Cd and Nd-Cd systems. Co-deposition of Cd and the rare earth metal (La, Nd) occurs to form the stable intermetallic compound on the W surface. The cathode deposit adhered with salt was powdered, placed in a glass slide and sealed thoroughly to ensure it was air tight for characterization by XRD analysis. Fig. 4.10 shows the XRD pattern of the cathode deposit obtained using LiCl-KCl-RECl₃-CdCl₂. The XRD pattern shows the formation of the intermetallic NdCd₁₁.

4.4.2 Electrochemical study of uranium at liquid cadmium electrode

4.4.2.1 Cyclic voltammetry

Cyclic voltammograms were recorded for LiCl-KCl-UCl₃ melt at cadmium pool and cadmium film electrodes. Fig. 4.11 shows the cyclic voltammograms of LiCl-KCl containing 2.44 x 10⁻⁵ moles cm⁻³ UCl₃ on a cadmium pool cathode at different temperatures. Reduction of UCl₃ on a cadmium cathode takes place at a less cathodic potential than that observed on the inert W electrode. Only a single peak couple is observed for the redox process on cadmium pool electrode. The reduction peak is attributed to under potential deposition of uranium metal on the cadmium electrode due to lowering of activity of uranium in cadmium. A shift of about 150 mV in the peak potential towards positive direction was observed. Similar observation was made by Shirai et al. [23] in their study on electrode reaction of UCl₃ in cadmium pool cathode in LiCl-KCl melt. Fig. 4.12 shows the phase diagram of the
Fig. 4.10 XRD pattern of Nd-Cd film formed by potentiostatic electrolysis at -1.55V vs. (Ag/Ag⁺) reference electrode in LiCl-KCl-NdCl₃-CdCl₃ melt for 5 hrs at 748 K.

Fig. 4.11 Cyclic voltammogram for LiCl-KCl-UCl₃ melt at different temperatures on cadmium pool cathode; Concentration of UCl₃: 2.44 x 10⁻⁵ moles cm⁻³; Ag/AgCl (X_{AgCl} = 0.001).
U-Cd system in the cadmium rich region [25]. It is deduced that uranium deposits as UCd$_{11}$ as it is the only stable intermetallic compound for this system.

\[
\text{U(III) + 11Cd +3e} \rightarrow \text{UCd}_{11}
\]  

(4.14)

Fig. 4.13 shows the cyclic voltammograms of LiCl-KCl-UCl$_3$ on a cadmium film electrode at various polarization rates. Unlike the cyclic voltammograms on the cadmium pool, two distinct peaks were seen on a cadmium film electrode. Fig. 4.14 compares the cyclic voltammograms obtained on W, cadmium pool and cadmium film electrodes. It may be seen that peak II$_c$ appears at a potential close to that for U(III)/U(0) on inert W electrode. Peak II$_c$ in Fig. 4.13 is attributed to the reduction of U(III) to uranium metal.
Fig. 4.13 Cyclic voltammograms of LiCl-KCl-UCl$_3$ on Cd film working electrode at different scan rates; Concentration of UCl$_3$: $7.31 \times 10^{-5}$ moles cm$^{-3}$; Temperature: 723 K.

Fig. 4.14 Cyclic voltammograms of LiCl-KCl-UCl$_3$ on different working electrodes; Concentration of UCl$_3$: $7.31 \times 10^{-5}$ moles cm$^{-3}$; Temperature: 748 K.
Fig. 4.15 Cyclic voltammograms of LiCl-KCl-UCl$_3$ on Cd film working electrode at different switching potentials; Concentration of UCl$_3$: 7.31 x 10$^{-5}$ moles cm$^{-3}$; Temperature: 748 K.

