

## ELECTROCHEMICAL BEHAVIOUR OF TITANIUM SUPPORTED IrO<sub>2</sub>/ZrO<sub>2</sub> ELECTRODES IN ACID AND ALKALINE SOLUTIONS AND IN FERRICYANIDE/FERROCYANIDE REDOX SYSTEMS

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### ABSTRACT

Mixed oxides of IrO<sub>2</sub> and ZrO<sub>2</sub> were prepared in various mole ratios and their cyclic voltammetric behaviour, and Tafel behaviour for oxygen evolution reaction in acid and alkaline solutions were studied. The service life of these electrodes were evaluated in 6 mol/dm<sup>3</sup> NaOH solutions and it is found that the electrodes containing 60 mole % of IrO<sub>2</sub> showed a maximum service life. The electrochemical behaviour of these electrodes were also studied in ferricyanide/ferrocyanide redox systems.

**Key Words:** IrO<sub>2</sub>/ZrO<sub>2</sub> electrodes, ferri-ferro cyanides redox systems, cyclic voltammetry, oxygen evolution reaction

### INTRODUCTION

The growth of electrochemical industries forces electrochemists with serious tasks to develop high quality materials for a wide range of production processes. Since in most cases the anodes operate in extremely severe conditions (aggressive media, high anodic potentials, high temperature etc.) the development and choice of stable anodes with little dissolution poses the greatest difficulties.

Though the pure precious metal oxides are the most efficient electrocatalysts [1-3], the life of these anodes were shortened [4,5] due to lack of stability of the oxide coating. The service life of these anodes could be increased by stabilising with valve metal oxides [6] such as ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> etc. It was reported [7] that RuO<sub>2</sub> was stabilised by the addition of ZrO<sub>2</sub> and gave a service life of about 200 hours in 6.0 mol/dm<sup>3</sup> NaOH at 80°C at 0.75 A/cm<sup>2</sup> whereas for the pure RuO<sub>2</sub> it was about 40 hours under the same conditions. The present paper mainly deals with the preparation and studies on the behaviour of various compositions of IrO<sub>2</sub>/ZrO<sub>2</sub> in acid/alkaline solutions. The behaviour of these anodes was studied in ferricyanide/ferrocyanide redox systems.

### EXPERIMENTAL

#### Preparation of electrodes

The electrodes were prepared as per Indian Patent No.134375. Plain titanium sheets (ASTM Grade II) of 1 x 18 x 0.1 cm were cleaned in trichloroethylene and etched in boiling 30% HCl for 15 minutes. The required amounts of IrCl<sub>3</sub> · 3H<sub>2</sub>O (51% metal content) and ZrOCl<sub>2</sub> · 8H<sub>2</sub>O were dissolved in minimum amount of concentrated HCl separately. The coating chelate was prepared by mixing the solutions depending upon the mole ratios of IrO<sub>2</sub> and ZrO<sub>2</sub> starting from IrO<sub>2</sub> of 5 mole % to 100 mole %. The thickness of the film is fixed as 3 μ for all anodes: isopropanol was used as an organic vehicle in all coating solutions.

The coating solution was brushed on to the etched titanium support and dried at 110°C for 3 mins. and then fired at 460°C for 10 mins. in the presence of air. The process was continued until no more solution remained. The anodes were finally baked at 500°C for 50 mins. The coated film showed resistance to peeling and bend tests.

#### Cyclic voltammetric oxygen evolution kinetics/redox behaviour

To study the cyclic voltammetric behaviour of electrodes in alkaline solutions, and kinetics of oxygen evolution in alkaline/acid solutions, a two-compartment cell was used with a glass frit (G<sub>3</sub>) separating the working and counter electrode sections. In the study of ferricyanide - ferrocyanide redox systems, a single compartment cell was used as counter electrode potentials were measured with respect to saturated calomel (SCE) or Hg/HgO, NaOH electrodes depending upon the nature of the system.

