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SHORT COMMUNICATION

Indirect reduction of p-nitroaniline to p-phenylenediamine at a Ti/TiO_2 electrode

C. RAVICHANDRAN, D. VASUDEVAN, P. N. ANANTHARAMAN
Central Electrochemical Research Institute, Karaikudi 623 006, India

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1. Introduction

p-phenylenediamine (p-PDA) is an industrially important compound used as antioxidant and antiozonant for plastics, elastomers, gasoline etc. It is used as a coupling agent in colour photography and as a fine grain developer in black and white photography. Coloured products obtained by oxidizing p-PDA are used for dyeing of furs and hairs. It is used in the synthesis of several azo dyes and sulphur dyes. It is also used for preparing polyurethanes, polyamides, polyimides and some conducting polymers. It also serves as a polymerization inhibitor [1]. It is used in photochemical measurements and its hydrochloride serves as a reagent for blood, H_2S, amyl alcohol and in testing of milk [2].

p-PDA is toxic and causes respiratory problems and dermatitis. However, by appropriate substitution of certain groups, the toxicity can be reduced [1].

Electrochemical reduction of p-nitroaniline (p-NA) to p-PDA has been studied by several authors [3–6]. Winslow [3] reported a yield of 45% in the reduction of p-NA to p-PDA at a porous carbon electrode in HCl medium. Mizuguchi *et al.* [4] used a platinum cathode in HCl–alcohol medium and reported a yield of 95%. In the above processes, chlorine disposal and anode corrosion pose problems and in the latter process, use of a platinum cathode and alcohol medium render the process uneconomical from an industrial viewpoint. The use of a titanous–titanic redox system gave a yield of 92.4% with 87.2% current efficiency [5, 6]. However, due to the tendency of Ti ions for complex formation, the same cannot be employed on an industrial scale. In the present paper, the use of a Ti/TiO_2 electrode as a catalytic electrode in the production of p-PDA and the inherent advantages of this method over the existing chemical or electrochemical methods have been highlighted. The optimum conditions for maximum yield of diamine have been worked out and studies have also been made on the reuse of the electrolyte. Cyclic voltammetry for the reduction studies on p-NA, carried out using Ti/TiO_2 strips as cathode, clearly show a mechanism involving heterogeneous redox catalysis of the Ti^{4+} by added p-NA.

2. Experimental details

2.1. *Galvanostatic electrolysis*

The experimental details regarding the preparation of Ti/TiO_2 electrode and the cell arrangement have been described previously [7]. 400 ml of 0.94/1.88/2.82 M H_2SO_4 containing p-NA (concentration as given in Tables 1 and 2) served as the catholyte and 100 ml of 0.94/1.88/2.82 M H_2SO_4 as the anolyte. Ti/TiO_2 (0.84 dm^2) and lead were used as the cathode and anode, respectively.

For experiments involving reuse of electrolytes, the same concentration of the acid was maintained for every reuse by adding the requisite amount of acid after standard estimation.

The diamine was isolated as the corresponding disulphate which was then neutralized and recrystallized from ethanol; its structure was confirmed from its melting point, i.r. spectra and the melting point of its acetyl derivative. The diamine in solution was estimated by the standard method [8].

3. Results and discussion

3.1. *Galvanostatic electrolysis*

The results of galvanostatic electrolysis carried out on

Table 1. Galvanostatic electrolysis data on the reduction of p-NA at a Ti/TiO_2 electrode

S. No.	*Weight of p-NA taken (g)*	*H_2SO_4 (moles cm^{-3})*	*Current density ($A\ dm^{-2}$)*	*Temp. (° C)*	*Insolubles (p-NA) (g)*	*Yield of p-PDA (estimated) (g)*	*Yield (%)*	*CE (%)*
1	14	1.88	2.5	40–50	7.68	4.91	77.8	45.1
2	14	1.88	5.0	40–50	–	9.8	89.9	86.8
3	14	1.88	7.5	40–50	6.58	4.8	64.8	55.0
4	14	0.94	5.0	40–50	5.70	6.4	78.8	75.7
5	14	2.82	5.0	40–50	–	9.5	87.2	85.9
6	14	1.88	5.0	30–40	7.30	4.48	81.5	61.1
7	14	1.88	5.0	50–60	–	6.62	60.7	73.7
8*	14	1.88	5.0	40–50	7.32	4.76	75.2	47.7

