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Electrocatalytic reduction of *o* and *m*-nitroanilines at a Ti/ceramic TiO_2 cathode

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Galvanostatic reduction of *o* and *m*-nitroanilines to the corresponding phenylenediamines has been carried out in aqueous H_2SO_4 medium at a Ti/ceramic TiO_2 cathode under varying conditions of acid strength, current density and temperature. The best conditions for obtaining maximum yields of the corresponding diamines have been established. Results show higher current efficiency for diamine formation at a Ti/ceramic TiO_2 cathode in comparison with those obtained at a copper cathode under identical conditions, thus indicating the electrocatalytic nature of the former. Experiments on the re-use of the electrolyte have also been carried out, the results of which show that the yields of the corresponding diamines are not affected up to the fourth re-use of the electrolyte. Cyclic voltammetric studies on the reduction of these compounds confirm that the reduction of the nitro group is catalysed by Ti^{4+}/Ti^{3+} redox species at the electrode.

1. Introduction

Modified electrodes are finding applications in electrosynthesis, electroanalysis, energy conversion systems, as well as bioelectrochemistry and photoelectrochemistry. These tailor-made electrodes can better meet the demands for higher activity, selectivity and stability. The Ti/ceramic TiO_2 cathode is one such type of electrode. The electrocatalytic reduction of several nitro and nitroso compounds using this electrode has been previously studied successfully in this laboratory. Synthesis of industrially important amines such as 5-aminosalicylic acid [1], *p*-phenylenediamine [2] and isomeric chloroanilines [3] serve as some examples for $-NO_2$ group reduction at this catalytic cathode. Work on the reduction of other electroactive functional groups is in progress.

The Ti/ceramic TiO_2 cathode developed by Beck and co-workers [4] offers unique advantages, such as ease of preparation, high electrocatalytic activity, high turn-over factor of the order of 10^6 [5], chemical and electrochemical stability and enhanced selectivity. In view of these advantages, the reduction of nitro compounds using this cathode may be superior to the existing chemical or electrochemical methods. Scale-up studies using this electrode are also in progress.

In the present paper, the reduction of *o*-nitroaniline (*o*-NA) and *m*-nitroaniline (*m*-NA) to the corresponding phenylenediamines (*o*-PDA and *m*-PDA) at the Ti/ceramic TiO_2 cathode is reported.

The *o*-PDA is prepared by reducing *o*-dinitrobenzene in the liquid phase with a noble metal catalyst or by iron and HCl. It may also be prepared by the reduction of *o*-NA with sodium sulphide in an autoclave or with zinc dust and NaOH. Treatment of *o*-dichlorobenzene or *o*-chloroaniline with aqueous NH_3 under pressure, or in the presence of copper, also yields *o*-PDA. The *m*-PDA is prepared by the reduction of *m*-dinitrobenzene with Fe and HCl or with ammonium polysulphide water gas mixture [6]. The yield of *m*-PDA by the chemical method under the best conditions is 94.3%.

o-PDA has been prepared by controlled-potential electrolytic reduction of *o*-NA at -100 mV at 75 °C in 25% H_2SO_4 [7] or of *o*-dinitrobenzene at -400 mV in 1 : 1 EtOH–2N H_2SO_4 at 20–40 °C at a mercury cathode (against SCE) [8]. King [9] reported a yield of 70% for the reduction of *o*-dinitrobenzene to *o*-PDA. Electrolytic reduction of *m*-dinitrobenzene to *m*-PDA, as studied by Bochringer and Sohne, gave a yield of 83% [10]. Electrolytic preparation from *m*-NA using $SnCl_2$ in HCl medium gave a yield of 98.7% [11]. However, chlorine evolution in the above case poses the problem of anode corrosion. In an attempt to eliminate these drawbacks, the reduction of these nitro compounds was studied at the Ti/ceramic TiO_2 cathode in aqueous H_2SO_4 medium.

o-PDA is used in the manufacture of dyes [12]. It is also useful as an analytical reagent for identifying 1,2-diketones, carboxylic acids and aldehydes by forming heterocyclic compounds [13]. *m*-PDA is used in the manufacture of dyes, rubber curing agents, ion exchange resins, decolorizing resins, formaldehyde condensates, resinous polyamides, block polymers, textile fibres, urethanes, petroleum additives, rubber chemicals, corrosion inhibitors, in photography and as a reagent for gold and bromine. The hydrochloride is used as a reagent for nitrite [12].

