Electrochemical Characterization Of $CaCl_2$-48 MOL % NaCl (0-2 % wt.% CaO) Melts And Study Of The Electrochemical Behavior Of Platinum As Anode In The Melt System

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Abstract:

Electrochemical investigations were carried out on $CaCl_2$-48 mol.% NaCl (0-2 wt.% CaO) melts at 650 ^oC, as part of a study to select an electrolyte melt containing $CaCl_2$ for direct electro-reduction of solid UO_2 to U metal. Decomposition potentials of $CaCl_2$-48 mol.% NaCl melt was measured using linear polarization method and found to be 3.33 V. Cyclic voltammetry of tungsten, graphite and platinum working electrodes against a Ni/NiO reference electrode was carried out with and without addition of CaO in the melt. In pure $CaCl_2$-48 mol.% NaCl melt, the cathodic Na-Ca alloy formation on tungsten ($2Na^+$-$Ca^{2+} + 2e^- <$ Na-Ca) occurred at -2.26 V and the anodic chlorine gas evolution on graphite ($2Cl^- < Cl_2 + 2e^-$) at +1.09 V. The anodic reaction on platinum, considered predominantly due to chlorine gas evolution and in a small measure to platinum dissolution, $Pt < Pt^{2+} + 2e^-$, was found to occur at +1.02V in the same melt. In $CaCl_2$-48 mol% NaCl-(1-2) wt.% CaO melts, the onset of oxygen evolution on Pt working electrode ($2O^{2-} < O_2 + 2e^-$) occurred at + 0.65 V and chlorine gas evolution at +1.04 V. The results indicated the possibility of using Pt as an anode with minimum consumption in the electro- reduction of UO_2 in $CaCl_2$-48 mol% NaCl-(1-2) wt.% CaO melt. The reaction, $2O^{2-} < O_2 + 2e^-$ was found to be diffusion controlled in the range of scan rates, 1-5 V/s and the diffusion coefficient of O^{2-} ions was calculated to be 9.9 x 10^{-6} cm^2 s^{-1} at 650 ^oC.

Keywords : platinum anode, direct oxide electro- reduction, pyroprocessing, uranium oxide, molten salt

1. Introduction

Reprocessing of spent oxide nuclear fuels (MOX) by pyroelectrochemical method in molten salt medium is an important area of study today [1]. In this method of reprocessing, the spent oxide fuel is first converted to a metallic alloy, which is subsequently electro-refined in LiCl-KCl melt at 500^{o}C to separate the constituent actinides present in it. Direct electrochemical reduction method is used in the conversion of the oxide fuel to metal alloy[2]. UO_2 is the major component of the spent MOX fuel and hence most of the studies reported in this area focused mainly on reduction of UO_2 to U. The electro-reduction of UO_2, generally in the form of porous pellets contained in a metal basket, has been carried out in LiCl-(1-3 wt%) Li_2O melt at 650 ^{o}C by employing platinum as the anode [3]. KAERI, South Korea has developed the process in a semi- engineering scale to achieve reduction of 50 kg/batch of UO_2 to U metal. The Korean facility, named PRIDE is the biggest reported demonstration facility to use the process to-date [4]. Basic studies on electro-reduction of UO_2 or MOX etc are also being carried out at ANL, USA and CRIEPI, Japan [5,6]. Most of the reported work in this area use LiCl as the electrolyte medium due to its favorable properties such as low melting temperature (~605^{o}C) and high solubility for oxide ions.