The cyclic voltammetric behaviour was studied in 1M NaOH solutions. For ferri/ferro cyanide redox studies, 0.05 M K<sub>3</sub> Fe(CN)<sub>6</sub> in 1M KNO<sub>3</sub> or 0.1M H<sub>2</sub>SO<sub>4</sub> solution was used. The steady state experiments were carried out in 1M H<sub>2</sub>SO<sub>4</sub> and 6M NaOH for acid and alkaline media respectively. In the evaluation of order of reaction, 2M H<sub>2</sub>SO<sub>4</sub> and 3M NaOH solutions were used. The data for Tafel curves were those obtained after waiting for 3 mins. at each point of measurement. All experiments were carried out at 30°C and by degassing the solutions with high purity nitrogen. All solutions were made up from Analar grade chemicals and triple distilled water.

#### Accelerated service life Test

Service life tests of the electrodes under study were carried out in 6M NaOH solution at 30°C, at 1 A.cm<sup>-2</sup> current density. Service life values were measured by recording the cell potential as a function of time during electrolysis under galvanostatic conditions. The service life for a given electrode is the time required for total failure of electrocatalytic surface layer. The time at which the latter occurred was immediately apparent as it resulted in a large increase in potential associated with complete failure of catalyst and the formation of an inactive anodic film on the titanium support.

### RESULTS AND DISCUSSION

#### Cyclic voltammetric behaviour

In the cyclic voltammogram for IrO<sub>2</sub>/ZrO<sub>2</sub> electrodes in 1M NaOH at 30°C (Fig. 1) a large background over the entire potential range (-1.1 V to -0.6 V vs Hg/HgO) was observed for the electrodes containing more than 10 mole % of IrO<sub>2</sub>. The amount of charging current is directly proportional to the roughness of electrodes [8,9].

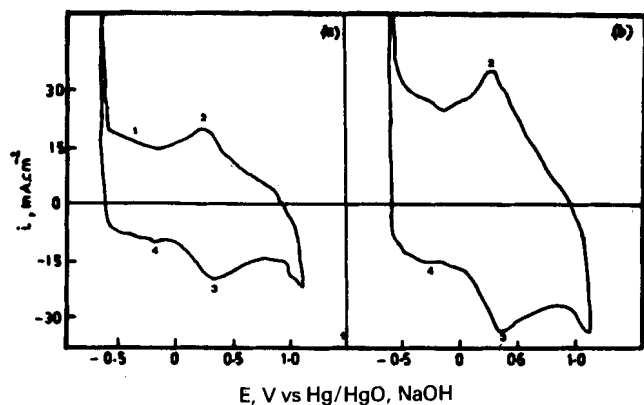
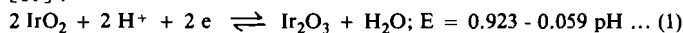
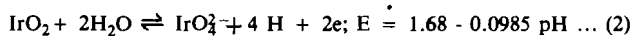


Fig.1: Cyclic voltammogram in 1 M NaOH solutions for (a) 20 mole % IrO<sub>2</sub> and 80 mole % ZrO<sub>2</sub> on titanium substrate, (b) 25 mole % IrO<sub>2</sub> and 75 mole % ZrO<sub>2</sub> on titanium substrate. Sweep rate = 50 mV/sec, temp: 30°C

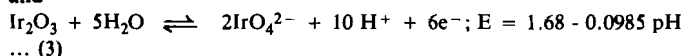
Two pairs of peaks are seen at about -0.3V vs Hg/HgO and + 0.3V vs Hg/HgO (Fig.1). The same observation has been made by earlier workers [10] on pure IrO<sub>2</sub>. The peaks 1 and 4 can be attributed to the reaction [11]:



whereas the peaks 2 and 3 may be due to the reaction:



and



respectively.

The qualitative and quantitative reproducibility of the cyclic voltammogram of IrO<sub>2</sub>/ZrO<sub>2</sub> is excellent. Repeated potential cycling between oxygen and hydrogen evolution does not affect the shape of the curve.

But in 1M H<sub>2</sub>SO<sub>4</sub> solution, only two peaks are observed at 0.9V (NHE) (Fig.2) and it may be attributed to IrO<sub>2</sub>/Ir<sub>2</sub>O<sub>3</sub> redox couples (Eq.1).

