The pH-dependence of thermally-coated Ti/TiO$_2$ electrodes in the absence and presence of nitrobenzene

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Cyclic voltammetric measurements on thermally coated Ti/TiO$_2$ electrodes in 0.05–3.0 M H$_2$SO$_4$, Na$_2$SO$_4$ and NaOH media were carried out to evaluate the cause of pH sensitivity of these electrodes. The electrode activity decreased in the order H$_2$SO$_4$ > NaOH > Na$_2$SO$_4$. Ionic strength had a significant influence on the electrode activity. In the redox catalysis of nitrobenzene reduction the pH dependence increased significantly. The electrode activity again decreased in the same order. In acid media the TiO$_2$ surface is protonated. In alkaline media OH$^-$ ions are specifically adsorbed on the TiO$_2$ surface. The concentration of these charged species, as well as the ease of counter ion transport through the charged layers during surface redox reactions in the oxide layer, is identified as the cause of the pH sensitivity of the electrodes. In acid media proton transport in the film occurs through a 'surface Grothus'-like mechanism. In alkaline medium proton abstraction by OH$^-$ ions from the trapped H$_2$O molecules may facilitate proton transport.

1. Introduction

The formation of a passive, compact oxide layer on titanium during anodic polarization is well known [1]. The photochemical properties of this n-type semiconductor [2, 3], including surface modification by ion-implantation [4, 5] and incorporation of redox mediators [6], have received considerable recent attention. Prevention of the formation of passive TiO$_2$ interlayers on dimensionally stable anodes in chlor-alkali cells has also been studied. Comprehensive reviews dealing with the physiochemical [7] and electrochemical investigations [8] in this area are available. However, during cathodic polarization, the pyrolytic Ti/TiO$_2$ electrode does not exhibit any inhibition to electron transfer [9]. This is mainly due to the presence of a mixed oxide system containing TiO$_2$, Ti$_2$O$_3$, TiO and Ti$_4$O$_7$ suboxides [1, 10, 11] which can readily undergo redox transitions in the cathodic potential regions. In HNO$_3$ media, for example, a Ti/TiO$_2$ cathode is successfully employed in the Purex process [12, 13]. In H$_2$SO$_4$, thermally coated Ti/TiO$_2$ electrodes exhibited heterogeneous redox catalytic properties towards the reduction of nitrobenzene [14, 15]. Recent investigations indicated that these electrodes can be effectively used for the reduction of a number of other aromatic nitrocompounds in H$_2$SO$_4$ media [16]. Despite these successes of thermally coated Ti/TiO$_2$ cathodes in acidic media their potential uses in neutral and alkaline media have not yet been examined. The pH sensitivity at rest potential has been briefly examined by impedance measurements [17]. However, the effect of pH on the electrochemical activity of Ti/TiO$_2$ electrodes during cathodic polarization has still to be investigated.

While investigating the cyclic voltammetric behaviour of over a dozen substituted aromatic nitrocompounds on thermally coated Ti/TiO$_2$ electrodes [16], m-nitrobenzene sulphonic acid (MNBSA) alone was found to give a strong reactant adsorption peak in acidic media. Further studies on the pH sensitivity of this adsorption peak confirmed that the peak was due to the acid-base interaction between the oxide layer of the electrode and the MNBSA function of the reactant molecule [18]. During this study, the electrochemical response of the Ti/TiO$_2$ electrode itself was found to depend significantly on the medium pH. In the present work an attempt is made to evaluate the cause of this pH dependence by studying the effect of pH and ionic strength on the cyclic voltammetric responses. For studying the heterogeneous-redox catalysis, nitrobenzene (which does not exhibit any separate adsorption peak like MNBSA) is employed. In addition to cyclic voltammetry, some impedance measurements to evaluate the adsorption effect on electron transfer are also reported.

2. Experimental details

High purity titanium sheets (Imperial Metal Industries Ltd, IMI-125 grade) of 1 cm × 5 cm dimensions were used for the preparation of thermally coated Ti/TiO$_2$ working electrodes. The procedure was a slightly modified version of that of Beck and Gabriel [14]. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Titanium sheet was sand blasted, treated with 50% HCl at 90 °C for 1 h, washed and dried. The activated titanium metal strip

was dipped in a solution of 0.05 M titanylacetylaceto-nate in isopropanol containing 7.5% (v/v) HNO₃, dried at 100–110 °C for 10 min and then heated at 500–550 °C for 25 min so that an oxide layer formed. The above coating and drying cycle was repeated at least five times to ensure a good coating of TiO₂ on the titanium. The electrode surface was covered with PVC adhesive tape, leaving an exposed area of 0.28 cm².

