

CATALYTIC ANODES IN ELECTROWINNING - INHIBITION OF POISONING BY MANGANESE IONS PART II - GALVANOSTATIC STUDIES

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ABSTRACT

The deactivation of the catalytic anodes caused by Mn^{2+} ion in electrowinning electrolytes has been studied under galvanostatic conditions. Gradual anode potential rise in presence of Mn^{2+} ion indicates the deterioration in the catalytic activity as a result of MnO_2 formation on the electrode surface. The addition of soluble phosphorous or arsenic compounds is found to restrict the rise in anode potential. Current efficiency studies made for MnO_2 deposition in presence of arsenic or phosphorous compound confirm the inhibiting tendency of these surface active substances on MnO_2 formation. Surface characterisation of polarised electrodes has also been made using Scanning electron microscope.

Key words: Catalytic anodes, electrowinning, galvanostatic studies, inhibition of Mn^{2+} .

INTRODUCTION

In recent years there have been many attempts to reduce power consumption in the production of metals by electrowinning process. The power requirement can be decreased by effecting a reduction in the cell voltage which in turn can be reduced by decreasing the oxygen over-voltage. Considerable work has been done on the development of improved anodes for electrowinning of metals. A straight forward reduction in oxygen overpotential is being realised by the substitution of dimensionally stable anodes for the conventional lead alloy anodes. Noble metal oxides like RuO_2 and IrO_2 show excellent characteristics as catalysts for oxygen evolution. Excellent corrosion resistance, increased purity of the cathode product and reduced maintenance cost are some of the added advantages.

The impurities and additives present in electrowinning electrolytes impose some restriction, on the application of catalytic anodes for metal winning operations. For example, the presence of manganese in solution is deterrant for the operation of catalytic anodes as the deposition of poorly conductive manganese oxides during electrowinning process, gradually cover the surface resulting in increased cell voltage.

This paper investigates the problem of deactivation of catalytic anodes by manganese ions studied under galvanostatic conditions. The effect of certain soluble compounds of arsenic and phosphorous on the inhibition of MnO_2 formation has been studied.

EXPERIMENTAL

Valve metal support particles were degreased with trichloroethylene and impregnated with the activating solution in an amount equivalent to 1.0 wt % Ru by weight of support particles. The impregnated particles were dried at 120°C and finally heated to 450°C for 1 hour, in an air stream. The electrocatalyst thus prepared was embedded in the surface of lead sheet to substantially cover the surface of the substrate. RuO_2 film electrodes of 2 cm² area on titanium substrate with Ru content of 0.5 mg cm⁻² were prepared by thermal decomposition technique. Platinum electrode of 5.2 cm² area was employed for current efficiency studies of MnO_2 deposition. Anodic polarization studies were carried out under galvanostatic conditions in 1M H_2SO_4 containing upto 20 g l⁻¹

Mn(II) ions at a current density of 400 mA cm⁻². As(III) addition in the form of sodium meta arsenite from 0 to 600 ppm and addition of P(V) in the form of H_3PO_4 from 0 to 1000 ppm were employed. Long term polarization studies with electrodes of 45 cm² area were carried out at a current density of 40 mA cm⁻² for a period of 8 hrs. Potentials were measured against saturated calomel electrode (SCE) and converted to normal hydrogen electrode (NHE). Scanning electron micrographs of RuO_2 film electrodes polarized at 40 mA cm⁻² in H_2SO_4 with and without Mn(II) and P(V) have been taken.

RESULTS AND DISCUSSION

Fig. 1 indicates potential-time curves for oxygen evolution of RuO_2 film electrode. In presence of Mn^{2+} the anode potential gradually

