

# Electrochemical behaviour of Ti-supported cobaltite anode in sulphuric acid

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Titanium electrodes coated with  $\text{Co}_3\text{O}_4$  -  $\text{IrO}_2$  have been characterised for their electrochemical activity and stability employing transient, cyclic voltammetric and accelerated polarization studies. Incorporation of  $\text{IrO}_2$  in  $\text{Co}_3\text{O}_4$  increases the life of the anode upto 70 atom%. The influence of intermediate layer of 'mixed-crystal oxides' of Ru and Ti introduced in between the titanium substrate and the outer layer ( $\text{Co}_3\text{O}_4$  -  $\text{IrO}_2$ ) has also been studied and compared.

**Key words:** Cobaltite anode, electrocatalysis, cyclic voltammetry, stability index

## INTRODUCTION

Development of durable anode with low oxygen overpotential and its characterisation assume importance in electrowinning of metals in view of shortage of power. In this context, the electrochemical behaviour of Ti-supported oxygen evolving catalysts has been studied by several authors [1]. Among them  $\text{IrO}_2$  -  $\text{Co}_3\text{O}_4$  seems to be the most promising one [2] but requires a detailed study. As introduction of an interlayer (IL) has been considered beneficial [3], an attempt is made to characterise and evaluate the cobaltite ( $\text{IrO}_2$  -  $\text{Co}_3\text{O}_4$ ) electrocatalysts supported on Ti with and without interlayer.

## EXPERIMENTAL

Oxide coatings IL(Ru-Ti) and outerlayer (Ir-Co) are formed on Ti by thermal decomposition method (723K) employing chloride salts, the load of Ru and Ir being 3 g and 1 g.  $\text{m}^{-2}$  respectively. The procedure adopted for accelerated polarisation and cyclic voltammetry (C.V.) studies are the same as described elsewhere [3]. The decay of potential has been measured using an Oscilloscope (Tektronix 7613) along with a D.C. power supply and a mercury wetted relay. The fall of potential in 750 ms has been measured arbitrarily, as beyond this duration the rate of decay was negligible. All potential values recorded are with reference to NHE.

## RESULTS AND DISCUSSION

### Accelerated polarisation tests

From Fig. 1 it is observed that the useful life of Ti/Ir-Co anode is maximum around 70 atom % Ir whereas in case of Ti/IL/Ir-Co, it is around 100 atom % Ir.

### Potential decay studies

As the activity is related to potential decay, it could be

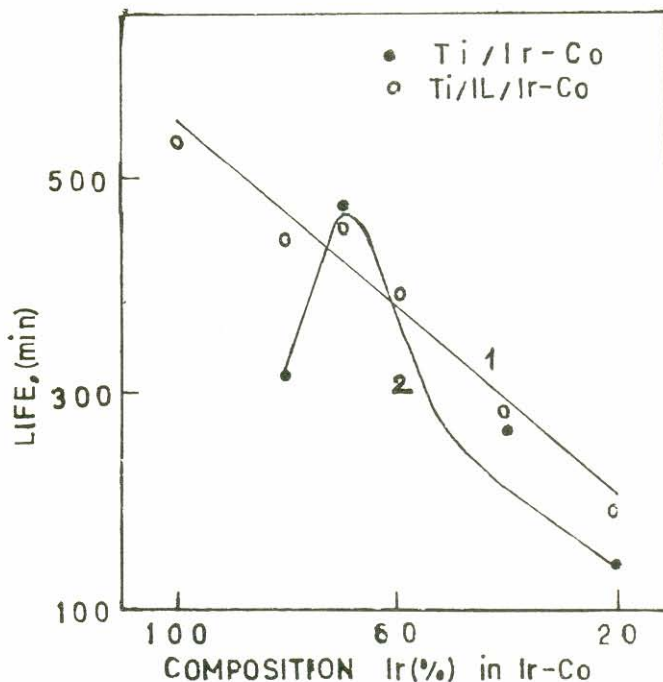


Fig. 1: Dependence of life on composition. Electrolyte: 1N  $\text{H}_2\text{SO}_4$ , current density  $1500 \text{ mA.cm}^{-2}$  (1) Ti/IL/Ir-Co (2) Ti/Ir-Co

measured from the same [4]. Figure 2 indicates the trend of dependence of fall in potential with composition. The observed catalytic activity is less around 60 atom % Ir than those at 100 to 70 atom % Ir, indicating that only at this region, maximum catalytic activity exists in both the systems.