A Wenking potentioscan (Model 75L FRG) coupled with Rikadenki X–Y recorder (model 101T, Japan) was employed for cyclic voltammetric measurements. Impedance measurements were carried out using a Solartron instrument (PAR model 368-1 a.c. impedance system).

For ensuring reproducibility, each experiment was verified using three electrodes prepared under identical conditions. A reproducibility of ± 10 mV in potential and $\pm 3\%$ in peak current values was achieved in these experiments. All other experimental details and the cell employed have been described previously [18].

3. Results and discussions

3.1. The effect of pH on the surface redox reaction

Typical cyclic voltammograms for the thermally coated Ti/TiO₂ electrode in 1.0 M H₂SO₄, Na₂SO₄ and NaOH solutions at different sweep rates are presented in Fig. 1(a)–(e), respectively. The cathodic peak potential (E_{pc}) was found to shift in the negative direction with increasing pH. The slope dE_p/dpH was found to be close to 30 mV (decade)$^{-1}$ over a wide pH range in these media [18]. This was attributed to the presence of a dual oxide layer consisting of an anhydrous interior oxide layer covered by a hydrated oxide layer close to the electrode electrolyte interface.

$$TiO_2 + H_2O \rightleftharpoons TiO(OH)_2 \qquad (1)$$
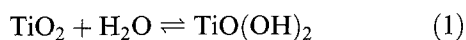
If either the hydrated species or the anhydrous species alone undergoes protonation along with electron transfer this type of unusual pH dependence of E_p can be observed. Such unusual pH sensitivities have also been noticed on nickel oxide electrodes [19, 20]. Another cause may be the 2e⁻, 1H⁺ reduction leading to the formation of charged species on the electrode surface [20].

$$2TiO_2 + H^+ + 2e^- \rightleftharpoons TiOOH + TiO_2^- \qquad (2)$$
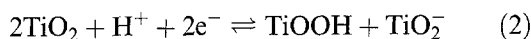
The striking observation in Fig. 1, however, is the dependence of peak current on pH. At constant sweep rates the cathodic peak currents (i_{pc}) always decrease in the order

$$i_{pc}(H_2SO_4) > i_{pc}(NaOH) > i_{pc}(Na_2SO_4)$$

The sharpness of the peak is also pH sensitive (Fig. 1). This may be quantified by either the half peak width value or $E_{pa} - E_{pc}$ (denoted hereafter as ΔE_p) value for each cyclic voltammogram. The ΔE_p values are found to increase in the direction of decreasing i_{pc};
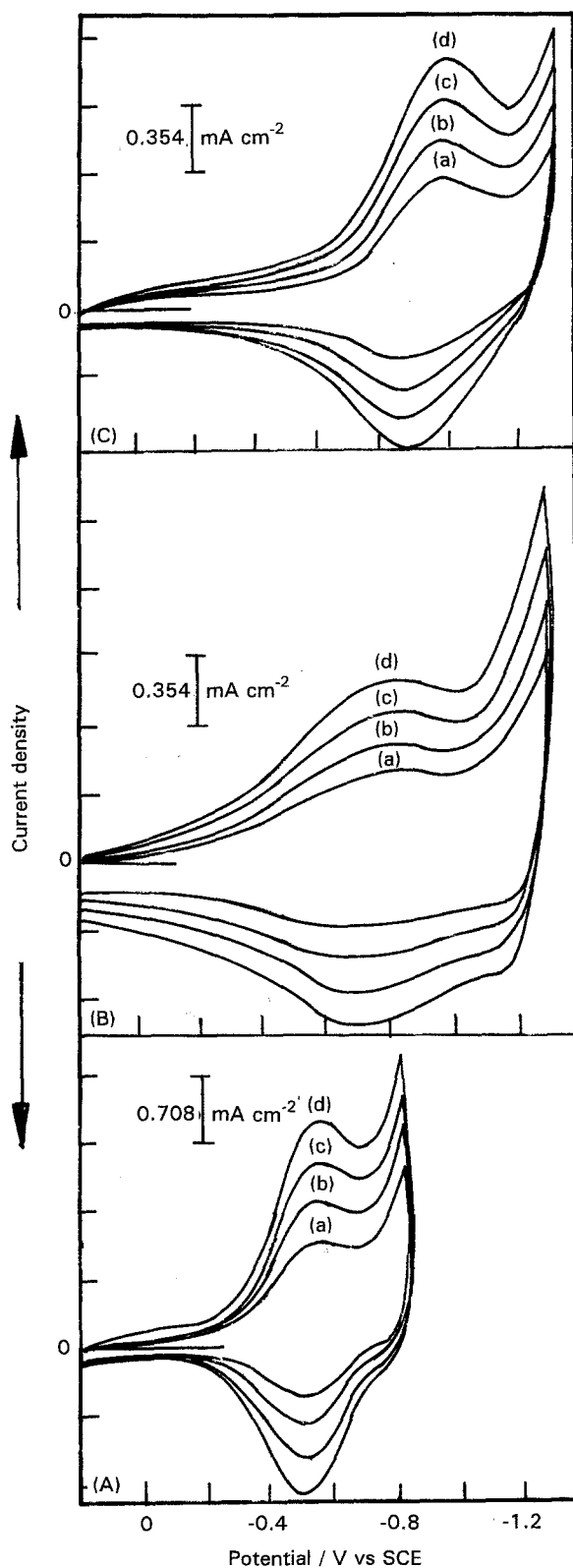

