# CATALYTIC ANODES IN ELECTROWINNING — INHIBITION OF POISONING BY MANGANESE IONS
## PART - I. CYCLIC VOLTAMMETRIC STUDIES

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## ABSTRACT

Poisoning of the catalytic anodes of $Mn^{2+}$ ion in metal winning electrolytes has been investigated. Addition of soluble phosphorous (V) and arsenic (III) compounds has been examined as a deterrent for $MnO_2$ deposition using cyclic voltammetric technique. Probable role of these compounds in the inhibition of anodic formation of $MnO_2$ is discussed. Platinum, $RuO_2$ film electrode and $RuO_2$ powder compact electrode have been studied in this context.

**Key words: Catalytic anodes, electrowinning, cyclic voltammetry, inhibition of $Mn^{2+}$**

## INTRODUCTION

Electrowinning of metals from sulphate solutions is one of the major steps in the hydrometallurgical methods of extraction from ores. Conventional materials employed for the anode consist of lead alloys containing silver, antimony, calcium or tin. Though alloying with elements like silver has reduced the corrosion rate, the overpotential for oxygen evolution has remained high. Oxygen evolution is the most common anodic reaction in industrial electrowinning operations in sulphate medium which accounts for 50 - 80% of the total cell voltage.

The introduction of titanium substrate dimensionally stable anodes (DSA) in chlor-alkali industries with accompanying significant energy saving led to attempts on the use of such anodes in other industrial electrolytic processes, such as electrowinning of metals. A straight forward reduction in oxygen overpotential is the primary advantage in such catalytic anodes. Materials like $RuO_2$ and $IrO_2$ show good characteristics as catalyst for oxygen evolution [1, 2]. Excellent corrosion resistance, increased purity of the cathode product and reduced maintenance cost are the added advantages.

In the electrowinning of metals from sulphuric acid solutions manganese is often present in the electrolyte. In the case of zinc electrowinning, manganese level is in between 0 to 10 gl$^{-1}$, whereas in cobalt electrowinning it varies from 0 to 20 gl$^{-1}$. The presence of manganese in solution is deterrant for the operation of catalytic anodes as a coating of $MnO_2$ is formed on the anode surface resulting in reduced catalytic activity. The deposit of poorly conductive manganese oxides in the course of metal electrowinning process, gradually covers the active coating resulting in increased cell voltage [3]. This paper attempts to understand the problem of manganese ion on the performance of catalytic anodes and to suggest possible remedial measures. In this context it is interesting to note that the presence of certain soluble compounds of arsenic and phosphorous inhibit the formation of $PbO_2$ at the anode in the electrowinning of lead [4,5]. The effect of similar compounds on the inhibition of $MnO_2$ formation has been studied using cyclic voltammetric technique.

## EXPERIMENTAL

$RuO_2$ powder for the compact electrodes were prepared by the thermal decomposition of ruthenium trichloride. The powder compacts of 200 mg cm$^{-2}$ loading having 13 mm diameter were prepared by adopting the method of pressing and sintering technique. $RuO_2$ film electrodes of 2 cm$^2$ area on titaniun substrates with Ru content of 0.5 mg cm$^{-2}$ were prepared by thermal decomposition technique. Platinum electrodes of 5.2 cm$^2$ area were also employed in some investigations. Cyclic voltammetric studies were carried out in 1M $H_2SO_4$ with Mn$^{+2}$ addition from 0 to 20 gl -1. As (III) addition in the form of sodium meta arsenite from 0 to 1000 ppm and addition of P(V) in the form of $H_3PO_4$ from 0 to 2000 ppm were employed. Cyclic voltammograms were recorded using a Wenking Potentioscan (Model POS 73) coupled with X-Y recorder (Digitronic 2000 series) at a scan rate of 10 mV s$^-$. Saturated calomel electrode was used as reference electrode and all potentials were quoted with respect to NHE.

## RESULTS AND DISCUSSION

Fig.1 shows the cyclic voltammograms of Pt in 1M $H_2SO_4$ containing 20 gl$^{-1}$ Mn$^{+2}$ ion with addition of As (III). In the absence of As(III), the peak formed at 1500 mV in the forward scan is due to $MnO_2$ formation. $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e$  E° = 1.23V [6] and the peak obtained around 1275 mV is due to reduction of $MnO_2$. With the increase of As(III) addition the peak heights for $MnO_2$ formation and
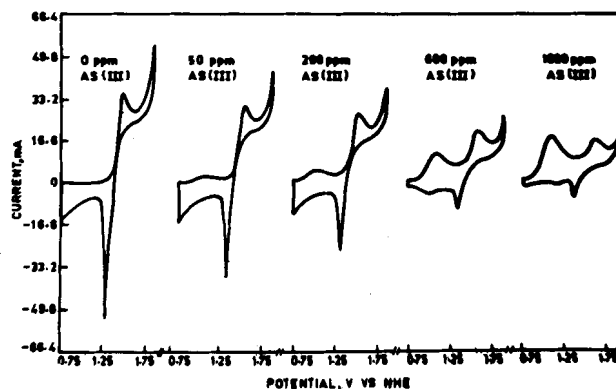


Fig.1 : Cyclic voltammograms of platinum in 1M $H_2SO_4$ containing 20 gl$^{-1}$ Mn(II) with additions of As(III) at 50 mV s$^{-1}$

reduction gradually decreases indicating the extent of these reactions taking place. Anodic peak formed at 1200 mV (NHE) is due to oxidation of arsenite to arsenate. The peak current increases proportionately, with addition of As(III) after which the current begins to drop.

