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An electrochemical technique for the reduction of aromatic nitrocompounds in H_2SO_4 medium on thermally coated Ti/TiO_2 electrodes

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An outline of the recently developed preparative method for the electroreduction of aromatic nitrocompounds using thermally coated Ti/TiO_2 electrodes in H_2SO_4 medium is presented. The method of preparation of stable and electrochemically active Ti/TiO_2 electrode is described. Cyclic voltammetry indicates wide variations in the heterogeneous redox catalysis of different aromatic nitrocompounds. Weak adsorption blocking due to insoluble film formation, catalytic hydrogen evolution and strong pH sensitive reactant adsorption effects are illustrated. Optimum conditions for the preparative scale electroreduction of these nitrocompounds are presented. The yields and current efficiencies were uniformly high for all the nitrocompounds involved. In addition to heterogeneous redox catalysis active hydrogen generated at the electrode surface also probably acts as efficient reducing agent on the preparative time scale. Reuse of electrolyte and stability of electrodes during prolonged electrolysis are also reported.

1. Introduction

Gas phase catalytic hydrogenation of aromatic nitrocompounds is the main route for the commercial production of aromatic amines on a large scale [1]. However, for nitrocompounds which are not stable at high temperatures (e.g., nitrophenols) and for aromatic amines that are required in smaller volumes, the aromatic nitrocompounds are reduced in aqueous solutions using active metal powders. This method leads to the formation of large volumes of metal oxides and hydroxides containing residual amines, whose disposal is becoming increasingly difficult in an environmentally conscious society.

Direct electroreduction of aromatic nitrocompounds using metal and graphite cathodes in H_2SO_4 and HCl media also stops at the phenyl hydroxylamine stage, and hence yields of amines are low and their isolation from the intermediates require additional unit operations [2]. In the case of a few nitrocompounds, like nitrophenols and nitroanilines [3, 4], the hydroxylamines undergo chemical transformations leading to the formation of easily reducible quinoneimines and diimines, to good overall yields of aromatic amines.

In analytical chemistry titanous chloride or titanous sulphate solutions are well-known reducing agents for the quantitative estimation of aromatic nitrocompounds [5]. In the early 1970s, it was found that by *in situ* regeneration of Ti^{3+} from the Ti^{4+} salt on a copper cathode, aromatic nitrocompounds could be conveniently and quantitatively reduced to their corresponding amines. Depending on the nature of the nitrocompounds, their solubility in H_2SO_4 and their reaction kinetics, some minor changes in operating conditions were required. In a few cases a two stage process was developed which involves generation of Ti^{3+} in the electrochemical cell and reducing the nitrocompound in a separate chemical reactor. However, the overall electrochemical technique was quite general and could be used for the reduction of 16 aromatic nitrocompounds [6]. For some nitrocompounds, 200–1000 A pilot plant electrochemical reactors were also operated [7]. The main difficulty in this technique was the hydrolysis of Ti^{4+} and Ti^{3+} salts under low acidity conditions and the problem of recovering the soluble portion of the aromatic amines from these salt solutions. The disposal problem of metal oxide sludge still remained, though at a much smaller scale [6].

A more efficient redox catalytic process for aromatic amines would involve the use of surface bound Ti^{4+}/Ti^{3+} redox species as redox mediators. In 1985, Beck and Gabriel [8] established that thermally coated Ti/TiO_2 electrodes act as such heterogeneous redox catalyst for the reduction of nitrobenzene. Among the thermally coated ceramic oxides investigated [9–11] the Ti/TiO_2 electrode was found to be efficient for cathodic reductions in H_2SO_4 media. The wear mechanism of this electrode at more negative potentials was also assessed [12, 13].

A more comprehensive study of the process covering a number of compounds was initiated in this laboratory in 1989. Cyclic voltammetric (CV) measurements showed even faster heterogeneous redox catalysis for nitroso compound when

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compared to nitrobenzene [14]. At higher temperatures and very high acid strengths, nitrobenzene reduction led to the formation of 4-aminophenol [15]. Electroreduction of 4-nitrosophenol could be achieved at relatively mild experimental conditions [16]. Under moderate operating conditions, a wide variety of aromatic nitrocompounds including 2- and 4-nitrophenols [17, 18], 1-nitronaphthalene [19], 5-nitrosalicylic acid [20], 2, 3 and 4-chloro nitrobenzenes [21], 2, 3 and 4-nitroanilines [22, 23], nitrobenzene and dinitrobenzene [24], nitrotoluenes [25], 1-chloro 2,4-dinitrotoluene [26] and 2-nitrobenzene sulphonic acid [27] could be reduced to their corresponding amines at fairly high efficiencies.

During the course of these investigations, a few modifications in the method of preparation of thermally coated Ti/TiO_2 electrodes were made. The stability and redox catalytic activity of these electrodes were found to be pH sensitive [27, 28]. In the cyclic voltammetric time scales, these compounds showed considerable differences in their adsorption and catalytic reduction behaviour. On the preparative time scales, however the compounds exhibited fairly similar reduction efficiencies. Under optimum conditions, the electrode itself exhibited good long term stability. This paper is an attempt to summarise the results, outline the overall understanding that emerges from these studies and point out scope for further work in this area.

2. Preparation of Ti/TiO_2 electrodes

Typical cyclic voltammetric (CV) responses of thermally coated Ti/TiO_2 electrode, prepared according to the procedure recommended by earlier workers [8–13] in 1.0 M H_2SO_4 at different sweep rates are presented in Fig. 1. Two redox peaks, which increase with sweep rate, are noticed. These peaks may be attributed to the successive reduction of Ti^{4+} to Ti^{3+} species and Ti^{3+} to Ti^{2+} species respectively [8–10]. However, the first cathodic peak is more probably due to the presence of partially decomposed Ti^{4+}-acetyl acetonate complex in the oxide matrix. The first cathodic peak completely disappears when the decomposition temperature exceeds 823 K [14].

