Fast breeder reactors using plutonium based fuels occupy an important place in the Indian nuclear energy programme, as they enable producing more fissile material than that is consumed. The Prototype Fast Breeder Reactor to be commissioned shortly is based on uranium-plutonium mixed oxide fuels whereas the future fast reactors of India will use metallic alloys of U-Pu-Zr or U-Pu as the fuels. Due to the high breeding potential of metallic alloy fuels, they have been chosen to expedite the growth of nuclear energy.

Currently used reprocessing technology is based on PUREX process, a solvent extraction process using tri-butyl phosphate in dodecane as the extractant. But, a high temperature non-aqueous process, known as molten salt electrorefining is more suited for the metallic fuels than the above process, as it offers several advantages such as more compact plant, less criticality problems, less waste volumes etc.
In the molten salt electrorefining process, [1, 2] the spent metallic fuel is anodically dissolved in molten LiCl-KCl eutectic mixture as their chlorides at 773 K. The Gibbs energy of formation of the metal chlorides is the primary determinant of the process. The alkali and alkaline fission products are completely oxidized and they remain in the salt throughout the process. The noble metals are not oxidized and they remain as metal in the anode. The chlorides of rare earths and actinides have intermediate stability. However, the rare earth chlorides are more stable than the actinide chlorides. Two kinds of cathodes are used in the process - a solid iron cathode and a liquid cadmium cathode. In the first stage, uranium is oxidized at the anode (as its chloride) and an equivalent amount of uranium chloride is reduced at the cathode. Plutonium and rare earth metals remain almost entirely in the salt or at the anode because of their relatively negative Gibbs energy of formation of their chlorides. The product obtained at the solid cathode is essentially pure uranium which will be used for fabrication of the blanket fuel. At the cadmium cathode, the activity coefficient of Pu is greatly lowered due to the formation of several intermetallic compounds with Cd. On the contrary, the activity coefficient of U in Cd is about four orders of magnitude larger at the operating temperature. So at the liquid Cd cathode, deposition of Pu is favoured. Similarly, the minor actinides are stabilized due to their very low activity coefficients in cadmium. A small amount of lanthanides also come into the liquid cadmium cathode since their behavior is similar to the trans-uranium metals. The product obtained at the liquid cadmium cathode is a mixture of plutonium, uranium and minor actinides which would be used for making fresh core fuel after blending with uranium and zirconium of required composition.

Minor actinides in the fuel are tolerated as they can be burnt in the reactor. But the lanthanides act as neutron poison and their proportion should be kept as minimum as possible. Under such circumstances, cadmium cannot be considered as the optimum solvent from the perspective of decontamination from the lanthanides. Studies from the liquid-liquid
metal reduction extraction in fluoride melts showed that aluminium has the highest potential for group selective separation of actinides and lanthanides [3]. The process variant being developed at Institute of Transuranium Elements (ITU), Karlsruhe, Germany is based on aluminium cathode. Selective recovery of actinides over lanthanides was achieved in this process [4].

Thus it is obvious that knowledge of the electrochemical behavior and the thermochemical properties of actinide and lanthanide chlorides are essential to achieve efficient separation. The basic electrochemical behavior of major elements involved in the electrorefining process, their standard electrode potentials and thermodynamic properties are well studied and reported in the literature. However the kinetics of the reduction process of the metal ions has not been studied to the same extent. The reduction behavior of actinide and rare earth elements at the interface between the LiCl-KCl eutectic melt and liquid Cd are not much studied.

From the perspective of selective separation of actinides from lanthanides, studies under identical conditions would provide inputs for better evaluation of the electrodes. In this thesis, studies on the behavior of an actinide (U) and two rare earth fission product elements (La, Nd) on W, Cd, Al and Ga electrodes in LiCl-KCl eutectic melt in the temperature range 698-773 K were carried out using transient electrochemical techniques. Also, there is need for developing a rapid and reliable method for in-situ monitoring of the composition of the actinides in the electrolyte during the pyrochemical processes. The concentration of uranium would vary to a large extent during the course of the electrorefining process. Hence the method to be selected should be suitable over a large concentration range. Hence studies on different transient techniques, namely, normal pulse voltammetry, square wave voltammetry, differential pulse voltammetry etc. were investigated for monitoring the concentrations of uranium and some lanthanides.
The thesis is divided into 8 chapters. A brief description of the contents of the chapter is given below.

