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EVALUATION OF STABLE CATALYTIC ANODES FOR OXYGEN EVOLUTION IN SULPHURIC ACID

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The electrochemical activity and stability of Ti/(RuO_2-TiO_2)/ (RuO_2- MnO_2) anodes have been characterised employing steady state, cyclic voltammetric and galvanostatic accelerated polarization techniques in 0.5M H_2SO_4. Their dependence on composition of RuO_2-MnO_2 has been highlighted based on the comparison of the data obtained by the above techniques. Attempt has also been made to derive 'Stability index' and 'Activity' from cyclic voltammetry data.

Key words: Electrocatalysis, titanium supported anode, anode stability, stability index

INTRODUCTION

Oxygen evolution reaction is the most common anodic reaction in metal electrowinning. Usually 50-80% of the total cell voltage is accounted for by the anode. Hence reduction in cell voltage coupled with increase in life of the anode will result in considerable savings in the industrial practice. Appropriate characterization of anode materials is a prerequisite in order to develop suitable catalytic electrodes.

The various factors to be considered while developing catalytic anodes are already covered [1]. The significant impact due to the employment of a valve metal anode coated with "mixed-crystal oxides" of valve and noble metals in the chlor-alkali industry is very well known [2]. The use of such electrodes has also been attempted to electrowinning from sulphate solution [3]. In these, appreciable quantities of noble metal oxides which are scarce and expensive are used. Investigations to stabilise the same by incorporating non-noble metal oxides like zirconium, tantalum, manganese are being carried out [4-6]. In addition, the introduction of an interlayer has been considered to be beneficial [1,7] and given the lead for further development of catalytic anodes with long life. In this communication attempt has been made to characterise and evaluate Ti/interlayer/(RuO_2- MnO_2) anode by steady-state, cyclic voltammetry and galvanostatic accelerated polarization techniques.

EXPERIMENTAL

Test electrodes of 8 x 1 x 0.1 cm size of titanium were prepared and polished with emery paper down to 4/0 grade and degreased with alcohol. The intermediate layer of 25% RuO_2-75% TiO_2 (expressed in mole %) was formed over the polished specimen according to the procedures already described [1]. The load of Ru chosen for the formation of the intermediate layer as well as the top one was 3 g m^{-2} each. To form the top active coating, appropriate quantities of ruthenium chloride and manganese nitrate were taken in isopropyl alcohol to form the required concentrations of individual chelate solutions. Suitable proportions of solutions were mixed to have different compositions of Ru and Mn. Such chelate solutions were coated over the intermediate layer coated-titanium test electrodes (Ti/IL) by the usual thermal decomposition method.

The kinetic parameters were studied by steady-state measurements. The experiments have been carried out by first prepolarising the electrode at 900 mV vs Hg/Hg_2SO_4/0.5M H_2SO_4 for 2 minutes and allowing the electrode to attain equilibrium. The potential was then increased by 20 mV steps successively and the current read after 2 minutes at each potential.

The cyclic voltammetric experiments were carried out and from the data charge the total charge, oxygen evolution current stability and catalytic activity of the electrode were measured. The accelerated tests were carried out by galvanostatic polarization techniques at 5 kA m^{-2}. H-type cell and AR grade 0.5M H_2SO_4 were used at 303 K for all the experiments. The potential values are expressed with respect to Hg/Hg_2SO_4/0.5M H_2SO_4 reference electrode. All potential values were not corrected for iR drop.

RESULTS AND DISCUSSION

Tafel slope behaviour

Typical Tafel plots for oxygen evolution at various compositions of RuO_2-MnO_2 on Ti/IL electrodes are shown in Fig. 1. The general character of the polarisation curves is the same. In addition, it is observed that slopes are not appreciably varying with compositions. Considering a relationship between processes of oxygen evolution reaction and formation of soluble oxidised species of the coating, it could be suggested that the rate of electrochemical anode destruction begins to change in the potential region of the bend, which is termed as critical potential [8]. Hence if one wants to determine the service life by galvanostatic technique, a current density higher than the one corresponding to the critical potential should be applied.