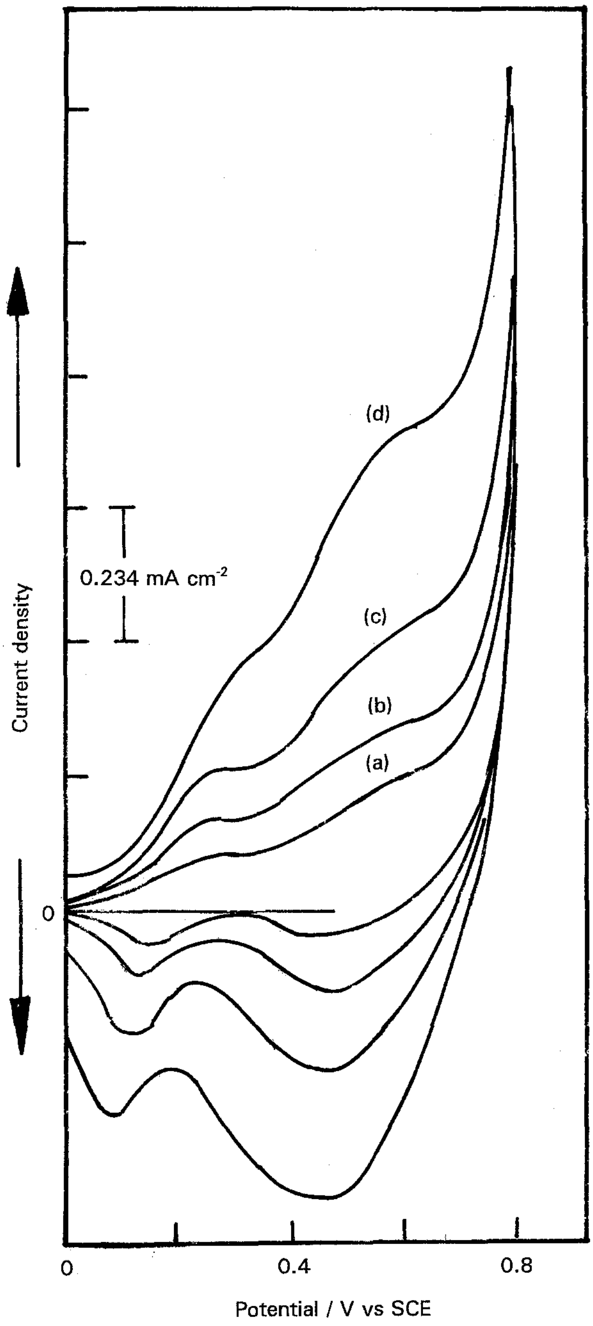

Fig. 1. Cyclic voltammetric behaviour of Ti/TiO_2 electrode in 2 M H_2SO_4 (electrode prepared as per the procedure reported by earlier workers (Section 2). Sweep rates: (a) 50, (b) 100, (c) 200 and (d) 300 mV s^{-1}.

The complete oxidative decomposition of acetyl acetonate ligand is also facilitated by addition of up to 7.5 vol % HNO_3 to the isopropanol/0.05 M Ti^{4+}-acetyl acetonate mixture. Typical CV curves obtained for an electrode prepared by adopting these modifications in 1.0 M H_2SO_4 are presented in Fig. 2(A). A single well-defined redox couple is noticed in this Figure.

The long term stability of the oxide electrode could be improved by sandblasting the titanium substrate and subsequently etching in 50% HCl for an hour before applying the Ti^{4+}-acetyl acetonate coating.

Incorporating these modifications, the following standard procedure was employed throughout the present study. High purity titanium sheets 5 cm × 1 cm (Imperial Metal Industries Limited IMI-125 grade) were used as substrates for cyclic voltammetric work. For galvanostatic preparative electrolysis titanium mesh (9 cm × 12 cm × 1 mm, pattern of expansion; L.W.D: 12.5 mm; B.W.D: 7 mm; sherand width: 2 mm; strand thickness: 1 mm) was the substrate. Titanium sheet/expanded mesh was sand blasted, treated with 50% HCl at 90 °C for 1 h, washed and dried. The activated titanium metal was dipped in a solution of 0.05 M titanyl acetylacetonate (Merck) in isopropanol containing 7.5 vol % HNO_3, dried at 100–110 °C for 10 min and then heated at 500–550 °C for 25 min so that an oxide layer was formed. The above coating and drying cycle was repeated at least five times to achieve an approximately 1 μm TiO_2 oxide layer thickness. The

