Bulletin of Electrochemistry 1 (1) Jan.—Feb. 1985, 46—49

ACTIVATED LEAD ELECTRODES FOR ELECTROWINNING OPERATIONS

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ABSTRACT

The need for new technology to recover metals with more energy efficiency has created increasing interest in sulphate electrowinning systems. Development of electrocatalytic anodes for oxygen evolution conditions is a subject of current interest. A kind of activated electrode with an electrocatalyst dispersed and embedded within a matrix of lead has been investigated. Cyclic voltammetric studies and anodic polarisation studies under oxygen evolution condition have been carried out in H_2SO_4 solutions. The effects of catalyst loading and acid concentration on anode potential have been discussed. RuO_2 and IrO_2 are the electrocatalysts studied.

INTRODUCTION

Hydrometallurgical methods have been proposed as more energy efficient and less polluting technologies. Electrowinning from sulphate solutions is one of the major steps in these approaches. The anode reaction in the electrolysis step is oxygen evolution ($E^\circ = 1.23$ V) and this accounts for 50-80% of the total cell voltage. It is therefore an important area where improvements can be worked out resulting in energy saving.

Stbstitution of the oxygen evolution reaction with reactions occurring at lower potentials, such as, oxidation of SO_2 to H_2SO_4 ($E^\circ = 0.17$V), oxidation of carbon to CO_2 ($E^\circ = 0.2$V) and production of acid and H_2 to H^+ ($E^\circ = 0.0$V) is one of the possibilities. More useful electrochemical reactions like oxidation of Mn^{2+} to MnO_2 and oxidation of $NaClO_3$ to $NaClO_4$ have also been suggested as alternatives [1].

A straightforward reduction in oxygen evolution potential itself with suitable electrodes can effect significant savings in electrowinning operations. This would have an added advantage that it would not call for a change in the existing cell designs. Conventional anodes in electrowinning are made of lead or lead alloys. Though alloying with elements like Ag, Ca, etc., has reduced the corrosion rate, the overpotential for oxygen evolution has remained high.

Following the introduction of dimensionally stable anodes (DSA) in chlor-alkali industries with significant energy savings and other operational advantages; the solid polymer electrolyte (SPE) cells for electrolysis of water are being developed with such anodes. Materials like RuO_2 and IrO_2 show good characteristics as electrocatalysts for oxygen evolution [2, 3]. Studies concerning the utilisation of this type of electrodes for metal winning processes have been reported in a preliminary way though it appears that there are still problem areas in their development. For sulfuric acid electrolytes, Ti-Pd alloys are recommended as the matrix while the suggested catalysts include RuO_2, IrO_2, $RuO_2 + TiO_2$, $Ir + IrO_2$, noble metal oxides and cermets stabilised with TiO_2, Nb_2O_5 etc.

The application in the case of electrowinning can advantageously think of lead in place of titanium and thereby avoid the difficulty due to passivation of the matrix. Inexpensive nature, simplified structure and manufacture and possibility of retrofitting in existing cells are the other advantages of lead based catalytic anodes. The catalytic particles can be embedded and anchored to the surface of the lead base. Oxygen evolution can take place at a low potential on the active sites and the lead base can largely remain electrochemically inactive. An attempt has been made in this work to investigate preparation of such anodes and test them under oxygen evolution conditions. Anodic ploarisation studies have been carried out with activated lead electrodes with incorporation of RuO_2 and IrO_2 without any valve metal combination. The effect of acid concentration and catalyst loading on anode potential has also been studied.