Characteristics of cyclic voltammetry

Fig.2 shows the cyclic voltammogram of the Ti/IL anode having 30% RuO_2-70% MnO_2 as the outer layer. It is observed that oxygen evolution takes place at 800 mV and a hump is the reverse scan at 500 mV.

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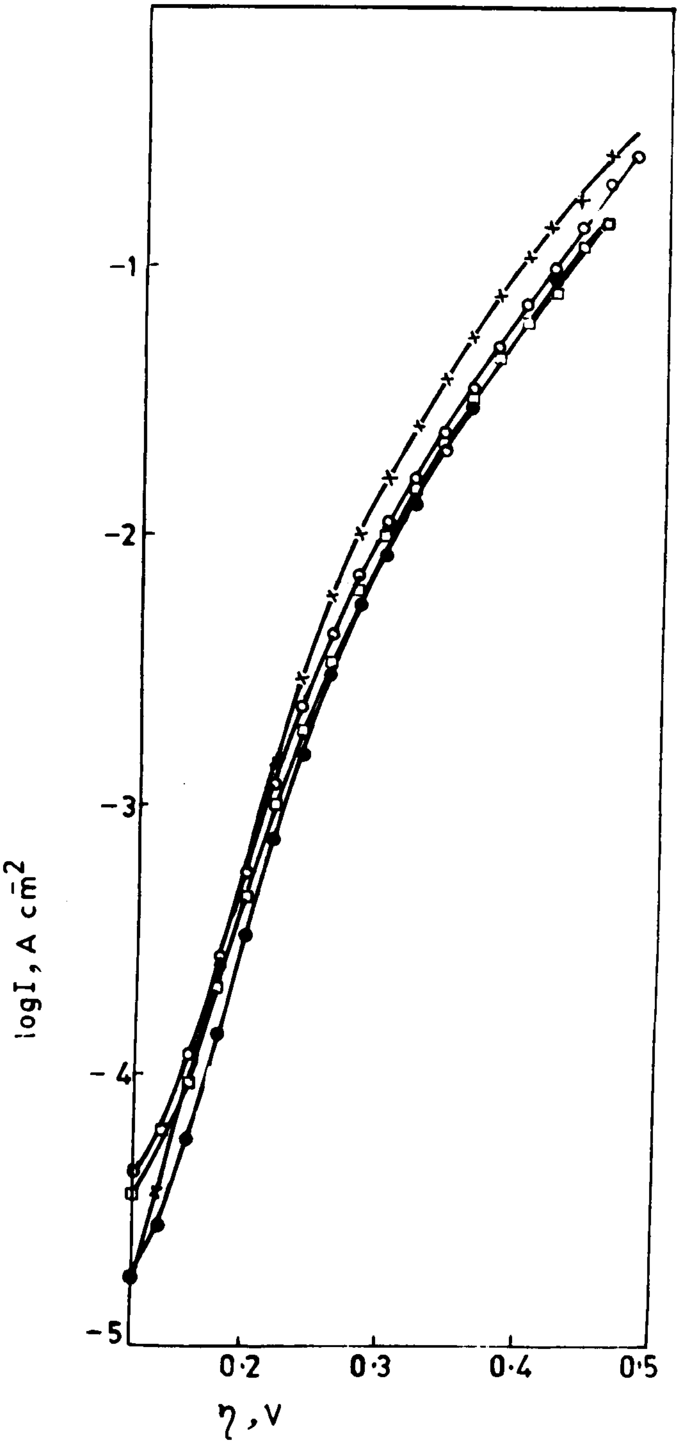

Fig 1 : Tafel plots for oxygen evolution at Ti/IL/(MnO_2 -RuO_2) in 0.5M H_2SO_4. Temperature 303 K. Mole % RuO_2 in the top layer (•)-95 (□)-80 (o)-60 and (x) -40.