Different electrolyte melt systems like LiCl-KCl [7] and fluoride melts [8] have been studied as alternate electrolytes for electrochemical reduction of UO_2. $CaCl_2$ has the maximum solubility of oxide ion among alkali halides and hence is an ideal electrolyte for the electrochemical reduction work. However, it is not preferred for electro-reduction of UO_2 due to its high melting temperature, which makes the U metal formed on the surface of the UO_2 pellet to sinter as an impervious layer at the high operation temperature of the cell (900 °C). This in turn prevents further deoxidation of the underlying UO_2 particles and thus leads to incomplete conversion of the oxide preform to metal. Sakamura et al has studied the effect of different alkali halides on electro-reduction of UO_2 [9]. Vishnu et al has reported the mechanistic aspects of UO_2 reduction in $CaCl_2$-NaCl melt using graphite anode [10]. Biju et al reported a study of the electro-reduction of UO_2 using graphite anode in the LiCl-Li_2O melt [11]. The $CaCl_2$-NaCl-CaO melt has some merits over pure $CaCl_2$ melt like lower melting temperature and good oxide ion solubility and hence could be a suitable electrolyte melt for electro-reduction of UO_2. However, a thorough study on the electrochemical characteristics of the system has not yet been carried out. Platinum has good stability against oxidizing conditions and hence is the preferred anode for electrochemical reduction studies in chloride melts. The knowledge on the electrochemical behavior of platinum anode in $CaCl_2$-NaCl-CaO melt is very important to assess its performance as anode in the system. The reaction potentials of different reactions in the melt system are also required for monitoring and controlling the electro-reduction process. In this background, we have carried out a study of the electrochemical characteristics of $CaCl_2$-48 mol % NaCl (0-2 wt% CaO)/Pt system to explore the feasibility of using the melt as an alternate electrolyte for electrochemical reduction of solid UO_2 to U. The results of the study are presented in this article.

2. Experimental

Sodium chloride (Merck, Emparta, 99.0%) and $CaCl_2.2H_2O$ (Merck, Emparta, 99.0%) and CaO (Alfa Aesar, 99.95%) were used in the work. NaCl was dried at 200 °C under vacuum and $CaCl_2.2H_2O$ was dried by following a procedure reported in our previous study [10]. CaO was used as received. Prior to use in the cell, graphite rod (10 mm dia, 100 mm long, Nikunj, India) was degassed under vacuum at 200 °C. All the dried salts, graphite rods and the CaO were stored inside a high purity argon atmosphere glove box with oxygen and moisture levels maintained at less than 5 ppm. The required amounts of dried $CaCl_2$ and NaCl were weighed, mixed and thoroughly ground inside the glove box and loaded in an ss crucible and placed inside an ss vessel with a flange on its open end. The flange had provisions for fixing and introducing/retracting the electrodes to/from the cell in leak-tight conditions. The required amount of CaO was added to the $CaCl_2$-NaCl salt to make the melt of the required composition. The cell was assembled inside the glove box, closed and taken out under argon atmosphere and placed in a furnace (Digiqual, India) kept outside the glove box. The furnace was heated to the required temperature by a programmable PID controller (Shinko, PCD, Japan) and the temperature was measured using a K-type thermocouple. After attaining the temperature of operation, all the electrodes were pushed into the molten salt to the required depth and kept for temperature equilibration. The cell was maintained under inert atmosphere by purging purified argon gas throughout the entire course of the experiments. Decomposition potential of $CaCl_2$-48 mol % NaCl melt was determined by applying a DC voltage across a graphite rod anode and a molybdenum coil cathode (8 mm dia, 40 mm long, coiled out of 300 mm long and 2mm dia. wire) and by measuring the corresponding cell current. Cyclic voltammetry of different working electrodes like graphite, platinum, tungsten in the melt was performed using AUTOLAB ( ) in conjunction with GPES software. An in-house built Ni/NiO system was used as the reference electrode in these experiments . The stability of the reference electrode was tested by measuring the calcium deposition potential on the W working electrode at times. All the experiments were carried out at 650 °C.

3. Results and discussion

3.1 Decomposition potential measurement of $CaCl_2$-48 mol % NaCl melt

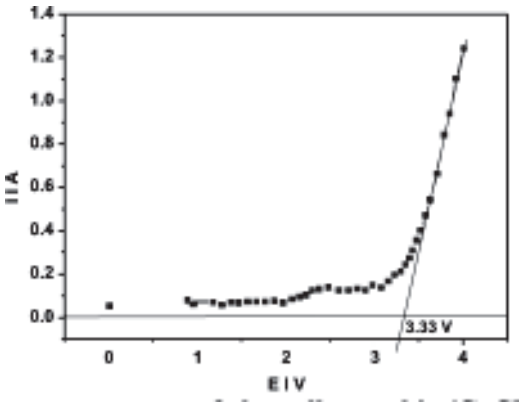


Figure 1:The current response of the cell, graphite/$CaCl_2$-48 mol.% NaCl/molybdenum during the decomposition potential measurement at 650 °C.

