# CHRONOPOTENTIOMETRY OF THORIUM, LANTHANUM AND YTTERBIUM IN FUSED LITHIUM CHLORIDE-POTASSIUM CHLORIDE

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Chronopotentiometric apparatus was used for studying fused salt chronopotentiometry. An eutectic mixture of LiCl.KCl was used as a base electrolyte. Chronopotentiograms were recorded either with a fast response recorder or os illoscope. The electrochemical behaviour of thorium, lanthanum and ytterbium in this medium was studied. The process in all the three cases were diffusion controlled The diffusion coefficients for thorium was $1.385 \times 10^{-5}$, lanthanum $0.19 \times 10^{-5}$ and ytterbium was $0.147 \times 10^{-5}$ at 450°C. The value of 'n' obtained from the log plots was two in case of lanthanum and ytterbium and one in the case of thorium.

Recently there has been an increased tendency to introduce the potential utility of fused salts in the field of nuclear energy, such as coolant in reactor, in fuel reprocessing system etc. Importance of thorium in breeder reactor technology as proposed in India is quite well known, and there is trend to investigate the electrochemistry of thorium.

Electrochemistry in fused salt media has already established its own importance in electrometallurgical processes and in electroanalytical chemistry. In general, potentiometry [1–4] and polarography [5–9] have been applied to analysis in molten salts. Electrodeposition of thorium from a bath of NaCl-KCl melt containing thorium ion was studied on bismuth electrode [10]. Thorium in the form of dendrites has been produced by many workers. Johnson [11] showed that thorium in the form of dendrites can be produced by electrolysis of thorium chloride dissolved in sodium chloride melt.

Smirnov et al [12,13] carried out some studies on thorium electrodeposition. Yang et al [14], in the potentiometric equilibrium study showed that $ThCl_4$ formed complexes with LiCl-KCl eutectic and its reduction to metal involves four electron exchange. Srinivasan [15] et al have reported on electrode potentials of thorium ion in some alkali halide melts. The chronopotentiometric technique finds extensive use in molten salts systems.

The chronopotentiometry of $ThF_4$ and $ThCl_4$ at and above 700°C using alkali chloride electrolyte and molybdenum indicator electrode [16] and the preparation of lanthanum metal by electrolysis of its fused chloride[17] have been reported. Some studies about the behaviour of rare earth ions in electrode process was carried out by Compbell [18], who calculated the redox potential of $Yb^{++}$ in LiCl-KCl eutectic from chronopotentiometric data.

The studies reported in this paper relate to chronopotentiometry of these ions in fused salt media. The study is confined to chloro compounds of thorium, lanthanum and ytterbium in LiCl-KCl eutectic at 450°C.

## EXPERIMENTAL PROCEDURE

**Constant current source :** A stabilised D.C. supply of 30 volts supplying a constant current varying between 50 to 1000 $\mu$A against the load resistance varying between 0 to 20 K$\Omega$ was used as a constant current source. In order to employ the apparatus for cyclic chronopotentiometry, a provision for current reversal was used with the help of a DPDT switch on a one centimeter thick perspex sheet to avoid current loss.

**Recorder :** The potential time curves in the range of $\tau$ - 2 sec. were recorded on a Honeywell Electronic 194 strip chart recorder and for '$\tau$'s less than that, Tektronix storage oscilloscope was used for recording the curves.

**Cell :** The electrolytic cell used is given in Fig. 1. The cell was fabricated from pyrex glass.

**Electrodes :** A three electrode system was employed for the studies : (1) a test or working microelectrode of platinum wire forms the cathode, (2) a reference electrode of Pt/0.1M $Pt^{+2}$ is employed and (3) a platinum wire serves as an auxiliary electrode.

**Preparation of supporting electrolyte :** LiCl-KCl eutectic was prepared from A.R. grade salts (BDH) by a method similar to that of Laitinen et al [19].

**Furnace :** The furnace used in these studies was a resistance, pit-type furnace, closed at the bottom to reduce the temperature gradient in the melt.

