Electrochimica Acta 139 (2014) 394–400

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A cyclic voltammetry study of the electrochemical behavior of platinum in oxide-ion rich LiCl melts

T. Biju Joseph, N. Sanil, L. Shakila, K.S. Mohandas*, K. Nagarajan

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102, India

ARTICLE INFO

Article history:
Received 6 June 2014
Accepted 1 July 2014
Available online 17 July 2014

Keywords:
Electrochemical reduction
LiCl-Li_2O system
Platinum anode
Li_2PtO_3
Oxygen evolution
Platinum dissolution

ABSTRACT

Electrochemical behavior of platinum in LiCl and LiCl-(1-3) wt% Li_2O melts at 650 °C was studied by cyclic voltammetry in the context of its use as anode in the direct electrochemical reduction of solid uranium oxide to uranium metal. By CV measurements with graphite and platinum (anodic polarization) and tungsten (cathodic polarization) working electrodes, the decomposition potential of LiCl and electrochemical potential of the reaction $Pt + 2LiCl \rightarrow PtCl_2 + 2Li$ were determined as 3.46 V and 3.14 V respectively. Three anodic reactions viz. (i) formation of Li_2PtO_3, (ii) oxygen evolution and (iii) platinum dissolution were found to occur on the platinum electrode in Li_2O containing LiCl melts. The Li_2PtO_3 formation was found to be a fast reaction with diffusion coefficient of O^{2-} ions in the melt as $4.53 \times 10^{-7} cm^2/s$. Oxygen evolution showed very high current densities when compared to that of the surface area limiting Li_2PtO_3 formation. The platinum electrode surface was corroded by formation of Li_2PtO_3 when the electrode was polarized for a longer period of time in the melt. The results of the study indicated that LiCl-2 wt.% Li_2O melt could be the optimum electrolyte composition in the electro-reduction of uranium oxide with platinum anode.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The recent discovery that a solid metal oxide can be directly reduced to metal by molten salt electrolysis and the perceived advantages of the process over the conventional metal production process have given an impetus for research in this area worldwide [1,2]. Several metals and alloys have been prepared in the laboratory from the respective oxides/mixtures of oxides by the electrochemical process. One of the major applications of the electrochemical process has been in the nuclear technology to reduce the actinide oxides to actinides in the context of pyrochemical reprocessing of spent oxide fuels. The electro-deoxidation process allows conversion of spent oxide fuel to an alloy of actinide and rare earth metals, which can be subsequently electro-refined in a molten salt electro-refiner cell to separate the actinides of interest [2–4]. The actinides thus recovered can be used to prepare metal fuel for fast reactors. Uranium oxide is the major component of spent oxide fuel and hence many research groups have been studying the electrochemical reduction bahaviour of uranium oxides in LiCl-Li_2O melts at 650 °C [2–6]. Platinum is used as anode in all these studies.

In a typical direct electro-reduction cell, oxygen ions are produced at the oxide electrode by cathodically polarizing it against a platinum or graphite counter electrode in a suitable molten electrolyte. The electro-generated oxygen ions dissolve in the electrolyte melt and are oxidized at the anode so that the oxide cathode slowly converts itself to metal. Obviously, the transport of oxygen ions between the cathode and anode are important to this process and hence it is necessary to maintain a suitable concentration of O^{2-} ions in the melt. Generally, this is achieved by addition of a small amount of the respective oxide of the electrolyte salt to it. While too low concentrations of O^{2-} ions in the chloride melt run the risk of reaction of platinum anode with Cl^- ions to form platinum chloride and hence the physical loss of the electrode, higher concentrations of O^{2-} ions could cause reoxidation of the reduced metal and also could aggravate the cell corrosion. These issues demand that an optimum concentration of O^{2-} ions be maintained in the melt during the electro-reduction process. Operation of an electro-reduction cell with platinum anode is critically dependant on its potential, which in turn is related to the concentration of the oxide ions present in the melt. Hence a thorough understanding of the electrochemical behavior of platinum electrode in the electrolyte melt is necessary for smooth operation of the electro-reduction cell.

---

* Corresponding author.
E-mail address: ksmd@igcar.gov.in (K.S. Mohandas).

http://dx.doi.org/10.1016/j.electacta.2014.07.025
0013-4686/© 2014 Elsevier Ltd. All rights reserved.

The study of the electrochemical behavior of platinum electrode in LiCl melt with different concentration of Li_2O is relevant in this context.

There have been few reports on the cyclic voltammetry studies on the electrochemical behavior of platinum electrode in LiCl-Li_2O melts at 650 °C. Sakamura et al. [7] reported the anodic behavior of platinum in LiCl melt containing 0.13 mol.% Li_2O. Sakamura [8] also studied the anodic behavior of platinum in LiCl melts containing up to 0.39 mol.% Li_2O and estimated the diffusion coefficient of O^{2-} ions in the melts with $x_{Li_2O} < 0.1$ mol.%. Jeong et al. [9], Choi et al. [10] and Herrmann and Li [11] have also studied the electrochemical behavior of platinum in LiCl melts. All these studies were carried out in LiCl melts containing a maximum amount of 1 wt.% Li_2O. However, most of the electrochemical reduction studies of actinide oxides with platinum anodes have been carried out in LiCl melts containing Li_2O concentrations varying from 0.5-3.0 wt %. Electrochemical behavior of platinum in LiCl melts containing more than 1 wt.% Li_2O was of interest in this context. We, therefore, carried out cyclic voltammetry of platinum electrode in the oxide ion rich (1-3 wt.% Li_2O) LiCl melts at 650 °C with a primary interest to understand the gross anodic behavior of platinum electrode in such melts and also to use the information in arriving at an optimum concentration of the electrolyte melt for the electroreduction process. Some efforts were also made to gain knowledge on the fundamental behavior of platinum electrode in LiCl-1 wt.% Li_2O melt and the relevant results of the study are also presented in this article.

