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"Stability Index" of Oxide Coated Titanium Anodes – A Novel Approach by Cyclic Voltametric Technique

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The significance of the oxide coated titanium anodes is mentioned. The importance of the accelerated polarization experiments to find out the life of the anode is indicated. The cyclic voltammetric behaviour of two different anode systems viz. Ti/(Ir-Co) and Ti/IL/(Ru-Mn) of different compositions was studied. The influence of temperature on the surface nature of the Ti/(Ir-Co) anodes is also found out by cyclic voltammetric technique. A novel approach to assess the stability of the anodes was attempted using cyclic voltammetric technique and compared the same with that of the conventional accelerated polarization tests. A linear relationship is found between the life of the anode and stability index. The technique adopted for finding out the life of the anode using accelerated polarization experiments is a time consuming one whereas the proposed 'stability index' method based on cyclic voltammetric experiments is a novel and expedient one.

Key words: Anode life, cyclic voltammetry, catalytic anodes, stability index

Introduction

For several industrial electrochemical processes involving oxygen evolution in acidic media such as electroplating, electrowinning and electrosynthesis, the selection of the anode material is a critical problem [1]. DSA-type electrodes, made of titanium base metal coated with platinum group metal/oxide catalysts are now widely used as anodes. The electrochemical behaviour of titanium as well as electrocatalytic oxides coated titanium anodes has been extensively studied [2-14].

The behaviour of the anode can be quantified by the stability of the working potential with respect to reference electrode. This can be defined as the ability of the anode to maintain its working potential constant under galvanostatic conditions in long term performance. In practice, the voltage between the working electrode and the counter electrode is measured as a function of time. Unfortunately, the estimation of the real service life of electrodes needs a prolonged period almost covering a field trial duration. Therefore, this parameter is often estimated by accelerated tests, which have the advantage of providing a quick answer on a laboratory scale. However, even this sort of experiment takes a very long time from several hundred hours to thousand hours at a very high current density in aggressive electrolytes. Thus, the duration of experiments alone, to find out the optimum composition of an anode system, will be sufficiently longer than a month. To obviate this problem, a novel approach is attempted to find out optimum composition/condition of an anode system in a test way by cyclic voltammetric technique.

Experimental

Titanium specimens with dimensions of 8.0 x 1.0 x 0.1 cm were mechanically polished with emery papers of OK brand, 0/0-4/0, moistened with isopropanol. Three sets of test electrodes were prepared. For the first set, the chloride salts of Co and Ir were taken in isopropyl alcohol in different proportions, brush coated over the polished titanium strips, dried at about 80 °C and baked at 500 °C for 10 min. The process of coating, drying and baking was repeated until all the chelate had been consumed. Electrodes thus prepared for each composition were finally annealed at 500 °C for one hour. Another set of electrodes were prepared with optimum composition (70 at % Ir - 30 at % Co) at various temperatures. In both the sets, the load of Ir was kept constant. A third set of electrodes viz Ti/IL/(Ru-Mn) were prepared as mentioned elsewhere [15]. Accelerated polarisation and cyclic voltammetric studies were carried out for the electrodes of each set.

In the case of electrochemical investigations, a working electrode with a geometrical area of 1 cm^2 was obtained by stopping off the rest. Electrodes were polarised at 30 °C in 1N H_2SO_4 using a simple H-type cell, the counter electrode being a cylindrical platinum wire gauze of large surface area. A fresh working electrode was used for each experiment. In the case of accelerated polarization tests, the electrodes were galvanostatically polarized at 1500 mA cm^{-2}; the length of time before a sharp rise in the anode potential occurs, is termed as the service life of the anode.

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The span of potential investigated in the cyclic voltammetric experiments was between –750 mV and +950 mV vs Hg/Hg_2SO_4/1 N H_2SO_4, at different sweep rates as mentioned in appropriate places. The anodic and cathodic charges viz. Q_a SP Q_c were calculated from the cyclic voltammograms by integrating the area using planixmeter.