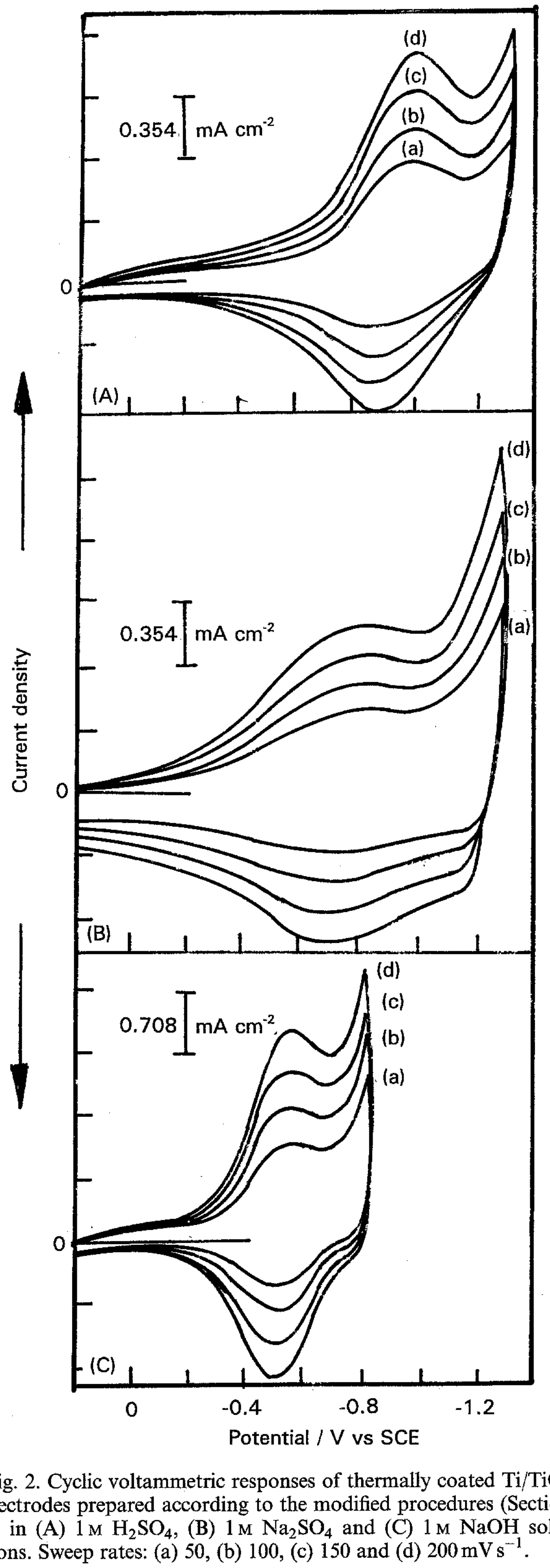

Fig. 2. Cyclic voltammetric responses of thermally coated Ti/TiO_2 electrodes prepared according to the modified procedures (Section 2) in (A) 1 M H_2SO_4, (B) 1 M Na_2SO_4 and (C) 1 M NaOH solutions. Sweep rates: (a) 50, (b) 100, (c) 150 and (d) 200 mV s^{-1}.

electrode surface was covered with PVC adhesive tape, leaving an exposed surface area of 0.28 cm^2 for cyclic voltammetric work.

3. Cyclic voltammetric studies

A typical single compartment glass cell was used for the cyclic voltammetry. A platinum counter electrode and a SCE reference electrode were used. Typically a 1 A potentiostat (Wenking Model 75L), a voltage scan generator (VSG-72) and an X–Y recorder (Rikadenki 101T) were employed. Wherever possible AR grade aromatic nitrocompounds were employed. In other cases, the nitrocompounds were distilled or recrystallized twice before use. All the cyclic voltammetric experiments were carried out at (25 ± 1) °C.

3.1. *Redox behaviour of the Ti/TiO_2 electrode*

Typical cyclic voltammetric curves of thermally coated Ti/TiO_2 electrodes in 1.0 M, H_2SO_4, Na_2SO_4 and NaOH solutions at different sweep rates are presented in Fig. 2(A)–(C), respectively. Well defined reversible redox peaks whose peak potentials (E_{po}) do not shift significantly with sweep rate and whose peak currents (i_{po}) increase linearly with sweep rates are observed. The peak potential also shifts in the negative direction with pH, suggesting the involvement of protons in the redox process

$$\mathrm{TiO_2 + e^- + H^+ \rightleftharpoons TiOOH} \tag{1}$$

Many cyclic voltammetric features suggest that the overall redox reaction is not as simple as the above equation suggests. The peak separation ($E_{pa} - E_{pc} = E_p$) would be zero for a surface redox process [29]. In the present case, however, the E_p value is

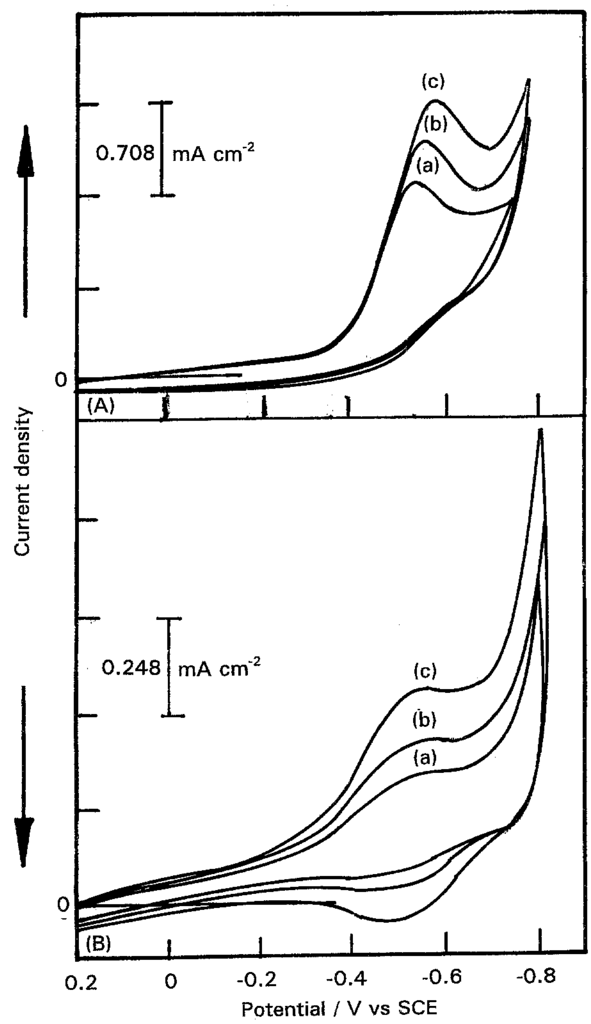

Fig. 3. Typical cyclic voltammetric responses of Ti/TiO_2 electrode in 1.0 M H_2SO_4 in the absence (A) and in presence (B) of 4 mM nitrobenzene. Sweep rate: (a) 10, (b) 20 and (c) 50 mV s^{-1}.