**Chapter 1: Introduction**

This chapter gives a brief description of the need of nuclear energy to meet the growing energy demand. It discusses about the various types of nuclear fuels and nuclear reactors with an emphasis on the metal fuelled fast breeder reactors for meeting the energy demand. The different non-aqueous processes for reprocessing of spent nuclear fuel are described and the molten salt electrorefining for reprocessing the spent metal fuel is discussed in detail. The need for research on alternate cathodes to cadmium in molten salt electrorefining process and the objective of the thesis are presented.

**Chapter 2: Experimental facilities and techniques**

The chapter is divided into two sections. The first section gives a brief description of the materials and the equipment used for the studies. The argon atmosphere glove box, purification of the LiCl-KCl salt mixture, preparation of electrolytes, the electrochemical cell, electrodes and the instrumentation are discussed. The second section gives a brief description and theory of the electrochemical techniques used for the studies such as cyclic voltammetry (CV), chronoptentiometry (CP), open circuit potentiometry (OCP), impedance spectroscopy (IS) and pulse techniques such as square wave voltammetry (SWV), normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV).

**Chapter 3: Electrochemical behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ in LiCl-KCl eutectic melt on inert tungsten electrode**

This chapter describes the results of the studies on the redox behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ at inert W electrode in LiCl-KCl eutectic melt. The reduction of La(III) ion to La metal and that of U(III) ion to U metal were found to take place in a single step with three electron transfer. On the other hand, reduction of Nd(III) ion to Nd metal on tungsten
electrode takes place in two steps- Nd(III)/Nd(II) and Nd(II)/Nd(0). The kinetics of the reduction process was studied by analyzing the semi-integrals of the cyclic voltammograms. The studies showed that the reduction of La(III)/La(0), Nd(II)/Nd(0) and U(III)/U(0) followed the quasi-reversible behavior. The reduction of Nd(III)/Nd(II) showed reversible electrode behavior. The heterogeneous rate constant for the reduction, La(III)/La(0) and Nd(II)/Nd(0) at 798 K were $4.1 \times 10^{-6}$ and $7.8 \times 10^{-6}$ cm$^{-1}$ respectively and that for U(III)/U(0) at 773 K was $1.8 \times 10^{-5}$ cm$^{-1}$. The apparent standard electrode potentials, $E^*_{\text{La(III)/La(0)}}$, $E^*_{\text{Nd(III)/Nd(II)}}$, $E^*_{\text{Nd(II)/Nd(0)}}$ and $E^*_{\text{U(III)/U(0)}}$ were estimated from the cyclic voltammograms and open circuit potential measurements. In order to validate our measurements using transient techniques, the equilibrium potential of U(III)/U(0) couple was determined using the emf method also. The electromotive force of the following galvanic cell was measured in the temperature range 680-823 K-

$\text{Ag(s) / AgCl in LiCl – KCl}_{eutt}(l) // \text{UCl}_3 \text{ in LiCl – KCl}_{eutt}(l) / U(s)$

The apparent standard potential values for the redox couple U(III)/U(0) obtained from cyclic voltammetry, OCP and emf measurement are in agreement with each other within ± 10 mV. The present data are in agreement with the values reported by Masset et al. in his critical review of the literature data [5].

**Chapter 4: Electrochemical behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ in LiCl-KCl eutectic melt on cadmium electrode**

The studies on the reduction behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ on liquid cadmium pool and film electrodes in LiCl-KCl eutectic melt are discussed in this chapter. Under potential deposition of the respective lanthanide metal through reduction of their chloride on this reactive due to the formation of the solvent rich intermetallic compound, LaCd$_{11}$ and NdCd$_{11}$ for the La-Cd and Nd-Cd systems respectively. The apparent standard electrode
potentials, $E_{La}^{\text{III}}/La(Cd)$ and $E_{Nd}^{\text{III}}/Nd(Cd)$ at 723 K were -2.728 (± 0.002) and -2.721 (± 0.002) V vs. Cl$_2$/Cl$^-$ respectively. The Gibbs energy of formation of the LaCd$_{11}$ and NdCd$_{11}$ intermetallic compounds at 723 K determined by OCP were -170.6 (± 0.9) and -153.1 (± 0.6) kJ mol$^{-1}$ respectively. The values are in agreement with those reported in the literature.