* At copper cathode

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Table 2. Galvanostatic electrolysis data on the reduction of p-NA at a Ti/TiO$_2$ electrode in 1.88 M H$_2$SO$_4$ solution showing the re-use of electrolyte

S. No.	*Amount of p-NA taken (g)*	*Yield of p-PDA disulphate (g)*	*Yield of p-PDA (after neutralization) (g)*	*Yield (estimated) of p-PDA in mother liquor (g)*	*Total yield (g)*	*Yield (%)*
1	42.0	78.70	22.50	3.20	25.7	78.2
2	31.5	56.23	14.71	4.23	18.9	76.8
3	31.5	55.86	13.93	4.91	18.8	75.8
4	31.5	56.01	14.20	4.72	18.9	76.1
5	31.5	55.98	14.01	4.86	18.9	75.9

p-NA at a Ti/TiO$_2$ cathode under varying conditions of current density, acid strength and temperature are listed in Table 1. It can be seen that the yield and current efficiency (CE) for the formation of p-PDA is maximum at a current density of 5 A dm^{-2} in 1.88 M H$_2$SO$_4$ at a temperature in the range 40–50° C. At lower/higher current density, hydrogen evolution becomes competitive, thereby reducing the yield and current efficiency (CE) considerably.

Increase in acid strength (H$_2$SO$_4$) from 0.94 to 1.88 M (S. No.'s 2 and 4) causes an increase in the solubility of p-NA as well as that of p-PDA and thereby increases the yield of the diamine to a great extent. On further increasing the acid strength (S. No. 5), slight reduction in the yield of the diamine is observed which may be due to formation of resin 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 40 to 50° C. Initial increase in the yield and CE with increase in temperature is due to improved convection conditions for the depolarizer transport. At higher temperature, however, the tendency for resin formation causes lowering in the yield and CE.

It can be seen from Table 1 that under conditions of low acid strength and at temperatures of about 30 to 40° C (S. No.'s 4 and 6), some unreduced p-NA was recovered. This observation may be attributed to lower availability of free H$_2$SO$_4$ since it may be used in converting the product diamine, which is a strong base, to the corresponding disulphate. Also, at current densities lower or higher than 5 A dm^{-2}, (S. No.'s 1 and 3), unreduced p-NA is seen at the end of electrolysis. This may arise due to the reduction in the strength of H$_2$SO$_4$ due to the competing hydrogen evolution reaction at these current densities, which in turn causes a decrease in the yield and CE.

Table 1 (S. No.'s 1 and 8) shows that the yield of the diamine and CE are considerably lower at a copper cathode than at a Ti/TiO$_2$ electrode under identical conditions. The above results clearly suggest the electrocatalytic activity of the Ti/TiO$_2$ electrode.

The high solubility of p-PDA, which can be separated as the corresponding disulphate in H$_2$SO$_4$ medium, suggests the possibility of electrolyte reuse. The results of the galvanostatic electrolysis experiments carried out on p-NA involving the reuse of the electrolyte (1.88 M H$_2$SO$_4$) are presented in Table 2. It can be

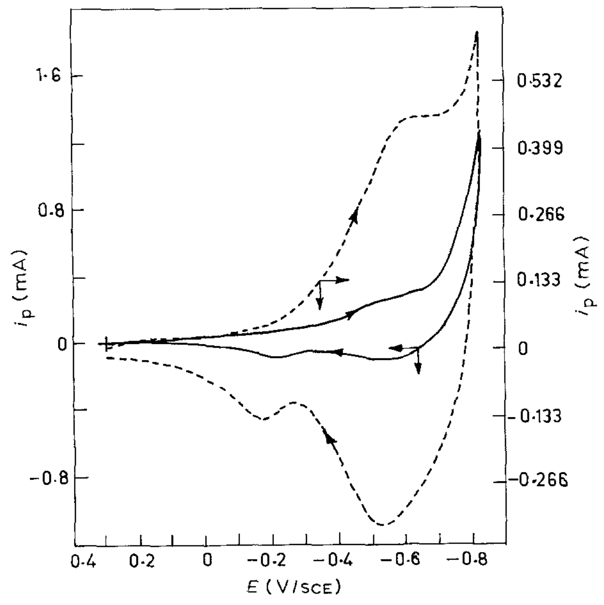

Fig. 1. CV's for the Ti/TiO$_2$ electrode in 2 M H$_2$SO$_4$ at different sweep rates (v): 0.005 V s^{-1} (——) and 0.200 V s^{-1} (– – –).