60 mV in acidic media. It further increases in alkaline and neutral media in that order. The peak shape is much broader in neutral media. The cathodic peak current (i_{pc}) value decreases with increasing E_p (Fig. 2).

In all these media, the electrodes exhibit good reproducibility and long term stability. Hence the pH sensitivity is not due to dissolution or deactivation of the electrode surface. In a thermally coated 3D oxide electrode, the electroreduction would require counter-ion diffusion (in this case proton) into the oxide layer to ensure charge balance. In acidic media, the proton diffusion occurs efficiently by a 'surface Grothus' mechanism. In alkaline media adsorbed OH^- ions assist proton transfer by abstracting protons in the hydroxide layer or trapped water molecules. The proton-transport is least efficient in neutral media. These trends are further enhanced during heterogeneous redox catalysis [27, 28].

Acidic solutions, in addition to maintaining higher redox activity of the electrode as mentioned above, also assist in the formation of amines during the reduction of aromatic nitrocompounds. Hence acidic medium was chosen for further redox catalytic studies.

3.2. *Catalytic reduction of aromatic nitrocompounds*

Typical cyclic voltammetric responses of the Ti/TiO_2 electrode in 1.0 M H_2SO_4 in the absence and presence of nitrobenzene under otherwise identical conditions are presented in Fig. 3. Nitrobenzene is also reduced in the same potential region where the Ti^{4+}/Ti^{3+} redox reaction occurs. The cathodic peak current increases significantly in the presence of nitrobenzene. On the reverse sweep, at slow sweep rates no anodic peak due to Ti^{3+} oxidation is noticed, since the Ti^{3+} is consumed in chemically reducing the nitrobenzene. At high sweep rates, since this heterogeneous redox catalytic reduction is incomplete, the anodic peak due to reoxidation of Ti^{3+} reappears.

The cyclic voltammetric responses for most of the nitrocompounds investigated also showed similar behaviour. Typical peak current enhancement ratios, i_{po}/i_{pc}, where i_{po} and i_{pc} refer to the peak currents in the presence and absence of 20 mM nitrocompounds are presented in Table 1. The wide variation in this ratio for different aromatic nitrocompounds suggests that the redox catalytic reaction rate is dependent on the nature of the substituent in the aromatic ring:

$$6TiOOH + ArNO_2 \longrightarrow 6TiO_2 + ArNH_2 + 2H_2O \quad (2)$$

Table 1. Comparison of cyclic voltammetric parameters for the electroreduction of concentrations of 20 mM aromatic nitrocompounds on Ti/TiO_2 electrodes in 1 M H_2SO_4 at a sweep rate of 20 mV s^{-1}

Sl	*Compound*	i_p/i_{pc}	$-E_{pc}$ /mV	*Ref.*
1	Nitrobenzene*	14.8	600	[14, 15]
2	4-Nitrosophenol	16.4	310	[14, 16]
3	2-Nitrophenol	12.5	580	[17, 18]
4	2-Chloro nitrobenzene†	4.0	650	[21]
5	3-Chloro nitrobenzene	11.3	620	[21]
6	4-Chloro nitrobenzene	7.4	610	[21]
7	2-Nitroaniline	3.4	570	[22]
8	3-Nitroaniline‡	–	–	[22]
9	4-Nitroaniline	4.3	600	[23]
10	2-Nitrobenzene sulfonic acid	5.8	660	[27]
11	Nitrobenzene§	14.5	730	[24]
12	2-Dinitrobenzene	27.2	630	[24]
13	2-Nitrotoluene	12.2	790	[26]
14	3-Nitrotoluene	12.7	760	[26]
15	4-Nitrotoluene	8.4	660	[26]
16	2,4-Dinitrotoluene	2.1	550	[25]
17	1-Chloro 2,4-dinitrobenzene	2.7	550	[25]
18	Nitrosalicyclic acid	2.5	680	[20]

* Nitrobenzene to 4-aminophenol.
† In the presence of 0.01% CTAB.
‡ No peak at all sweep rates.
§ Nitrobenzene to aniline.