EXPERIMENTAL

RuO_2 and IrO_2 samples were prepared by the thermal decomposition of corresponding trichlorides at 450°C. Electrode compacts of 13 mm dia and 12 mm length were prepared by the method of pressing and sintering. Lead powder of -200 mesh size with catalytic materials RuO_2 or IrO_2 spread over the surface at one end of the electrode was pressed at 4 tons for 1 minute and then the specimen was ejected out. The green compact was heated at 150°C for half-an-hour. A lead wire was soldered at the other end of the electrode. The entire surface of the electrode specimen was covered with an epoxy resin leaving 1 cm^2 area for polarisation studies. Catalyst loading was varied from 10 to 200 mg cm^{-2}. Cyclic voltammetric studies were carried out with specimens of 200 mg cm^{-2} catalyst loading in 1M H_2SO_4 using a Wenking potentioscan (Model POS73) coupled with an X-Y recorder (Digitronic 2000 series). Potential cycle was made between 0.0V and 1.50V at a scan rate of 5 mV Sec^{-1}. Anodic polarisation studies for oxygen evolution were carried out under galvanostatic conditions at different current densities of 20, 40, 60, 80 and 100 mA/cm^{-2} in 0.1M, 0.5M and 1M H_2SO_4 solutions. Long term polarisation studies were carried out with lead-based electrodes with different loadings of RuO_2 and IrO_2 at a current density of 40 mA cm^{-2} in 1M H_2SO_4 for a duration of 8 hours. A platinum foil was used as the counter electrode. Potentials were measured against a saturated calomel electrode (SCE) and converted to normal hydrogen electrode (NHE).

Polarisation studies were also carried out with lead electrodes prepared under similar conditions.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of Pb and RuO_2 in 1M H_2SO_4 at a scan rate of 5 mV sec^{-1}. Oxygen evolution starts at 2.1V for Pb and at 1.4V for RuO_2 electrodes. The peaks and humps

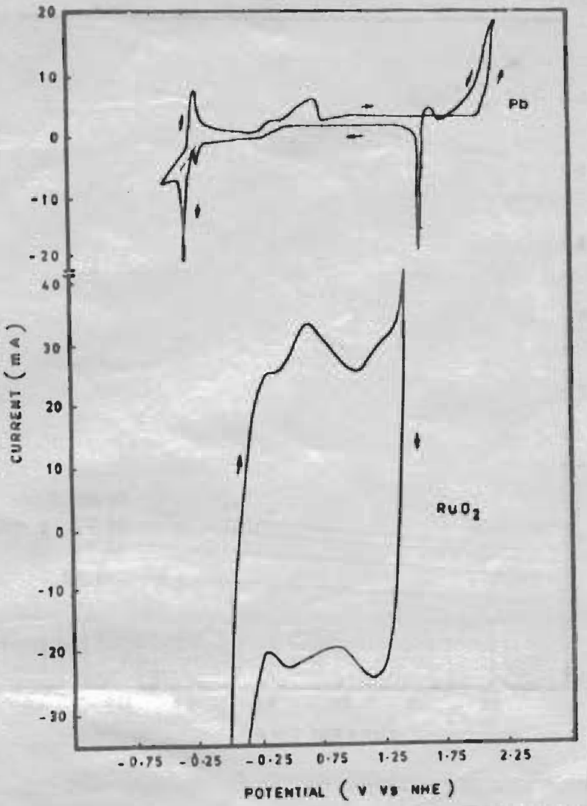

Fig. 1 : Cyclic voltammograms of Pb and RuO_2 at 5 mV S^{-1} in 1M H_2SO_4

seen in the voltammogram for lead are due to $Pb/PbSO_4$ and $PbSO_4/PbO_2$ couples. Discussion on the precise nature of the surface processes taking place on RuO_2 electrode is beyond the scope of the present work but a list of likely redox couples would include OH_{ads}/H_2O, O_{ads}/OH_{ads} Ru^{2+}/Ru^{4+} etc. [4].