Results and discussions

Activity and surface nature

Figure 1 represents the cyclic voltammograms of the anodes of (Ir-Co) systems with different composition. Curve 1a is the cyclic voltammogram of Ti/100% IrO_2 in 0.5 M H_2SO_4 in the potential range of hydrogen and oxygen evolution. The nature of the CV remains almost unaltered in general upto 30 at % cobalt oxide. However, further increase leads to a change indicating an adverse effect which is felt both in activity and service life (stability) as found in the Table 1. The activity and stability are maximum at (70 at % Ir- 30 at % Co).

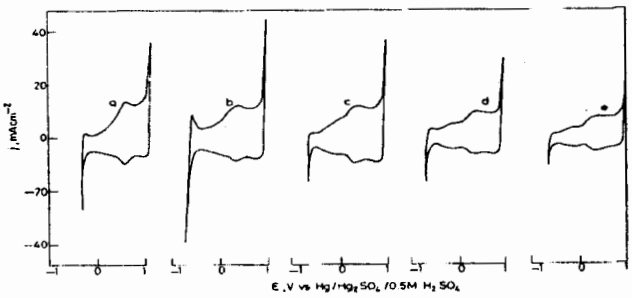

Fig.1. Influence of incorporation of cobalt oxide to IrO_2 in Ti/(Ir-Co) anode.
a) 100 % Ir, b) 70 at % Ir-30 at % Co, c) 60 at % Ir-40 at % Co, d) 40 at % Ir-60 at % Co, e) 20 at % Ir-80 at % Co, Scan rate: 100 mVs^{-1}

Table 1. Data relating the composition and the service life of (Ir-Co) anodes at 15 KA m^{-2} in 0.5 MH_2SO_4.

No.	Compn. of Ir in Ir-Co anode systems (%)	Service Life (h)	Activity i_{PO2} (mA cm^{-2})
1	100	0.2	----
2	90	--	15
3	80	5.2	----
4	70	7.8	29
5	60	4.0	25.5
6	50	----	----
7	40	5.7	18
8	20	2.3	15.4

The voltammograms (Fig. 2) of the anodes having the composition of (70 at % Ir-30 at % Co) prepared at different temperatures, depict the influence of temperature on the changes in the surface nature. It is seen from the Table 2 that the value of the total charge decreases as the temperature is increased and the anodic peak current ipO_2 (activity) for oxygen evolution also follows the same trend.

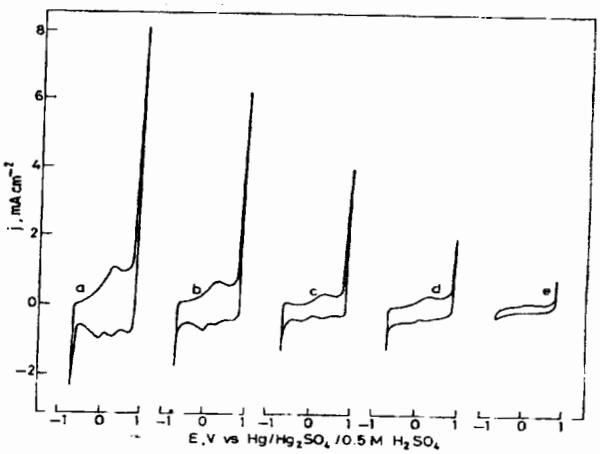

Fig.2. Cyclic voltammogram of Ti/(Ir-Co) prepared at different temperatures. a) 500 °C, b) 550 °C, c) 600 °C, d) 650 °C and e) 700 °C. Scan rate: 100 mVs^{-1}

Table 2. Effect of temperature on total charge and oxygen evolution current (ipO_2) of Ti/(Ir-Co) anode.