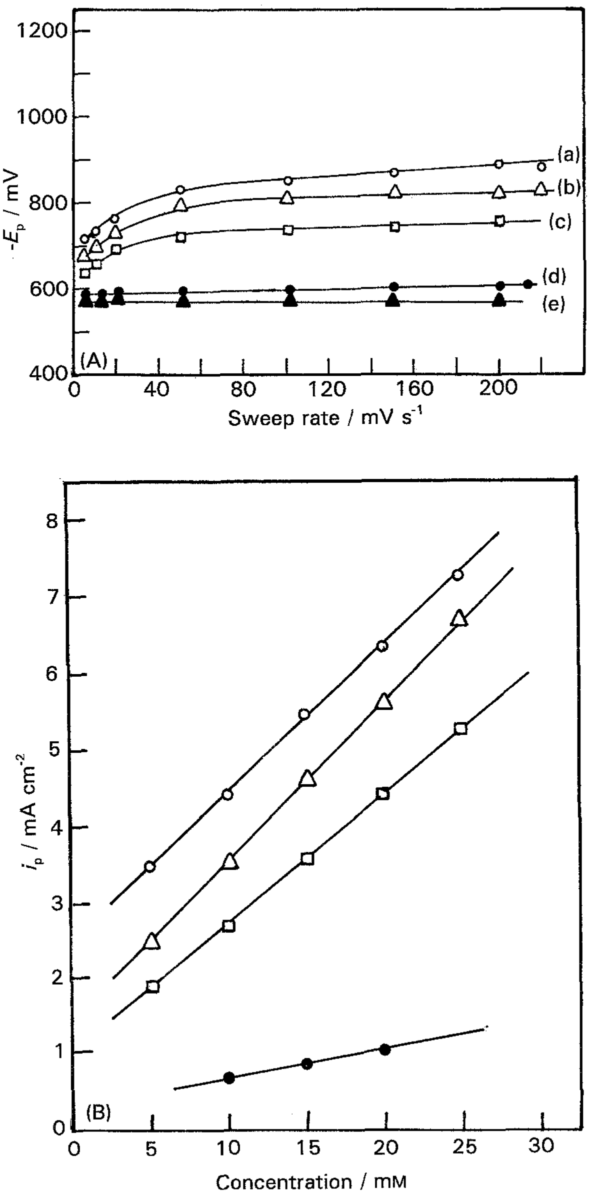

Fig. 4. Comparison of the peak potential (E_p) variation with sweep rate (A) at a concentration of 20 mM isometric nitrate (dinitro) toluenes and i_p against concentration plots (B) for the electroreduction of the isometric nitro(dinitro)toluenes at a sweep rate of 20 mV s^{-1}. Key: (a, ○) 2 NT, (b, △), 3 NT, (c, □) 4 NT, (d, ●) 2,4 NT and (e, ▲) Ti/TiO_2.

The chemical reaction for 4-nitrosophenol reduction (which requires only four TiOOH species) appears to be fast compared to other nitrocompounds:

$$OH-C_6H_4NO + 4TiOOH \longrightarrow OH-C_6H_4NH_2 + 4TiO_2 + H_2O \quad (3)$$

The reduction potential for this compound is also more positive when compared to all other compounds. Hence, direct electroreduction, at least partially, cannot be ruled out in this case:

$$OH-C_6H_4NO + 4H^+ + 4e^- \longrightarrow OH-C_6H_4NH_2 + H_2O \quad (4)$$

Direct correlation between structural parameters of the nitrocompounds involved and their redox catalytic reaction rate could not be established. However, this reaction rate seems to depend more on the solubility of the nitrocompound and its adsorption on the electrode surface. It is well-known that adsorbed organic molecules generally inhibit electron transfer and hence shift the reduction peak potential to more negative values [29]. In a heterogeneous redox catalytic reaction, adsorption of the reactant would shift the E_{pc} in the negative direction, as usual. But the chemical reaction rate (Equation 2) in the adsorbed state would increase.

In Table 1, for example, in the cases where E_{pc} is more negative (say beyond −700 mV) the peak current enhancement factors are also found to be higher. The relationship between E_{pc} and i_{pc} at different sweep rates are more clearly illustrated in Figs. 4(A) and (B) for the four nitrotoluenes. 2-Nitrotoluene which exhibits maximum negative shift (Fig. 4(A)) also exhibits high i_{pc} values (Fig. 4(B)) and vice versa.

In addition to the general cyclic voltammetric behaviour discussed above, some compounds also exhibit specific effects in their cyclic voltammetric responses. These are briefly outlined below.

