

CATALYTIC ANODES FOR ELECTROWINNING — PART I: EFFECT OF METHANOL ADDITION

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A significant reduction in energy consumption in metal electrowinning from sulphate solutions can be achieved by the use of catalytic anodes in combination with methanol addition to the electrolyte. The effect of current density on methanol oxidation has been studied on different types of catalytic anodes like RuO₂ film electrode and sponge electrode. The effect of periodic current reversal on the anodic process has also been investigated.

Key words: Catalytic anode, electrowinning, methanol oxidation

INTRODUCTION

Electrolysis energy in electrowinning of metals like zinc accounts for nearly 80% of the total energy. Reduction of this energy component can offer rich rewards. Many years of development and experimentation with different electrolytes, different current densities, smaller anode-cathode distances and different anode materials have not significantly reduced this energy requirement. The most promising approach to this problem in electrowinning operation appears to be the use of other oxidation processes in place of oxygen evolution. An anodic reaction suitable for a fuel cell can be considered for electrowinning. Among soluble fuels, methanol is most practical to be used in an electrowinning cell.

The use of methanol in zinc electrowinning has been reported by several workers [1,2]. The catalytic activity of the precious metal coated titanium anode has been proved by carrying out the electrolysis under periodically reversed current conditions [3].

The use of catalytic anodes based on catalysts like RuO₂ and IrO₂ is one of the recent trends in metal electrowinning processes. Here titanium or lead can be substrate material. The anodic stability of these electrocatalysts under oxygen evolution conditions poses problems in the development of usable electrowinning anodes. Attempts to develop an electrocatalyst on a substrate stable in H₂SO₄ have not been so successful as to encourage commercial adoption. In this paper a new approach where a combination of methanol addition and catalytic anodes is employed has been investigated and results reported.

EXPERIMENTAL

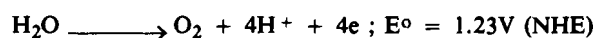
RuO₂ film electrodes were prepared by forming a thin coating of RuO₂ onto titanium strip by adopting the method of thermal decomposition of ruthenium trichloride solution. Similarly RuO₂ sponge electrodes were prepared using titanium sponge of 3 mm size and embedding the activated sponge particles onto lead substrate. These electrodes were used in the polarisation studies. Potentiodynamic studies were carried out with RuO₂ film electrode using a Wenking Potentiostat (POS 73) and an X-Y recorder (Model Digitronic 2000 series). Platinum foil was used as the auxiliary electrode. An H-type glass cell of 200 cm³ capacity was used.

Steady state galvanostatic studies were carried out using a galvanostat of 1 ampere capacity. 1M H₂SO₄ was used as electrolyte in all the experiments. Methanol addition was varied from 0 to 5 wt%. Galvanostatic studies with periodic current reversal was also investigated. All the solutions were prepared from the AR grade samples and double distilled water. All the measurements were carried out at 302 ± 1K. The current densities employed were based on the apparent area of the working electrodes.

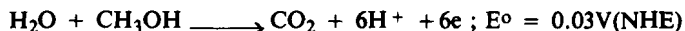
A saturated calomel electrode was used as the reference electrode and all potentials are quoted with respect to this reference unless otherwise stated.

RESULTS AND DISCUSSION

Fig.1 shows the effect of methanol addition on the potentiodynamic behaviour of the RuO₂ film electrode in H₂SO₄ electrolyte. In absence of methanol in the electrolyte in the anode reaction is oxygen evolution as indicated by a steep current rise at higher anodic potential.



Addition of methanol results essentially in the evolution of CO₂; evolution occurs relatively at lower anodic potential.



The anode reaction involving methanol oxidation has a lower positive potential than the deposition of water to give oxygen occurring in conventional electrowinning, with the result that cell potential is reduced. It is evident from these curves that the advantage of anode potential reduction is more pronounced at lower current densities. At a current density of 2.5 mA cm⁻² the anode potential reduction is nearly 150 mV.

As the current density rises this trend is progressively reduced. Thus at a current density of 45 mA cm⁻² the potentiodynamic curves recorded in presence and absence of methanol are found to merge indicating that there is no effect due to methanol addition.