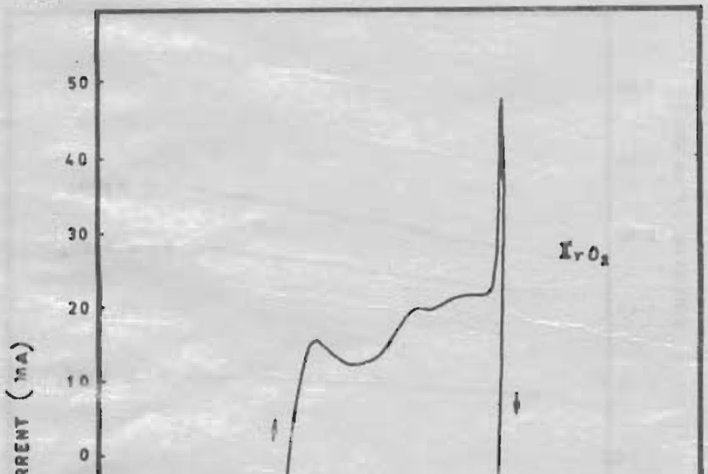

Fig. 2 : Cyclic voltammogram of IrO_2 at 5 mV S^{-1} in 1M H_2SO_4

Figure 2 shows the cyclic voltammogram of IrO_2 electrode in 1M H_2SO_4 with a scan rate of 5 mV Sec^{-1}. The peaks seen in the voltammogram may be due to surface processes involving couples like Ir/Ir_2O_3 , Ir_2O_3/IrO_2 etc. and may be also due to the adsorption of oxygenated species.

Cyclic voltammetry has been studied [5] as a technique for determining the surface area of RuO_2 electrodes. Since both charge and surface area are linear functions of oxide loading, it is possible to determine reasonably reproducible surface area values.

Anodic polarisation curves for oxygen evolution obtained galvanostatically on lead-based electrodes with different amounts of catalyst loading in 1M H_2SO_4 are shown in Figure 3. The increase in catalytic activity with increasing oxide loading evidentl reflects the increasing surface area and hence the increasing number of active sites available for the reaction. Depolarisation up to the extent of 500 mV is observed for all the current densities studied. The effect of acid concentration on the activity of the Pb electrode with 10 mg cm^{-2} RuO_2 loading is shown in Figure 4. Depolarisation for O_2 evolution obviously increases with decrease in acid concentration. Figure 5 shows the anode potential-time curves for O_2 evolution on lead and activated lead electrode with loading of RuO_2 in the range 10 to 200 mg cm^{-2}. With increase of catalyst loading, the anode potential decreases upto the extent of 10 to 50 mV and a reduction of nearly 500 mV is observed between electrode with catalyst loading of 10 mg cm^{-} and lead throughout the polarisation period, namely 8 hours.

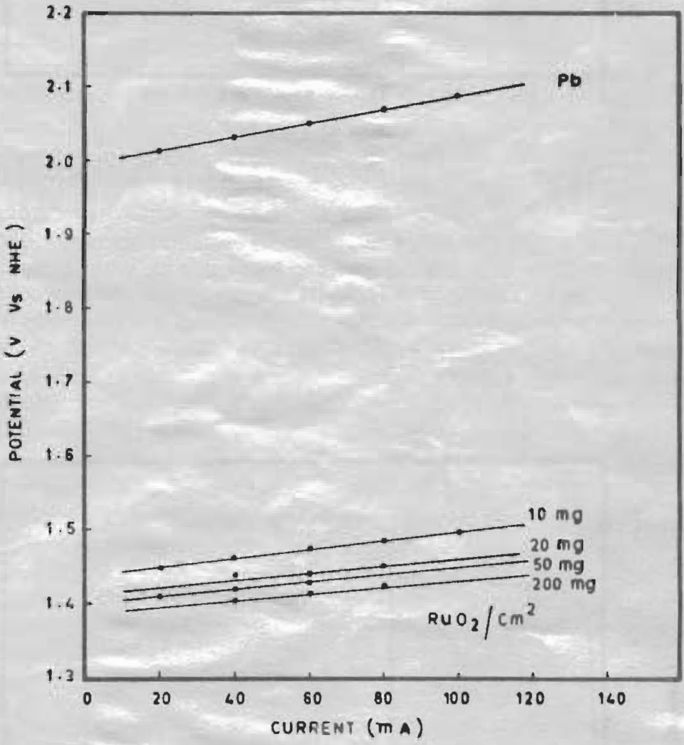

Fig. 3 : Anodic polarisation curves for O_2 evolution obtained galvanostatically on lead and activated lead electrodes with different loadings of RuO_2 in 1M H_2SO_4

Figure 6 shows the anodic polarisation curves for O_2 evolution an lead with different loadings of IrO_2. Catalytic activity increases