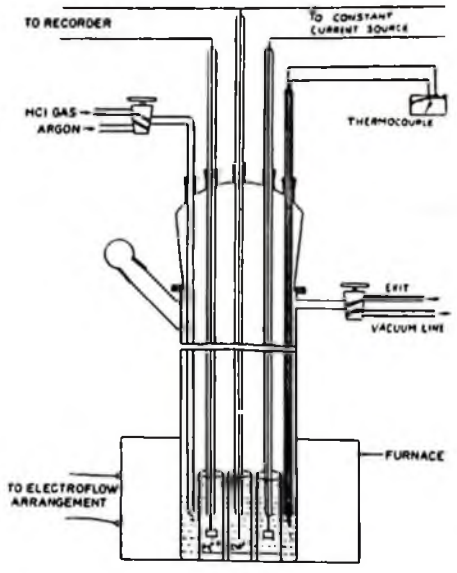



FIG 1
FUSED SALT CELL

**Reagents and chemicals :** Anhydrous thorium chloride was obtained by forming a hydrated ammonium chloride complex in acidified water solution, dehydrating this compound and finally decomposing the double salt and subliming the ammonium chloride compound.

Anhydrous lanthanum and ytterbium chlorides were prepared by dissolving the oxide in dilute hydrochloric acid, adding about 6.0 mole of ammonium chloride per mole of metal and next about 50 ml of relatively concentrated hydrochloric acid. The mixture was evaporated to dryness. All the salts were stored in a dessicator over magnesium perchlorate.

## PROCEDURE

The cell was standardised with lead salt as follows. The cell and capsules were cleaned with hot nitric acid. The fritted portion of the tube was heated to incandescence to remove all impurities. All the electrodes were cleaned by dipping them in hot nitric acid and drying overnight.

Chronopotentiograms of pure supporting electrolyte were taken first. The solute of dry A.R. grade chloride was weighed in a clean fritted capsule and dropped into the melt along with the electrode in position. The constant current source was connected to the respective electrodes by wires with shielded cables terminating in alligator clips. The recording equipment was checked for required characteristics. The recorder was set to match the sweep at the rate which spread the transition time over a large measurable area.

The desired melt temperature of 450°C was obtained by adjusting the auto-transformer. Chronopotentiogram was obtained by closing the switch and allowing the constant current to pass between the electrodes. The direction of current was reversed at the end of the reduction transition time, to obtain oxidation curve whenever desired.

The bulk concentration of the lead chloride was re-established in the vicinity of the polarised indicator electrode by bubbling purified argon and also by reversing current which was passed through the cell just enough to remove the deposited metal from the electrode. This was indicated by the e.m.f. displayed on the recorder.

The temperature measurement was accomplished with the help of a calibrated thermocouple to an accuracy of $\pm 2$°C. The area of the microelectrode was calculated by the conventional methods.

The method employed for measurement of transition time '$\tau$' and quarter wave potential $E_{\tau}/4$ are the same as that employed in aqueous chronopotentiometric work [19].

The same procedure was followed for thorium, lanthanum and ytterbium.

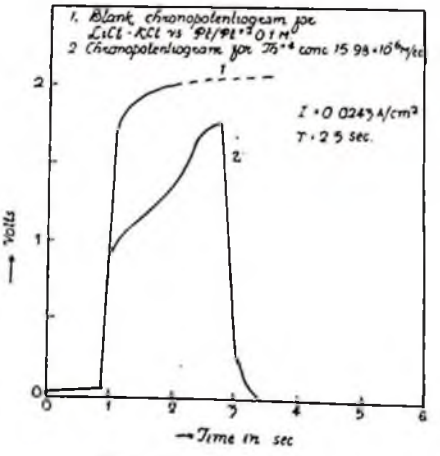



Fig 2 Cyclic Chronopotentiogram

## RESULTS AND DISCUSSION

**Thorium :** Verification of Sand's equation : In order to verify whether Sand's equation is obeyed or

not, reduction of $Th^{+4}$ ion in LiCl-KCl melt was studied at 450°C at different concentrations using varying current densities.

Specimen curves have been given in Fig.2. Curve 1 is for the supporting electrolyte only. It shows a deviation in the curve at 1.88± 0.02 V showing the reduction of $Li^+$ ion. As there is a large excess of $Li^+$ ions present, the electrolysis continues, and there is no further deviation in the potential time curve. Curve2, for thorium ion, on the other hand shows a deviation much earlier and further deviation defines clearly the transition time. Table 1 gives the results obtained. It can be seen that the value of $I\tau^{\frac{1}{2}}/C$ is constant within the experimental error showing that the mass transport is controlled solely by the process of diffusion and Sand's equation is obeyed. From the average value of $I\tau^{\frac{1}{2}}/C$ obtained from a number of readings, the diffusion coefficient was calculated to be $1.385 \times 10^{-5}$ $cm^2$ $sec^{-1}$, which is close to reported values[16].