No.	Temp. (°C)	Total Charge (mC)	O_2 evoln. Current, i_{PO2} (mA cm^{-2})
1	500	228.8	9.0
2	550	166.9	7.3
3	600	110.6	4.0
4	650	87.5	2.3
5	700	37.5	0.8

Figure 3 represents the reverse scan of the Ti/(70 at % Ir-30 at % Co) prepared at different temperatures. A well defined peak at 100 mV is more predominant below 600 °C and the same is vanishing above 600 °C. The anodes prepared at low temperatures dissolve comparatively easily and hence its contribution in terms of dissolution current will be greater. Both these factors viz. dissolution current and O_2 evolution current together accounts for higher i_pO_2 for anodes prepared at low temperatures. In addition, the formation of well defined peaks in the reverse scan may correspond to the adsorption of the dissolved species of the oxides of Co/Ir (Fig.3) which occurred during the simultaneous

processes of anodic dissolution and oxygen evolution. The contribution due to sintering effect of the electrocatalyst during the preparation of the anodes at higher temperature results in lower surface area (viz. charge) and lower activity (viz. i_pO_2) as indicated in Table 2. Thus the anode prepared at 600 °C possesses good stability and activity due to the minimum dissolution during oxygen evolution.

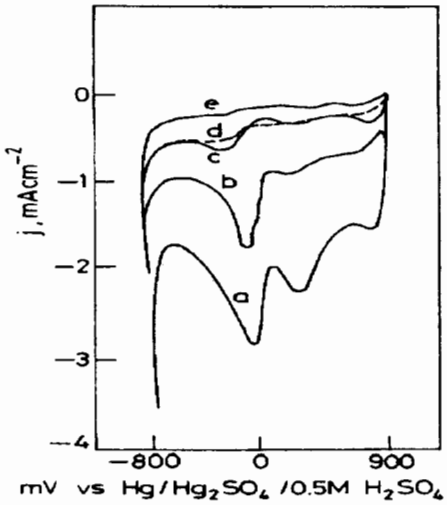

Fig. 3. Reverse scan of the cyclic voltammogram of Ti/(Ir-Co) anodes prepared at different temperatures. Scan rate: 100 mVs^{-1} a) 500 °C, b) 550 °C, c) 600 °C, d) 650 °C and e) 700 °C.

It is reported in the literature that the oxygen evolution current at constant potential is considered as the measure of catalytic activity [16, 17]. This is applicable for an ideal insoluble anode where 100% current goes towards oxygen evolution alone. In the case of anodes where current efficiency for oxygen evolution is less than 100%, the oxygen evolution current measured 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.

Stability index

Hitherto it has been the practice to determine the overall performance of an anode based on the results of the accelerated polarisation test in highly aggressive electrolytes [18]. It is obvious that during oxygen evolution, a portion of the current will be accounted for the dissolution of the anode and the dissolved species will be adsorbed at the surface which can be identified in the reverse scan of cyclic voltammetry. However, the interfacial phenomena is complicated one. Since there may occur varied types of reactions, very slow to fast, it is likely to miss the electroactive species of the dissolved oxides of the anode if the scan rate is arbitrarily chosen.

Hence each composition of the anode system viz. (Ir-Co) was subjected to different scan rates and the voltammetric behaviour was studied. The anodic/cathodic charge ratio was calculated using Planix integrator and its relationship with scan rate is given in Fig.4. Portions of the curves are parallel to the X-axis for scan rates higher than 100 mV/s. But it is quite interesting that the behaviour of the electrodes is complicated at lower scan rates the cause of which is not clear at present. Hence, for comparison and characterisation of the present anode systems, application of higher scan rates (100-300 mV/s) is preferable.

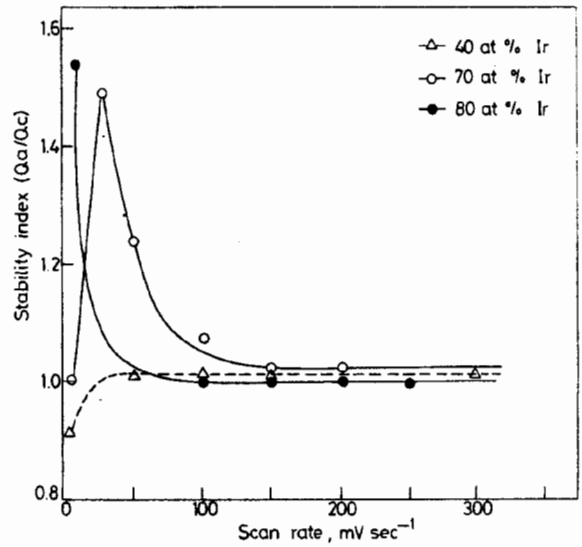

Fig.4. Scan rate vs stability index (Q_a/Q_c) for Ti/(Ir-Co) anode.