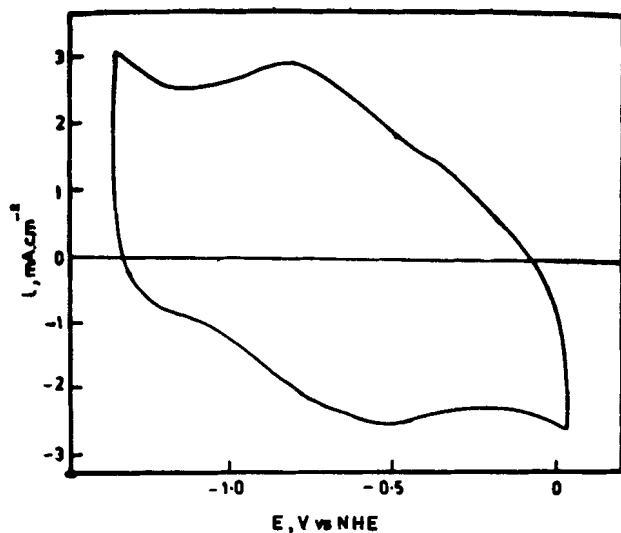


Fig.2: Cyclic voltammogram in 1M H<sub>2</sub>SO<sub>4</sub> solutions for 10 mole % IrO<sub>2</sub> and 90 mole % ZrO<sub>2</sub> on titanium substrate. Sweep rate:50 mV sec<sup>-1</sup>, Temp:30°C

### Overvoltage behaviour

Figure 3 shows the overvoltage variation with IrO<sub>2</sub> content at constant current density of 10 mA.cm<sup>-2</sup> in 1M H<sub>2</sub>SO<sub>4</sub> and 6M NaOH respectively.

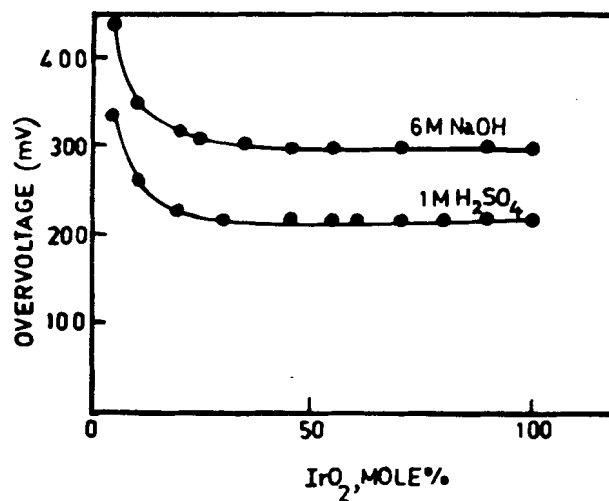


Fig. 3 : Overvoltage at constant current density of 10 mA cm<sup>-2</sup> vs IrO<sub>2</sub> in 1M H<sub>2</sub>SO<sub>4</sub> and 6M NaOH respectively

It is noted in both cases that electrodes containing 5 mole % of IrO<sub>2</sub> has maximum overvoltage, and it goes on decreasing up to 35 mole %; afterwards the overvoltage was constant over a wide range up to 100 mole % of IrO<sub>2</sub>. This type of observation is noticed in acid as well as in alkaline solutions.

### Kinetics and reaction mechanism for oxygen evolution

Typical Tafel curves for electrodes of 30 mole % of IrO<sub>2</sub> obtained galvanostatically in 1M H<sub>2</sub>SO<sub>4</sub> and 6M NaOH respectively were well reproduced and their anodic Tafel slopes were 60 mV and 40 mV respectively (Fig. 4).