from the peak position and from the nature of the corresponding anodic peak (stripping peak) which resembles that for dissolution of insoluble species. Peak I$_c$ was studied by switching the potential before peak II$_c$ and the cyclic voltammogram appeared as shown in Fig. 4.15. The shape of the voltammogram resembles that for a soluble-soluble couple. It may be observed from Fig. 4.14 that the onset potential for reduction of U(III) ion on Cd pool is close to the onset potential for peak I$_c$. Hence peak I$_c$ is attributed to the underpotential reduction of uranium on cadmium surface. We consider that since the amount of cadmium on the film electrode is limited, initially a peak for underpotential deposition of uranium on cadmium surface occurs and once the surface of the film is saturated with the U-Cd alloy, with no fresh cadmium at the surface, the electrode behaves as an inert electrode. Hence a peak for reduction of U(III) ion to U metal is
observed subsequently. Similar behavior was observed by Murakamiz et al. in their study on the electrochemical behavior of zirconium on cadmium film surface [42]. Such behavior was not observed in case of lanthanides, since their redox potentials for RE(III)/RE(0), lie beyond the electrochemical window of the cadmium electrode. Hence from the above discussion it may be inferred that peak Ic corresponds to under potential deposition of uranium on cadmium.

From the cyclic voltammograms obtained at 10 mVs⁻¹ on cadmium pool electrode, the number of electrons transferred for the reduction of U(III)/U(Cd) was calculated using Eq. 4.3 applicable for a soluble-soluble redox couple. The value of n was close to three. The apparent standard potentials, \( E^\ast_{U(III)/U(Cd)} \) at different temperatures were estimated using Eq. 4.4 - Eq. 4.7. The potentials thus obtained versus the reference electrode, Ag/AgCl (\( X_{AgCl} = 0.0031 \)), was converted to the scale of Cl₂/Cl⁻ reference electrode using Eq. 3.21 and Eq. 3.22 stated in chapter 3. The apparent standard potential, \( E^\ast_{U(III)/U(Cd)} \) at different temperatures are shown in Table 7.

Table 4.7 Apparent standard potentials (±0.003 V) for U(III)/U(Cd), estimated from cyclic voltammogram on Cd pool, \( X_{UCd} = 0.00267 \); Ag/AgCl (\( X_{AgCl} = 0.0031 \)) | Temperature, K | \( E^\ast_{U(III)/U(Cd)} \), V vs. Ag/Ag⁺ | \( E^\ast_{U(III)/U(Cd)} \), V vs. Cl₂/Cl⁻ | \( E_{1/2,U(III)/U(Cd)} \), V vs. Ag/Ag⁺ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>-1.323</td>
<td>-2.552</td>
<td>-</td>
</tr>
<tr>
<td>698</td>
<td>-1.311</td>
<td>-2.545</td>
<td>-</td>
</tr>
<tr>
<td>723</td>
<td>-1.299</td>
<td>-2.538</td>
<td>-1.331</td>
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<tr>
<td>740</td>
<td>-1.293</td>
<td>-2.535</td>
<td>-</td>
</tr>
<tr>
<td>773</td>
<td>-1.218</td>
<td>-2.468</td>
<td>-1.320</td>
</tr>
</tbody>
</table>
The values were compared with the apparent standard potential for U(III)/U(0) couple, $E^*_{U(III)/U(0)}$ which was obtained by emf method discussed in chapter 3. It was expected that the difference in the potentials should correspond to the Gibbs energy formation of the intermetallic, UCd$_{11}$. Fig. 4.16 shows the apparent standard potentials obtained from this study and the standard electrode potentials for U(III)/U(0) and U(III)/U(Cd) couple reported by Shirai et al. [23]. Shirai et al. had measured the redox potentials for U(III)/U(0) couple at various concentrations at different temperatures by equilibrium measurement. They had obtained the standard reduction potential, $E^0_{U(III)/U(0)}$ at different temperatures using the Nernst equation. They had derived the half wave potential, $E_{1/2,U(III)/U(Cd)}$ from the cyclic voltammograms recorded on cadmium pool cathode using the relation for soluble-soluble couple (Eq. 4.3). They had considered the half wave potential, $E_{1/2,U(III)/U(Cd)}$ as the standard reduction potential for the reduction of U(III) on Cd. The $E_{1/2,U(III)/U(Cd)}$ reported by them is more negative than their $E^0_{U(III)/U(0)}$ values for U(III)/U(0) couple as may be seen in Fig. 4.16. Also it may be observed from the figure that the difference between the potentials increases with increase in temperature. As stated earlier, according to the phase diagram of the uranium-cadmium system, UCd$_{11}$ is the only intermetallic compound of the system and it decomposes peritectically to liquid + α U beyond 746 K, whereas in both the studies, that is, study by Shirai et al. and this work find underpotential reduction of uranium on the cadmium cathode for temperatures beyond 746 K. But the discrepancy has not been discussed by Shirai et al and no explanation has been given. We also do not know the reason for the behavior.