Since the adsorption of the dissolved species could be sensed in the cathodic sweep, they could be encountered in the cathodic charge also. That is, if the dissolution is more, the cathodic charge will be higher. Or, in other words, if the charge ratio Q_a/Q_c is higher, dissolution of the anode will be lower and vice versa. Hence the charge ratio (Q_a/Q_c) could be taken as an indication of the stability of the anode and is denoted as the stability index.

Therefore, under this assumption, charge ratio was calculated for all the compositions of Ti/(Ir-Co) system and their relationship is presented in Fig.5. It is found that the charge ratio, otherwise known as the stability index derived from cyclic voltammetric experiments, follows the same trend as that of the service life obtained by conventional accelerated polarisation experiments. (cf. Table 1). The optimum composition of the anode is 70 at % Ir-30 at % Co as found by the two techniques.

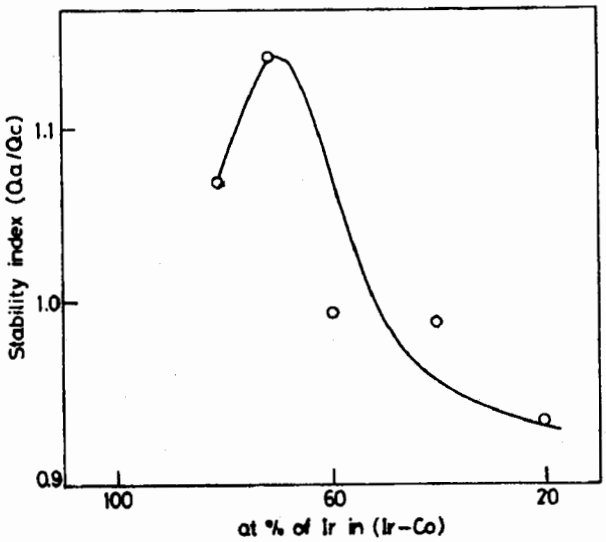

Fig 5. Influence of composition of Ti/(Ir-Co) anode on the stability index (Q_a/Q_c), Scan rate: 100 mVs^{-1}

Figure 6 represents the influence of the temperature of preparation of the It/(Ir-Co) anode having the optimum composition on the stability index. The stability of the anode is maximum at 600 °C which is in concordance with the life of the anode obtained from the accelerated polarisation experiments as seen from the inset in the figure.

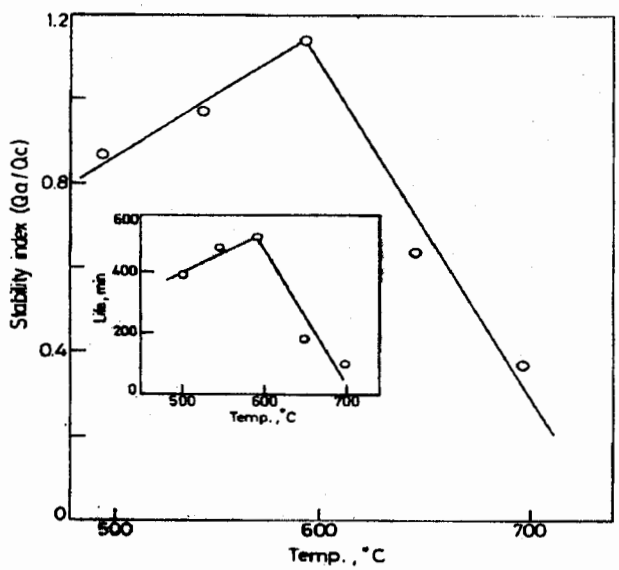

Fig.6. Influence of temperature of preparation of Ti/(Ir-Co) anode system having the optimum composition on the stability index.

Load of Ir: 1 g m^{-2}; Electrolyte: 0.5 M H_2SO_4; Set potential: -750 to +950 mV vs $Hg/Hg_2SO_4/H_2SO_4$; Scan rate: 100 $mVsec^{-1}$

Inset: Influence of temperature of preparation of the Ti/(Ir-Co) anode system on the service life obtained by accelerated polarisation experiments.