However, in case of the U-Cd system, the extent of shift in the potential in the cyclic voltammograms did not agree with those expected from the Gibbs energy of formation of the intermetallic UCd$_{11}$ reported by Johnson et al. [6] by molten salt emf measurement. According to the phase diagram of the uranium-cadmium system, UCd$_{11}$ is the only intermetallic compound and it decomposes peritectically to liquid + α U beyond 746 K. But we could observe peak in the cyclic voltammograms at positive potentials beyond 746 K. Similar observation was made by Shirai et al. also [7]. To understand the anomalous behavior of U on cadmium cathode, we have studied the U-Cd system in the cadmium rich region by galvanic cell emf method in the temperature range 653 to 764 K.

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

Measurements were made with saturated U-Cd alloy and unsaturated U-Cd alloy. 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.[6] The peritectic temperature of UCd$_{11}$ was evaluated to be 748 K which is consistent with the phase diagram. The discrepancy found in the cyclic voltammograms and OCP transients were fairly understood by comparing the values of the equilibrium potentials obtained from these measurements with those measured in the saturated and unsaturated U-Cd alloy from the galvanic cell.

**Chapter 5: Electrochemical behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ in LiCl-KCl eutectic melt on solid aluminium electrode**
This chapter discusses the reduction behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ on solid aluminium electrode by electrochemical methods in the temperature range 698-773 K. The reduction of LaCl$_3$ and NdCl$_3$ occurred at more positive potential than that for inert cathode due to the formation of the intermetallic compound Al$_{11}$RE$_3$. The apparent standard electrode potential of La(III)/La(Al) and Nd(III)/Nd(Al) at 723 K were -2.539 (± 0.002) and -2.496 (± 0.002) V vs. Cl$_2$/Cl$^-$ respectively. The Gibbs energy of formation of the intermetallics estimated from OCP were -179.5 (± 0.6) and -168.8 (± 0.6) kJ mol$^{-1}$ respectively. Studies on the redox behavior of UCl$_3$ on solid aluminium electrode showed the underpotential reduction of U(III) ion on aluminium electrode at a potential ~ 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. From the values of the Gibbs energy of formation of the intermetallics, UAl$_4$ and UAl$_3$ reported by Chiotti et al. [8], it was found that they differ merely by 1 kJ mol$^{-1}$ and the difference in the corresponding emf is < 10 mV. Taking this into consideration, it was concluded that the compound formed on the Al surface corresponds to both the intermetallics, UAl$_4$ and UAl$_3$. Similar behavior was earlier reported by Cassayre et al. [9].

Chapter 6: Electrochemical behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ in LiCl-KCl eutectic melt on gallium surface