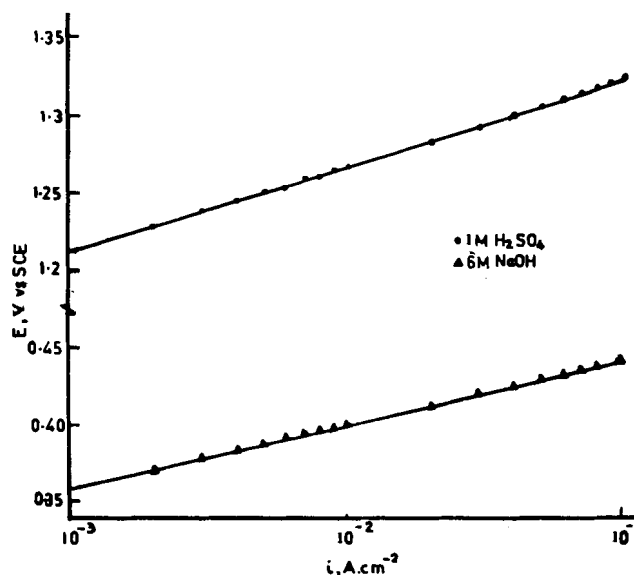


Fig. 4 : Typical Tafel curves for electrode of 30 mole % of IrO<sub>2</sub> and 70 mole % of ZrO<sub>2</sub> in 1M H<sub>2</sub>SO<sub>4</sub> and 6M NaOH respectively, Temp: 30°C

The Tafel value obtained for electrodes of 5 mole % of IrO<sub>2</sub> is greater than 120 mV. The Tafel slopes obtained for other electrodes of IrO<sub>2</sub>/ZrO<sub>2</sub> are found to be the same within an error of a few millivolts per decade both in acid and alkaline solutions.

From the current - potential curves obtained galvanostatically in acid solution of different pH, the anodic potentials at given current densities are plotted against activity of H<sup>+</sup> ions (Fig. 5) by using the activity data for H<sub>2</sub>SO<sub>4</sub> aqueous solution and a slope

$$\left( \frac{\delta E}{\delta \log a_{H^+}} \right)_i$$

of about -0.06V was obtained. The dependence of current density at the given potential on activity of H<sup>+</sup> ions is shown in Fig. 5, and the order of reaction  $(\delta \log i / \delta \log a_{H^+})_E$  with respect to H<sup>+</sup> ions is found to be -1.

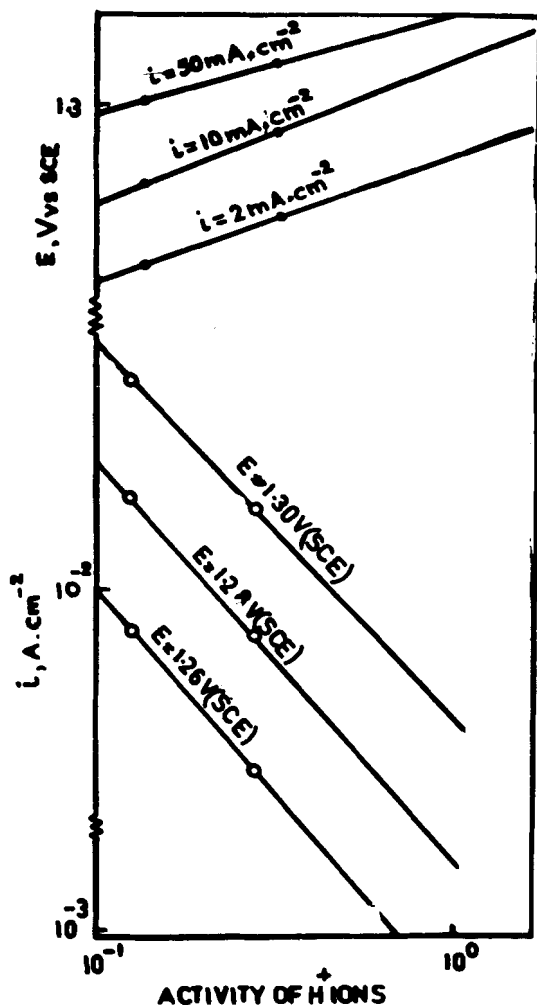


Figure 5 : Activity (a<sub>H<sup>+</sup></sub>) dependence of anodic potential at const. current density and of current density at constant potential for 30 mole % IrO<sub>2</sub> and 70 mole % ZrO<sub>2</sub> electrode in H<sub>2</sub>SO<sub>4</sub> solutions, Temp. 30°C

The same type of behaviour was observed in all electrodes containing more than 10 mole % of IrO<sub>2</sub>.