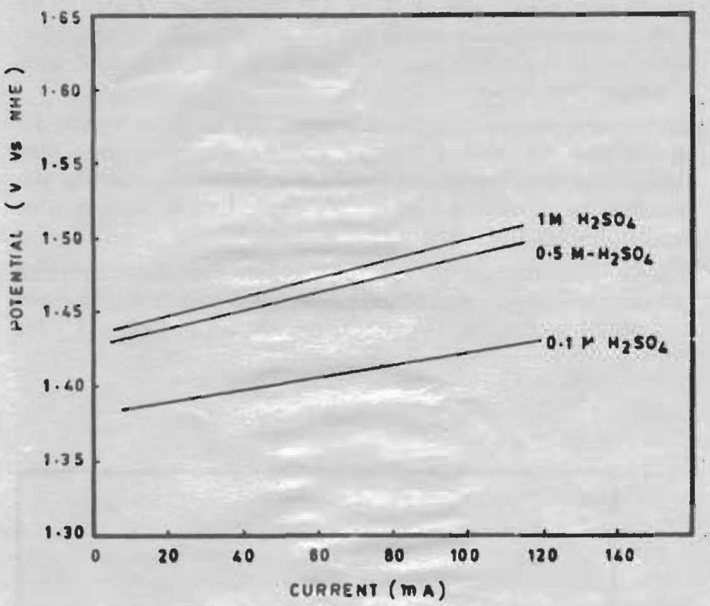

Fig. 4 : Anodic polarisation curves for O_2 evolution obtained galvanostatically on activated lead electrode with 10 mg cm^{-2} loading of RuO_2 in H_2SO_4 solutions of different concentrations

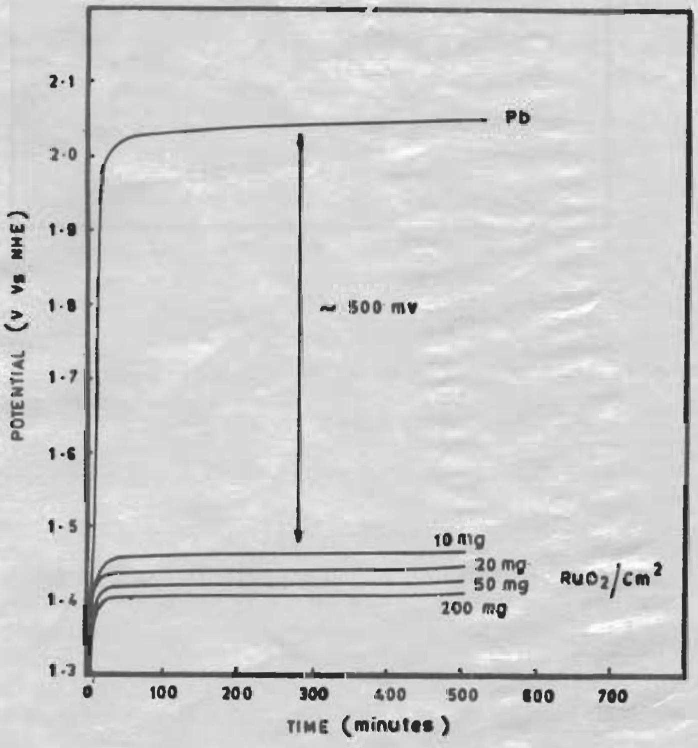

Fig. 5 : Anode potential - time curves for lead and activated lead electrodes with different loadings of RuO_2 in 1M H_2SO_4