Fig. 1. Typical cyclic voltammograms for the thermally coated Ti/TiO₂ electrode in 1.0 M H₂SO₄ (A), Na₂SO₄ (B) and NaOH (C) solution at different sweep rates. Sweep rate: (a) 50, (b) 100, (c) 150 and (d) 200 mV s⁻¹.

namely,

$$\Delta E_p(H_2SO_4) < \Delta E_p(NaOH) < \Delta E_p(Na_2SO_4).$$

Although slightly more difficult to quantify because of the closeness of the hydrogen evolution process, half peak width values also show a qualitatively similar trend.
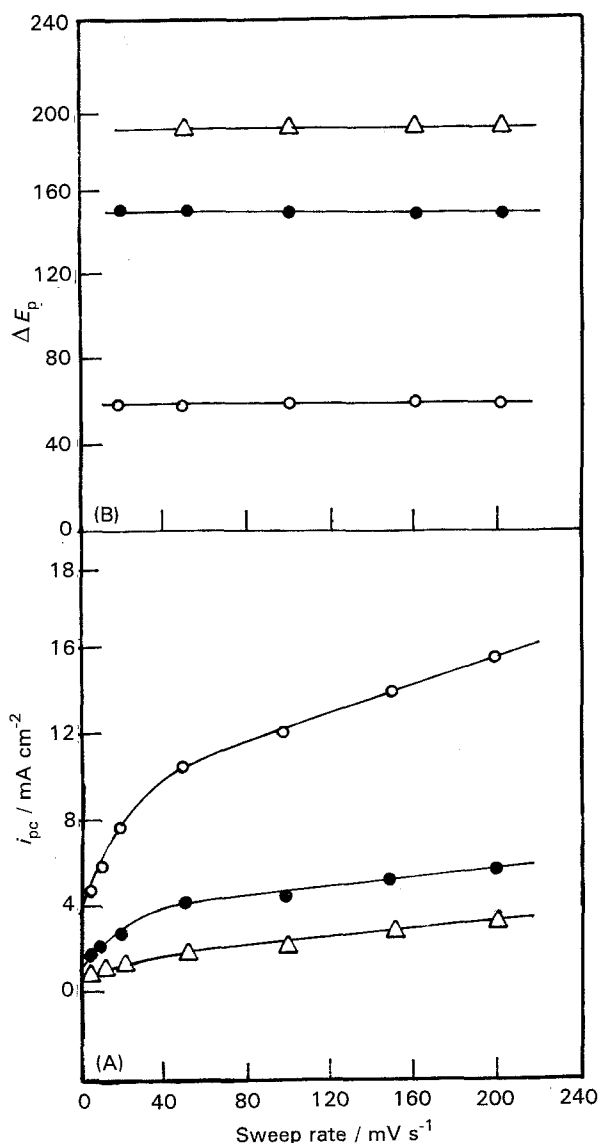
Fig. 2. The effect of sweep rate in i_{pc} (A) and ΔE_p (B) values in acid, neutral and alkaline media at 20 mM concentration of nitrobenzene. Key: (O) 1.0 M H₂SO₄; (●) 1.0 M NaOH; (△) 1.0 M Na₂SO₄.