3.3. *Solubility effect*

Cyclic voltammograms were generally recorded in the

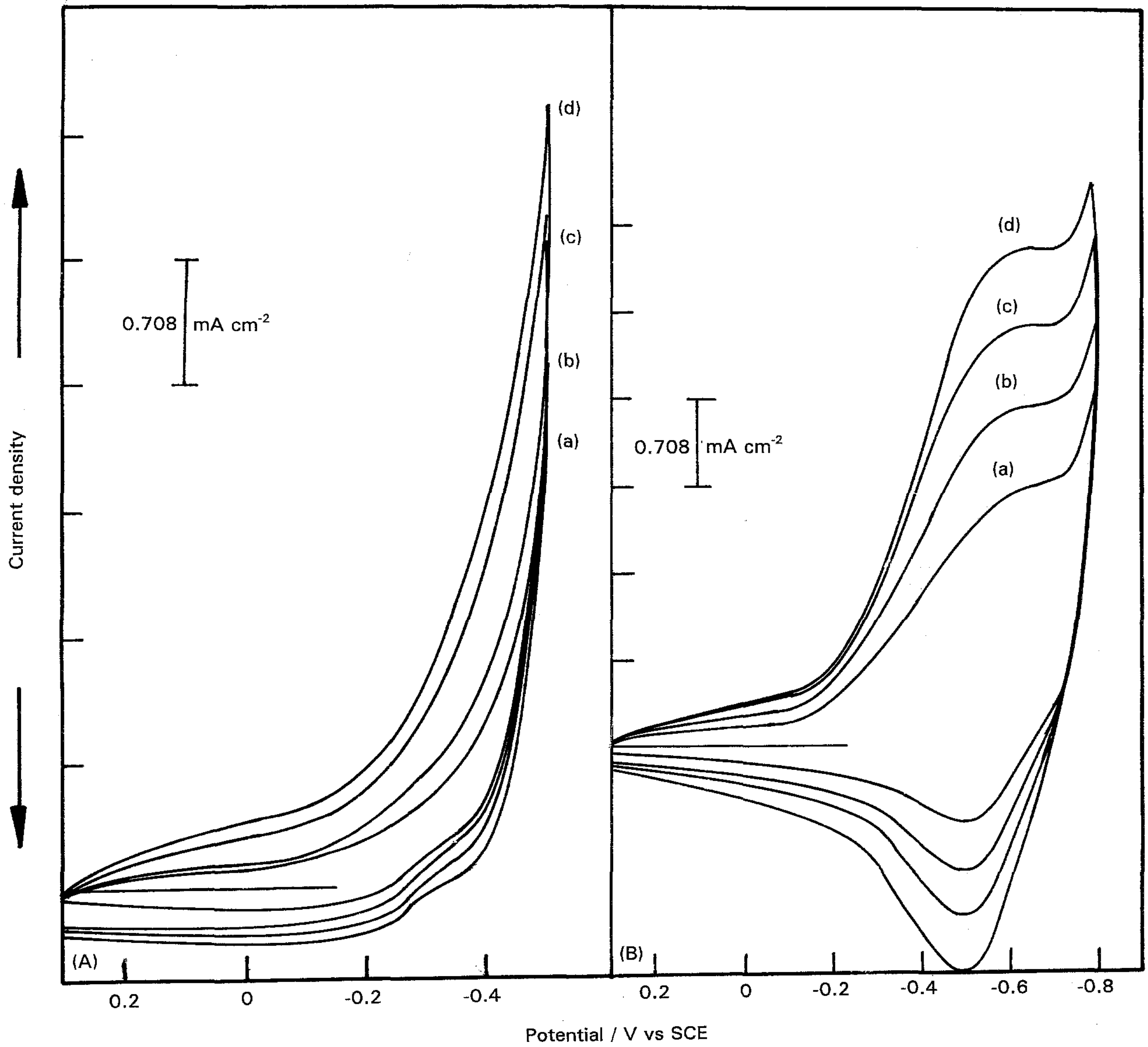

Fig. 5. Cyclic voltammetric behaviour of the Ti/TiO_2 electrode in 1.0 M H_2SO_4 containing 5 mM of 2-CNB (without CTAB) (A) and with CTAB (B). Sweep rate: (a) 50, (b) 100, (c) 150 and (d) 200 mV s^{-1}.

low concentration range of 1–20 mM aromatic nitrocompound. In this range most of the nitrocompound investigated exhibit good solubility in 1.0 M H_2SO_4. However, 2-chloronitrobenzene was found to be an exception. Even at 5 mM concentration the solution is rather turbid for this compound. Because of this low solubility the compound becomes strongly adsorbed on the electrode surface and apparently inhibits the Ti^{4+}/Ti^{3+} redox reaction. The hydrogen evolution reaction (background current), however, is not suppressed (Fig. 5(A)). Small concentrations of cationic surfactant cetyl trimethyl ammonium bromide (CTAB), however, improve the solubility of the nitrocompound. Redox catalysis is also noticed for this compound in the presence of CTAB (Fig. 5(B)).

3.4. *Catalytic hydrogen evolution*

Figure 6 shows typical cyclic voltammograms of the Ti/TiO_2 electrode in the presence of 3-nitroaniline. The redox peak due to Ti^{4+}/Ti^{3+} species is again not clearly noticed. This cannot be attributed to the solvent effect. 3-Nitroaniline is highly soluble in 1 M H_2SO_4:

$$3NH_2C_6H_4NO_2 + H^+ \rightleftharpoons 3NH_3^+C_6H_4NO_2 \qquad (5)$$

In this case the protonated nitroaniline may enhance catalytic hydrogen evolution, by the following reaction:

$$3NH_3^+C_6H_4NO_2 + e^- \rightleftharpoons 3NH_2C_6H_4NO_2 + \tfrac{1}{2}H_2 \qquad (6)$$

Now, 2 and 4-nitroanilines are stabilized by the electron withdrawing effect of the nitrogroup. Hence the redox behaviour of Ti/TiO_2 electrodes in the presence of these compounds exhibit normal cyclic voltammetric patterns (Table 1).

3.5. *Acid–base interaction with the electrode surface*

3-Nitrobenzene sulphonic acid is one of the strongly acidic nitrocompound investigated. In acidic media the TiO_2 surface itself exists in the protonated state:

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

The anionic species of the dissociated acid can easily interact with this positive charge on the electrode surface to form a strongly bound surface species which would be expected to give a separate post adsorption peak [29]. Such a pH sensitive post adsorption peak is noticed, in addition to the main redox catalytic peak for this compound (Fig. 7). The pH response of this

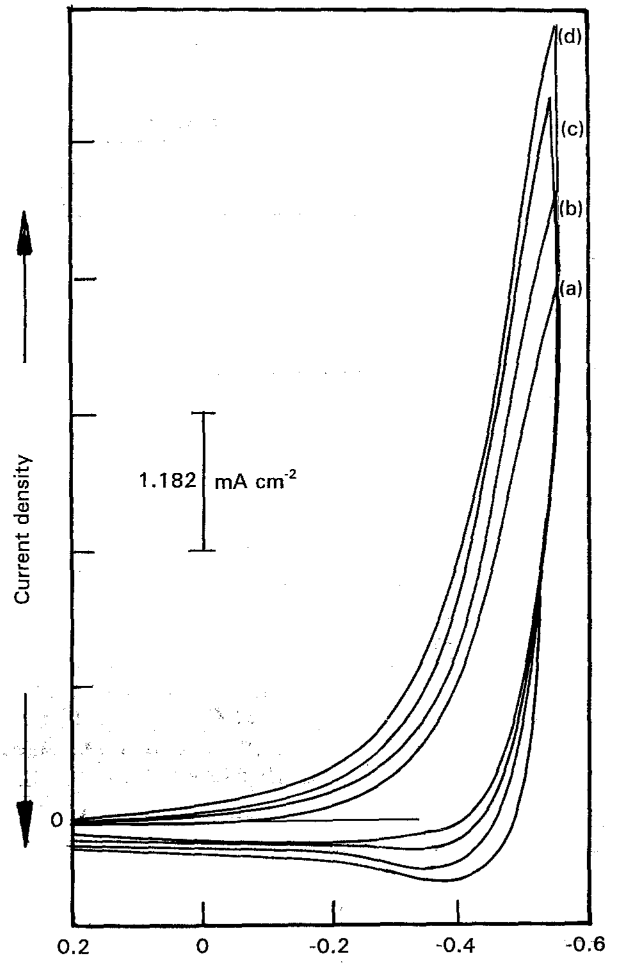

Fig. 6. Typical cyclic voltammograms obtained for the electroreduction of 5 mM 3-NA on Ti/TiO_2 electrode in 1.0 M H_2SO_4. Sweep rate: (a) 50, (b) 100, (c) 150 and (d) 200 mV s^{-1}.