2. Experimental details

2.1. *Galvanostatic electrolysis*

The experimental details regarding the preparation of

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Table 1. Galvanostatic electrolysis data on the reduction of o-NA at a Ti/ceramic TiO_2 cathode in aqueous H_2SO_4 medium

S. No.	*Weight of o-NA taken/g*	*H_2SO_4/ mol cm^{-3}*	*Current density/ A dm^{-2}*	*Temp./°C*	*Insolubles (o-NA)/g*	*Yield of o-PDA (estimated)/g*	*Yield/%*	*c.e./%*
1	14	0.56	5.0	30–40	2.32	8.2	90.0	90.0
2	14	0.94	5.0	30–40	–	10.1	92.0	91.9
3	14	1.88	5.0	30–40	–	8.7	79.4	79.4
4	14	0.94	2.5	30–40	3.35	7.6	91.1	69.3
5	14	0.94	7.5	30–40	1.40	8.9	89.8	80.8
6	14	0.94	5.0	20–30	2.52	8.0	89.4	77.9
7	14	0.94	5.0	40–50	–	9.1	82.6	82.6
8*	14	0.94	5.0	30–40	1.63	7.8	80.6	44.4

* At copper cathode.

Ti/ceramic TiO_2 cathode and the divided cell arrangement employed have been described previously [14]. 400 ml of 0.56/0.94/1.88/2.82 M H_2SO_4 containing *o*-NA/*m*-NA (the amount as given in the Tables) served as the catholyte and 100 ml of 0.94/1.88/2.82 M H_2SO_4 as the anolyte. A Ti/ceramic TiO_2 electrode (0.84 dm^2) and lead were used as the cathode and anode, respectively.

For experiments involving the re-use of the electrolyte, the same concentration of the acid was maintained for every re-use by adding the requisite amount of acid after standard estimation.

The diamines were isolated as the corresponding disulphates which were then neutralized and recrystallized from ethanol; their structures were confirmed from their melting points, i.r. spectra and the melting points of their diacetyl derivative. The diamine in solution was estimated by the standard method [15].

2.2. *Cyclic voltammetry*

Cyclic voltammetry (CV) for the reduction studies on *o*-NA and *m*-NA was carried out in 1 M H_2SO_4 using a Ti/ceramic TiO_2 strip as cathode (area 0.283 cm^2). An aqueous SCE and a platinum foil served as reference and counter electrodes respectively. The undivided cell set up for CV studies is the same as that employed earlier [1].

3. Results and discussion

3.1. *Galvanostatic electrolysis*

The results of galvanostatic electrolysis carried out on *o*-NA and *m*-NA at a Ti/ceramic TiO_2 cathode under varying conditions of current density, acid strength and temperature are listed in Tables 1 and 2, respectively. It can be seen from Table 1 that the yield and current efficiency (c.e.) for the formation of *o*-PDA (S.No. 2) is maximum at a current density of 5 A dm^{-2} in 0.94 M H_2SO_4 at a temperature in the range 30–40 °C. At lower/higher current densities, hydrogen evolution becomes competitive, thereby reducing the yield and c.e. considerably. Initial increase in the acid strength (H_2SO_4) from 0.56 M to 0.94 M (S.No.'s 1 and 2) causes an increase in the solubility of *o*-NA as well as that of *o*-PDA and, thereby, increases the yield of the diamine considerably. On further increasing the acid strength (S.No. 3), the considerable decrease observed in the yield and the c.e. is due to resin formation at high acid strength.

The effect of temperature (S.No.'s 2, 6 and 7) shows that the yield of the diamine is a maximum at about 30–40 °C. Initial increase in the yield and c.e. with increase in temperature is due to improved convection conditions for the depolarizer transport. At still higher temperature, however, the tendency for resin formation causes lowering in the yield and c.e.