The effect of sweep rate (V) on the i_{pc}, as well as ΔE_p values, in all the three media are compared in Fig. 2(A) and (B), respectively. i_{pc} against V plots in all the three media indicate two slopes. At slower sweep rates the i_{pc} increases faster, but at higher sweep rates a much slower increase in i_{pc} is noticed. The sweep rate range, where such a transition occurs, also decreases in the order H₂SO₄ > NaOH > Na₂SO₄ (Fig. 2(A)). In contrast to i_{pc} values the ΔE_p values remain practically constant over the entire pH range.

In all the three media, CV responses in different concentrations of the supporting electrolyte, namely, 0.05 to 3.0 M were recorded. The pH of the medium also changes along with the ionic strength. The E_{pc} values presented in Table 1 for example show a shift in the negative direction with increasing pH (this table is arranged with solution compositions listed in the direction of increasing pH).

The cathodic peak current is always found to increase with supporting electrolyte concentration, reach a maximum value around 0.5 to 1.0 M

Table 1. Cyclic voltammetric data for the behaviour of Ti/TiO₂ electrode at various concentrations of supporting electrolyte in acid, neutral and alkaline media

Concentration of supporting electrolyte/M	i_{pc} /mA cm⁻²	$-E_{pc}$ /mV	$-E_{pa}$ /mV	ΔE_p /mV
H₂SO₄				
3.0	1.611	580	460	120
2.0	1.628	580	490	90
1.0	2.371	570	510	60
0.5	1.238	620	530	90
0.1	1.227	680	550	130
0.05	1.097	700	500	200
Na₂SO₄				
3.0	0.940	800	620	180
2.0	0.950	800	620	180
1.0	0.960	820	570	250
0.5	1.130	890	590	300
0.1	1.060	900	570	330
0.05	0.880	910	560	350
NaOH				
3.0	0.980	1040	820	220
2.0	1.044	1040	820	220
1.0	1.185	970	820	220
0.5	1.539	980	780	210
0.1	1.469	1020	770	250
0.05	1.364	1030	760	270

concentration and then decrease. The maximum i_{pc} occurs at 1.0 M concentration in H₂SO₄ medium but at 0.5 M concentration in Na₂SO₄ and NaOH media (Table 1).

With increasing H₂SO₄ concentration, the ΔE_p value decreases with increasing i_{pc} and then increases with decreasing i_{pc} (Table 1). In Na₂SO₄ and NaOH media, however, the ΔE_p value decreases with ionic strength and reaches a constant minimum value at higher ionic strengths.
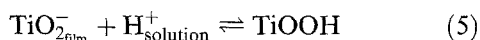
The explanation for the sensitivity of thermally coated Ti/TiO₂ electrodes to pH and ionic strength derives from the equilibrium and transport properties of protons in the films. The isoelectric point in TiO₂ surfaces in aqueous solutions were found to be around pH 4.8–6.0 [21, 22]. Protonation and OH⁻ ion adsorption occurs in the acidic and basic pH regions, respectively, according to the following equilibria:

$$TiOOH^+ \overset{-H^+}{\rightleftharpoons} TiO_2 \overset{OH^-}{\rightleftharpoons} TiO_2.OH^- \qquad (3)$$
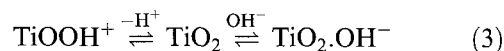
The shift of E_{pc} in the negative direction with increasing pH may be explained on the basis of these equilibria. However, the minimum i_{pc} value and maximum ΔE_p value in neutral (Na₂SO₄) solutions cannot be accounted for on this basis.

It appears that proton transport within the oxide film plays a decisive role in determining the redox behaviour of the Ti/TiO₂ electrode. Electroreduction of any redox film requires counter-ion (in this case proton) diffusion from the electrolyte side of the interface into the oxide layer to achieve charge

neutralization in the film [23].

$$TiO_{2_{film}} + e^- \rightleftharpoons TiO_{2_{film}}^- \qquad (4)$$

$$TiO_{2_{film}}^- + H_{solution}^+ \rightleftharpoons TiOOH \qquad (5)$$

In acidic media, the proton is the diffusing species through the pores and cracks of the oxide layer and also through the bulk of the hydrated outer, and fairly dry, inner oxide layers of the oxide film. As noted in the case of RuO_2 films [24], this proton transport can take place through a 'surface Grothus mechanism'. Hence, in acidic medium proton transport is faster. In alkaline media, the adsorbed OH^- ions assist proton transport by proton abstraction from the trapped water molecules. Hence, it is expected that the proton transport rate would decrease in the order $H_2SO_4 > NaOH > Na_2SO_4$. This accords with the order of decreasing i_{pc} values and increased ΔE_p values noted in the present case.