E° for the reaction

$$AsO_4^{-3} + 4H^+ + 4e \rightleftharpoons AsO_2^- + 2H_2O \text{ is } 0.977 \text{ V (NHE) } [7].$$

The effective range of the arsenic compound addition is around 600 ppm as indicated by peak current for $MnO_2$ reduction and further addition of arsenic compund alters the peak current very little.

Similar cyclic voltammetric studies carried out with the addition of phosphorous compounds in the form of phosphoric acid is shown in Fig. (2).
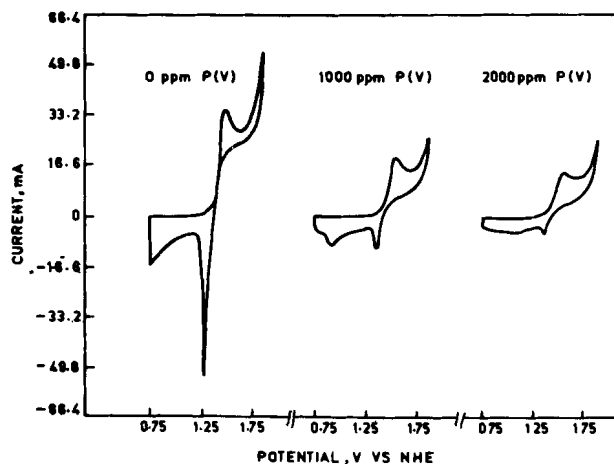
Fig. 2 : Cyclic voltammograms of platinum in 1M $H_2SO_4$ containing 20 gl⁻¹ Mn(II) with addition of P(V) at 50 mV s⁻¹

Cyclic voltammogram obtained with effective range of P(V) concentrations from 1000 to 2000 ppm are shown in the figure. $MnO_2$ is formed on the electrode surface in the forward scan and it is reduced in the reverse scan as indicated by sharp cathodic peak at 1275 mV. This peak current value in absence of P(V) compound is nearly 59 mA which is reduced to less than 15 mA in presence of P(V) indicating the inhibition of $MnO_2$ formation.
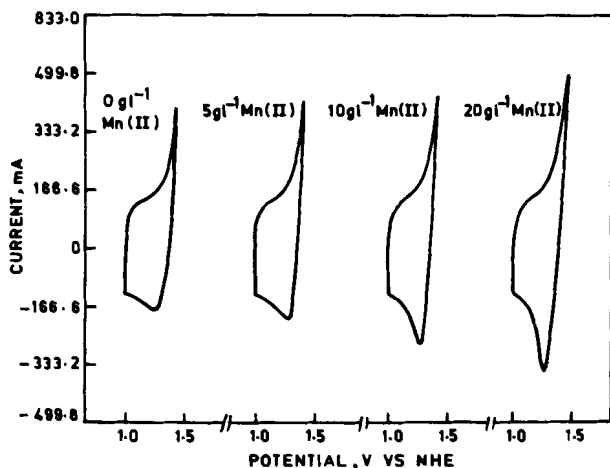
Fig. 3 : Cyclic voltammograms of $RuO_2$ powder compacts of 200 mg cm⁻² loading in 1M $H_2SO_4$ with addition of Mn(II) at 50 mV s⁻¹

Fig.3 shows the cyclic voltammograms of $RuO_2$ powder compacts of 200 mg cm⁻² loading in 1M $H_2SO_4$ with addition of Mn⁺². With the increase of Mn²⁺ addition from 0 to 20 gl⁻¹, amount of $MnO_2$ deposited onto the catalytic anode surface progressively increases as indicated by increase in the peak height in the cathodic potential sweep to the extent of 200 mA. The effect of As(III) addition in this case is shown in Fig.(4).
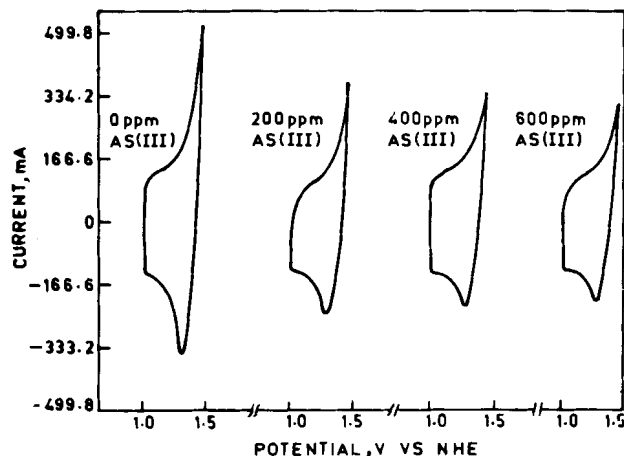
Fig. 4 : Cyclic voltammograms of $RuO_2$ powder compacts of 200 mg cm⁻² loading in 1M $H_2SO_4$ containing 20 gl⁻¹ Mn(II) with additions of As(III) at 50 mV s⁻¹

