Anodic Behaviour Of Platinum Electode In $CaCl_2$-(0-3)wt% CaO Melts

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Abstract :

Solid metal oxides, configured as cathode in an electro-reduction cell, can be chemically reduced to metals by lithium or calcium metal electro-generated on it by molten salt electrolysis with graphite or platinum anode. Molten $CaCl_2$-CaO system at ~900 °C is a suitable electrolyte medium for producing calcium metal with platinum anode. In the context of electrochemical reduction of solid ThO_2 in $CaCl_2$-CaO melt, electrochemical behaviour of platinum electrode in molten $CaCl_2$-xwt% CaO (x = 0, 0.5, 1, 2, 3) was studied with cyclic voltammetry at 900 °C. In pure $CaCl_2$ melt, the limiting anodic reaction occurred at 0.99 V w.r.t Ni/NiO reference electrode and it is inferred that a mixed reaction of platinum dissolution and chlorine gas evolution occurred at the potential. In $CaCl_2$- 0.5wt% CaO melt, the onset potential for oxygen evolution on platinum was found to be at 0.77 V and that for platinum dissolution and chlorine evolution at 1.02 V. The onset potential for oxygen evolution in $CaCl_2$-1wt% CaO melt and platinum dissolution and chlorine evolution was found to be shifted to more anodic potential of 1.15 V. As the concentration of CaO in the melt was increased from 1wt% to 3wt%, the potential window of oxygen evolution increased from 0.47 V to 0.98 V and correspondingly, the potential of platinum dissolution and chlorine evolution was also shifted from 1.15 V to 1.66 V. Potentiostatic electrolysis experiments carried out in the oxygen evolution potential window of $CaCl_2$ -1wt% CaO melt did not indicate formation of platinum oxide, but showed small mass loss of platinum. The diffusion coefficient of O^{2-} ions for oxygen evolution reaction was determined to be $2.4 \pm 0.003 \times 10^{-4}$ cm^2s^{-1} at 900 °C. The results of the study showed that platinum can be used as anode in the electrochemical reduction of ThO_2 in $CaCl_2$-1wt% CaO melt with minimal consumption in the anodic processes.

Keywords: $CaCl_2$-CaO melt, Platinum anode, Platinum dissolution, Oxygen evolution, Diffusion coefficient

1. Introduction

Electrochemical de-oxidation of solid metal oxides to corresponding metals and alloys by in-situ electro-generated reductant metal (Ca or Li) in $CaCl_2$-CaO [1] or LiCl-Li_2O melt [2-3] has gained a lot of importance recently. In this method generally solid metal oxides are configured as cathode and graphite or platinum as the anode in the electrolytic cell. Graphite anodically reacts with O^{2-} ions producing CO and CO_2 gases in these processes [3].These reaction by-products take part in various parasitic reactions leading to decrease in process efficiency [4-6] and hence it is desirable to use an inert oxygen evolving anode, e.g. platinum in these processes. Behaviour of platinum as anode in electrochemical reduction of metal oxides in LiCl-Li_2O melt [2,7] is known but such information w.r.t platinum in $CaCl_2$-CaO melt is very scarce [8]. In the context of electrometallothermic reduction of solid ThO_2 in $CaCl_2$-CaO melt, the anodic behaviour of platinum electrode was required and hence was studied by cyclic voltammetry in $CaCl_2$-xwt% CaO (x = 0, 0.5, 1, 2, 3) melts and by potentiostatic electrolysis experiments in $CaCl_2$-1wt.% CaO melt at 900 °C.The diffusion coefficient of O^{2-} ions for oxygen

evolution reaction on platinum at 900 °C was calculated with the help of the results obtained in the chronopotentiometry measurements with platinum electrode in $CaCl_2$-1wt% CaO melt. The results of the study are reported in this article.

2. Experimental

2.1 Preparation of anhydrous salt (electrolyte)

Commercially available $CaCl_2.2H_2O$ (Merck, Emparta, ACS grade, purity 99% min.) was pre-dried at 150 °C under argon atmosphere followed by vacuum drying at 200 °C for complete removal of moisture present. The CaO content in the dried salt was determined as 0.004wt% by acid-base titration. Anhydrous CaO (Alfa Aesar, purity 99.95%) stored inside a high purity argon atmosphere glove box, was used in the preparation of $CaCl_2$-CaO electrolytes.