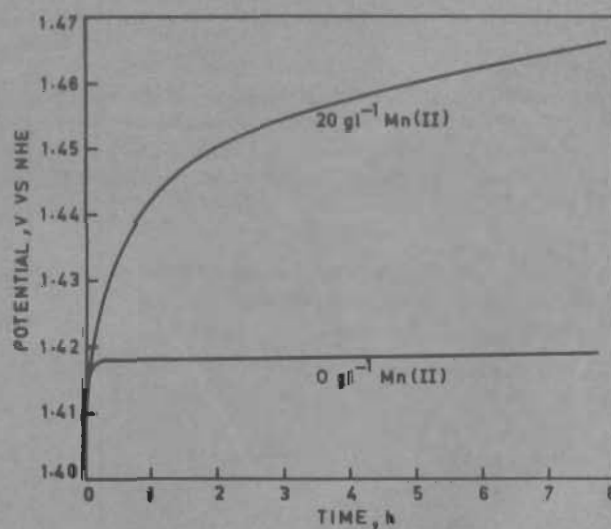


Fig.1 : Anode potential-time curves for oxygen evolution on RuO_2 film electrode of Ru 0.5 mg cm⁻² loading in 1M H_2SO_4 with additions of Mn(II)

increases as the catalytic surface is poisoned by MnO_2 deposition. An increase of 50 mV in anode potential for a period of 8 hrs. duration was noticed. The MnO_2 formation may be represented by the equation:

$$\text{Mn}^{2+} + 2 \text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \quad E^\circ = 1.23\text{V}$$

The gradual increase in the anode potential can be explained by the gradual coverage of the active coating by deposition of electrically poorly conductive manganese oxides.

The effect of P(V) and As(III) on the anode potential under oxygen evolution conditions is shown in Fig. 2.

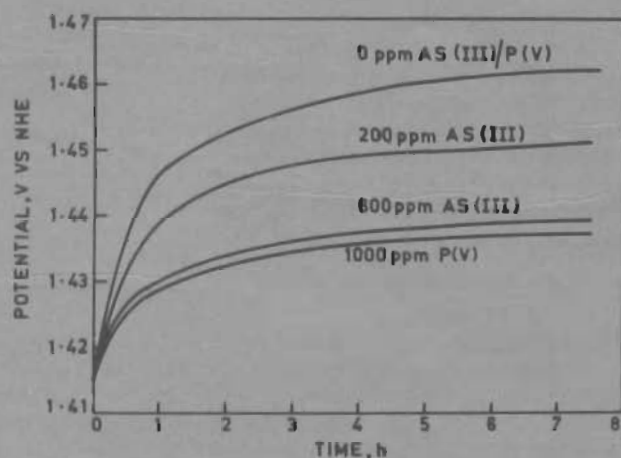


Fig. 2 : Anode potential-time curves for oxygen evolution on RuO_2 film electrode of $\text{Ru } 0.5 \text{ mg cm}^{-2}$ loading in $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)}$ with additions of As(III) or P(V)

The reduction in rise of anode potential by MnO_2 deposition with 200 ppm As(III) is 15 mV for 8 hrs. and it is around 30 mV for 600 ppm As (III) and 1000 ppm P(V) additions. The influence of arsenic and phosphorous compounds on the inhibition of MnO_2 formation can be explained on the basis of preferential adsorption of these compounds on the electrode surface [1-3].

Table I shows current efficiency for MnO_2 deposition with different amounts of As(III) additions, under the conditions of $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)}$ at a current density of 100 Am^{-2} ; with the increase of As(III) addition, the current efficiency for MnO_2 deposition decreases from 12.8% to 0.25%.

TABLE I : Current efficiency for MnO_2 deposition in $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)}$ with arsenic (III) additions

As(III) addition (ppm)	Current efficiency for MnO_2 deposition (%)
0	12.820
50	7.768
200	2.270
600	0.246

Table II gives current efficiency data for MnO_2 deposition with P(V) additions. In this case the current efficiency decreases from 12.8 to 0.86%.

TABLE II : Current efficiency for MnO_2 deposition in $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)}$ with phosphorous (V) additions

Phosphorous (V) addition (ppm)	Current efficiency for MnO_2 deposition (%)
0	12.820
100	8.2812
500	2.7130
1000	0.8630

Table III shows the anode potential for RuO_2 sponge electrode in presence of Mn(II) and the influence of P(V) addition. The rise in anode potential is 422 mV for a period of 7 days which reduces to 126 mV in presence of 1000 ppm of P(V).