Reduction in peak height to the extent of 150 mA was noticed which indicates the inhibition of $MnO_2$ formation by As(III) species. Behaviour of $RuO_2$ film electrode in presence of Mn²⁺ is shown in Fig.5.
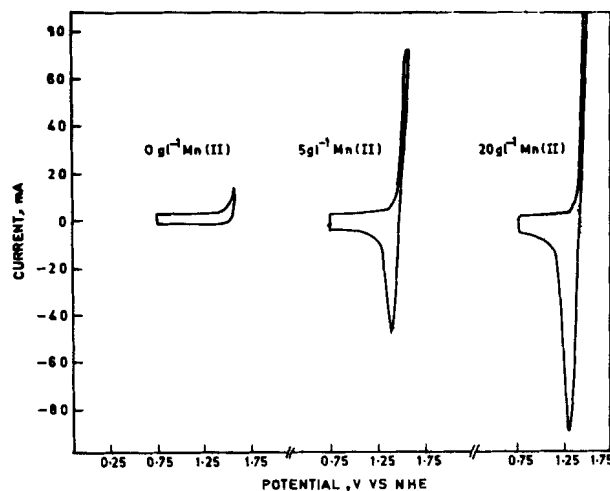
Fig. 5 : Cyclic voltammograms of $RuO_2$ film electrode of Ru 0.5 mg cm⁻² loading in 1M $H_2SO_4$ containing 20 mg I⁻¹ Mn(II) with additions of Mn(II) at 50 mV S⁻¹

The peak current for $MnO_2$ reduction in the cathodic sweep is 50 mA for 5 gl⁻¹ Mn²⁺ and increases to 90 mA for 20 gl⁻¹ Mn²⁺. Fig. 6 indicates the effect of As(III) in the inhibition of $MnO_2$ formation. Peak current for $MnO_2$ reduction in the cathodic sweep is decreased from 90 mA to 55 mA from 0 ppm to 1000 ppm As(III) addition respectively.
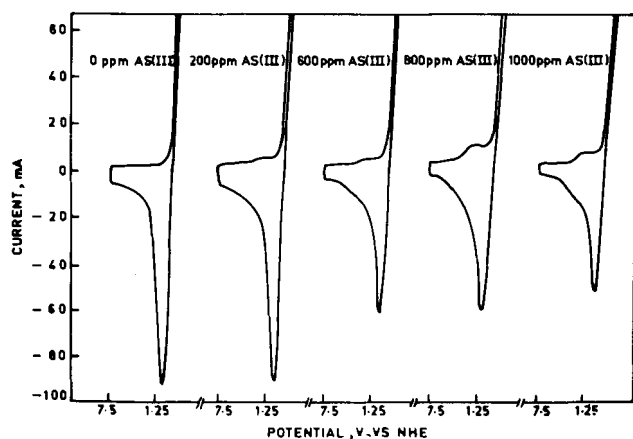
Fig. 6 : Cyclic voltammograms of RuO$_2$ film electrode of Ru 0.5 mg cm$^{-2}$ loading in 1M H$_2$SO$_4$ containing 20 gl$^{-1}$ Mn(II) with additions of As(III) at 50 mV s$^{-1}$

The influence of arsenate ion in inhibition of the formation of PbO$_2$ has been explained on the basis of preferential adsorption at the electrode surface. Similar inhibition of electrode reactions by the readily adsorbed extraneous species such as chloride and thiocyanate has been reported for the anodic oxidation of oxalic acid on a platinum surface [8]. Anions especially arsenate and phosphate, having higher ionic radii, tend to give higher surface coverage. The presence of phosphorous compounds such as phosphoric acid and organic phosphates prevents anodic formation of PbO$_2$ [9]. The inhibition of MnO$_2$ formation by arsenic and phosphorous compounds can be explained on the basis of preferential adsorption of such compounds on the electrode surface.

## CONCLUSIONS

Poisoning of the catalytic anodes by Mn$^{2+}$ ions in metal winning electrolytes has been studied. Cyclic voltammetric studies with platinum, RuO$_2$ film electrode and RuO$_2$ powder compact electrode indicated the inhibition of MnO$_2$ formation by arsenic and phosphorous compounds. The inhibition may be due to preferential adsorption of these compounds on the electrode surface.

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