For a three-dimensional, heterogeneous, porous electrode of the type considered here, quantitative correlations of model parameters with experimental results are difficult. However, qualitatively all the results presented above fit well with the proton transport controlled redox electrode process. The decreasing sensitivity of i_{pc} to sweep rate in alkaline and neutral media (Fig. 2A) may be attributed to the slower ion transport when compared to the sweep rate. The higher ΔE_p values noticed in these media are not connected with the quasireversibility of the electron-transfer process. Hence, the ΔE_p value at constant electrolyte composition is independent of sweep rate (Fig. 2B).

Although proton transport, as a counter-ion in the film, is the limiting factor that determines the peak current values, it is the effective concentration and

nature of charged centres in the oxide layers which determines the proton transport rate itself. This is the cause of the sensitivity of i_{pc} and ΔE_p to pH as well as ionic strength. The sensitivity of these parameters to sweep rate is thus not so straightforward.

Increased ionic strength in the electrolyte enhances counter-ion diffusion and, hence, i_{pc} increases and ΔE_p decreases with ionic strength (Table 1). Beyond 0.5 M concentrations ion–ion interactions and ion-pair formation may inhibit counter-ion transport to some extent. Hence, the maximum efficiency of the electrode is observed around 0.5 to 1.0 M. In strong acidic media, cathodically induced electrode dissolution and damage may also take place [25].

$$TiO_2 + 4H^+ + e^- \rightleftharpoons Ti^{3+} + 2H_2O \qquad (6)$$
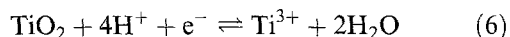
3.2. Effect of pH on heterogeneous redox catalysis

Typical cyclic voltammetric responses of Ti/TiO_2 electrodes in 1.0 M H_2SO_4, Na_2SO_4 and NaOH containing 12 mM nitrobenzene at different sweep rates are presented in Fig. 3(A)–(C), respectively. In all the three media, only one irreversible single reduction peak in the potential region of the Ti^{4+}/Ti^{3+} redox reaction is noticed. This suggests the heterogeneous redox catalytic reduction of nitrocompounds. In acid media the reaction invariably leads to the formation of amines, as indicated by preparative electrolysis [16]:

$$6TiO_2 + 6H^+ + 6e^- \rightleftharpoons 6TiOOH \qquad (7)$$

$$6TiOOH + ArNO_2 \longrightarrow 6TiO_2 + ArNH_2 + 2H_2O \qquad (8)$$
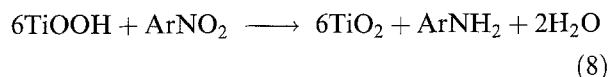
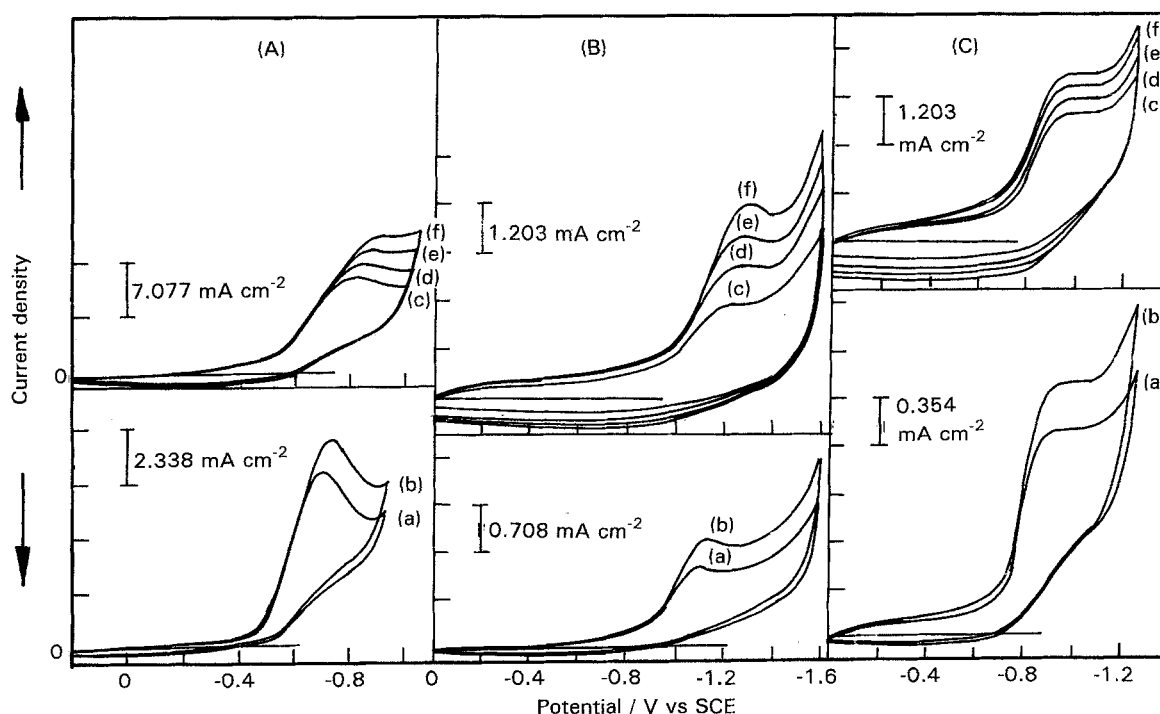In all the three media, the cathodic peak current does not increase linearly with $V^{1/2}$ (Fig. 3) suggesting that