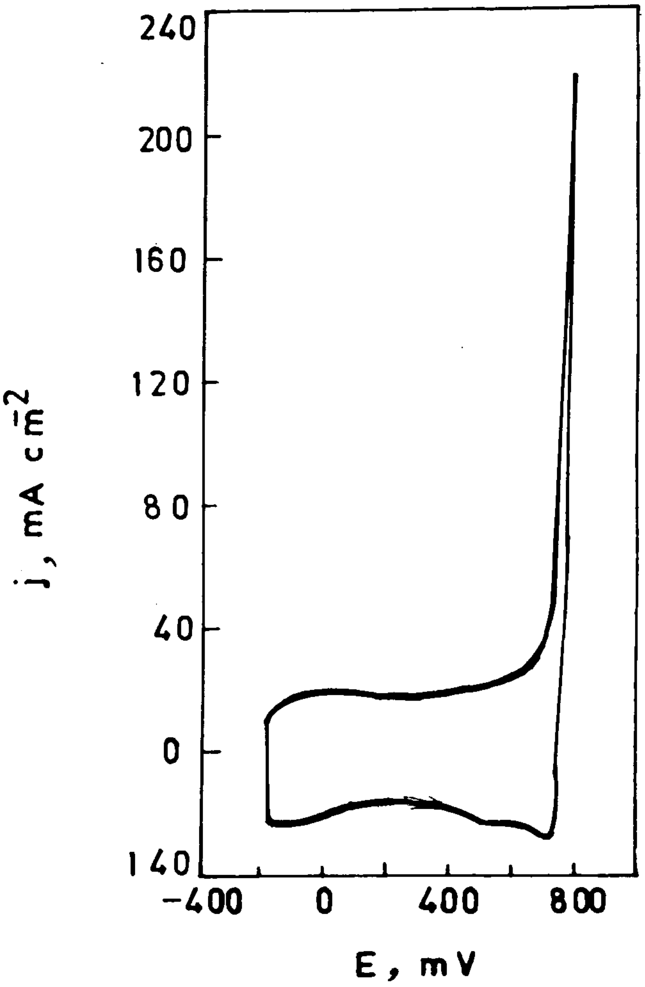

Fig. 2: Cyclic voltammogram in 0.5M H_2SO_4 of Ti/IL/(30% RuO_2-70% MnO_2); Scan rate: 300 mVs^{-1}

In electrocatalysis with oxides the strength of absorption of the oxygenated species and its desorption, is as a rule regarded as determining the electrocatalytic activity. The anode, when cycled between -200 and 600 mV acts as a pseudo capacitor [9] as shown in the Fig. 3. The electrode is reversible in the potential range studied at higher scan rate (cf.Fig. 3b). These results imply that this system is a good electrocatalyst.

Fig. 4 represents the behaviour of the anode when operated from -1000 to +800 mV. Hydrogen evolution is observed at -980 mV and a shoulder formation is found around 0 mV in the forward scan indicating the oxidation of some species. A comparison of the Figs.2 and 4 shows that the anode surface is not undergoing any appreciable change in the potential range of -200 to + 800 mV even though it was operated from hydrogen evolution to oxygen evolution region.

Influence of scan rate

Fig. 5 illustrates the effect of scan rate between the potential range - -700 and + 800 mV. It is found that the formation of a reversible