The plot of the voltage vs current obtained from the decomposition potential measurement of $CaCl_2$-48 mol % NaCl melt is presented in figure 1. The extrapolation of the straight line part of the i-Vplot data to the x-axis gives the decomposition potential as 3.33 V. The value corresponds to the decomposition of the melt into Na-Ca alloy (on the Mo cathode as per the reaction $2Na^+$-$Ca^{2+} + 2e^- <$ Na-Ca) and chlorine gas (on graphite anode as per the reaction $2Cl^- < Cl_2 + 2e^-$).

3.2 Cyclic voltammetry studies

3.2.1 In $CaCl_2$-48 mol % NaCl melt

Cyclic votammograms recorded on tungsten and graphite working electrodes in the above melt are given in figure 2(a) and 2(b) respectively. It is seen from the forward scan of figure 2a (in the direction starting from 0.0 V to -2.5 V) that the limiting reaction occurs at -2.26 V w.r.t Ni/NiO which corresponds to Ca-Na alloy formation due to the combined discharge of Ca and Na ions ($2Na^+$-$Ca^{2+} + 2e^- <$ Na-Ca) on the tungsten working electrode. The anodic current peak 1 observed during the backward scan is attributed to the dissolution of the alloy into the melt. From figure 2 (b), the forward scan (in the direction starting from 0.0 V to +1.5 V) the anodic limit is observed at +1.095 V which corresponds to the oxidation of chloride ions to chlorine gas on graphite working electrode according to the reaction $2Cl^- < Cl_2 + 2e^-$.

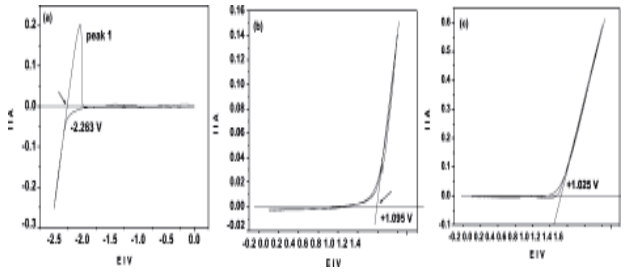


Figure 2: CVs recorded in pure $CaCl_2$-48 mol% NaCl melt on (a) tungsten WE and (b) on graphite WE at 650 °C and (c) Pt WE at 650 C. Scan rate 50 mV/s

From the voltages of these limiting reactions on both the working electrodes, the electrochemical window of the melt was calculated as 3.35 V. This value is in close agreement with the decomposition potential measured (3.33V) by the DC polarization method and explained in the previous section.

Cyclic voltammetric response of platinum working electrode in the same melt is given in figure 2 (c). Linear increase of current is noticed to commence from ~ +1.02 V. This potential is only slightly less than that measured on inert graphite working electrode (1.09 V, Fig. 2b), for the corresponding chlorine evolution reaction $2Cl^- < Cl_2 + 2e^-$. From this it can be inferred that the limiting anodic reaction on Pt in the melt is a combined reaction of chlorine evolution ($2Cl^- < Cl_2 + 2e^-$) and platinum dissolution $Pt < Pt^{2+} + 2e^-$. From the data it may be possible to infer that the chlorine gas evolution on the electrode will suppress the platinum dissolution.

3.2.2 In $CaCl_2$-48 mol % NaCl- (1-2) wt % CaO melt

Cyclic voltammograms recorded on platinum working electrode in $CaCl_2$-48 mol % NaCl- (1) wt % CaO melt and $CaCl_2$-48 mol % NaCl-(2) wt % CaO melt are given in figure 3 (a) and 3 (b)

respectively. In both the plots the anodic current is observed to rise at +0.65 V during forward scan. This can be attributed to the oxidation of oxide ion to oxygen gas on the Pt WE. The 'oxygen evolution window' is seen starting from this potential and extending up to +1.039 V and + 1.11 V in melt containing 1wt.% CaO and 2 wt.% CaO respectively. Another rising portion in anodic current is also observed from these voltages onwards. The potential region from and beyond these potentials corresponds to the combined reaction of chlorine gas evolution as well as platinum dissolution as described in the previous section 3.2.1. It is observed from the CVs that the platinum dissolution is shifted to more positive potentials with addition of CaO to $CaCl_2$ melt. The potential was also slightly increased with increase in the oxide ion concentration. Similar anodic behavior was observed in LiCl-Li_2O melts [12] too, but the shift was less pronounced than in the present melts.