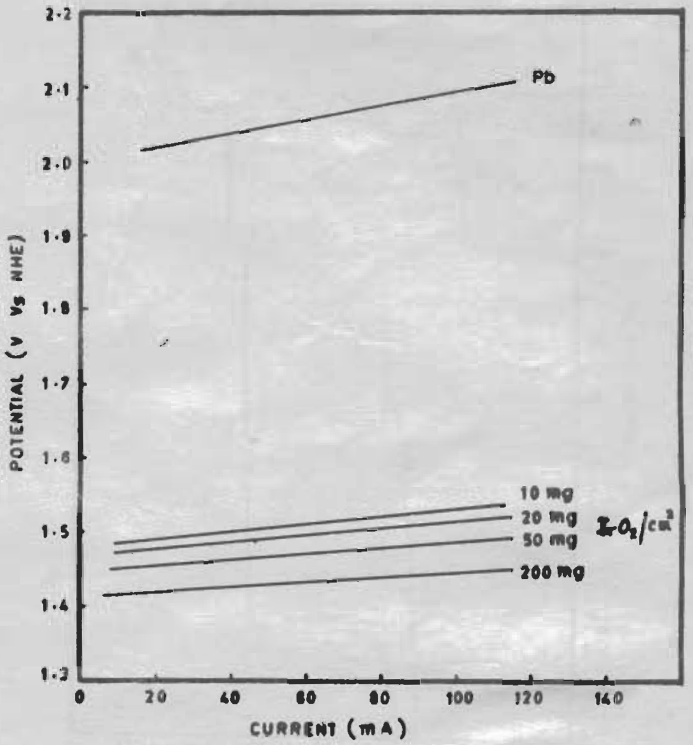

Fig 6 : Anodic polarisation curves for O_2 evolution obtained galvanostatically on lead and activated lead electrodes with different loadings of IrO_2 in 1M H_2SO_4

with increasing amounts of catalyst loading. Activity is found to be slightly less when compared with RuO_2 electrodes. Acid concentration is also a factor contributing to the depolarisation effect of catalytic material as shown in Figure 7. Long term

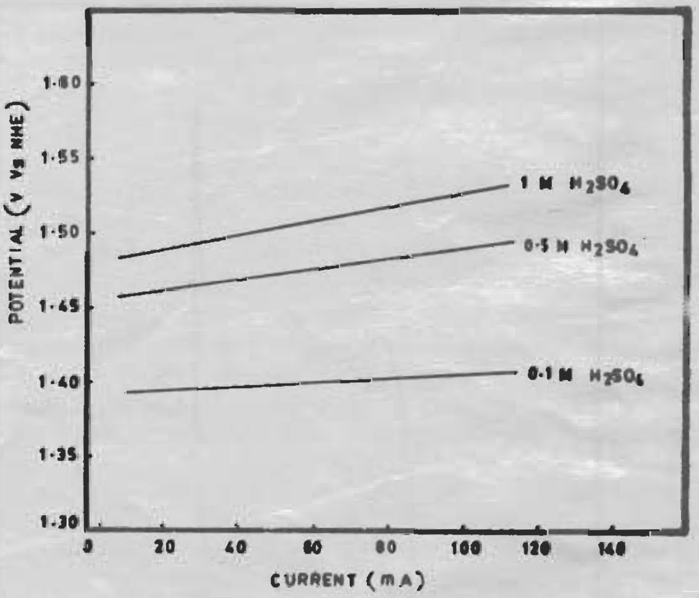

Fig. 7 : Anodic polarisation curves for O_2 evolution obtained galvanostatically on activated lead electrode with 10 mg cm^{-2} loading of IrO_2 in H_2SO_4 solutions of different concentrations

polarisation studies with lead-based IrO_2 electrodes as shown in Figure 8 indicate a reduction of nearly 500 mV in anode potential, a factor of utmost importance for energy-saving measures in electrowinning operation.

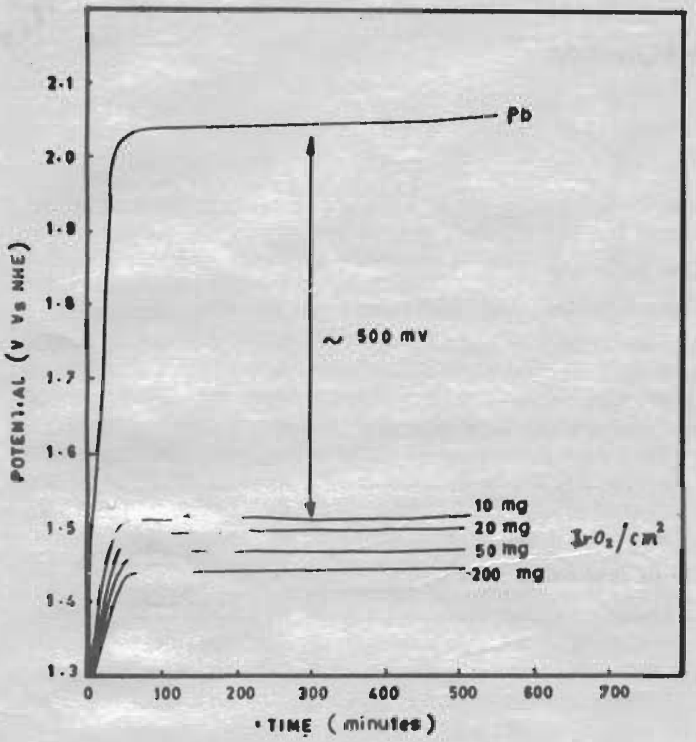

Fig. 8 : Anode potential-time curves for lead and activated lead electrodes with different loading of IrO_2 in 1M H_2SO_4