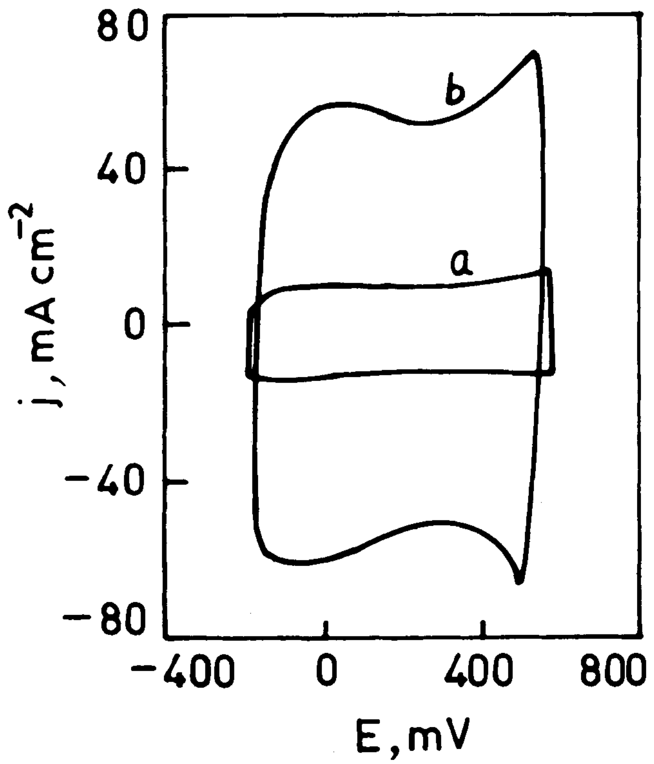

Fig.3: Charging curves plotted at different scan rates (a) 100 and (b) 500 mVs^{-1}

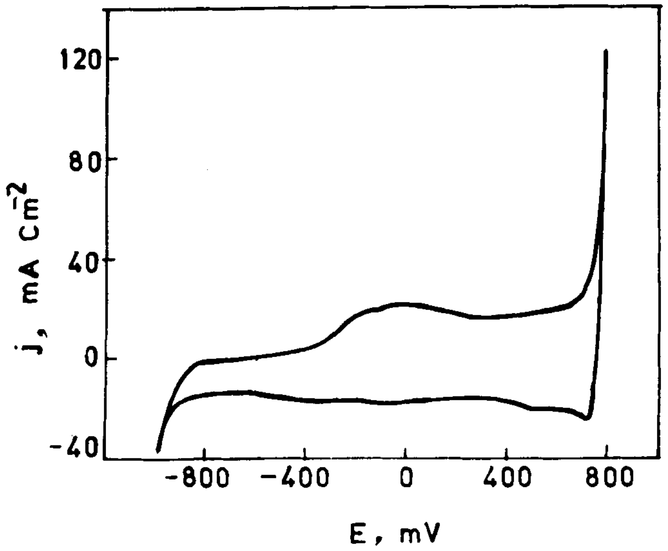

Fig. 4: Cyclic voltammogram obtained for Ti/IL/(30% RuO_2-70% MnO_2) in 0.5M H_2SO_4. Scan rate: 100mVs^{-1}. Range of the potential sweep covered is -1000 to +800 mV