Fig. 3. The cyclic voltammetric responses of Ti/TiO_2 electrode in 1.0 M H_2SO_4 (A), Na_2SO_4 (B) and NaOH (C) containing 12 mM concentration of nitrobenzene at different sweep rates. Sweep rate: (a) 10, (b) 20, (c) 50, (d) 100, (e) 150 and (f) 200 mV s^{-1}.
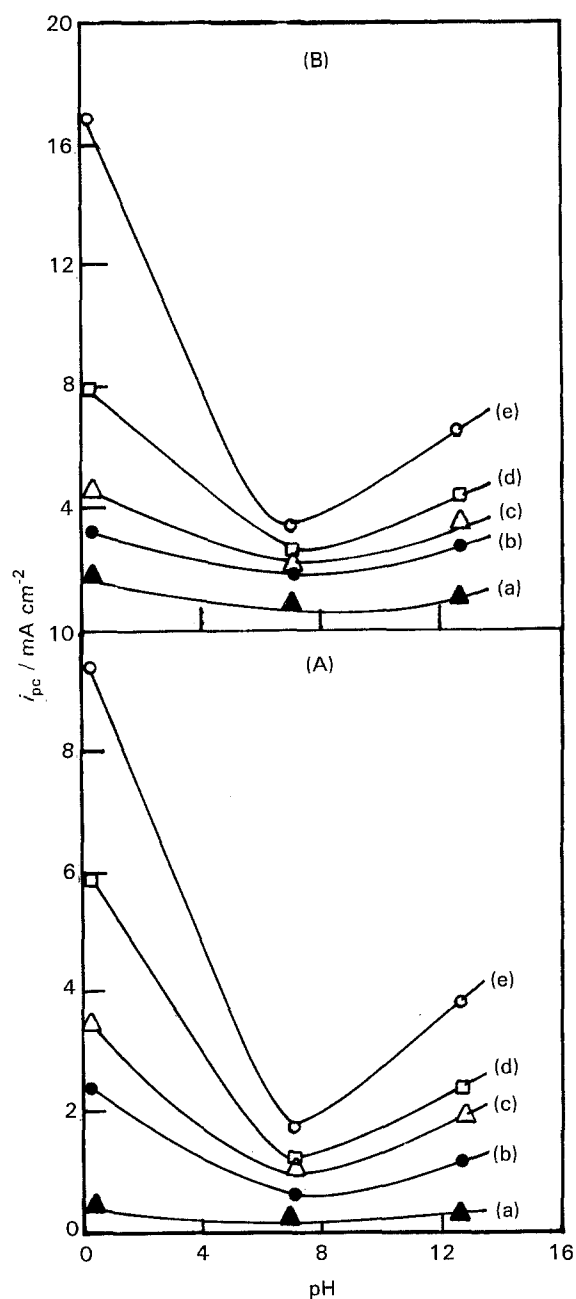
Fig. 4. pH against i_{pc} plot at $10\,\mathrm{mV\,s^{-1}}$ (A) and $100\,\mathrm{mV\,s^{-1}}$ (B) sweep rates for different concentrations of nitrobenzene. Concentrations: (a) 0, (b) 6, (c) 10, (d) 20 and (e) 40 mM.

the overall reaction rate is controlled partially by diffusion and chemical Reaction 8.