Load of Ir: 1 gm^{-2}; electrolyte: 0.5 M H_2SO_4; Current density: 1500 $mAcm^{-2}$;
Temperature: 30 °C

Similar attempts were made for the other anode systems like Ti/IL/(Ru-Mn) and it is found that fixing up of the optimum compositions/conditions from the present stability index method holds good (Fig.7). Hence for a particular anode system, the value of the charge ratio can be taken as the index of stability.

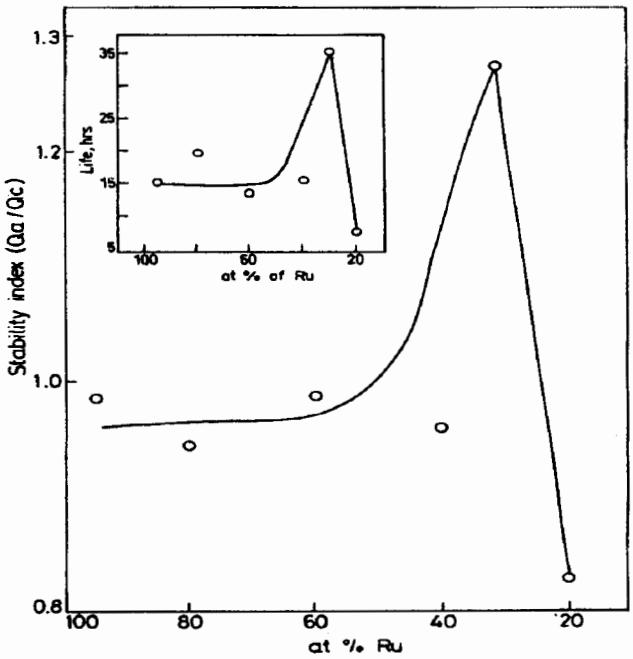

Fig.7. Influence of composition of Ti/IL/(Ru-Mn) anode system on the stability index obtained by cyclic voltammetric experiments

Load of Ru: 3 gm^{-2} in the inter layer (IL) and 3 gm^{-2} in the active layer
Electrolyte: 0.5 M H_2SO_4; Set potential: -750 mV to + 950 mV, Scan rate: 100 mVs^{-1}

Inset: Influence of composition of the anode system and the service life.

Load of Ru: 3 g m^{-2} in the inter layer (IL) and 3 g m^{-2} in the active layer; Electrolyte: 0.5 M H_2SO_4; Anode current density : 1500 $mAcm^{-2}$; Temperature: 30°C

Figure 8 represents the relationship between the stability index (Q_a/Q_c) and service life of Ti/(Ir-Co) anodes. A linear relationship is found. The same behaviour is also found for Ti/IL/(Ru-Mn) systems (Fig.9). This indicates that the charge ratio and the life of the anode are directly proportional to each other.

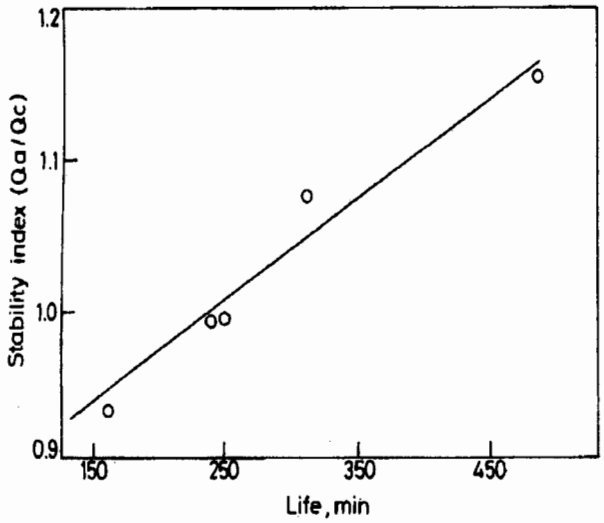

Fig.8. Service life vs stability index (Q_a/Q_c) of Ti/(Ir-Co) anode. Scan rate: 100 mVs^{-1}