Table I: Electrochemical Parameters of IrO<sub>2</sub> Electrodes

Solution	Parameters	Ideal value	Observed value
Acidic	Anodic Tafel slope	0.06 V	0.059 V
	$(\delta E / \delta \log a_{H^+})_i$	+ 0.06 V	+ 0.063 V
	$(\delta \log i / \delta \log a_{H^+})_E$	- 1.0	- 1.20
Alkaline	Anodic Tafel slope	0.040 V	0.041 V
	$(\delta E / \delta \log a_{OH^-})_i$	- 0.040 V	- 0.040 V
	$(\delta E / \delta \log a_{OH^-})_E$	1.0	0.96

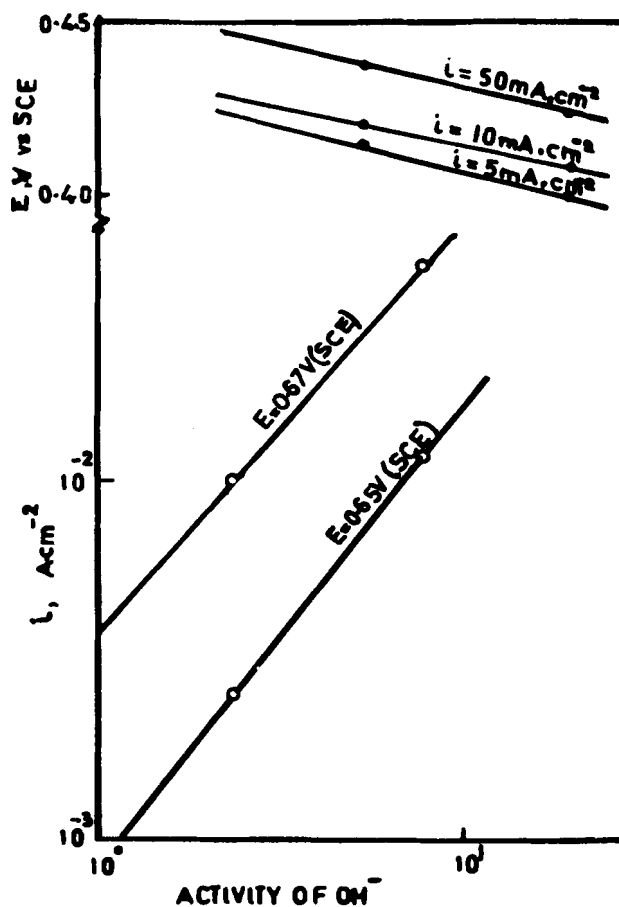


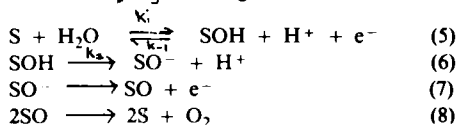
Figure 6 : Activity (a<sub>OH<sup>-</sup></sub>) dependence of anodic potential at constant current density and, of current density at constant anodic potential for 30 mole % IrO<sub>2</sub> and 70 mole % ZrO<sub>2</sub> electrode, Temp. 30°C

The typical electrochemical parameters both in acid and alkaline solutions for the 50 mole % IrO<sub>2</sub> : 50 mole % ZrO<sub>2</sub> electrodes are summarised in Table I.

On the basis of experimental parameters obtained, the theoretical rate expression for oxygen evolution in acid solution may be presented in a more convenient way as

$$E = \text{Constant} + (RT/F) \ln i + (RT/F) \ln a_{H^+} + \dots \dots (4)$$

The reaction mechanism may be deduced from the observed parameters under Langmuirian conditions of adsorption [12,13]. The suggested mechanism [14] involving surface site 'S' is:



The second step given in Eq. 5 is rate determining, and the overall current density is given as :

$$i = nF \frac{k_1 k_2}{k_{-1}} \cdot a_{H^+}^{-1} \cdot \exp\left(\frac{EF}{RT}\right) \dots \dots (9)$$

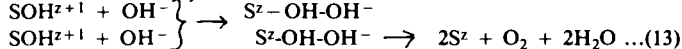
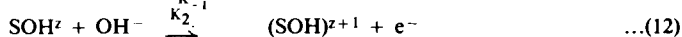
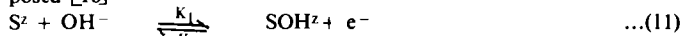
This is in good agreement with data obtained. The same observation was made on pure IrO<sub>2</sub> [15].