The apparent standard potentials, $E^*_{U(III)/U(Cd)}$ are more negative than the apparent standard potentials for U(III)/U(0) couple, $E^*_{U(III)/U(0)}$, at temperatures below 746 K in our study similar to the observation made by Shirai et al. Their difference, ΔE, is less than
those expected from the Gibbs energy formation of UCd\(_{11}\) reported by Johnson et al.[25] and Veleckis et al.[26] obtained by galvanic cell emf method and by vapour pressure measurement respectively. However it was observed that the difference in the potentials becomes zero \(\sim 746\) K in our study as expected from the phase diagram unlike in the case of Shirai et al. report. In order to know the equilibrium potential of U on cadmium at different temperatures, open circuit potential measurements were carried out.

![Graph showing electrode potentials for U(III)/U(0) and U(III)/U(Cd) couples from cyclic voltammetry and emf method.](image)

Fig. 4.16 Electrode potentials for U(III)/U(0) and U(III)/U(Cd) couples from cyclic voltammetry and emf method.
4.4.2.2 Open-circuit chronopotentiometry-LiCl-KCl-UCl₃

Open circuit potential measurements were carried out on cadmium film cathode using LiCl-KCl-UCl₃ melt at different temperatures. The cadmium film was polarized at -1.5 V for a short period (60-120 sec) and the open-circuit potential of the electrode is measured under zero current condition as a function of time. The potential increased towards anodic direction with the evolution of plateau at about -1.4 and -1.22 V. Fig. 4.17 shows the open circuit potential measurements on a cadmium film electrode. The plateau at about -1.4 V, may be attributed to the couple U(III)/U(0) from the potential of the plateau, which is the equilibrium potential of the U(III)/U(0) couple. Since UCd₁₁ is the only intermetallic of the U-Cd system, we attribute the plateau at about -1.22 V to the coexistence of UCd₁₁ and Cd. The potential further increases in the anodic direction and stabilizes at the equilibrium potential of Cd(II)/Cd(0) couple. Initially, the potential time transients at various temperatures were obtained by electrodepositing uranium for 300 s at a potential of -1.6 V in the melt LiCl-KCl containing UCl₃ on fresh tungsten electrode at various temperatures. The details were discussed in chapter 3. The potentials measured on cadmium film cathode with respect to the reference electrode, Ag/AgCl (X_{AgCl} = 0.0031), was rescaled with reference to that of a U(III)/U(0) electrode. The potential of the plateau on cadmium film electrode referred to the uranium electrode is considered as the emf of the cell represented by Eq.1.

Table 8 shows the equilibrium potential for U(III)/U and those for U(III)/U(Cd) recorded from open circuit potential measurements. The difference between the potential values lie between 187-208 mV in the temperature range 653-743 K. The values are much higher than those reported by Johnson et al. [25] for the formation of UCd₁₁. Also, we had observed the plateau corresponding to the alloy in the OCP transients for temperatures above
Table 4.8 Equilibrium potentials (±0.003 V), $E_{U(III)/U(0)}$ and $E_{U(III)/U(Cd)}$ from open circuit potentials measurement.

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>$E_{U(III)/U(0)}/$ V</th>
<th>$E_{U(III)/U(Cd)}/$ V</th>
<th>$\Delta E/ V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>653</td>
<td>-1.443</td>
<td>-1.256</td>
<td>0.187</td>
</tr>
<tr>
<td>670</td>
<td>-1.433</td>
<td>-1.242</td>
<td>0.191</td>
</tr>
<tr>
<td>698</td>
<td>-1.417</td>
<td>-1.219</td>
<td>0.198</td>
</tr>
<tr>
<td>723</td>
<td>-1.402</td>
<td>-1.199</td>
<td>0.203</td>
</tr>
<tr>
<td>743</td>
<td>-1.391</td>
<td>-1.183</td>
<td>0.208</td>
</tr>
</tbody>
</table>