It is quite interesting to note that in the presence of nitrobenzene also the sequence $i_{pc}(\mathrm{H_2SO_4}) > i_{pc}(\mathrm{NaOH}) > i_{pc}(\mathrm{Na_2SO_4})$ remains true (Fig. 3). The pH effect on i_{pc} at different nitrobenzene concentrations at low (Fig. 4(A)) and high sweep rates (Fig. 4(B)) are more directly brought out in Fig. 4. These data clearly show that the redox catalysis is substantially more efficient in acidic medium, followed by alkaline medium and it is least efficient in neutral medium.

In neutral and alkaline medium the reduction of nitrocompounds may involve formation of other products involving a lesser number of electrons. Even with this assumption, however, it is difficult to explain the practical independence of i_{pc} on

nitrobenzene concentration in neutral media. It is obvious that efficient counter-ion transport and redox reaction rate is essential for an efficient redox catalytic sequence involving Reactions 7 and 8. Hence, the efficiency of redox catalysis also follows the efficiency of reduction of the TiO₂ layer. In fact the pH sensitivity of the Ti/TiO₂ electrode becomes much more apparent in heterogeneous redox catalytic processes.

To understand the cause of the extremely low efficiencies in neutral and alkaline media, a few a.c. impedance measurements were carried out in all the three media, both in the absence and presence of nitrobenzene. The impedance pattern, recorded in the form of Nyquist plots were qualitatively similar, both at the rest potential region, and in the cathodic peak potential region. Typical impedance spectra (Fig. 5) recorded in acidic (A and B) and alkaline (C and D), media in the absence (A and C) and presence (B and D) of nitrobenzene at the corresponding peak potential regions. The overall impedance response is similar to a conventional equivalent circuit involving charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and mass transport. The charge transfer resistance and double layer capacitance were calculated assuming a conventional equivalent circuit. These data are summarised in Table 2.

These data suggest that R_{ct} values show only minor variations in the neutral and alkaline media in the absence of nitrobenzene. In the rest potential region (where the background current in acidic medium is quite low in the cyclic voltammograms presented in Fig. 1), R_{ct} in acidic solutions is found to be even higher than that in neutral and alkaline media. These trends are in fact reversed when comparing the R_{ct} values in the corresponding peak potential region. In the absence of nitrobenzene, the C_{dl} values in neutral and alkaline media are significantly higher than in acidic medium. The cause of this observation is not clear.