2.2 Electrodes

Platinum wire (purity 99.95%, 1 mm dia.) tied to a SS rod and high density (HD) graphite rod (6mm dia., 100 mm long, density 1.85 g/cc) which was tightly screwed to a SS rod current lead were used as the working electrodes and molybdenum coil, prepared out of Mo wire (Alfa Aesar, purity 99.95%, 2 mm dia.) tied to a SS rod was used as the counter electrode in the different electrochemical experiments. A Ni/NiO reference electrode made of a Ni wire (Alfa Aesar, purity 99.95%, 1.6 mm dia.) embedded in NiO powder (Sigma Aldrich, purity 99.8%) in a one-end-closed alumina tube with a pinhole (<1 mm dia.) at the closed end was used for monitoring the electrode potentials during molten salt electrochemical measurements.

2.3 Experimental setup

Molten salt experiments were carried out in a specially designed leak tight reactor made of SS316L.The reactor was placed in a pit-type resistance heating furnace (Digiqual) kept under continuous purging of pure argon gas (Fig. 1a). Loading of electrodes and salt in the molten salt reactor was carried out inside an argon atmosphere glove box having purity ≤ 5ppm of O_2/H_2O. The properly assembled reactor (Fig. 1b) was then placed in the pit-type furnace and was slowly (≤3°/min) heated to the required process temperature (900 °C). For $CaCl_2$-CaO melts, weighed amount of CaO was added to molten $CaCl_2$ to achieve the desired concentration and thereafter the reactor was maintained at 900 °C for 8-10 hours for complete dissolution of CaO in the molten salt.

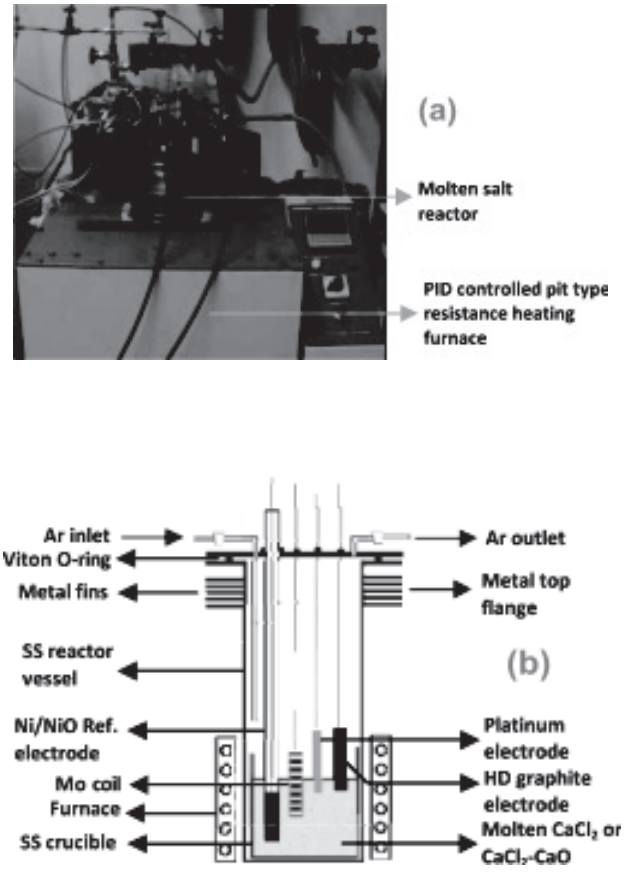


Figure 1: (a) Photograph of the experimental set up and (b) Schematic of the molten salt reactor assembly

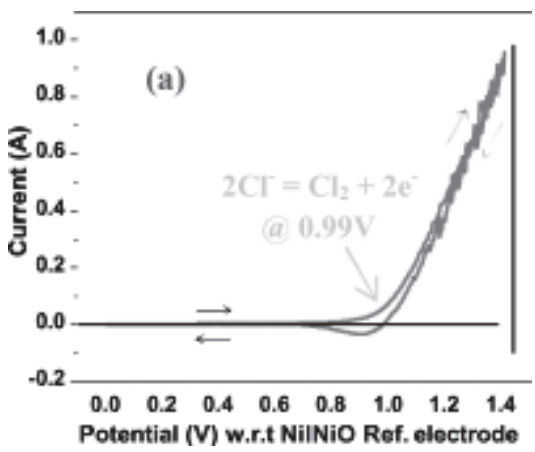
2.4 Electrochemical experiments

The molten electrolyte ($CaCl_2$ or $CaCl_2$-CaO) was first pre-electrolysed for complete removal of moisture and redox active impurities, by applying 2.5 V (in the case of pure $CaCl_2$ electrolyte) or 1.5 V (in the case of $CaCl_2$-CaO electrolytes) between Mo coil cathode and HD graphite rod anode and with the help of a DC power supply (Agilent, N6753A).The pre-electrolysis was carried out until background currents decreased and stabilised. Cyclic voltammetry (CV) (anodic polarisation) of platinum working electrode (area