It can be seen from Table 1 that under conditions of low acid strength and at low temperatures (S.No.'s 1 and 6), some unreduced *o*-NA was recovered. This observation may be attributed to lower availability of free H_2SO_4 since it may be used in converting the product diamine, which is a strong base, to the corresponding disulphate. Table 1 (S.No.'s 2 and 8) also shows that the yield and c.e. are considerably lowered at a copper cathode compared with the Ti/ceramic TiO_2 cathode under identical conditions. The above results clearly suggest the electrocatalytic nature of the latter electrode.

The results on the galvanostatic electrolysis of *m*-NA under similar experimental conditions are shown in Table 2. The yield and c.e. for the formation of *m*-PDA is maximum at a current density of 5 A dm^{-2} in 0.94 M H_2SO_4 at a temperature in the range 40–50 °C. The above results are similar to those observed for the reduction of *o*-NA and hence a similar explanation holds good.

The high solubility of *o*-PDA and *m*-PDA, which can be separated as the corresponding disulphates in H_2SO_4 medium, suggests the possibility of electrolyte re-use. The results of the galvanostatic electrolysis experiments carried out on *o*-NA and *m*-NA involving the re-use of electrolyte (choosing the best experimental conditions from Tables 1 and 2, respectively) are presented in Tables 3 and 4, respectively. It can be seen that the yields of the corresponding diamines are not affected even after the fourth re-use of the electrolyte. This makes the process economical on a large scale.

It is interesting to observe that in the reduction of *m*-NA, unreduced *m*-NA was recovered at the end of every re-use. It is likely that as the more soluble

Table 2. Galvanostatic electrolysis data on the reduction of m-NA at a Ti/ceramic TiO_2 cathode in aqueous H_2SO_4 medium

S. No.	*Weight of m-NA taken/ g*	*H_2SO_4/ mol cm^{-3}*	*Current density/ A dm^{-2}*	*Temp./°C*	*Insolubles (m-NA)/g*	*Yield of m-PDA (estimated)/g*	*Yield/%*	*c.e./%*
1	14	0.56	5.0	40–50	3.64	7.2	88.3	69.0
2	14	0.94	5.0	40–50	2.83	8.2	93.7	74.7
3	14	1.88	5.0	40–50	2.53	8.1	90.5	74.2
4	14	2.82	5.0	40–50	2.17	7.5	89.6	68.2
5	14	0.94	2.5	40–50	5.05	6.2	88.6	56.6
6	14	0.94	7.5	40–50	3.46	7.5	90.5	68.2
7	14	0.94	5.0	30–40	4.51	6.7	90.2	61.1
8	14	0.94	5.0	50–60	3.27	7.8	92.4	70.8
9*	14	0.94	5.0	40–50	7.96	4.2	88.9	38.4

* At copper cathode.

m-PDA (which exists as disulphate) forms progressively during the reduction of *m*-NA, the latter separates out.

The *o*-PDA and *m*-PDA prepared as above, melted at 104 °C (103–104 °C) and 63 °C (62–63 °C) [12], respectively, and the corresponding diacetyl derivatives at 186 °C (185 °C) and 191 °C (191 °C) [6], respectively, which are in close agreement with the literature values given in parentheses. The i.r. spectra of *o*-PDA and *m*-PDA prepared as above exactly matched those of the authentic samples [16]. The diamines were stored in air-tight amber coloured bottles since they would otherwise become darkened on exposure to air.