TABLE III : Effect of phosphorous (V) on anode potential of RuO_2 sponge electrode in $1\text{M H}_2\text{SO}_4$ containing $5 \text{ gl}^{-1} \text{ Mn(II)}$ at 400 Am^{-2} .

Phosphorous (V) addition (ppm)	Anode potential rise for 7 days (mV)
0	422
1000	126

Fig. 3 shows the scanning electron micrograph of RuO_2 film electrode polarized in $1\text{M H}_2\text{SO}_4$ which indicates multi-layered pore free structure of RuO_2 . Fig. 4 is the SEM of RuO_2 film electrode polarised in $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)}$ ions where massive crystalline deposition of MnO_2 is seen. Fig. 5 is the SEM of RuO_2 film electrode polarized in $1\text{M H}_2\text{SO}_4$ containing $20 \text{ gl}^{-1} \text{ Mn(II)} + 1000 \text{ ppm P(V)}$. Absence of the characteristic massive crystalline structure indicates the inhibition of MnO_2 formation.

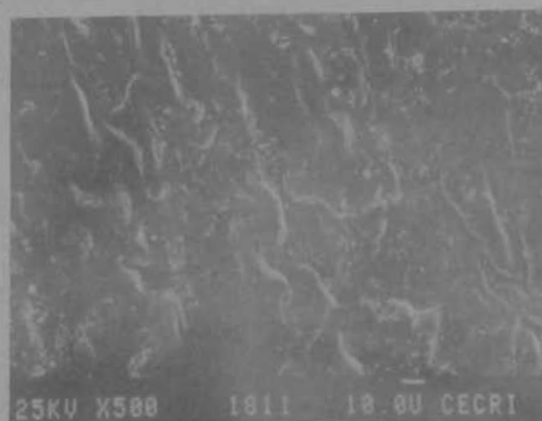


Fig. 3 : SEM photograph of RuO_2 film electrode polarised in $1\text{M H}_2\text{SO}_4$

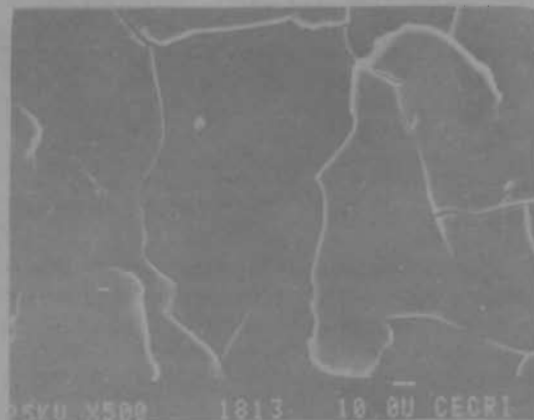


Fig. 4 : SEM photograph of RuO_2 film electrode polarised in $1\text{M H}_2\text{SO}_4 + 20\text{ gl}^{-1}\text{ Mn(II)}$

CONCLUSION

Poisoning of the catalytic anodes by Mn(II) ion in metal winning electrolyte has been studied. Anode polarization studies under galvanostatic condition with platinum, RuO_2 film electrode and RuO_2 sponge electrodes 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.

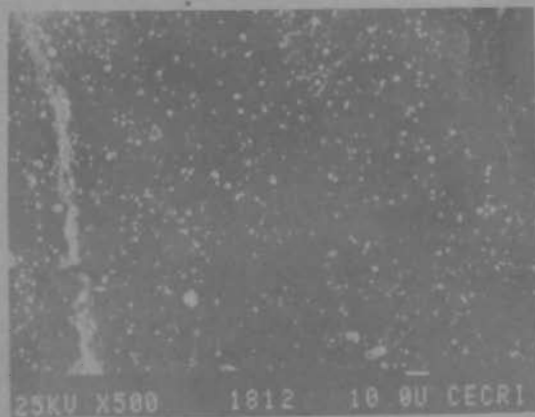


Fig. 5 : SEM photograph of RuO_2 film electrode polarised in $1\text{M H}_2\text{SO}_4 + 20\text{ gl}^{-1}\text{ Mn(II)} + 1000\text{ ppm P(V)}$

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