Fig. 4.17 Open circuit potential transient of LiCl-KCl-UCl₃ on Cd film working electrode at different temperatures; Concentration of UCl₃: $7.31 \times 10^{-5}$ moles cm⁻³; Applied potential: -1.5 V.
746 K. The same observations were made on repeated measurements. As discussed earlier, we had observed peak for underpotential deposition on cadmium cathode in the cyclic voltammograms recorded beyond 746 K and Shirai et al. also have reported $E_{\text{U(II)/U(I)}(\text{Cd})}$ at 773, 798 and 823 K in their work. These observations are contradictory to the phase diagram, as it may be noted from the phase diagram that UCd$_{11}$ decomposes to U(α) + liquid beyond 746 K.

The anomalous behavior of uranium on cadmium cathode is not well understood. In order to have a better understanding of the uranium-cadmium system, we had studied the uranium cadmium system on the cadmium rich side by galvanic cell emf method.

### 4.4.2.3 Galvanic cell emf measurement

We had studied the U-Cd system on the cadmium rich side in the temperature range 653 to 764 K by setting up an emf cell as denoted below

$$U(s)/UCl_3 \text{ in LiCl} – KCl_{(l)}/U – Cd(\text{alloy})$$

(4.15)

Studies were carried out in the region of unsaturated alloy and in the region of saturated alloy. Preparation of the alloy was as discussed in the experimental section. The emf values of the cell are given in Table 9. The emf values were reproducible during the heating and cooling cycles. Variation of the emf with temperature for the saturated alloy is shown in Fig. 4.18. The emf data below 746 K were fitted by a polynomial equation given below

$$emf = 1.4941 - 3.65 \times 10^{-3}T + 2.21 \times 10^{-6}T^2$$

(4.16)

The Gibbs energy of UCd$_{11}$ from α-uranium and pure liquid cadmium is given by

$$\Delta G_f^{\alpha} = -zFE + 11RT \ln a_{Cd}$$

(4.17)

Where $z$=3, the number of electrons participating in the electrode reaction, $F$, the Faraday constant and $a_{Cd}$, the activity of cadmium in the saturated solution. Assuming
that the solution is ideal with respect to cadmium and from the solubility data [25], the standard Gibbs energy formation of UCd$_{11}$ was estimated and the values are shown in Table 9.

The Gibbs energy of formation of UCd$_{11}$ (cal mol$^{-1}$), obtained by measuring the vapour pressure of cadmium reported by Veleckis et al. is given by the following relation in the temperature range 578-650 K [43].

\[ U(\alpha) + 11Cd(liq) \rightarrow UCd_{11}(c) \quad \Delta G'' = -143600 + 188.5T \]  
(4.18)

And that by Johnson et al. obtained from galvanic cell emf method is given by the following relation in the temperature range 573-746 K [43]

\[ \Delta G''(UCd_{11}) = -113800 + 151.5T \]  
(4.19)

We had derived the following relation from the emf data of our measurement

\[ \Delta G''(UCd_{11}) = -115500 + 154.4T \]  
(4.20)

Our measurement is very much in agreement with those of Johnson et al. whereas those of Veleckis et al. not in agreement. However, the three equations extrapolate to $\Delta G^o = 0$ at about 746 K which is the peritectic temperature of UCd$_{11}$ and are consistent with the phase diagram. It shows that the Gibbs energy of formation from all the three studies are in agreement. The enthalpy and entropy values being different are to be explained as they are fit parameters rather than the actual enthalpy and entropy values, as has been discussed by Kubaschwaski et al. [44].

The activity of uranium on cadmium was calculated from Eq. 4.21 and the values are given in Table 10.

\[ emf = \frac{RT}{3F} \ln a_{U(Cd)} \]  
(4.21)

The excess Gibbs energy of U in cadmium is given by,

\[ \Delta \bar{G}_U^e = RT \ln \gamma_{U(Cd)} = -3F \Delta E - RT \ln x_{U(Cd)} \]  
(4.22)
Table 4.9 The emf (±0.002 V) of unsaturated and saturated U-Cd alloy vs. uranium metal.