0.322 cm^2) in $CaCl_2$-xwt% CaO (x = 0, 0.5, 1, 2, 3) melts and HD graphite rod working electrode (area 1.225 cm^2) in pure $CaCl_2$ melt was carried out with the help of AUTOLAB PGSTAT 302N potentiostat. Potentiostatic electrolysis experiments and chronopotentiometry (CP) measurements were also carried out with the platinum wire working electrode (area 0.322 cm^2) in $CaCl_2$-1wt% CaO electrolyte. The Ni/NiO reference electrode showed good potential stability during the electrochemical measurements.

2. Results and Discussions

2.1 Cyclic voltammetry of platinum electrode in pure $CaCl_2$ melt under anodic polarisation condition The CV of anodically polarised graphite electrode in pure $CaCl_2$ melt is shown in Fig. 2a. The anodic current was noticed to increase at 0.99 V and it increased linearly with increase in potential. Obviously the linearly increasing current is due to the chlorine evolution reaction on the electrode as per the reaction $2Cl^- \rightarrow Cl_2 + 2e^-$. The current behaviour of a platinum electrode under similar anodic polarisation condition is depicted in Fig. 2b. In this case too the anodic current is seen to increase at 0.99 V, suggesting thereby the possibility of chlorine evolution on the electrode. Further the potential (0.99 V) closely relates to that of platinum dissolution ($Pt \rightarrow Pt^{2+} + 2e^-$) potential and hence it is possible that this reaction is also taking place along with the Cl_2 evolution reaction on the electrode. Small mass loss of platinum observed during electrolysis with platinum anode supports the possibility of platinum dissolution.



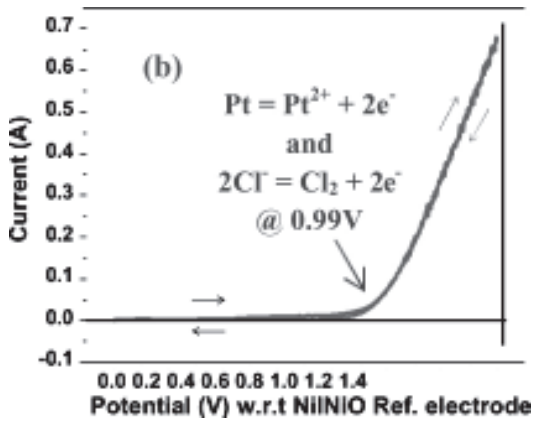


Figure 2: Cyclic voltammograms (anodic polarisation) of (a) HD graphite rod and (b) platinum wire electrodes in pure $CaCl_2$ melt (scan rate = 50mV/s)

3.2 Cyclic voltammetry of platinum electrode in $CaCl_2$-CaO melts under anodic polarisation conditions In the CV of platinum electrode (anodic polarisation) in $CaCl_2$-0.5 wt% CaO melt, commencement of an anodic current was noticed at 0.77 V w.r.t Ni/NiO reference electrode and its magnitude was found to increase with increase in the applied potential. The current peaked at 1.02 V and thereafter showed a different pattern as shown in Fig. 3a. The anode current in the potential window of 0.77 V-1.02 V can be considered to be due to the O_2 evolution reaction on the electrode as per the reaction $2O^{2-} \rightarrow O_2 + 4e^-$. Its magnitude was noticed to increase with increase in the CaO content in the melt (Fig. 3b, 3c and 3d). The anodic current beyond 1.02 V was most probably due to the mixed reaction of platinum dissolution and Cl_2 evolution. A small shift of about 90 mV was noticed in the onset potential of oxygen evolution in the plots in Fig. 3b, 3c and 3d compared to that in Fig. 3a. The reason for this shift is not clear.The potential window of oxygen evolution can be seen to increase with increase in the concentration of CaO in the melt. It increased from 0.25 V in $CaCl_2$-0.5wt% CaO melt to 0.47 V in $CaCl_2$-1wt% CaO melt (Fig. 3b). The window was further seen to widen to 0.72 V in $CaCl_2$-2wt% CaO melt (Fig. 3c) and to 0.98 V in $CaCl_2$-3wt% CaO melt (Fig. 3d). Due to this widening of the potential window, the platinum dissolution potentials of the electrode were pushed to higher anodic potentials. This