**Table 1 Chronopotentiometric Data on Thorium Chloride in LiCl-KCl at 450°C**

Area of the platinum working electrode : $A_1 = 0.0338 cm^2$; $A_2 = 0.0770$ $cm^2$; Reference electrode : $Pt/Pt^{+2}$ 0.1M; Auxiliary electrode : Platinum

| Concentration moles $cc^{-1}$ C | Current density $A/cm^2$ I | $\tau^{\frac{1}{2}}$ sec | $I\tau^{\frac{1}{2}}/C$ A sec. $\frac{1}{2}$ ml. $mole^{-1}$ | $D \times 10^5$ $cm^2$ $sec^{-1}$ | $E\tau/4$ −V |
|---|---|---|---|---|---|
| $10.20 \times 10^{-6}$ | 0.01154 | 1.166 | 1319 | 1.486 | 1.45 |
| $11.39 \times 10^{-6}$ | 0.0090 | 1.60 | 1264 | 1.2773 | 1.48 |
| $25.37 \times 10^{-6}$ | 0.0243 | 1.340 | 1283 | 1.404 | 1.40 |
| | 0.0270 | 1.20 | 1277 | 1.383 | — |
| | 0.0216 | 1.580 | 1345 | — | — |

D Mean $1.385 \times 10^{-5}$ $cm^2$ $sec^{-1}$

From the reduction waves of $Th^{+4}$ ions the $E\tau/4$ values were found out as outlined by Delahay[20] and Table 1 also lists $E\tau/4$ values and it can be concluded that $E\tau/4$ values for thorium ion reduction is 1.4 ± 0.05 volt. The comparative data with $Pt/Pt^{+2}$ (0.1M) reference is not available.

**Lanthanum :** Fig.3 shows that reduction of the supporting electrolyte ions start at about 1.88±0.02V vs $Pt/Pt^{+2}$ 0.1M reference electrode. $La^{+3}$ ion under the conditions of our studies showed an unusual behaviour. The $E\tau/4$ value indicating the reduction varied with change in current density. It was found to be −0.22 volts vs Pt $Pt^{+2}$ 0.1M for low current densities of the order of 0.008 $A/cm^2$. However, at higher current densities like 0.0135 $A/cm^2$, the $E\tau/4$ value was found to be -1.06 volts vs $Pt/Pt^{+2}$ 0.1M. However, no attempt was made to find out an exact current density limit where this transition took place. Further observations were carried out at high current densities only. Specimen results obtained in the concentration range of 37mM to 137mM of $La^{+3}$ under varying current densities have been listed in Table 2. The transition time varied from 1 sec to 4 sec. It can also be seen that $I\tau^{\frac{1}{2}}/C$ is constant within experimental limits showing that the reaction is solely controlled by diffusion and Sand's equation is obeyed. Therefore diffusion coefficient value was calculated and found to be $0.19 \times 10^{-5} cm^2$ $sec^{-1}$ at 450°C.

It is clear from the equation

$$E = E\tau/4 - \frac{RT}{nF} \ln \frac{i_{\frac{1}{2}}}{\tau^{\frac{1}{2}} - i_{\frac{1}{2}}}$$

that for a reversible electrode process the plot of E vs log $\left(\frac{\tau^{\frac{1}{2}} - i_{\frac{1}{2}}}{i_{\frac{1}{2}}}\right)$ shall give a straight lind whose reciprocal slope shall give the number of electrons 'n' taking part in the electrode reaction. For a reversible reaction involving 4 electron reduction the reciprocal slope would be 2.303 RT/4F (about 0.036 at 450°C.)

The value of average slope in our study was 5 and from that the number of electrons exchanged indicated

**Table 2 Chronopotentiometric Data on Lanthanum Chloride in LiCl-KCl at 450°C**

Area of platinum working electrode : 0.037 $cm^2$; Reference electrode : $Pt/Pt^{+2}$ 0.1M; Anxiliary electrode : Platinum wire

| | Concentration moles/c.c. C | Current density A/$cm^2$ I | $\tau\ \frac{1}{2}$ sec. | I $\tau\ \frac{1}{2}$/C A sec. ml. $mole^{-1}$ | D × $10^5$ $cm^2$ $sec^{-1}$ | E $\tau$/4 |
|---|---|---|---|---|---|---|
| | 37.49 × $10^{-6}$ | 0.0081 | 1.183 | 255 | 0.222 | 0.2 |
| Low | | | | | | |
| | 38.41 × $10^{-6}$ | 0.0067 | 1.34 | 235 | 0.185 | 0.19 |
| | 112.07 × $10^{-6}$ | 0.0135 | 2.09 | 251 | 0.200 | 1.07 |
| High | | | | | | |
| | 137.96 × $10^{-6}$ | 0.0216 | 1.41 | 220.7 | 0.170 | 1.06 |