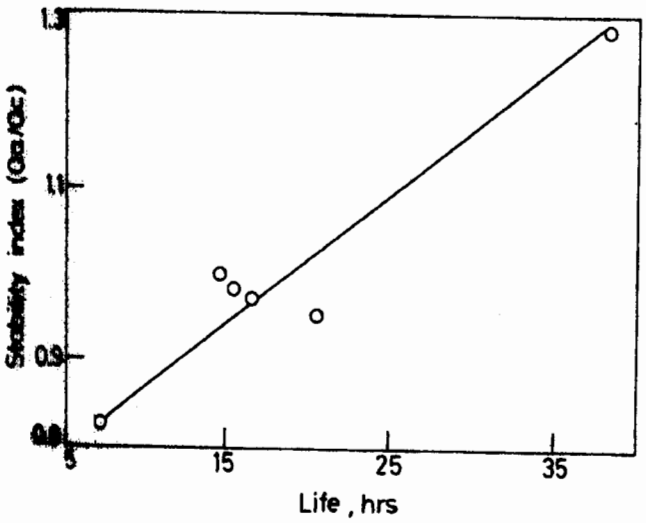

Fig.9. Service life vs stability index of the Ti/IL/(Ru-Mn) anodes. Scan rate: 100 mVs^{-1}

Even though there is no literature evidence for our findings, we attempted to verify the same with the available two cyclic voltammograms and the corresponding lives of two compositions of (RuO_2-ZrO_2) anode systems as detailed below.

The service life and the corresponding cyclic voltammograms of (RuO_2-ZrO_2) system (Fig.10) for two compositions viz. 80 and 20 mole % Ru available in literature [19] were taken as such, calculated the charge ratio and compared with the corresponding lives as found in Table 3. It is found that this is in conformity with our present finding viz higher the charge ratio higher is the anode life.

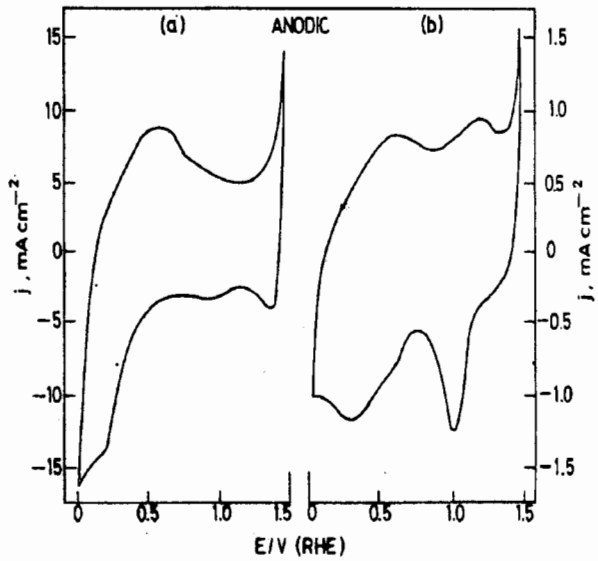

Fig.10. Cyclic voltammograms (potential span : 0-1.50, scan rate : 30 mV sec^{-1}) recorded for (RuO_2-ZrO_2) coated titanium anodes in nitrogen stirred 6 mol dm^3 NaOH [19].
Temp: 80 °C, Oxide loading: 4 $mgcm^{-2}$, Oxide film composition: a) 80 mol% RuO_2 and b) 20 mol% RuO_2

Table 3. Data on composition, service life and calculated stability index (Q_a/Q_c) of (RuO_2-ZrO_2) anode system.

No.	Compn. mol % Ru	Life (h)	Stability Index
1	80	215	1.14
2	20	5	0.947

Conclusion

The ipO_2 is the measure of catalytic activity for an ideal insoluble anode where 100% current goes towards the oxygen evolution. In other cases, the current measured at the oxygen evolution potential includes both the dissolution current and oxygen evolution current. However, this may be taken as an index for catalytic activity provided the contribution by the side reaction is negligible. Even though the accelerated polarization experiments are adopted as conventional tool for fixing up the optimum composition/conditions, it is a time consuming one. But the proposed "Stability Index" method, based on cyclic voltammetric experiments is a novel and expedient one.

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