The stability of RuO_2 appears to depend largely on the presence of oxygen-bridged cations in a largely anhydrous lattice in which overlap of metal orbitals across the oxygen bridges provides a facile route for electron-transfer – hence the metallic conduction properties of this oxide. Pure RuO_2 lacks the stability required for industrial applications. One way of achieving the increased stability is the use of mixed oxide coating. The addition of TiO_2 will reduce the amount of noble metal required for a given oxide loading and probably improve the adhesion of the oxide layer to the metallic support.

From the Pourbaix diagram for ruthenium it could be forecast that the stability of ruthenium dioxide as an oxygen evolving anode could be difficult to achieve over a broad range of pH conditions. In acid solutions at potentials greater than 1.3V, the formation of RuO_2 is feasible, which may result in dissolution of the active layer [6].

$RuO_2 + 2H_2O = RuO_4 + 4H + 4e; E^{\circ} = 1.387V - 0.0591$ pH.

However, RuO_2 formed thermally is reported to be more stable than RuO_2 formed on Ru by anodic oxidation at potentials $>$ 1.0V. The oxide prepared by thermal decomposition is composed of anhydrous RuO_2 which has a high resistance against dissolution. Thus the degree of hydration in the oxide film is considered to be one of the factors influencing the polarisation characteristics in H_2SO_4 solutions. Comparatively better anodic stability can be envisaged with IrO_2 electrodes as predicted by the following reaction [7] :

$IrO_2 + 2H_2O = IrO_4^{2-} + 4H^+ + e; E^{\circ} = 2.057V - 0.1182pH$

A major reason for deterioration of the titanium-base anode is the base metal attack which is caused either by shedding of the active layer or by the dissolution of coating. Failure of the anodes in the chlor-alkali electrolysis is characterised by the onset of passivation followed by quick rise in anode potential. However, the situation is different with the activated lead electrodes where lead base remains electrochemically inert under oxygen evolution conditions. A potential rise of 10 to 15 mV is observed in the long term polarisation studies with lead based RuO_2 and IrO_2 electrodes and it is too early to give definite reasons for this. Removal of active sites as a result of shedding or dissolution of the coating, lead base attack to some extent as a consequence of oxygen penetration in the oxide coating, stoichiometry change in the oxide coating and deposition of foreign insulating matter are the possibilities.

The impurities and additives in electrowinning electrolytes may impose further restrictions upon the selection of a suitable anode surface for electrowinning. Plant scale operation in electrowinning of zinc prescribes a limit of about 50 mg l^{-1} of chloride in the electrolyte to keep the attack on lead anodes to the minimum. Anodic polarisation studies carried out in the present investigation with addition of 1 g/l chloride indicate no visual base metal attack. The materials investigated in this context are RuO_2 and IrO_2 which are also known to be good electrocatlysts for chlorine evolution. The manganese present particularly in zinc electrowinning electrolytes may present problems by being deposited as an insulating layer on the surface of anodes [8]. Remedial measures have also been reported to overcome this problem. Detailed investigations in this regard is a separate study by itself.

CONCLUSION

The investigations carried out under oxygen evolution condition indicate an anode potential reduction to the extent of 500 mV which may result in considerable energy savings in the electrowinning operation. The other important observation made here is that lead base remains electrochemically inactive. Though the present study is limited to 10 mg cm^{-2} as the lowest catalyst-loading, economically acceptable catalyst loadings have to be worked out with the combination of proper valve metal particles. Finding an electrocatalyst and a substrate stable to the highly acidic conditions existing at the surface of an electrowinning anode are still major problems to be solved at an economically acceptable cost. Rising costs of power forecast for the future could indicate that both research and development should continue towards the attainment of the objective of the development of low oxygen overvoltage electrowinning anodes.

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