D = Mean 0.1942 × $10^{-5}$$cm^2$ $sec^{-1}$.

E $\tau$/4 for lanthanum shows inconsistency with change in cathode current density

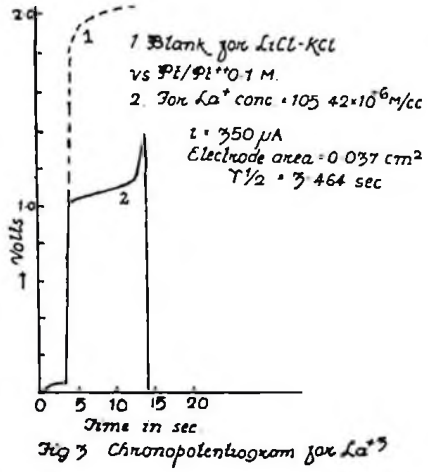



Fig 3 Chronopotentiogram for $La^{+3}$

would be one. The plot of E vs $\log\left(\frac{\tau\ \frac{1}{2} - t\frac{1}{2}}{t\frac{1}{2}}\right)$ is shown in Fig.4.

For a 3 electron reduction the reciprocal slope must be 2.303 RT/3F. But the value of the slope obtained from a number of such plots was 14 on the average. From this it is indicated that the number of electrons exchanged, under the given experimental conditions is two. This would indicate that probably there is a displacement reaction giving rise to $La^{++}$ which in its turn is getting reduced at the electrode. The plots of $\log\left(\frac{\tau\ \frac{1}{2} - t\frac{1}{2}}{t\frac{1}{2}}\right)$ vs E at higher and lower current density results showed difference in the 'n' value. Plots with the higher current densitiy results indicated a value of 2 whereas the ones at lower current densities showed a 'n' value of 1. This is difficult to explain. Popov et al[21] have observed somewhat similar behaviour in the case of molybdenum (IV) in LiCl-KCl melt at 450°C. Though there is no such indication of $La^{+3} \rightarrow La^{+2} \rightarrow La^{\circ}$ given by others, Campbell[18], in case of rare earth ions like $Sm^{+3}$ $Yb^{+3}$ etc. has established this by potential measurements.

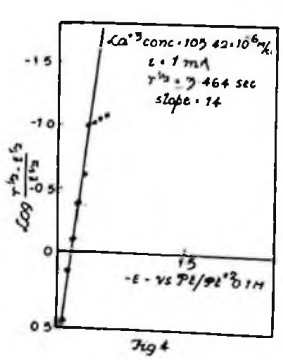



Fig 4

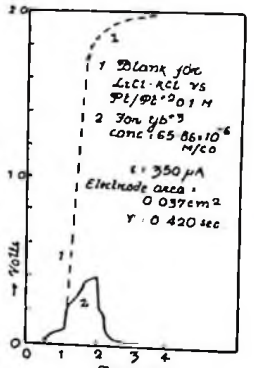



Fig 5 Chronopotentiogram for Ytterbium

**Ytterbium** : The nature of the reduction wave for $YbCl_3$ was studied. The reduction starts at about −0.18V vs 0.1M Pt (II) Pt reference electrode. From the nature of the chronopotentiogram it could be seen that the reaction might be reversible. A good oxidation wave was obtained. The whole reaction proceeded in a single step. Reproducible values were obtained. The quarter wave potential was about −0.25 ± 0.03 volt A typical chronopotentiogram for $YbCl_3$ added is given in Fig.5. The Sand's equation was checked for the reduction

step using different current densities at three varying concentrations and the results are given in Table 3. $I\tau^{\frac{1}{2}}/c$ value indicated diffusion controlled reaction. The value of diffusion coefficient calculated was $0.1474 \times 10^{-5}$ cm² sec⁻¹ on the average.