### Cyclic voltammetry studies

Figure 3 represents the CV of Ti/100%  $\text{IrO}_2$  in 1N  $\text{H}_2\text{SO}_4$ . A reversible peak is formed at 870 mV probably due to change in valency state. Incorporation of cobalt oxide

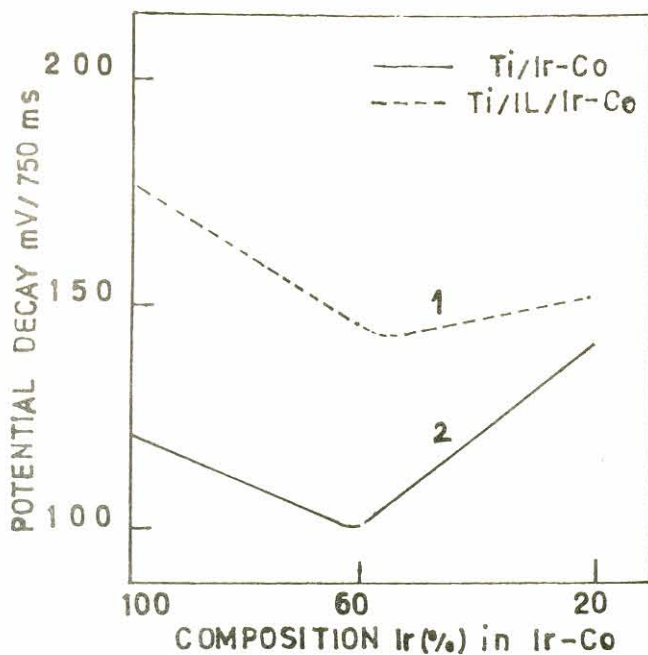


Fig. 2: Relationship between fall in potential and composition  
Electrolyte: 1N  $H_2SO_4$ , current density:  $125 \text{ mA}\cdot\text{cm}^{-2}$  (1) Ti/IL/Ir-Co (2) Ti/Ir-Co

does not alter materially the nature of the voltammogram. There is no appreciable difference in the general nature of the voltammogram on introduction of the interlayer, except the absence of desorption peak found at  $-30 \text{ mV}$  in the case of Ti/(Co - Ir) anode.

#### Catalytic activity ( $i_{pO_2}$ )

The dependence of  $i_{pO_2}$  vs composition is presented in Fig. 4. Incorporation of cobalt increases the activity and it is maximum at around 30 atom %, whereas, in the case with interlayer, the maximum catalytic activity is observed at around 80 atom %.

#### Stability index ( $Q_a/Q_c$ )

The stability index i.e. the ratio of the anodic charge to the cathodic charge [5] is an expedient method for optimising the composition of an anode system.  $Q_a/Q_c$  was found out by the graphical integration of the CV curves and presented in Fig. 5. The stability of the anode is maximum at 70% Ir - 30% Co. In the case of anode with the IL, it is maximum for 100%  $IrO_2$  and it decreases with increase of cobalt oxide content. The stability index is in accordance with the results of the accelerated polarisation experiments depicted in Fig. 1.

#### CONCLUSIONS

It has been found possible to adopt cyclic voltammetry as a convenient tool for characterising the catalytic activity and