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>$N_u$/unsat’d</th>
<th>emf/ V</th>
<th>Temperature/ K</th>
<th>$N_u$/sat’d</th>
<th>emf / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>680.5</td>
<td>0.006</td>
<td>0.0356</td>
<td>680.5</td>
<td>0.0120</td>
<td>0.0356</td>
</tr>
<tr>
<td>681</td>
<td>0.006</td>
<td>0.0323</td>
<td>680.9</td>
<td>0.0120</td>
<td>0.0373</td>
</tr>
<tr>
<td>700</td>
<td>0.006</td>
<td>0.0268</td>
<td>699</td>
<td>0.0120</td>
<td>0.0244</td>
</tr>
<tr>
<td>743.8</td>
<td>0.006</td>
<td>0.0227</td>
<td>700</td>
<td>0.0120</td>
<td>0.0264</td>
</tr>
<tr>
<td>763.9</td>
<td>0.006</td>
<td>0.0113</td>
<td>700.7</td>
<td>0.0120</td>
<td>0.0244</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>724</td>
<td>0.0120</td>
<td>0.0121</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>724.5</td>
<td>0.0120</td>
<td>0.0128</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>725.5</td>
<td>0.0120</td>
<td>0.0133</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>744.3</td>
<td>0.0120</td>
<td>0.0051</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>762.9</td>
<td>0.0120</td>
<td>-0.0017</td>
</tr>
</tbody>
</table>

Fig. 4.18: Plot of emf as a function of temperature from galvanic cell emf method.
Chapter 4

The activity coefficients of uranium in liquid cadmium was calculated using Eq. 4.22 and are shown in Table 10. The activity coefficient value reported by Johnson et al. in the temperature range 671-798 K is 47-100 [25]. The activity coefficient value reported by Sakamura et al. in the temperature range 673-773 K is 54-104 [40]. Our values are in very good agreement with the reported values. Roy et al. estimated the activity coefficient of uranium in cadmium by studying the distribution coefficient of uranium in salt phase and in cadmium phase at 723 K [45]. They had reported the value as 15. The order of activity coefficient of all the measurement is same.

During the emf measurement, the equilibrium potentials of the uranium electrode and the U-Cd alloy electrode were monitored with respect to the reference electrode, Ag/AgCl (X_{AgCl} = 0.0031). Their difference is the emf reported above. The values were compared with the standard potentials reported by Shirai et al. [23] and the apparent standard potentials obtained from the cyclic voltammograms in this study as shown in Fig. 4.16. It may be observed that the equilibrium potentials for the uranium electrode and U-Cd alloy (sat’d) electrode shift to less cathodic values with increase in temperature and intersect at ~ 746 K. The result is in very good agreement with that expected from the reported phase diagram. The equilibrium potentials of the unsaturated alloy are also shown in Fig. 4.16. The values are not much different from the saturated alloy in the concentration range of uranium in cadmium studied.

We had compared the data from the emf study and the cyclic voltammograms to understand the behavior of uranium on cadmium electrode. From Fig. 4.16, it is evident that, there is a change in the slope of the apparent standard potential, $E_{U(III)/U(CI)}^*$ for values below 746 K and those above. The trend is similar to that observed for the values of the equilibrium potentials of the saturated alloy. Comparing the values of the emf, from the galvanic cell method and ΔE (the difference in the apparent standard potentials,
Table 4.10 Thermodynamic properties of U-Cd system – measurements made by galvanic cell emf method

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>$N_a$</th>
<th>$\Delta_f G_{\text{UCd}_1}^{0}$ / kJmol$^{-1}$</th>
<th>$a$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>680.9</td>
<td>0.012</td>
<td>-10.4</td>
<td>0.181</td>
<td>15</td>
</tr>
<tr>
<td>699</td>
<td>0.012</td>
<td>-7.6</td>
<td>0.325</td>
<td>27</td>
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<td>700.7</td>
<td>0.012</td>
<td>-7.3</td>
<td>0.324</td>
<td>28.4</td>
</tr>
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<td>-3.7</td>
<td>0.620</td>
<td>51.7</td>
</tr>
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<td>0.012</td>
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<td>0.627</td>
<td>52.2</td>
</tr>
<tr>
<td>725.5</td>
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<td>0.641</td>
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</tr>
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<td>744.3</td>
<td>0.012</td>
<td>-0.6</td>
<td>0.923</td>
<td>76.9</td>
</tr>
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<td>762.9</td>
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<td>101.1</td>
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<td>0.162</td>
<td>29.9</td>
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<tr>
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<td>0.192</td>
<td>35.5</td>
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<tr>
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<td>0.264</td>
<td>43.8</td>
<td></td>
</tr>
<tr>
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<td>0.346</td>
<td>57.4</td>
<td></td>
</tr>
<tr>
<td>763.9</td>
<td>0.006</td>
<td>0.597</td>
<td>99.5</td>
<td></td>
</tr>
</tbody>
</table>