TABLE 3

**Chronopotentiometric Data on Ytterbium Chloride in LiCl-KCl at 450°C**

Area of platinum working electrode : 0.037cm²; Reference electrode : $Pt/Pt^{+2}$ 0.1M Auxiliary electrode : Platinum wire

| Conc moles/cc C | Current density A/cm² I | $\tau^{\frac{1}{2}}$ sec. | $I\tau^{\frac{1}{2}}/c$ A sec. $\frac{1}{2}$ml. mole⁻¹ | DX $10^5$cm² sec⁻¹ | E $\tau/4$ |
|---|---|---|---|---|---|
| $35.54 \times 10^{-6}$ | 0.0054 | 1.414 | 214.8 | 0.1356 | 0.25 |
| $38.85 \times 10^{-6}$ | 0.0121 | 0.7483 | 233.0 | 0.1692 | 0.255 |
| $44.32 \times 10^{-6}$ | 0.0081 | 1.096 | 200.0 | 0.1376 | 0.255 |

D Mean : $0.1474 \times 10^{-5}$ cm² sec⁻¹

As described earlier, that a plot of E vs $\log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}}$ shall give a straight line, the reciprocal slope of this line shall give the number of electrons 'n' taking part in the electrode reaction. Such a plot is given in Fig.6. The value of the slope of the above plot indicated that only 2 electrons are involved in the reduction step under the above stated concentrations and temperatures. This indicated that probably $Yb^{+3}$ ion reacts with $Li^+$ ion to become $Yb^{+2}$ which undergoes reduction. This has been confirmed by Campbell[18] in his potential measurement studies of $Sm^{+3}$, $Eu^{+3}$, and $Yb^{+3}$.

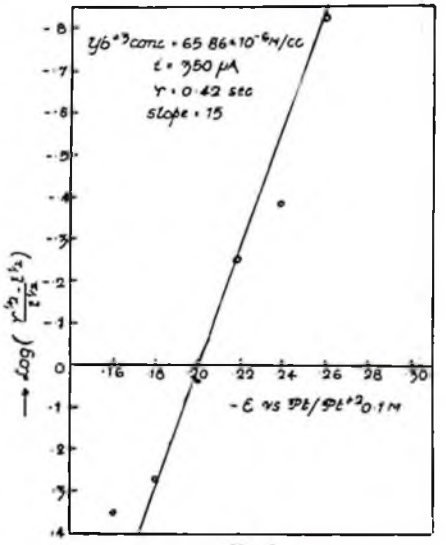


Fig 6

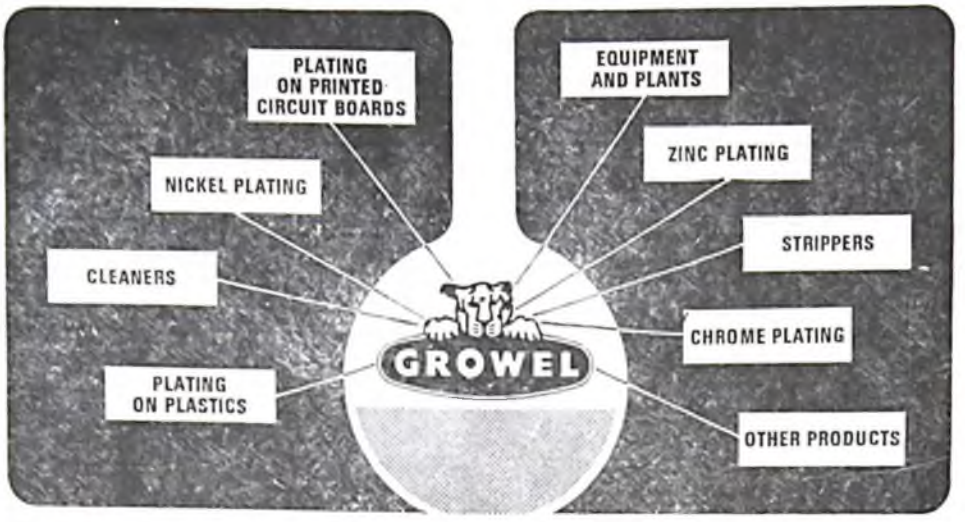
Even though other electrochemical data would be obtained by this technique, it could not positively indicate the number of electrons exchanged especially in case of thorium, as the extent of reversibility could not be ascertained under the conditions. It will have to be obtained from other techniques like microcoulometry.

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