Fig. 2 shows the effect of methanol addition on anode potential reduction for the RuO₂ film electrode in steady state galvanostatic

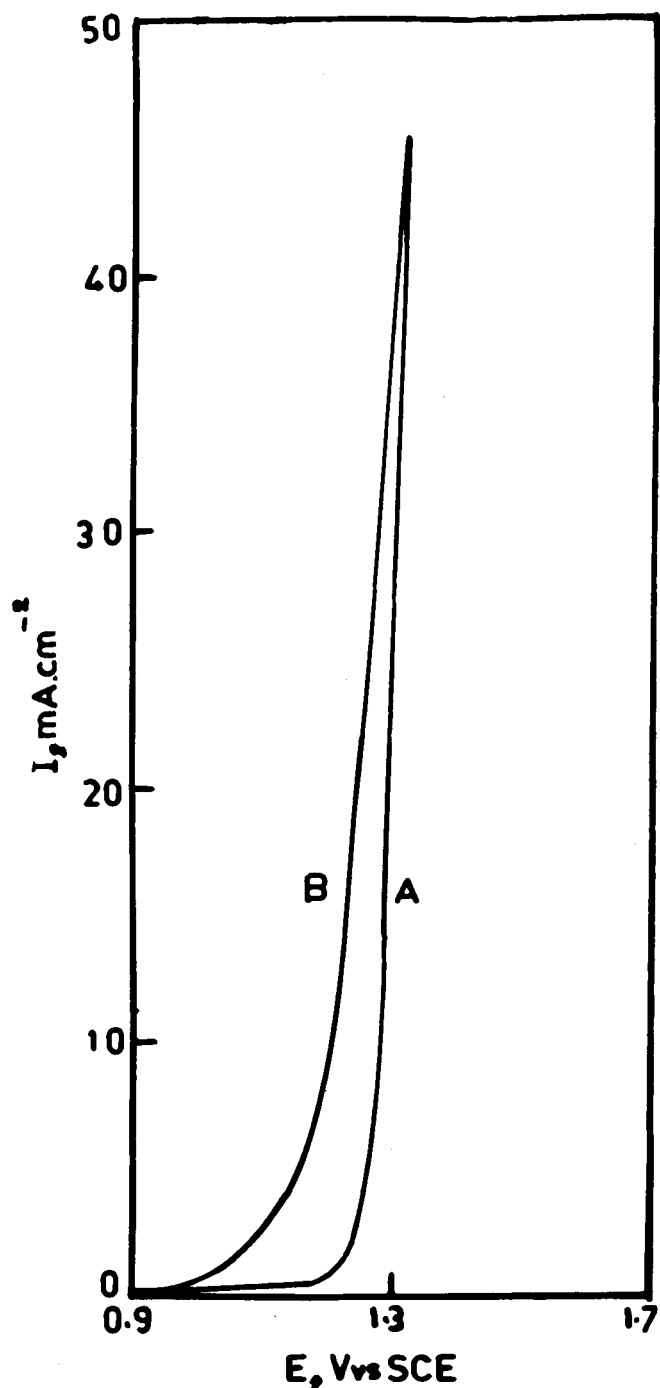


Fig. 1: Potentiodynamic curves of RuO_2 film electrode, A, in $1M H_2SO_4$ and B, in $1M H_2SO_4 + 3 wt\% CH_3OH$ at $10 mVs^{-1}$

measurements. Comparison of the polarization curves obtained in presence and absence of methanol indicates that the anode potential reduction is more prominent at lower current densities.

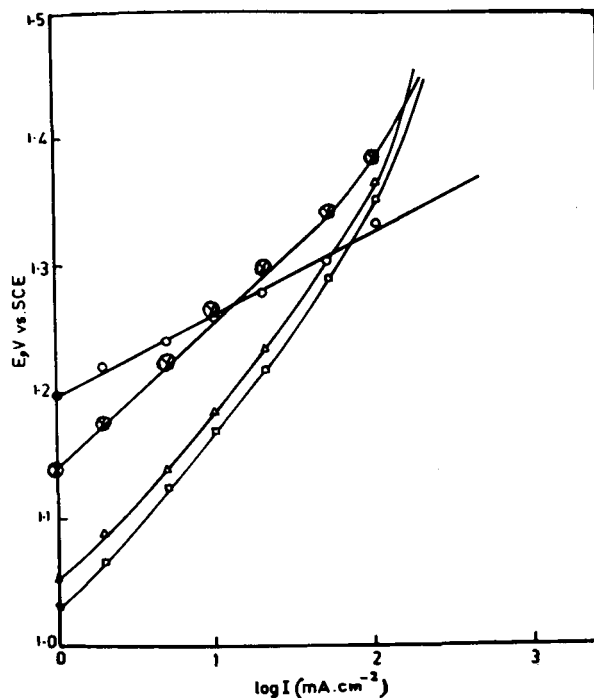


Fig. 2: Anodic polarisation curves of RuO_2 film electrode in $1M H_2SO_4$ with additions of CH_3OH (O) 0 (\odot) 1.0 (\triangle) 3.0 (\square) 5.0wt%

Methanol addition upto 3 wt% results in gradual decrease in anode potential and further addition influences the anode potential very little. The slopes of the polarization curves are more at higher current densities when compared to those at lower and moderate current densities. This phenomenon is typical of an organic oxidation where partial oxygen evolution at higher current densities makes the process a complex one. It has been reported [4] that current efficiency in organic oxidation processes is inversely proportional to current density. Various competitive reactions both organic and oxygen evolution are responsible for this. Generally an increase in current density favours oxygen evolution to the detriment of other oxidations. Greater depolarization obtained for methanol at lower current densities indicates better efficiency for methanol oxidation. At higher potentials and current densities the fraction of oxygen evolved increases.