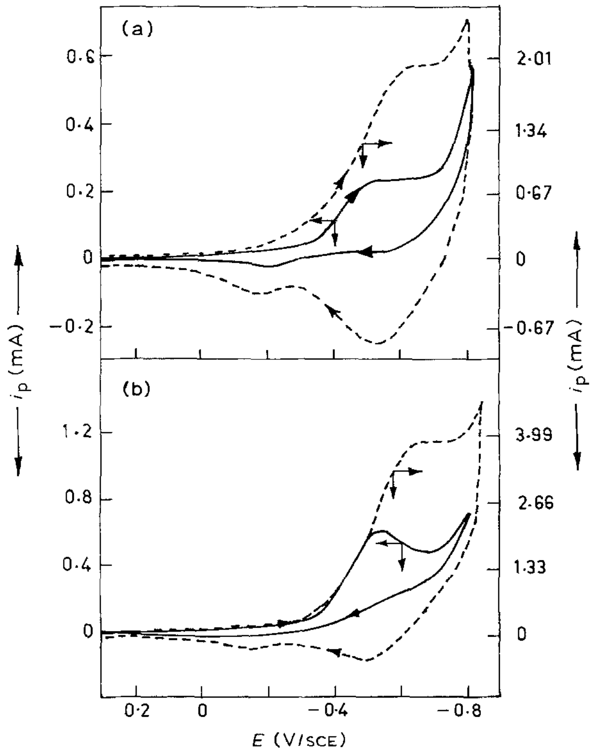

Fig. 2. CV's for the Ti/TiO$_2$ electrode in 2 M H$_2$SO$_4$ solution in the presence of p-NA [2 × 10^{-2} M(a) and 5 × 10^{-2} M(b)] at different sweep rates: 0.005 V s^{-1} (——) and 0.200 V s^{-1} (– – –).

seen that the yield of the diamine was not affected even after the fourth reuse of the electrolyte. This makes the process economical on a large scale.

The diamine obtained as above and its acetyl derivative (prepared) melt at 140° C (140° C) and 162–164° C (162–163° C) which are in close agreement with the literature values [9, 10] given in the brackets. The IR spectra for p-PDA prepared as above exactly matched with that of an authentic sample. The diamine was stored in an air-tight amber-coloured bottle since it would otherwise become darkened on exposure to air.

3.2. *Cyclic voltammetric studies*

The cyclic voltammetric (CV) response for the Ti/TiO_2 electrode (fabricated using the method employed in the production of ceramics) in 2 M H_2SO_4 at sweep rates (v) of $0.005\,V\,s^{-1}$ and $0.2\,V\,s^{-1}$ are shown in Fig. 1. Two redox peaks are clearly visible at $0.2\,V\,s^{-1}$ sweep rate though they are less distinct at $0.005\,V\,s^{-1}$ sweep rate. The two redox peaks arise due to the reduction of $Ti(OH)_4$ and TiO_2, respectively, to the corresponding Ti(III) compounds [11] as shown below:

$$Ti(OH)_4 + H^+ + e^- \rightleftharpoons Ti(OH)_3 + H_2O \quad (1)$$

$$TiO_2 + H_2O + H^+ + e^- \rightleftharpoons Ti(OH)_3 \quad (2)$$

The cyclic voltammograms for the Ti/TiO_2 electrode in 2 M H_2SO_4 solution in the presence of p-NA[2×10^{-2} M(a) and 5×10^{-2} 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 p-NA, magnification 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,

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

It can also be seen from Fig. 2 that the disappearance of the anodic peak is more clear in the time scale of the lower sweep rate, as may be expected in the case of an EC_{cat} reduction [12] as above.

4. Conclusion

The Ti/TiO_2 electrode has been found to give higher yields of the diamine with higher CE when compared to the conventional copper cathode in the reduction of p-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 p-PDA.

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