$E^{\circ}_{U(III)/U(II)}$ and $E^{\circ}_{U(III)/U(Cd)}$, we noted that the value of $E^{\circ}_{U(III)/U(Cd)}$ is more negative by ~40 mV. Hence we infer that our measurement by cyclic voltammetry is fairly in agreement with that expected from the emf method.
The appearance of a peak in cyclic voltammograms above 746 K, could be attributed to the large solubility of uranium in liquid cadmium (0.84 - 2.32 wt % in the temperature range 723 - 746 K). The concentration of uranium in cadmium cathode in our experiments could have been in the region of the unsaturated alloy seen in the phase diagram in Fig. 4.12. The peaks in cyclic voltammograms above 746 K may not correspond to UCd$_{11}$ as we had presumed. They probably correspond to the unsaturated U-Cd alloy. The large difference in the equilibrium potentials from the OCP measurement, may be due to the above reason.

Fig. 4.21 compares the cyclic voltammograms obtained for LiCl-KCl melt containing UCl$_3$, LaCl$_3$ and NdCl$_3$ on cadmium pool cathode. It may be observed that their reduction potentials differ hardly by 150 mV. Hence the separation of actinides from lanthanides cannot be very high on a cadmium cathode.

4.4.2.4 Potentiostatic electrolysis

Potentiostatic electrolysis was carried out on the liquid cadmium pool electrode in LiCl-KCl-UCl$_3$ melt at 723 K for more than 10 hours at a potential of -1.3 V. This potential is more positive than that required for deposition of pure uranium metal on an inert electrode. The amount of uranium deposited on cadmium cathode was estimated from the coulombs passed. The electrolysis was stopped and the cell was cooled, when the amount of uranium in cadmium was in the region of unsaturated alloy. The solidified cathode deposit was retrieved by breaking the alumina container. The deposit was washed with ethylene glycol to remove the adhering salt and subsequently sliced into many pieces to view the cross section. The cross section of the cathode deposit was characterized by XRD analysis. Fig. 4.19 shows the XRD pattern for the top most slice of the cathode deposit. The XRD pattern shows the presence of Cd and the intermetallic, UCd$_{11}$ [33]. SEM-EDAX analysis of the samples was carried out to study the morphology and
Fig. 4.19 XRD pattern of the cathode deposit of uranium on cadmium pool cathode formed by potentiostatic electrolysis at -1.3 V vs. Ag/AgCl reference electrode at 723 K [46].

Fig. 4.20 SEM micrograph of the cathode deposit of uranium on cadmium pool cathode formed by potentiostatic electrolysis at -1.3 V vs. AgCl/Ag reference electrode at 723 K and the corresponding EDAX analysis.
Fig. 4.21 Comparison of cyclic voltammograms for UCl$_3$, LaCl$_3$ and NdCl$_3$ in LiCl-KCl melt on cadmium pool cathode.

elemental composition. Fig. 4.20 shows the SEM micrographs and EDAX analysis of the same cathode deposit sample. Elemental analysis from EDAX analysis shows the U-Cd ratio as 1:11 corresponding to UCd$_{11}$. The results indicate that underpotential deposition of uranium occurs on cadmium cathode due to formation of U-Cd alloy. On cooling, the liquid alloy solidifies as Cd(s) and UCd$_{11}$ which is revealed in the XRD pattern [45].