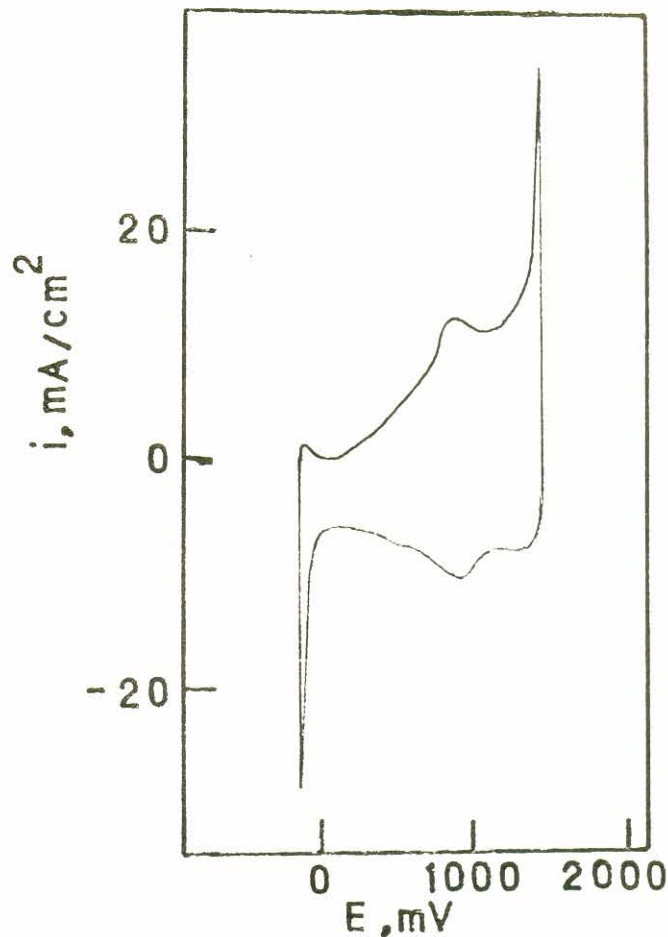


Fig. 3: Cyclic voltammogram in 1N  $H_2SO_4$  of Ti/100% Ir, Scan rate 100 mV/sec

stability of anode. The decay potential method though gives an idea of the catalytic activity, yet the results of accelerated polarisation procedure represent the overall behaviour of the anode. The interlayer, which is prolonging the life of the anode in the case of single component as outer layer, is not beneficial in the case of the 'mixed-crystal oxides'. This offers scope for further investigation.

#### REFERENCES

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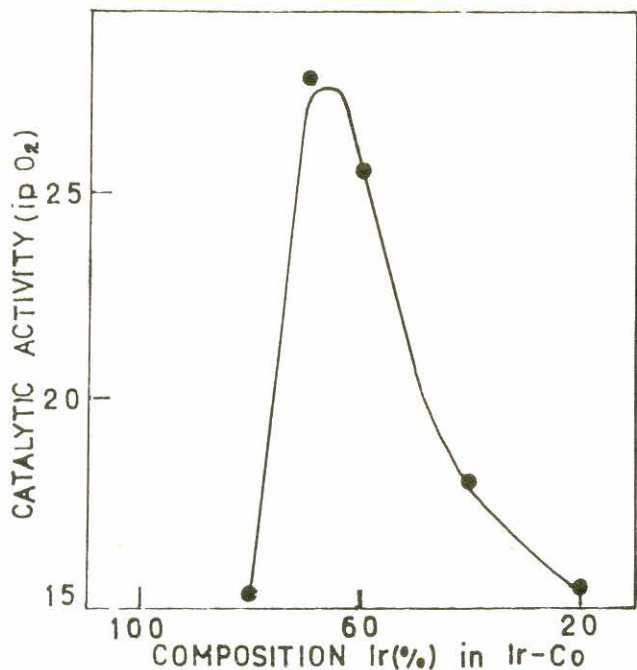


Fig. 4: Influence of composition on the catalytic activity for Ti/Ir-Co. Electrolyte: 1N  $H_2SO_4$

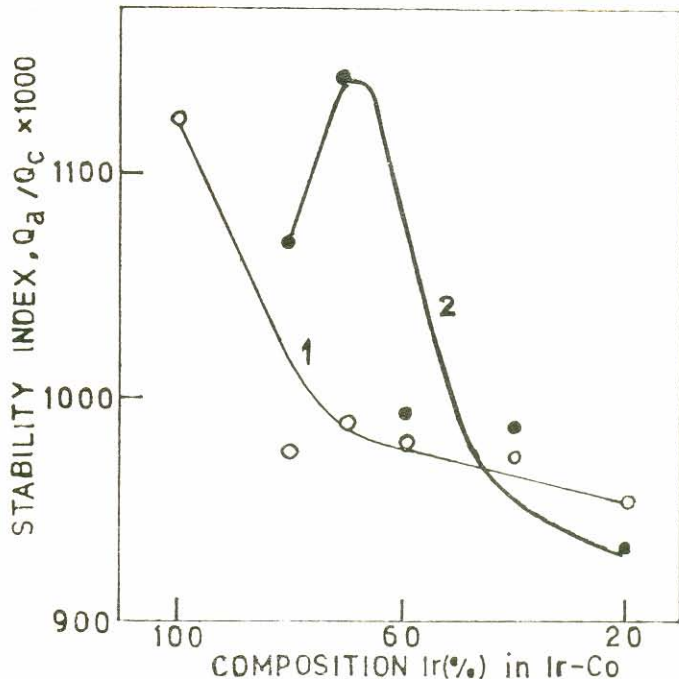


Fig. 5: Variation of charge ratio  $Q_a/Q_c$  with composition Electrolyte: 1N  $H_2SO_4$  (1) Ti/IL/Ir-Co, (2) Ti/Ir-Co

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