The mechanism for oxygen evolution in alkaline solution may be determined as above. From i-E relationships in alkaline solution, the plots of log i vs log a<sub>OH<sup>-</sup></sub> and E vs log a<sub>OH<sup>-</sup></sub> (Fig.6) can be obtained and respective slope values, (δ log i / δ log a<sub>OH<sup>-</sup></sub>)<sub>E</sub> (equal to about 1) and (δ E / δ log a<sub>OH<sup>-</sup></sub>)<sub>i</sub> (equal to about -0.04V) are obtained.

Based on the experimental parameters, the theoretical rate expression may be written as :

$$E = \text{Constant} + \frac{2 \times 2.3 RT}{3F} (\log i - \log a_{OH^-}) \quad \dots(10)$$

Under langmuirian conditions, the following mechanism has been proposed [16]



The second step (Eq.12) is assumed to be the rate-determining step and the overall current density is given as

$$i = nF \frac{k_1 k_{ij}}{k_{-1}} \cdot a_{OH^-} \cdot \exp \frac{(1 + \beta) EF}{RT}$$

This agrees well with Eq.10 by assuming 'β' is equal to ½.

**Accelerated service life**

From the plot of service life versus mole % of IrO<sub>2</sub> content (Fig.7) it is found that the service life increases up to 35 mole % of IrO<sub>2</sub>, beyond which the service life becomes constant up to 80 mole % of IrO<sub>2</sub> content and decreases thereafter. The 5 mole % IrO<sub>2</sub> electrode showed a very high overvoltage from the beginning and it failed within 10 hours of testing. But the maximum service life of about 500 hours was obtained for electrodes of 35 mole % to 80 mole % of IrO<sub>2</sub> content and only 300 hours was obtained for pure IrO<sub>2</sub> electrode.

The above data and test give an idea that the IrO<sub>2</sub> can be well stabilised by addition of ZrO<sub>2</sub> if the IrO<sub>2</sub> content is more than 35 mole % and less than 80 mole %. And above 80 mole %, the electrode could not get the required mechanical stability and a low service life of 300 hours was achieved; but below 35 mole %, the required amount of catalyst might not be available, and hence the life is insignificant.

It was found that iridium got deposited on the cathode during prolonged electrolysis. The presence of Ir was qualitatively identified with the help of electron probe microanalyser.

In NaOH solution, the IrO<sub>2</sub> becomes IrO<sub>4</sub><sup>2-</sup> and got deposited at the cathode; hence it may be assumed that during prolonged operation in 6M NaOH solution deterioration of IrO<sub>2</sub> takes place [17] to form IrO<sub>4</sub><sup>2-</sup> as given below

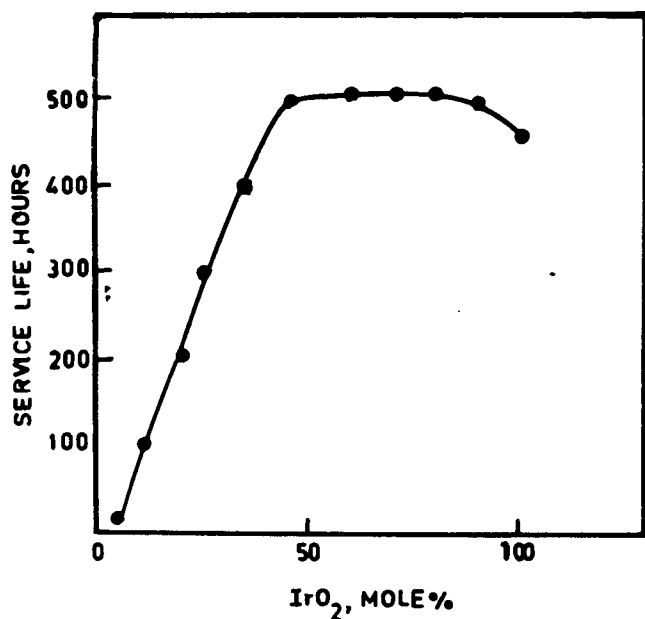
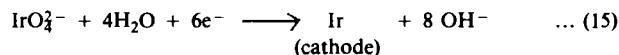
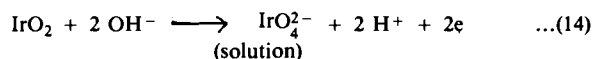