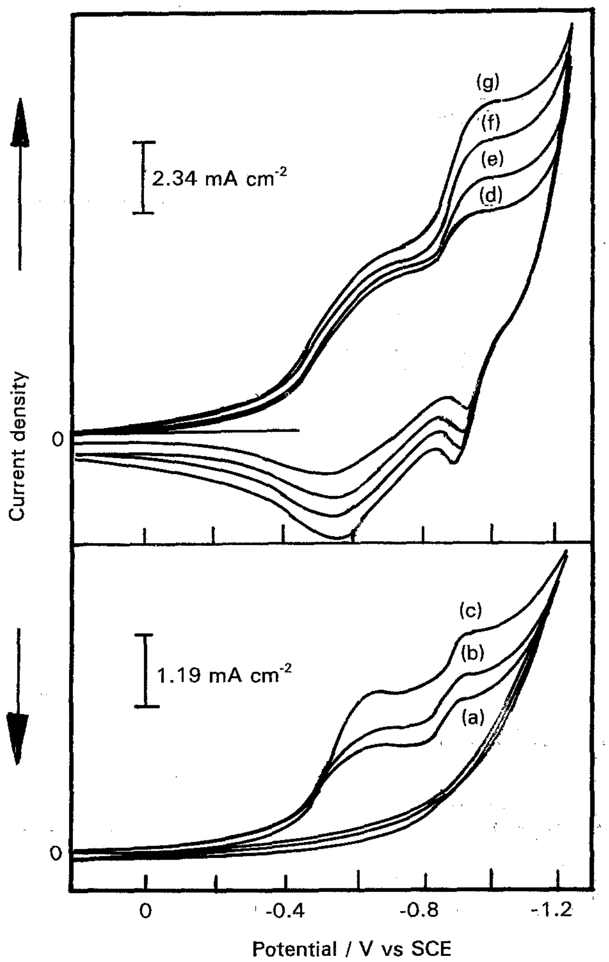

Fig. 7. Cyclic voltammograms of 12 mM 2-nitrobenzene sulphonic acid on a Ti/TiO_2 electrode in 10 M H_2SO_4. Sweep rates: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

adsorbed peak has been investigated over a wide pH range to confirm the above process [27].

4. Preparative electrolysis

Preparative scale experiments were carried out in a 1 dm^3 capacity glass cell. The cell cover was equipped with openings for introducing the porous diaphragm, thermometer, condenser and electrodes. About 500 cm^3 of sulphuric acid of varying concentrations was used as catholyte and the same sulphuric acid solution was used as anolyte. A Ti/TiO_2 electrode of 84 cm^2 surface area and a lead anode (55 cm^2) were used as cathode and anode, respectively. After the completion of the electrolysis, the aromatic amine content of the catholyte was estimated by the nitrous acid method [30] or excess bromination method or Koppeschaar's method [31], depending on the suitability of the amines formed.

4.1. *Effect of operating parameters*

The optimum experimental conditions obtained for each nitrocompound obtained from these preparative scale experiments are summarized along with the corresponding yields and current efficiencies in Table 2.

If the nitrocompound exhibits fairly good solubility in H_2SO_4 a lower acid strength of 10–20 vol % would be sufficient for efficient electroreduction. Nitroanilines and nitrophenols are good examples of this group. In the case of highly soluble *m*-nitrobenzene sulfonic acid and 2-nitrotoluene even 5 vol % H_2SO_4 was found to be sufficient. For nitrocompounds of very low solubility optimum acid strengths were found to be 30–40 vol % H_2SO_4. In the case of highly insoluble 2-chloro nitrobenzene, for example, in addition to using 50 vol % H_2SO_4 as the electrolyte medium, 0.01% CTAB was also found to be necessary for efficient overall electroreduction.

Nitrobenzene (NB) is an interesting case with respect to the optimum acid strength. For electroreduction of NB to aniline the optimum acid strength was found to be 10 vol % H_2SO_4. In 50 vol % H_2SO_4 the intermediate phenylhydroxylamine undergoes para-transformation to 4-aminophenol. This transformation is further assisted by higher operating cell temperature (80–85 °C).

In general higher operating temperatures are required whenever the solubility of the reactants is poor. The requirement of higher acid strength is always accompanied by the requirement of higher operating temperature (Table 2). Solid aromatic nitrocompounds also generally require higher operating temperatures for optimum results.

A significant observation in the present work is that the optimum current density for most of the nitrocompounds was found to be 5 A dm^{-2}. This is in spite of the wide variations observed in the cyclic voltammetric behaviour (see Table 1). The yield and current efficiency values are also found to vary only within a narrow range for such a wide variety of aromatic nitrocompounds studied (Table 2). It appears that in addition to the electroreduction through heterogeneous redox catalysis, the active hydrogen generated in the channels of the oxide layer also efficiently reduces all these nitro compounds, as well as their partially reduced reaction intermediates.