3.2. *Cyclic voltammetric studies*

The cyclic voltammetric (CV) response for the Ti/ceramic TiO_2 cathode (fabricated using the method employed in the production of ceramics) in 1 M H_2SO_4 at sweep rates (v) of 0.005 V s^{-1} and 0.2 V s^{-1} is shown in Fig. 1. Two redox peaks are seen, though the first cathodic peak is extremely small. These are due to reversible reduction of the $Ti(OH)_4$ and TiO_2, respectively, to the corresponding Ti(III) compounds [1]. The peak separation between the cathodic and anodic peak potentials of the redox peak is close to 0.030 V. This suggests the occurrence of a preprotonation reaction involving a dimeric TiO_2 species which undergoes a two-electron reduction in a rate determining step as shown below.

$$2TiO_2 + H^+ \rightleftharpoons [(TiO_2)_2H^+] \tag{1}$$

$$[(TiO_2)_2H^+] + H^+ + 2e^- \xrightarrow{rds} 2TiOOH \tag{2}$$

The cyclic voltammograms for the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 solution in the presence of *o*-NA [2 × 10^{-3} M (a) and 166.67 × 10^{-3} M (b)] at 0.005 V s^{-1} and 0.2 V s^{-1} sweep rates are shown in Fig. 2. It can be seen that on increasing the concentration of *o*-NA, increase in the cathodic peak height with simultaneous decrease in the anodic peak height occurs. This observation clearly illustrates the catalytic regeneration of Ti^{4+} at the electrode surface which is due to a fast reaction between the Ti^{3+} and the nitro compound. That is,

$$6Ti(OH)_3 + RNO_2 \longrightarrow 6TiO_2 + RNH_2 + 8H_2O \tag{3}$$

or

$$6TiOOH + RNO_2 \longrightarrow 6TiO_2 + RNH_2 + 2H_2O \tag{4}$$

It is also clear from Fig. 2 that at higher concentrations, the anodic peak completely disappears. Also, at lower sweep rates, the disappearance of the anodic peak is more clearly seen. This behaviour may be expected in the case of an EC_{cat} reduction as above [1].

At lower concentrations of *o*-NA, the response was diffusion-limited in the sweep-rate range of 0.3 to 0.005 V s^{-1}. This may be explained by considering that

Table 3. Galvanostatic electrolysis data on the reduction of o-NA at a Ti/ceramic TiO_2 cathode in 0.94 M H_2SO_4 solution showing the re-use of electrolyte

S. No.	*Amount of o-NA taken/g*	*Yield of o-PDA disulphate/g*	*Yield of o-PDA (after neutralization)/g*	*Yield (o-PDA) estimated in mother liquor/g*	*Yield/%*
1	70	69.7	47.9	1.1	90.3
2	77	70.3	53.5	1.2	90.8
3	77	69.9	53.3	1.2	90.5
4	77	70.1	53.3	1.2	90.4
5	77	69.9	53.5	1.2	90.6

Table 4. Galvanostatic electrolysis data on the reduction of m-NA at a Ti/ceramic TiO_2 cathode in 0.94 M H_2SO_4 solution showing the re-use of electrolyte

S. No.	*Amount of m-NA taken/g*	*Insolubles (m-NA)/g*	*Yield of m-PDA disulphate/g*	*Yield of m-PDA (after neutralization)/g*	*Yield (m-PDA) estimated in mother liquor/g*	*Yield/%*
1	126	22.0	109.8	72.5	1.3	90.7
2	140	24.6	122.0	80.6	1.4	90.4
3	140	24.8	122.0	80.5	1.4	91.0
4	140	24.8	121.7	80.7	1.3	90.9
5	140	24.8	121.6	80.6	1.2	90.8

the electrochemical step involving the reduction of Ti^{4+} to Ti^{3+}, as well as the chemical step involving the regeneration of Ti^{4+}, occur at a much faster rate compared to the diffusion of *o*-NA to the electrode surface. However, as the concentration of *o*-NA was increased to 166.67×10^{-3} M and above, the trend in the current function values observed was that expected for an electrochemical step with a follow-up catalytic reaction. This is understandable since at higher concentrations of *o*-NA, the diffusion step becomes less important.

The cyclic voltammograms for the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 solution in the presence of *m*-NA (2×10^{-3} M) at $0.005\,V\,s^{-1}$ and $0.2\,V\,s^{-1}$ sweep rates are shown in Fig. 3. Similar behaviour has been observed as for the reduction of *o*-NA and, hence, the same explanation holds good. However, the cyclic voltammetric response is poor in the case of *m*-NA.