Similar studies carried out with sponge electrode give rise to polarization curves given in Fig. 3. The sponge electrode, by virtue of its higher surface area, results in greater depolarization. Because of higher surface area, the effective current density is lower resulting in effective methanol oxidation. Anode potential rise is investigated in long term polarization studies. The rise is quite low for sponge electrode compared to film electrode at a fixed c.d. The rise at a c.d. of $5 mA cm^{-2}$ is 62 mV for film electrode and it is 8 mV for sponge electrode whereas at a c.d. of $10 mA cm^{-2}$

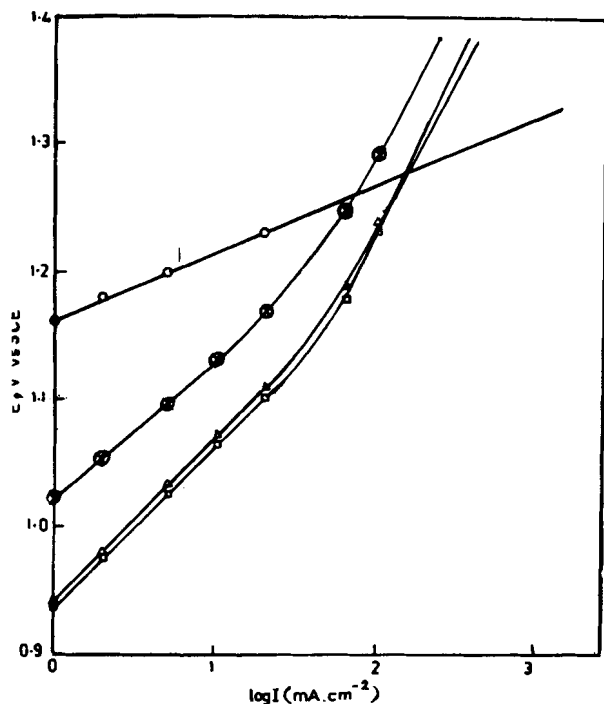


Fig.3: Anodic polarisation curves of RuO_2 sponge electrode in $1\text{M H}_2\text{SO}_4$ with additions of CH_3OH . (O) 0 (\odot) 1.0 (\triangle) 3.0 (\square) 5.0 wt%

it is 120 and 23 mV respectively. Higher current densities as already explained promote oxygen evolution and the reduction in anode potential due to methanol oxidation is partially lost. Moreover, at higher current densities, the formation of other oxidation products apart from CO_2 is likely.

The effect of periodic current reversal (PCR) on the polarization characteristics is illustrated in Table I. It is observed that

TABLE-I: Effect of periodic current reversal with sponge electrode at 20 mAcm^{-2} in $1\text{M H}_2\text{SO}_4$ with 3 wt% CH_3OH

Type of electrolysis	Duration/secs.		Anode potential rise for 6 hrs mV
	t_f	t_r	
DC	—	—	30
PCR	20	2	60
PCR	160	4	36

t_f : forward current

t_r : reversal current

this technique is not useful in arresting the anode potential rise. On the other hand, the polarization is found to be more when compared to direct current electrolysis. It has been reported [5] that PCR technique is useful for methanol oxidation on Pt. Here oxides of Pt formed during anodic polarization conditions can inhibit methanol oxidation and application of periodic current reversal techniques may help in the reduction of such surface oxides promoting oxidation of methanol. In the present study the electrodes investigated are essentially noble metal oxides for which this technique is not found to be effective.

Anode potential measurements with and without the application of PCR to the RuO_2 film electrode in methanol-free sulphuric acid solutions indicate a steady potential value of 1.33V in D.C. electrolysis of 6 hr at 20 mA cm^{-2} in $1\text{M H}_2\text{SO}_4$, which rises to 4V under PCR conditions. These results indicate the deterioration of active coating in the PCR applications. This is due to reduction of the oxide catalyst during the current reversal and subsequent shedding or dissolution of the coating raises the anode potential.

CONCLUSION

Methanol oxidation associated with lower anode potential is effective only at lower current densities. The RuO_2 loaded sponge electrode having higher surface area is found to be more useful than the RuO_2 film electrode in the present study. The application of periodic current reversal for the effective oxidation of methanol is not found to be useful for RuO_2 based electrodes in contrast to the reported useful application of the same technique for platinum based electrodes. The economy of the industrial application of this concept has to be considered from the view points of local conditions like power cost and cost of methanol.

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