condition is very helpful for the platinum anode to remain in the oxygen evolution potential region for a longer duration of time during an electro-reduction experiment and thus to avoid the damage of the anode by the dissolution reaction discussed above. Hence $CaCl_2$ melts with higher concentrations of CaO are desirable for electrochemical reduction of metal oxides e.g. ThO_2 with platinum anode.

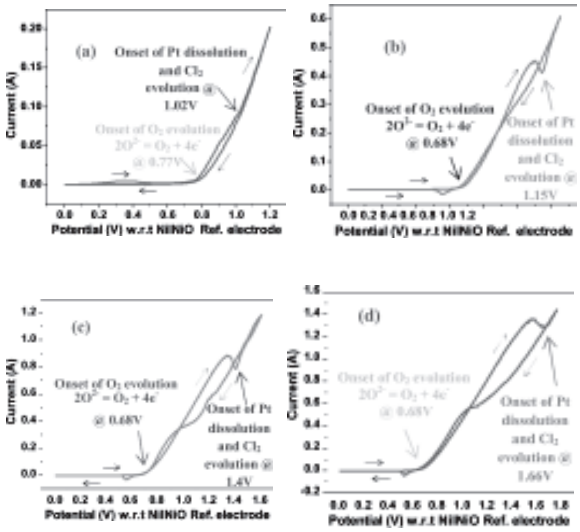


Figure 3: Cyclic voltammograms (anodic polarisation) of platinum electrode in (a) $CaCl_2$-0.5wt% CaO, (b) $CaCl_2$-1wt% CaO, (c) $CaCl_2$-2wt% CaO, (d) $CaCl_2$-3wt% CaO melts (scan rate = 25mV/s)

3.3 Potentiostatic electrolysis on platinum electrode in $CaCl_2$-lwt% CaO melt under anodic polarisation conditions

Potentiostatic electrolysis experiments were carried out in $CaCl_2$-1wt% CaO melt with platinum working electrode and Mo counter electrode at two different potentials (0.85 V and 0.95 V w.r.t Ni/NiO reference electrode) in the potential window of O_2 evolution (for 15 mins each). Mass loss of platinum electrode after electrolysis experiments was found to be very low (0.003 g at 0.85 V and 0.006 g at 0.95 V). Y. Sakamura et al [8] reported blackening of the immersed portion of the platinum electrode in $CaCl_2$ melt at similar conditions due to formation of Pt_3O_4, but no such black coating was seen on the platinum electrode in our experiments (Fig. 4). Theoretical studies by N. Seriani et al [9] also showed that metallic Pt is thermodynamically more stable than Pt-O compounds at 900°C even at oxygen pressures >1 atm. From the results, it is possible to infer that platinum electrode can be used as anode in the electrochemical de-oxidation of ThO_2 with minimal consumption.



Figure 4: Photograph of the platinum electrode after potentiostatic electrolysis experiment at 0.95 V. No surface modification is noticed upon polarisation of the electrode in the melt

3.4 Diffusion coefficient of O^{2-} ions for oxygen evolution on platinum electrode in $CaCl_2$-l wt% CaO melt

The diffusion coefficient of O^{2-} ions ($D_{O^{2-}}$) for oxygen evolution on platinum electrode was evaluated with the help of chronopotentiometry (CP) measurements at various applied currents at 900 °C in $CaCl_2$-1w% CaO melt. Fig. 5a shows a typical chronopotentiogram of platinum electrode recorded at applied current of 0.388 A. The duration of the potential plateau of the chronopotentiogram in Fig. 5a is a measure of the transition time (ι) of the reaction under consideration (oxygen evolution). Linear variation of the inverse square root of transition time (ι) with different applied currents (*i*) (Fig. 5b) showed that the process was diffusion controlled. The $D_{O^{2-}}$ for oxygen evolution on platinum electrode was calculated using Sand Eq.

$$i\tau^{1/2} = 0.5nFAC \quad D_{O^{2-}}\nu^{1/2} \quad D^{1/2}_{O^{2-}}$$

where *i* is the applied current (A), ý is the transition time (s), n is the number of electrons involved in the oxygen evolution reaction i.e. 4, F, the Faraday constant, A, the area of the platinum electrode

(cm^2), $C_{O}2-$, the concentration of O^{2-} ions (mol/cm^3) in the melt. The diffusion coefficient of O^{2-} ions for oxygen evolution reaction on platinum electrode was determined to be 2.4 ± 0.003 x 10^{-4} cm^2 s^{-1} at 900 °C.