It was observed from CV studies on the electrode behaviour under different strengths of H_2SO_4 (0.05–2 M), that the hydrogen evolution potential, as well as the peak potential for the reduction of Ti^{4+} to Ti^{3+}, are shifted to more positive values. However, the positive shift was greater in the case of the former, thus lowering the difference in potentials between the reduction of the Ti^{4+} peak and hydrogen evolution. Hence, there may be competitive hydrogen evolution at higher acid strengths which may also reduce the yield and c.e., as observed from the results of galvanostatic electrolysis.

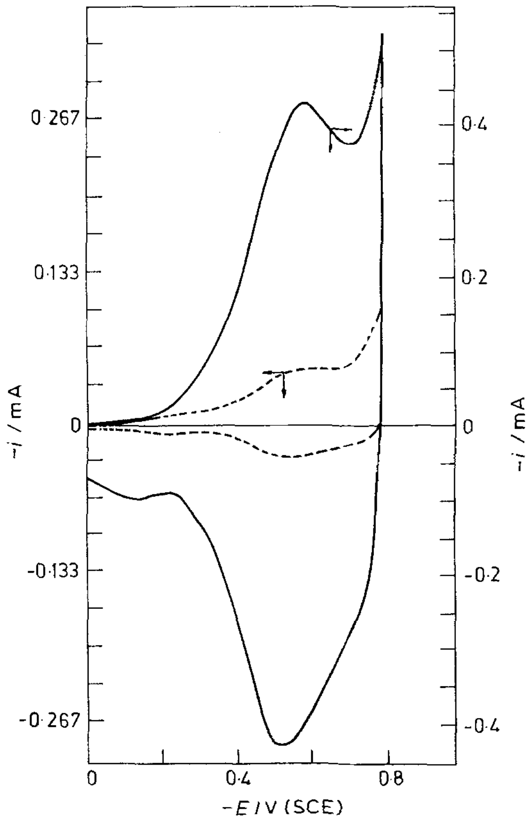

Fig. 1. CV response for the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at sweep rate (v) of $0.005\,V\,s^{-1}$ and $0.2\,V\,s^{-1}$.

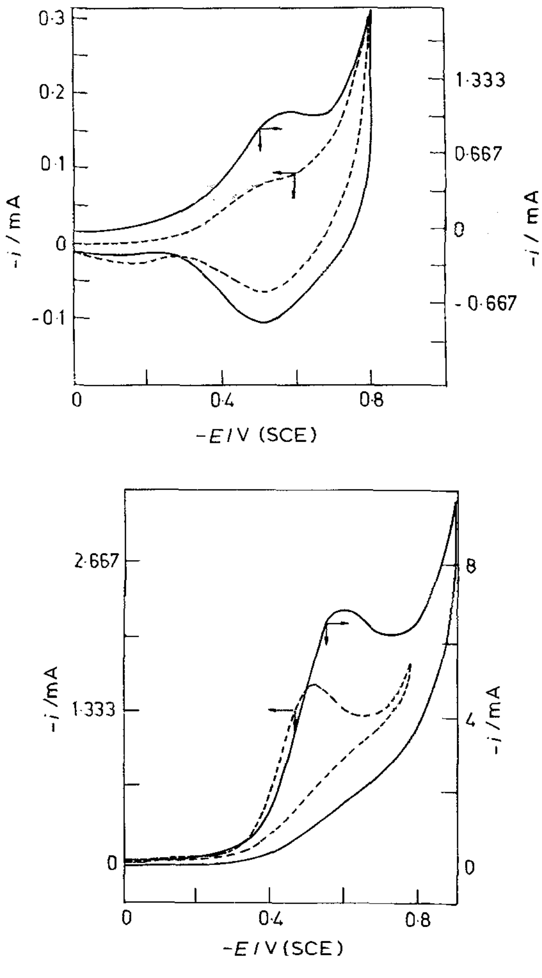

Fig. 2. CV response for the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 solution in the presence of *o*-NA [2×10^{-3} M (a) and 166.67×10^{-3} M (b)] at $0.005\,V\,s^{-1}$ and $0.2\,V\,s^{-1}$ sweep rates.