4.5 Summary

The electrode behavior LaCl$_3$ and NdCl$_3$ in LiCl-KCl eutectic melt was studied on liquid cadmium pool and film electrode using cyclic voltammetry. The reduction occurred at more positive potential than that on an inert electrode. The activity of La/Nd is lower on the Cd electrode due to the formation of intermetallic compound. The apparent standard electrode potentials, $E^{\ast}_{\text{La(III)/La(Cd)}}$ and $E^{\ast}_{\text{Nd(III)/Nd(Cd)}}$ were estimated for the temperatures in the range 698-773 K. The equilibrium potentials, $E_{\text{La(III)/La(Cd)}}$ and
\[ E_{\text{Nd(III)/Nd(Cd)}} \] were obtained from the OCP measurement. The equilibrium potentials thus obtained was converted to emf by comparing the potential against the equilibrium potential of RE(III)/RE(0) obtained from OCP measurement mentioned in chapter 1. This method is used for first time here. The Gibbs energy of formation of the alloys, LaCd\(_{11}\) and NdCd\(_{11}\) were obtained from the open circuit potential measurement. The activity of La/Nd in cadmium, the excess Gibbs energy and the activity coefficient of La/Nd in cadmium are reported from the open circuit potential measurement for first time. XRD pattern of the electro-deposit showed the formation of intermetallic compounds LaCd\(_{11}\) and NdCd\(_{11}\) on the Cd cathode for La-Cd and Nd-Cd systems respectively. The studies reported on Nd-Cd system in this work is not reported in open literature earlier.

Only one report was found in literature (by Shirai et al.) for the redox behavior of UCl\(_3\) on Cd pool electrode. The studies were reported for the temperature range 698-823 K. They had reported the underpotential deposition of uranium on Cd pool electrode due to the formation of UCd\(_{11}\). However from the phase diagram, we find that UCd\(_{11}\) is unstable above 746 K. Also the Gibbs energy formation of UCd\(_{11}\) reported by them was much higher than those reported by Johnson et al. who had studied the U-Cd system by emf method.

Hence, to understand the anomalous behavior of UCl\(_3\) on cadmium electrode, the reduction mechanism of UCl\(_3\) on cadmium pool and film electrodes was investigated by cyclic voltammetry and open circuit potentiometry in the temperature range 698-798 K. Our studies on the open circuit potential measurement on Cd electrode did not yield any fruitful result. Underpotential deposition of uranium on the cadmium cathode was revealed from the cyclic voltammograms. The shift in potential towards the positive direction was presumed to be due to the formation of the intermetallic compound, UCd\(_{11}\). However, the extent of shift in potential did not agree with those reported in literature.
Also we had observed appearance of peak for UCd$_{11}$ in the cyclic voltammogram beyond 746 K which is the peritectic temperature of UCd$_{11}$.

The discrepancies were fairly understood from our studies by galvanic cell emf method. In order to know the equilibrium potential of the U-Cd alloy both in saturated and unsaturated region with respect to the reference electrode, emf measurement was carried out. Apart from measuring the emf between the uranium electrode and the alloy, the potentials of the alloy was monitored against the AgCl/Ag reference electrode over a wide temperature range for the saturated and unsaturated alloy. From the potential values obtained from the cyclic voltammograms and emf studies in this work, we could relate the appearance of peak above 746 K to the underpotential deposition of uranium forming the unsaturated alloy. The large solubility of uranium in cadmium (0.84 -2.32 wt % in the temperature range 723 -746 K) could be the reason for the discrepancies observed. We have not come across any cyclic voltammetry study for such systems with large solubility.

The SEM-EDX analysis and the XRD pattern of the cathode deposit obtained in the region of unsaturated alloy by potentiostatic electrolysis of LiCl-KCl-UCl$_3$ melt on cadmium pool cathode at 723 K reveal the formation of the intermetallic UCd$_{11}$.

The uranium cadmium system on the cadmium rich side was studied in the temperature range 653 - 764 K by galvanic cell emf method. The Gibbs energies of formation of UCd$_{11}$ in the temperature range 680 to 744 K were evaluated and the values were in good agreement with those reported by Johnson et al. The peritectic temperature of UCd$_{11}$ was evaluated to be 748 K which is consistent with the phase diagram [24] and those reported by Johnson et al.[25], Veleckis et al. [26] and Kurata et al.[38] are 751 K, 762 K and 748 K respectively. The activity coefficients of uranium in the solvent rich
region were computed in the temperature range 680-764 K were found to be in the range 14-100 and are in good agreement with the literature value.

4.6 References