Fig.7 : Variation of service life in hours with mole % of IrO<sub>2</sub> content

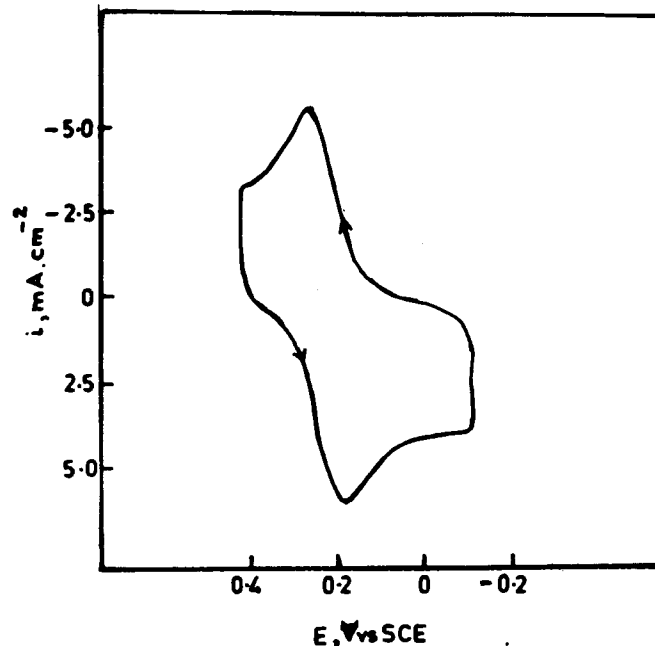


Fig.8 : Cyclic voltammogram for 20 mole % IrO<sub>2</sub> and 80 mole % ZrO<sub>2</sub> electrode in 0.05M K<sub>3</sub> Fe(CN)<sub>6</sub> in 1M KNO<sub>3</sub> solutions, sweep rate = 50 mV/sec, Temp. 30°C

**Ferri/ferrocyanide redox studies**

Figure 8 shows a typical cyclic voltammogram on IrO<sub>2</sub> electrode in 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1M KNO<sub>3</sub> solutions. A value of E<sub>p</sub> = 60 mV was obtained for one electron charge-transfer reaction of ferri-ferrocyanide system. The formal reduction potential was obtained as 0.2 V vs SCE.

The same type of cyclic voltammograms and E<sub>p</sub> = 60 mV were obtained in almost all electrodes containing more than 30 mole % of IrO<sub>2</sub>.

The same behaviour was observed in 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1M NaOH solution having E<sub>p</sub> = 60 mV and at the same (0.2 V vs SCE) formal reduction potential (Fig. 9).

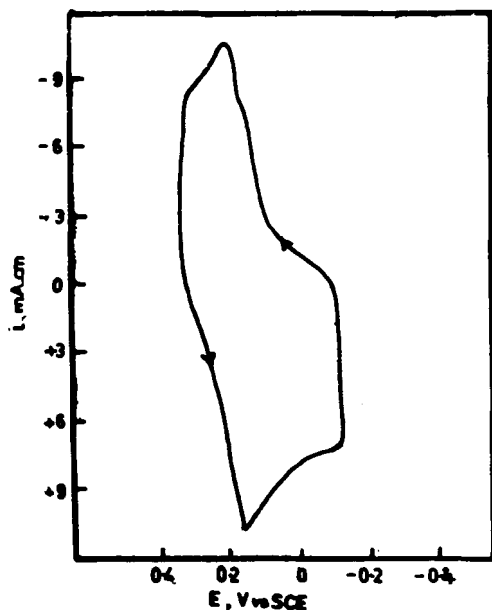


Fig.9 : Cyclic voltammogram for 20 mole % IrO<sub>2</sub> and 80 mole % ZrO<sub>2</sub> electrode in 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1M NaOH solutions, sweep rate = 50 mV/sec, Temp. 30°C