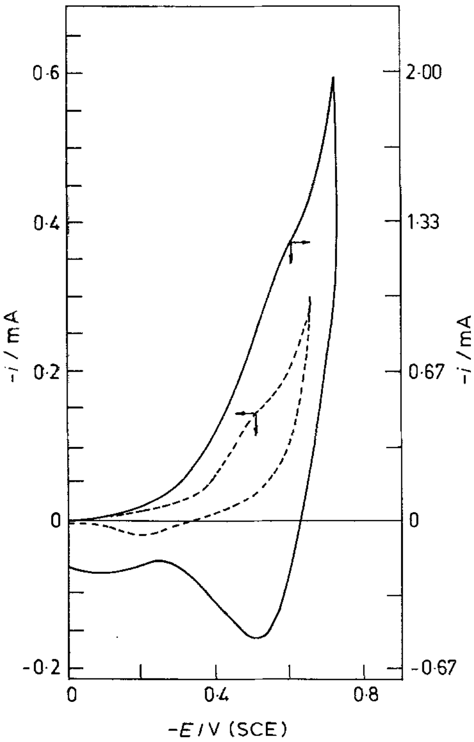

Fig. 3. CV response for the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 solution in the presence of *m*-NA (2×10^{-3} M) at 0.005 V s^{-1} and 0.2 V s^{-1} sweep rates.

4. Conclusion

The Ti/ceramic TiO_2 cathode has been found to give higher yields of the diamine with higher c.e. when compared to the conventional copper cathode in the reduction of *o*-NA and *m*-NA. Also, the present method offers a pollution free, cost effective and direct route (without complications by side products) as compared to the existing methods for the production of *o*-PDA and *m*-PDA.

References

[1] D. Vasudevan, S. Chellammal and P. N. Anantharaman, *J. Appl. Electrochem.* **21** (1991) 839.
[2] C. Ravichandran, D. Vasudevan and P. N. Anantharaman, *ibid.* **22** (1992) 179.
[3] C. Ravichandran, D. Vasudevan, S. Thangavelu and P. N. Anantharaman, *ibid.* in press.
[4] F. Beck and W. Gabriel, *Angew Chem. Int. Ed. Engl.* **24** (1985) 771.
[5] F. Beck, *Electrochim. Acta* **34** (1989) 811.
[6] Robert S. Browning and 22 others, 'Encyclopedia of Industrial Chemical Analysis', Vol. 11, (edited by Foster Dee Snell and Leslie S. Ettre), John Wiley & Sons, New York (1971) p. 438 and p. 445.
[7] M. L. Guyader, *Compt. Rend.* **254** (1962) 4182.
[8] A. Talles and D. Peltier, *ibid.* **259** (1964) 400.
[9] M. V. King, *J. Org. Chem.* **26** (1961) 3323.
[10] C. F. Bochringer, D.R.P. 116942 (1900).
[11] C. J. Brockman, 'Electroorganic chemistry', John Wiley & Sons, New York (1926) p. 210.
[12] The Merck Index, 'An Encyclopedia of Chemicals, Drugs and Biologicals', (edited by Susan Budavari), Merck and Co., Inc., USA (1989) p. 1157.
[13] W. A. Anderson *et al.* Kirk-Othmer, 'Encyclopedia of Chemical Technology', Vol. 2, (edited by Galen J. Bushey, Anna Klingsberg and Lorraine Van Nes), John Wiley & Sons, New York (1978), p. 353.
[14] C. Ravichandran, S. Chellammal and P. N. Anantharaman, *J. Appl. Electrochem.* **19** (1989) 465.
[15] A. R. Day and W. Taggart, *Ind. Eng. Chem.* **20** (1928) 545.
[16] The Aldrich Library of Infrared Spectra, (edited by C. J. Pouchert), Aldrich Chemical Company, Inc., USA (1981) pp. 739–41.