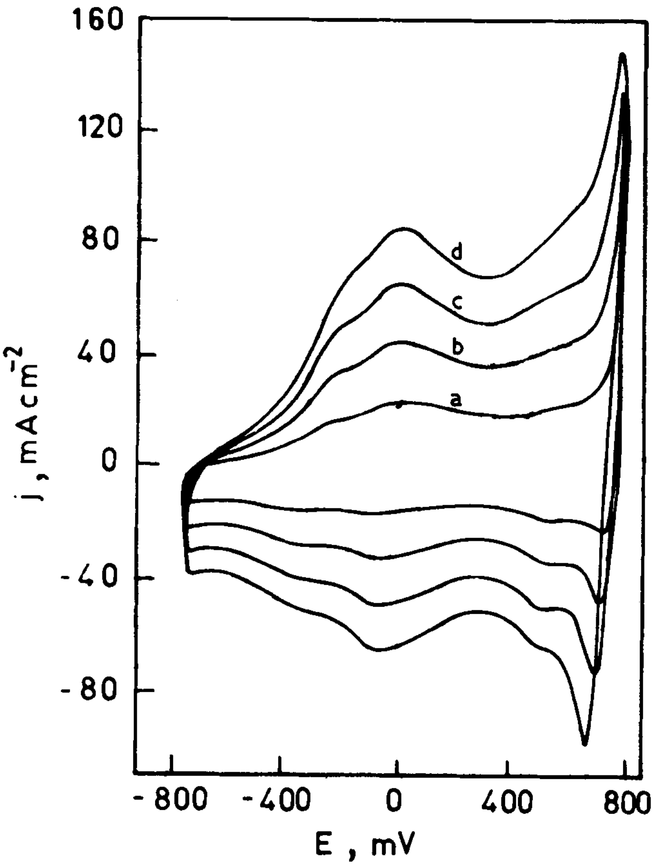

Fig. 5: Effect of scan rate on the CV curves obtained for Ti/IL/(30% RuO_2-70% MnO_2) in 0.5M H_2SO_4. Scan rate: (a) 100 (b) 200 (c)300 and (d) 400 mVs^{-1}

hump is perceptible around 0 mV with increased scan rate. The hump suggests the presence of an oxy-complex of Ru and Mn [10].

The small hump that emerges at 500 mV in the reverse scan of Fig. 2 becomes predominant as the scan rate is increased. The hump indicates the reaction Mn^{2+}/Mn^{4+} which is corroborated by the thermodynamic data [10].

Determination of overpotential of oxygen

Fig. 6 denotes the cyclic voltammograms of the systems Ti/IL, Ti/IL/RuO_2, Ti/IL/(30% RuO_2-70% MnO_2). It is inferred that the values of ηO_2 for electrodes marked I, II and III are 340, 280 and 220 mV respectively. Keeping the substrate and the composition of the intermediate layer as constant, introduction of MnO_2 to the extent 70 mole % to RuO_2 leads to a further lowering of η O_2 to the extent of 60 mV. This significant observation is worth pursuing from the point of view of energy saving.

Surface area and activity

The voltammetric charge of an insoluble anode can be a measure of its active surface area. Fig. 7 represents the relationship

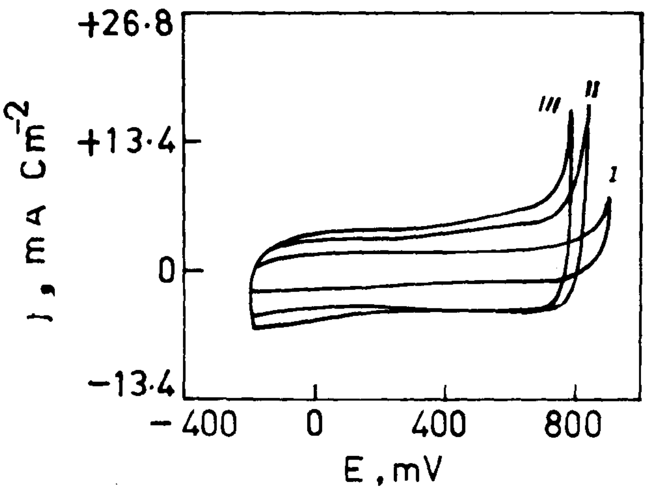

Fig. 6: Cyclic voltammograms of:I-Ti/IL, II-Ti/IL/RuO_2, III-Ti/IL/(30% RuO_2 – 70% MnO_2), Scan rate 100 mVs^{-1}

between the bulk composition vs the anodic charge density. A maximum value is obtained at 70% MnO_2-30% RuO_2. Similar characterization has also been reported for RuO_2-ZrO_2 electrodes [4]. The influence of the composition on the total charge also follows the same trend.

Hitherto it is practice to determine the overall performance of an anode based on the results of the accelerated polarization tests in highly aggressive electrolyte [1,11,12]. A novel approach is attempted to fix up the optimum compositions of a catalytic anode which will have maximum stability by cyclic voltammetric study.

The oxygen evolution current at constant potential is considered as the measure of the catalytic activity [5,13]. This is applicable for an ideal insoluble anode where 100% current goes towards oxygen evolution. In case of anodes where current efficiency for oxygen evolution is < 100% the oxygen evolution current measured at constant potential will not wholly represent the catalytic activity. However, this may be taken as an index for catalytic activity provided the contribution by the side reaction is negligible.