4.2. *Reuse of electrolyte*

One of the main advantages of using H_2SO_4 as the

Table 2. Optimum experimental conditions and related yields for the electroreduction of aromatic nitrocompounds

Sl	*Compound*	*Amount of reactant*/g	*Acid strength taken*/%	*CD* /A dm^{-2}	*Temp.* /°C	*Yield* /%	*CE* /%	*Ref.*
1	Nitrobenzene*	6	50	2.5	80–85	90.0	94.5	[15]
2	4-Nitrosophenol	7	10	1.8	30–35	82.0	76.0	[16]
3	4-Nitrophenol	8	10	2.5	40–45	97.0	98.0	[18]
4	1-Nitronaphthalene	12	30	8.1	70–80	92.3	84.5	[19]
5	2-Nitrophenol	20	20	5.0	40–50	95.0	93.2	[17]
6	2-Chloro nitrobenzene	12	50	5.0	40–50	89.1	97.2	[21]
7	3-Chloro nitrobenzene	12	40	5.0	50–60	82.9	83.0	[21]
8	4-Chloro nitrobenzene	12	20	5.0	60–70	85.9	95.4	[21]
9	2-Nitroaniline	14	10	5.0	30–40	92.0	91.9	[22]
10	3-Nitroaniline	14	10	5.0	40–50	93.7	74.7	[22]
11	4-Nitroaniline	14	10	5.0	40–50	89.9	86.8	[23]
12	2-Nitrobenzene sulfonic acid	13	5	5.0	35–40	95.2	93.4	[27]
13	Nitrobenzene†	12	10	5.0	40–50	95.5	93.6	[24]
14	2-Dinitrobenzene	11	20	5.0	70–80	92.2	91.1	[24]
15	2-Nitrotoluene	14	5	5.0	20–30	84.8	83.5	[26]
16	3-Nitrotoluene	14	10	5.0	30–40	88.5	86.2	[26]
17	4-Nitrotoluene	14	20	5.0	50–60	93.1	93.0	[26]
18	2,4-Dinitrotoluene	16	20	5.0	65–70	94.6	92.5	[26]
19	1-Chloro-2,4-Dinitrobenzene	16	20	5.0	50–55	92.7	88.3	[25]
20	5-Nitrosalicylic acid	7	20	2.1	30–35	76.0	90.0	[30]

* Nitrobenzene to 4-aminophenol.

† Nitrobenzene to aniline.

Table 3. Comparative results of preparative experiments involving product recovery and five times reuse of electrolytes

Sl	*Compound*	*Amount of reactant taken*/g	*Recovered amine sulphate*/g	*Yield*/%	*Ref.*
1	2-Chloro nitrobenzene	99.2	75.7	65.4	[21]
2	3-Chloro nitrobenzene	79.4	64.0	61.6	[21]
3	4-Chloro nitrobenzene	47.0	31.8	65.5	[21]
4	2-Nitroaniline	75.6	69.9	90.5	[22]
5	3-Nitroaniline	137.2	119.4	90.8	[22]
6	4-Nitroaniline	33.6	60.6	76.9	[22]
7	2-Nitrobenzene sulfonic acid	79.5	56.3	92.8	[27]
8	Nitrobenzene*	126.0	148.5	87.2	[24]
9	2-Dinitrobenzene	45.1	67.4	83.0	[24]
10	2-Nitrotoluene	52.2	66.9	79.9	[26]
11	3-Nitrotoluene	44.0	54.7	84.4	[26]
12	4-Nitrotoluene	67.2	79.1	90.8	[26]
13	2,4-Dinitrotoluene	88.8	125.5	81.4	[26]
14	1-Chloro-2,4-Dinitrobenzene	90.0	64.1	85.0	[25]

* Nitrobenzene to aniline.

electrolyte medium is the high solubility of the product aromatic amines as sulphates in this medium. Fairly high concentrations can thus be built up and subsequently isolated as solid sulphates. The same electrolyte can thus be conveniently recycled a number of times. Such electrolyte reuse experiments were carried out for 14 aromatic nitrocompounds by reusing the electrolyte five times for each compound. The average quantity of nitrocompounds employed in each experiment and average results obtained are summarized in Table 3. For most of the nitrocompounds fairly high yields were also noticed during reuse experiments (Table 3). However, slightly lower yields were obtained for chloronitrobenzenes.

In the earlier technique using homogeneous redox catalysis by Ti^{4+}/Ti^{3+} also [6] the amines were recovered as amine sulphates and electrolyte was reused. However, final recovery of amines from solution involves neutralization when titanium salts also become hydrolysed making the isolation of the amines more difficult. The present method totally eliminates this difficulty.

4.3. *Stability of the electrode*

In the preparative electrolysis experiments Ti/TiO_2 electrodes showed excellent stability over fairly long periods. Thermally coated Ti/TiO_2 plates could also be used in these experiments. Only after 900 h of use was considerable damage to the thermally coated oxide layer noticed. No hydrogen embrittlement effect or removal of oxide coating from this substrate was noticed during this experiment. Even after 900 h of use the electrode activity did not decrease significantly. However, it is desirable to recoat such electrodes before reuse.

Whenever high acid strengths (more than 50 vol %) and high temperature are simultaneously employed damage to the TiO_2 coating is noticed. Such conditions, for example, are required for the electroreduction of nitrobenzene to 4-aminophenol. In this case the electrodes required frequent re-coating to achieve reproducible results.

5. Summary

The preparative method for aromatic amines from aromatic nitrocompounds described here is a simple and environmentally friendly technique which can be commonly adopted for producing a number of compounds. As of now the energy cost for a 6F reaction of this type appears to be rather high. Fairly low energy cost and more environment consciousness may bring this technique to prominence in the future. Electroreduction of nitrocompounds, which are 4F reactions, under identical conditions are also attractive.

Electroreduction of oxalic acid to glyoxalic acid and maleic acid to succinic acid are currently being investigated on these electrodes. In acidic solutions these thermally coated Ti/TiO_2 electrodes offer wide scope for further investigations.

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