The feasibility of using gallium cathode for efficient actinide-lanthanide separation in molten LiCl-KCl eutectic is explored in this chapter. Lambertin et al. [10] had studied the reduction behavior of CeCl$_3$ and PuCl$_3$ on gallium cathode in CaCl$_2$ and NaCl-KCl melts at 1073 K using electrochemical transient techniques. Their studies showed the feasibility of selective deposition of Pu in gallium cathode. However there is no electrochemical study reported on U-Ga, La-Ga and Nd-Ga systems in the literature to our knowledge. The redox
behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ on Ga surface using CV and OCP is reported in this chapter. The measurements were made using the LiCl-KCl-GaCl$_3$-MCl$_3$ (M-U, La, Nd) melt in the temperature range 698-785 K at the W electrode using CV and OCP. The metal ions reduced on the pre-deposited gallium surface at more positive potentials forming the Ga-rich intermetallic compounds, LaGa$_6$, NdGa$_6$ and UGa$_3$ respectively for La-Ga, Nd-Ga and U-Ga systems. In case of the La-Ga system, there was a change in the trend of the peak potentials in the cyclic voltammograms and the emf values from the OCP transients recorded at temperatures 765 and 785 K. The observation is consistent with the phase diagram of La-Ga system as LaGa$_6$ decomposes peritectically to Liq. + LaGa$_2$ beyond 750 K. The apparent standard potentials, $E^*_{\text{La(III)/La(Ga)}}$, $E^*_{\text{Nd(III)/Nd(Ga)}}$ and $E^*_{\text{U(III)/U(Ga)}}$ at 723 K were -2.392 (±0.001), -2.374 (±0.001) and -2.083 (±0.001) V vs. Cl$_2$/Cl$^-$ respectively. The Gibbs energy of formation of the alloys, LaGa$_6$, NdGa$_6$ and UGa$_3$ estimated from OCP measurements at 723 K were -217.3 (±0.6), -209.3 (±0.6) and -129.3 (0.6) kJ mol$^{-1}$ respectively. The values for UGa$_3$ were in very good agreement with those reported in the literature. However there were no reports to compare the values for LaGa$_6$ and NdGa$_6$. Further studies need to be carried out by potentiostatic electrolysis to ascertain the alloys formed.

**Chapter 7: Electrochemical pulse techniques for in-situ monitoring the concentration of uranium in molten LiCl-KCl**

Electroanalytical pulse techniques could serve quick and reliable methods for in-situ monitoring of the composition of analyte in multi-component systems. Iizuka *et al.* [11] studied the applicability of NPV and SWV for determining the actinide concentration in molten chloride electrolyte. In Argonne National Laboratory, ANL, a semi-quantitative analysis of the SWV was carried out in molten chlorides containing Zr, U, Pu & Dy [12]. In this chapter we discuss the results of NPV, DPV and SWV for determining the concentration of uranium in the concentration range 0.01 to 11 wt %. Linear relationship was observed for
the reduction current with the concentration of UCl$_3$ in the electrolyte in the concentration range 0.1 -4 wt % for DPV and fairly a linear relationship was found in the concentration range 0.1 -11 wt % for NPV. The SWV showed higher sensitivity, but a linear relationship for the reduction current was not observed throughout the range. Two different linear dependences, one for lower concentration range and the other for the higher concentration ranges of UCl$_3$. Studies using simulated melt showed that the presence of the lanthanides products does not affect the determination of uranium.

**Chapter 7: Conclusions and scope for further studies**

This chapter summarizes the major findings of this study

(1) The apparent standard potentials of various redox couples were obtained under identical conditions from the studies. This serves as a database for our further studies. A brief discussion is made on the selectivity of the electrodes.

(2) We could estimate the equilibrium potential of the Nd(III)/Nd(0) couple from OCP measurement which is not possible by galvanic cell emf method due to the disproportionation reaction of Nd(II) ion to Nd(III) ion and Nd metal.

(3) The discrepancy found in the behavior of U on Cd cathode was understood by galvanic cell emf measurements using saturated and unsaturated U-Cd alloys.

(4) Studies on the redox behavior of LaCl$_3$, NdCl$_3$ and UCl$_3$ on Ga surface are reported for first time.

(5) The pulse parameter for measuring the concentration of uranium over wide concentration range for three electroanalytical pulse techniques was optimized.

**Scope for further studies**

(1) The studies using different cathodes, namely, W, Cd, Al and Ga can be extended to investigate the redox behavior of the chlorides of Pu and minor actinides so as to have a complete database.
From the difference in potential values of the actinides and lanthanides, their activity coefficient at different substrate, it is possible to model and evaluate the selectivity of the electrodes.

Studies on the pulse techniques have to be optimized for U, Pu, minor actinides in the presence of major fission products to simulate the process condition.

References


**Publications in Refereed journals**

**a. Published**


**b. Under Review**


**Proceeding and presentations at national/international conference**


3. “Investigation on the electrochemical behaviour of neodymium chloride in molten LiCl-KCl eutectic”, S.Vandarkuzhali, Sudhhasattwa Ghosh, S. Nedumaran, Manish


**Awards**

NA

Signature of Student :

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**Doctoral Committee**

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