Fig. 8 gives the dependence of activity (j) and charge ratio (Q_a/Q_c) which may reflect on the stability index with composition. It is observed that from 95% to 40% RuO_2, the stability of the anode is more or less the same (curve-1), while the activity (curve-2) shows the increasing trend appreciable. This reveals that incorporation of MnO_2 increases the electrocatalytic activity indicating an increase in the active centres. The activity is predominant between 95% and 40% RuO_2. Both (Q_a/Q_c) and activity approach maximum at 30% RuO_2-70% MnO_2 under the experimental conditions. Further increase in MnO_2 is not beneficial. Results of accelerated polarization tests support this finding. The relationship between Q_a/Q_c(calculated from the cyclic voltammetric curve) and life agrees well in the case of RuO_2-ZrO_2 system [4] also.

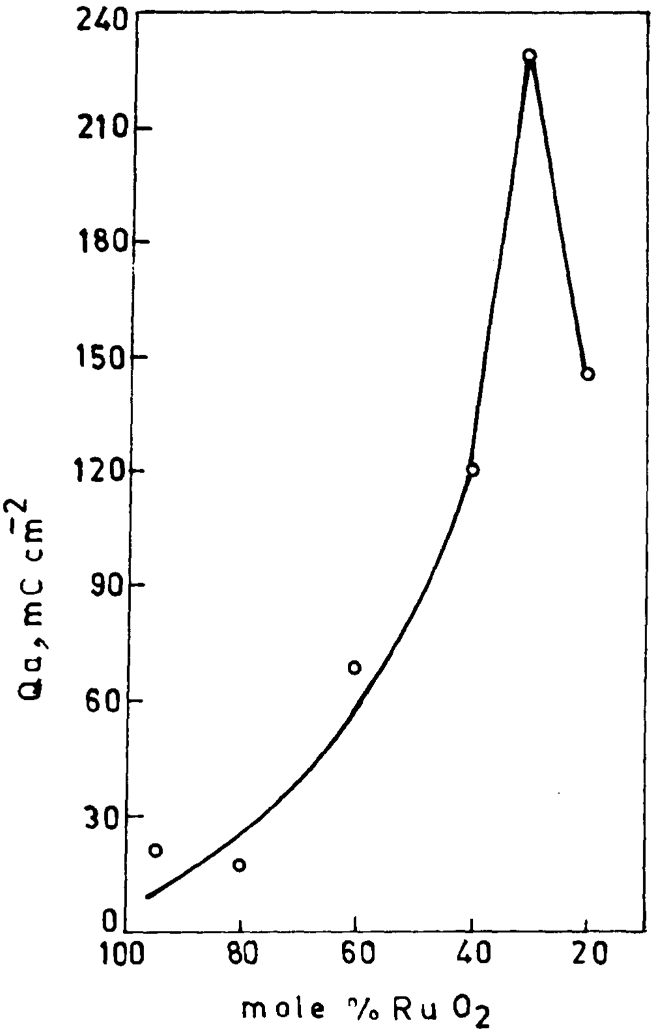

Fig.7: Relationship between composition vs anodic charge density

Accelerated polarization test

Fig. 9 shows the relation between life and composition. The service life has been determined by procedures described elsewhere [1]. It can be seen that incorporation of 70% MnO_2 to the RuO_2 doubled the service life. Electrodes containing other compositions in the coating have inferior performance. All electrodes operate at potentials approximately 1.1V which is greater than the critical potential ∼0.8V (cf.Fig. 1) right from the beginning of polarization thereby promoting dissolution and breakdown of the oxide layer. However, it is evident from the results that life is maximum at 30% RuO_2-70% MnO_2. This may be due to the fact that 30% RuO_2 and 70% MnO_2 form a homogeneous crystallochemical system of its own with improved physical, chemical and electrochemical properties so as to exhibit maximum catalytic activity and stability.