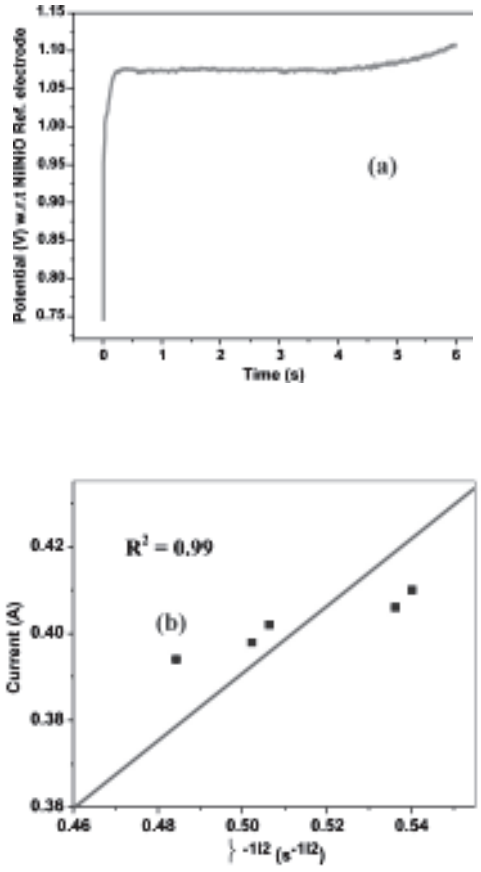


Figure 5: (a) Typical chronopotentiogram of platinum electrode recorded at an applied current of 0.388 A and (b) applied current – (transition time)$^{-1/2}$ profile at 900 °C in $CaCl_2$-1wt% CaO melt

3. Conclusions

The electrochemical behaviour of platinum electrode was studied in $CaCl_2$-x wt% CaO (x = 0, 0.5, 1, 2, 3) melts by cyclic voltammetry. Results showed that the potential window of O_2 evolution on platinum electrode widened with increase in CaO concentration in the melt. Low mass loss of platinum electrode was observed during potentiostatic electrolysis experiments at different potentials within the potential window of O_2 evolution in $CaCl_2$-1wt% CaO melt. The results indicate the possibility of using platinum as anode in electrochemical reduction of ThO_2 in $CaCl_2$-1wt% CaO melt with minimal consumption. The diffusion coefficient of O^{2-} ions for oxygen evolution reaction on platinum electrode was found to be 2.4 ± 0.003 x 10^{-4} cm^2 s^{-1} at 900 °C in this melt.

4. Acknowledgement

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5. References

1. R. F. Descallar-Arriesgado, N. Kobayashi, T. Kikuchi and R. O. Suzuki, Electrochimica Acta, 2011, Vol. 56, 8422-8429.

2. E. Y. Choi and S. M. Jeong, Progress in Natural Science: Materials International, 2015, Vol. 25, 572-582.

3. T. B. Joseph, N. Sanil, K. S. Mohandas and K. Nagarajan, JES, 2015, Vol. 162, E51-E58.

4. K.S. Mohandas**,** Minerals Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C), 2013, 122, 197-212.

5. D. S. M. Vishnu, J. Sure and K. S. Mohandas, Carbon, 2015, 93, 782-792.

6. V. A. Kovrov, A.V. Suzdaltsev, A. P. Khramov and Y. P. Zaikov, "Electrode processes at the electrolysis of molten calcium chloride", Proceedings of The twelfth Israeli-Russian Bi- national Workshop 2013, July 2013, 290-297.

7. T. B. Joseph, N. Sanil, L. Shakila, K. S. Mohandas and K. Nagarajan, Electrochimica Acta, 2014, Vol. 139, 394-400.

8. Y. Sakamura, M. Kurata and T. Inoue, JES, 2006, Vol. 153, D31-D39.

9. N. Seriani, W. Pompe and L. C. Ciacchi, JPC B, 2006, Vol. 110, 14860-14869.

10. A. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, John Wiley & Sons, N.Y., 1980.