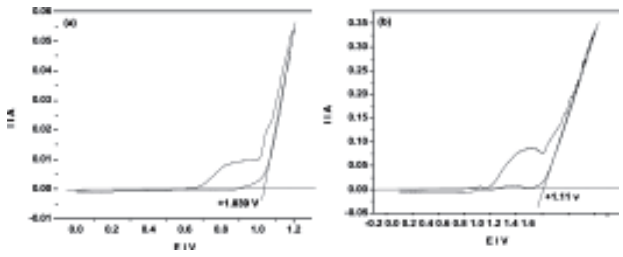


Figure 3 : Cyclic voltammograms of Pt WE in (a) $CaCl_2$-48 mol % NaCl-1 wt % CaO melt and (b) $CaCl_2$-48 mol % NaCl-2 wt % CaO melt at 650 °C, scan rate 50 mV/s.

Unlike in the case of LiCl-Li_2O melts, no peaks were seen before the oxygen evolution reaction on platinum in these melts. As reported before [12] platinum anode is known to corrode and physically degrade due to the formation of lithium platinate, Li_2PtO_3 in the LiCl-Li_2O melts, according to the anodic reaction $2Pt + 4Li^+ + 3O^{2-} < 2\,Li_2PtO_3 + 2\,e^-$. The potential of formation of this compound is more cathodic to that of oxygen evolution in LiCl-Li_2O melts. The absence of such a compound formation in $CaCl_2$-CaO melts suggests that the stability of the electrode could be better so that platinum could be used as an anode with minimum consumption for electro-reduction work in these melts.

3.2.3 Effect of scan rate in $CaCl_2$-48 mol % NaCl-1wt.% CaO melt on Pt WE

The CVs recorded on Pt WE in $CaCl_2$-48 mol % NaCl-1wt. % CaO with different scan rates in the range 1-5 V/s are depicted in figure 4 (a) and the corresponding plot of the peak current versus square root of scan rate is given figure 4 (b) respectively. The CVs were recorded with switching potentials less than that of platinum dissolution so as to study the oxygen evolution reaction at the Pt electrode. The anodic current was not pronounced in the CVs recorded at lower scan rates (not shown) but became more defined at higher scan rates of 1 V/s and above. The oxidation current increased with increase in the scan rate and the peak potentials shifted anodically with scan rate. Cathodic current peaks corresponding to the anodic current peaks were observed, but with very low peak currents. This electrode behavior indicated that oxidation of oxide ions on platinum electrode is irreversible in nature. The plot of the peak current vs square root of scan rate, shown in figure 4 (b), is a straight line passing through the origin and this further shows that the oxidation process is diffusion controlled in the range of scan rates studied.

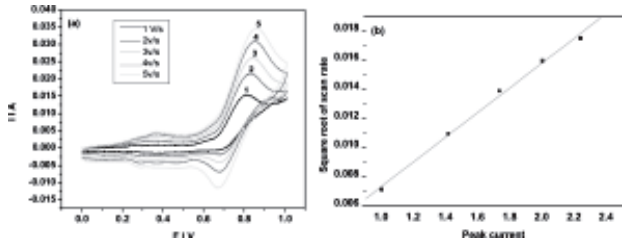


Figure 4: CVs recorded on Pt WE in $CaCl_2$-48 mol % NaCl-1wt % CaO melt (a) with scan rates of 1-5 V/s and (b) plot of the peak current versus square root of scan rate.

The diffusion coefficient of oxide ions has been calculated as 9.9 x 10^{-6} cm^2 s^{-1} at 650 °C using the expression $i_{pc} = 0.4463\ nFAC(nF/RT)^{1/2}(\mu D)^{1/2}$ where i_{pc} = the anodic peak current, n= no. of electrons, F=Faraday's constant, A = area of the electrode, C= concentration of the species, R=gas constant, T=temperature in K, μ= scan rate and D = diffusion coefficient.

4. Conclusions

The molten salt system, $CaCl_2$-48mol% NaCl-(0-2) wt.% CaO was electrochemically characterized using linear polarization and cyclic voltammetry techniques. Electrochemical behavior of Pt in the melt was investigated for its use as anode in the direct electrochemical reduction of UO_2 in calcium chloride containing melts and the results show that Pt can be used as anode with low consumption in the process. The oxygen evolution reaction on Pt was found to be irreversible and diffusion controlled in the scan rate of 1-5 V/s and the diffusion coefficient of oxide ion was calculated to be 9.9 x 10^{-6} cm^2 s^{-1} at 650 ^oC.

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