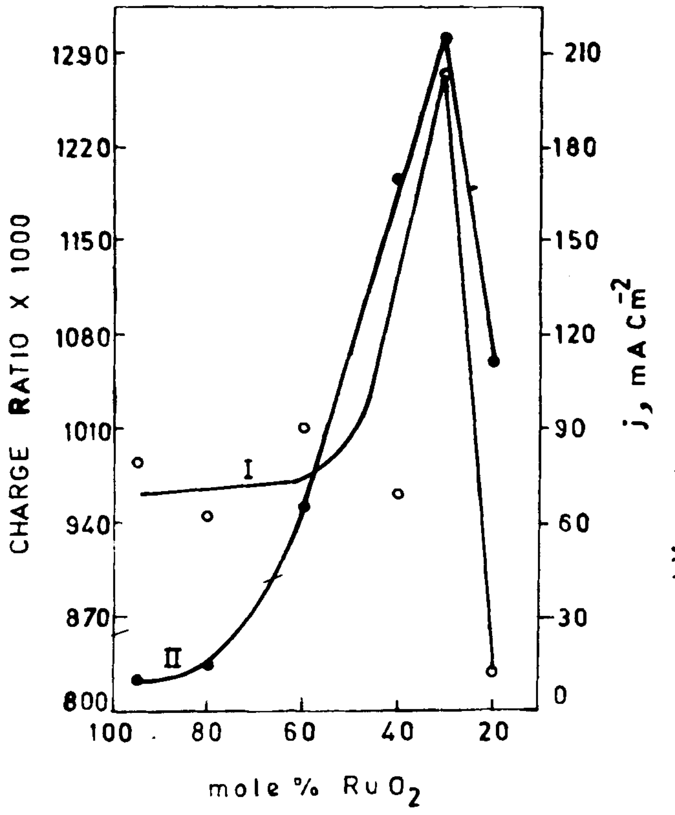

Fig. 8: Dependence of activity (j) and charge ratio (Q_a/Q_c) with composition

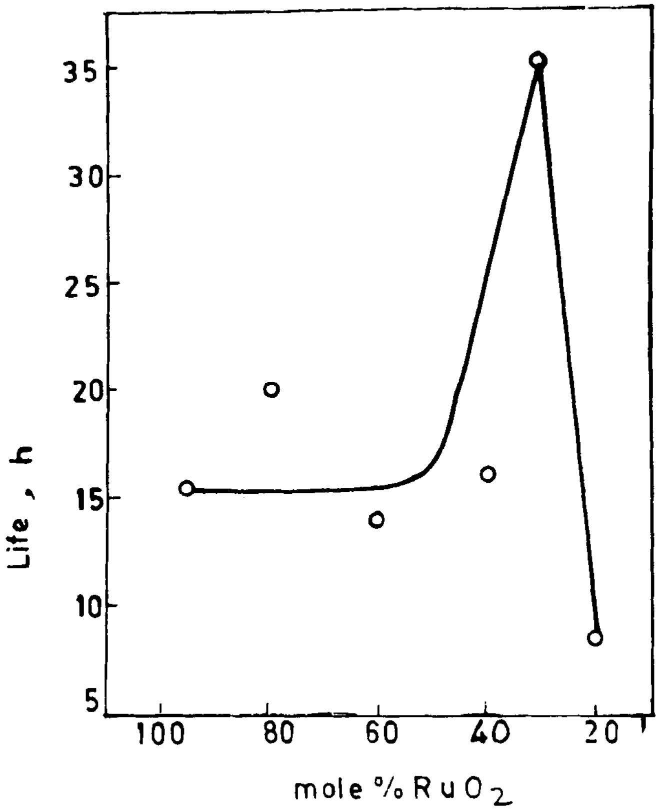

Fig. 9: Relationship between life and composition

CONCLUSION

Incorporation of 70% MnO_2 to RuO_2 on a Ti substrate already coated with fixed composition of "mixed-crystal oxides" of Ti and Ru substantially increased the service life of anodes with respect to oxygen gas evolution and lowers the oxygen overpotential. Tafel slopes do not vary appreciably with composition. Determination of activity and stability index lends itself as an additional tool in arriving at optimum composition.

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