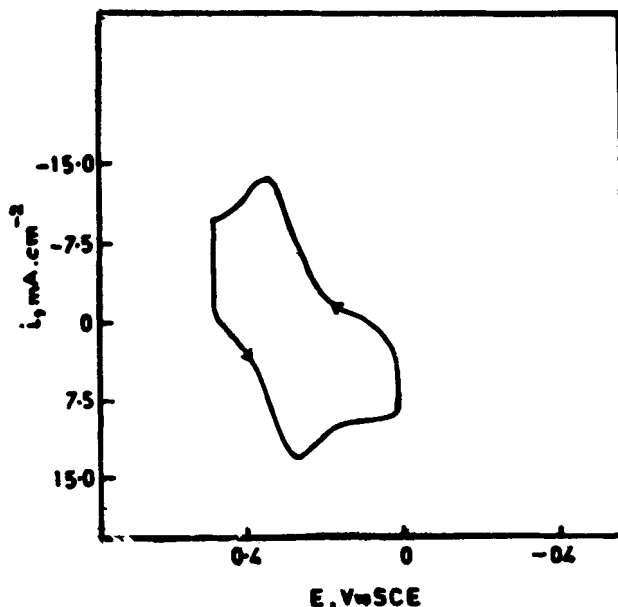


Fig.10 : Cyclic voltammogram for 20 mole % IrO<sub>2</sub> and 80 mole % ZrO<sub>2</sub> electrode in 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1M H<sub>2</sub>SO<sub>4</sub> solutions, Sweep rate = 50 mV/sec, Temp. 30°C.

In 0.05M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1M H<sub>2</sub>SO<sub>4</sub> solutions (Fig.10) E<sub>p</sub> value was about 60 mV, but the formal reduction potential was shifted to more than some 150 mV as the ferricyanide/ferrocyanide complex is not stable in acid medium and it represents purely a Fe<sup>3+</sup>/Fe<sup>2+</sup> system only [18]

**SUMMARY**

(i) The cyclic voltammetric behaviour of IrO<sub>2</sub>/ZrO<sub>2</sub> electrodes are similar to that of pure IrO<sub>2</sub> electrodes and four peaks are observed, which correspond to IrO<sub>2</sub> to Ir<sub>2</sub>O<sub>3</sub>; IrO<sub>2</sub> to IrO<sub>4</sub><sup>2-</sup>; IrO<sub>4</sub><sup>2-</sup> to Ir<sub>2</sub>O<sub>3</sub> and Ir<sub>2</sub>O<sub>3</sub> to IrO<sub>2</sub> reactions..

(ii) The reaction mechanisms for oxygen evolution are similar to that of pure IrO<sub>2</sub> electrodes in acid solutions, but the kinetic parameters and reaction mechanism observed in this investigation greatly deviates from earlier workers [13] in alkaline solutions in which a reaction order of 2 was obtained with respect to OH<sup>-</sup> ion activity (1M to 2M KOH). In the present studies (3M to 6M NaOH) the order of reaction is 1 and the reaction is followed by a different mechanism [14].

(iii) The service life of IrO<sub>2</sub> (35 mole %) electrodes can be well stabilised by the addition of ZrO<sub>2</sub> and life can be enhanced. During prolonged operation in alkaline media, deterioration of IrO<sub>2</sub> to soluble IrO<sub>4</sub><sup>2-</sup> occurs with possible deposition at the cathode as Ir or IrO<sub>2</sub>.

(iv) The ferri/ferrocyanide redox reaction was reversible even at the electrode of 10 mole % IrO<sub>2</sub> stabilised with ZrO<sub>2</sub> in neutral as well as in alkaline solutions.

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