2. Experimental

2.1. Chemicals

Anhydrous LiCl (99.99% purity, Alfa Aesar) and Li_2O (99.5% purity, Alfa Aesar) were used. The LiCl was further dried by heating under vacuum at 150 °C for 5 days to avoid presence of adsorbed moisture. The chemicals were stored in an argon atmosphere glove box prior to use in the experiments.

2.2. Apparatus

The CV studies were carried out in a stainless steel reactor vessel. The flanged vessel could be made leak-tight by use of an O-ring seal between its flange and top mating flange. The mating flange had four ports on it through which three electrodes and a thermocouple could be introduced in a leak-tight manner to the melt kept at the bottom of the reactor in a high density alumina crucible (NASKAR Ceramics, Kolkota, India, 50 mm OD X 70 mm long). Separate working electrodes were used for the anodic and cathodic CV scans in both LiCl and LiCl-Li_2O melts. Pt wire (99.9%, 1 mm dia. wire, Hindustan platinum, India) and graphite rod (3 mm dia., supplied by Graphite India) were used in the anodic polarisation and W wire (99%, 1.5 mm dia.) for the cathodic polarization. Both Pt coil (3 mm dia. coil made out of 1 mm dia. x 300 mm long wire) and Ta coil (3 mm dia. coil made out of 1 mm dia. x 300 mm long wire) were used as the counter electrodes. Individual electrode materials were connected to an SS rod, which acted as the current lead to the electrodes. They were electrically insulated from the cell body as well as from each other by the use of suitable alumina sleeves. A platinum wire immersed in the melt served as a quasi-reference electrode. The melt temperature was measured using a K-type thermocouple placed in a one end closed alumina tube.

The handling of the salts and assembly of the cell were carried out inside an argon atmosphere glove box. Approximately 150 g of the vacuum dried LiCl was used in each experiment. The assembled cell was heated to 650 °C and appropriate amount of Li_2O was subsequently added to the molten LiCl to make the desired composition of LiCl-Li_2O mixture. The reactor was allowed to stay at the temperature for 8-12 hours to allow complete dissolution of the Li_2O in the molten LiCl. Moisture-free argon gas was purged through the reactor vessel throughout the course of the experiments. Electrochemical measurements were carried out by using a potentiostat/galvanostat (AUTOLAB PGSTAT 30, M/s ECOCHEMIE, Netherlands equipped with IF030 interface). The voltammograms were processed using GPES 4.9 software. XRD analysis of the platinum compound was carried out using a PHILIPS xPERT diffractometer with Cu-Kα radiation.

The electrode potentials measured against the platinum pseudo-reference electrode were standardized against reversible Li^+/Li couple. The lithium reduction potentials obtained from the cyclic voltammetry of a tungsten working electrode in the respective melts were used in the standardization.

3. Results and discussion

Preliminary studies showed that tungsten and graphite electrodes are inert during cathodic and anodic polarizations respectively in LiCl melt and hence used to measure the electrochemical window of the melt.

3.1. Electrochemical characterization of LiCl melt

The typical CV patterns obtained during cathodic polarization of tungsten and anodic polarization of graphite electrodes in LiCl melt at 650 °C are given in Fig. 1a and 1b respectively. No significant current was noticed on W electrode until about 0.00 V vs Li^+/Li and thereafter the current increased linearly with increase in the electrode potential. The reversal of the potential resulted in a current wave as depicted in Fig. 1a. The electrochemical reactions during the forward and reverse sweep are ascribed to lithium metal deposition ($Li^+ + e^- \rightarrow Li$) and lithium metal dissolution ($Li \rightarrow Li^+ + e^-$) respectively. Similarly, the anodic polarization of graphite showed no significant current until about 3.0 V. Small currents, ascribed to adsorption of Cl^- ions on the graphite electrode, were noticed between 3.0 -3.3 V and as the potential was swept beyond 3.3 V, the current increased steeply indicating the onset of the reaction $Cl^- \rightarrow 1/2Cl_2 + e^-$. The linear portions of both Fig. 1a and 1b were extrapolated to zero-current to obtain the reversible lithium reduction and chlorine evolution potentials of the melt as 0.00 V and + 3.45 V respectively. From the two reversible potentials, the electrochemical window of LiCl is deduced as 3.45 V. The $\Delta_f G^o$ of LiCl at 650 °C is reported as -333.8 kJ/mol.[12] and using Nernst equation the reversible decomposition potential of LiCl is calculated as 3.46 V. The potential deduced from the CV measurements shows excellent agreement with that calculated from the free energy data.

3.2. Electrochemical behavior of platinum in LiCl melt

Typical CV of a platinum wire electrode (1 mm dia., area: 0.07 cm^2) obtained during anodic polarization in LiCl melt is given in Fig. 2. The CV of the graphite electrode is also given in the fig. for comparison. Current on the platinum electrode was noticed to increase linearly with potential beyond 3.0 V due to the oxidation of platinum as per the reaction $Pt \rightarrow Pt^{2+} + 2e^-$. The platinum dissolution potential was determined as 3.14 V by extrapolation of the straight line portion of the plot to zero current. From the lithium reduction (0.00 V vs Li^+/Li) and platinum oxidation potentials, the reaction potential of $Pt + 2LiCl \rightarrow PtCl_2 + 2Li$ has been calculated as 3.14 V. Using the data, the Gibbs energy of the reaction at 650 °C has been worked out as 605.92 kJ as against the reported value of 594.53 kJ [12].

Download English Version:

https://daneshyari.com/en/article/185372

Download Persian Version:

https://daneshyari.com/article/185372

Daneshyari.com