The effect of nitrobenzene on the impedance response is quite striking. In acidic media, R_{ct} and C_{dl} values remain practically unchanged. In neutral media the R_{ct} value increases many times and C_{dl} values are correspondingly suppressed. In alkaline media significant increase in R_{ct} values and decrease in C_{dl} values are also noticed. This trend is common to the measurements at rest potential region, as well as in the peak potential region. In acidic medium nitrobenzene does not adsorb on and hence block the electron transfer of the positively charged protonated oxide layer (see Equation 2). Significant blocking adsorption takes place in alkaline medium. In the neutral medium, which falls in the isoelectric point range of TiO₂ electrodes [21, 22], maximum nitrobenzene adsorption and hence the blocking of the charge transfer process occurs. Thus, the lower dependence of i_{pc} values on pH in the absence of nitrobenzene is significantly increased in its presence (Fig. 4).
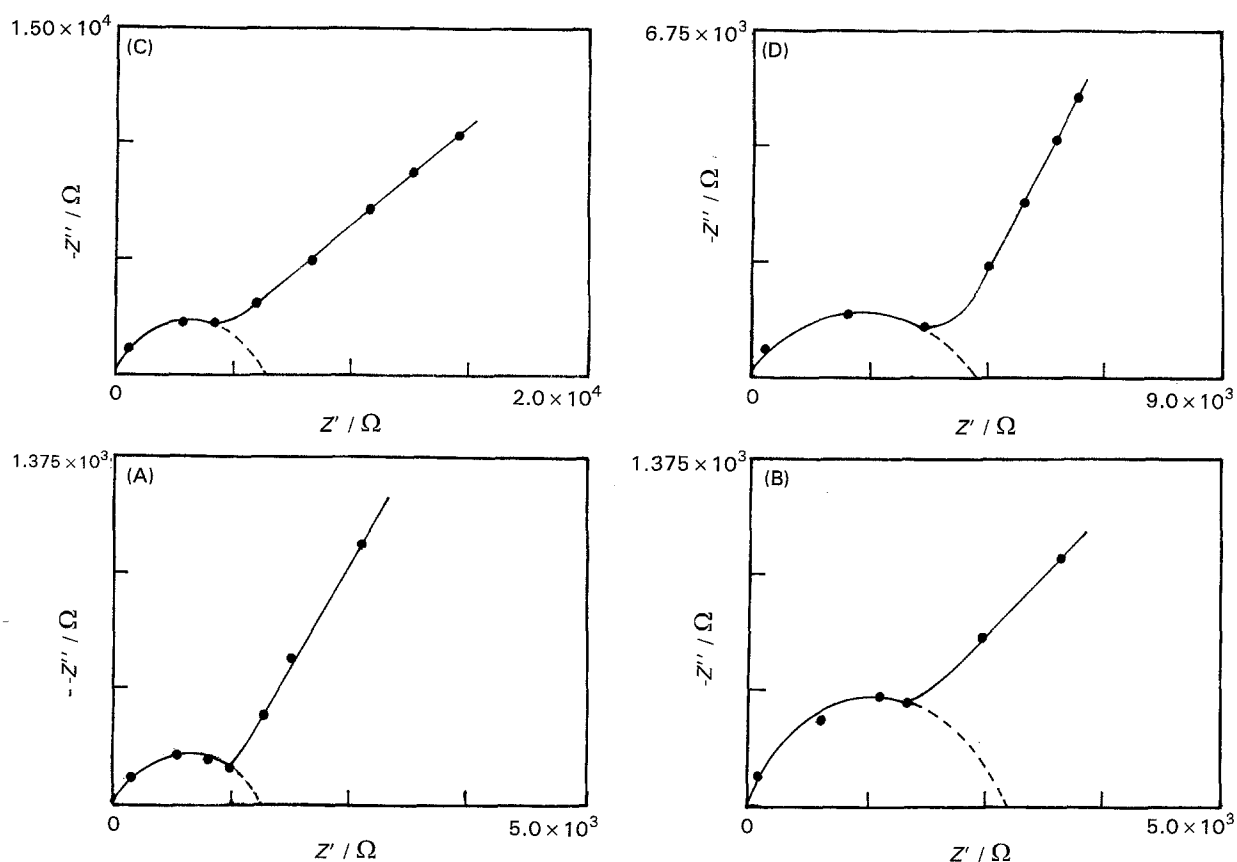
Fig. 5. Nyquist plots for Ti/TiO_2 electrode in acidic (A and B) and alkaline (C and D) media in the absence (A and C) and in presence (B and C) of 12 mM nitrobenzene.

4. Conclusions

All the experimental evidence presented here indicates that the pH dependence of the Ti^{4+}/Ti^{3+} redox reaction of the thermally coated Ti/TiO_2 electrode is primarily due to the counter-ion diffusion rate in the oxide film which decreases in the order acid > alkali > neutral solutions. The pH sensitivity becomes even more predominant in the heterogeneous redox catalysis of nitrobenzene reduction. Nitrobenzene specially adsorbed on the neutral TiO_2 layer around the isoelectric point further inhibits the heterogeneous redox catalytic efficiency of the electrode.

The present study suggests that Ti/TiO_2 electrodes can operate efficiently as a heterogeneous redox catalytic cathode only in acidic medium. Practically these electrodes are now employed as cathodes only in nitric [12, 13] and sulphuric acids [14–16]. It may also be worthwhile to see if this type of pH sensitivity also exists for other thermally coated three dimensional oxide electrodes.

Acknowledgement

Table 2. Impedance data for Ti/TiO_2 electrode in the absence and presence of nitrobenzene

1 M Concentration of supporting electrolyte	$R_{ct}/\Omega\,cm^{-2}$		$C_{dl}/\mu F$		Potential /mV
	Without compound	With compound	Without compound	With compound	
At rest potential					
H_2SO_4	2950	2982	21.502	21.271	183
Na_2SO_4	361	21084	44.085	11.989	128
NaOH	718	11492	33.032	13.856	101
At reduction potential					
H_2SO_4	1214	1248	9.384	9.306	−570
Na_2SO_4	1806	29692	58.088	18.655	−820
NaOH	1553	3718	16.247	21.062	−970

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