

Reduction of 1-nitroso-2-naphthol at a Ti/ceramic TiO₂ cathode in different media

D. VASUDEVAN*, P. N. ANANTHARAMAN

Central Electrochemical Research Institute, Karaikudi-623 006, India

Received 11 November 1992; revised 29 October 1993

The cyclic voltammetric behaviour of a Ti/ceramic TiO₂ cathode has been studied in 50% (v/v) ethanolic 1 M H₂SO₄, 0.1 M Na₂SO₄ and 1 M NaOH solutions, both in the absence and presence of various concentrations of added 1-nitroso-2-naphthol (NN). Catalytic reduction of NN at the Ti/ceramic TiO₂ cathode occurs by the electrogenerated Ti³⁺ species. Galvanostatic electrolytic reduction of NN at a Ti/ceramic TiO₂ cathode carried out in these media gave 1-amino-2-naphthol in high yield with a high current efficiency. The cyclic voltammetric and galvanostatic studies on the reduction of NN in these media have also been carried out at a glassy carbon electrode (GCE) for comparison.

1. Introduction

The behaviour of a Ti/ceramic TiO₂ cathode in 50% (v/v) ethanolic 1 M H₂SO₄ and the electrocatalytic reduction of several nitrocompounds to the respective amino compounds in high yields at this cathode has been reported earlier in this journal [1–4]. As part of the present work, the cyclic voltammetric studies on the behaviour of the Ti/ceramic TiO₂ cathode have been extended to 50% (v/v) ethanolic 0.1 M Na₂SO₄ and 1 M NaOH media. The influence of different concentrations of added NN on the behaviour of the cathode in the three different media has also been investigated. Galvanostatic electrolytic reduction of NN was also carried out in these media using a Ti/ceramic TiO₂ cathode and lead anode and the product formed was characterized by its melting point and i.r. spectral data. Both cyclic voltammetric and galvanostatic electrolysis studies on the reduction of NN in these media have also been carried out at a GCE for comparison.

Literature data on the electrochemical studies on NN are limited to polarographic studies in aqueous or aqueous methanolic solutions in acid, neutral or basic media [5–8]. A single four-electron wave corresponding to the reduction of the nitroso group to the amino group was observed in acid and basic media. However, two waves were observed in the neutral media. Also, due to ease of complex formation, polarographic estimations of a number of metal ions such as Co²⁺, Cu²⁺ and Zn²⁺, employing NN as the titrating agent, have been reported [9, 10].

2. Experimental details

2.1. Cyclic voltammetric studies

Cyclic voltammetric studies were carried out in an

undivided cell using a potentiostat and a scan generator in conjunction with an XY recorder. An aqueous SCE and a platinum foil served as the reference and counter electrodes respectively while a Ti/ceramic TiO₂ electrode (area 0.283 cm²) or a GCE (area 0.071 cm²) served as the working electrode. 50% (v/v) ethanolic 1 M H₂SO₄, 0.1 M Na₂SO₄ and 1 M NaOH served as the electrolyte, which are quoted in the following as acid, neutral or basic media, respectively (electrolytes, solutions). An AR sample of NN (Loba Chemie) was used. The depolariser (NN) in the concentration range of 1–10 mM was employed. The experimental solution was deaerated using pure nitrogen gas. All the measurements were carried out at 30°C.

2.2. Galvanostatic electrolysis studies

The Ti/ceramic TiO₂ cathode for galvanostatic electrolytic studies was prepared by a method similar to that reported by Beck and coworkers [11, 12], by sandblasting the expanded titanium sheet of required area, pickling of the above sheet in 50% HCl and finally applying the coating solution consisting of titanium acetylacetonate (2.189 g) in concentrated HNO₃ (5 ml) and H₂O (3 ml) made upto 50 ml with isopropanol using a micropipette. The electrode was dried at 90°C for 10 min and then baked in air in a muffle furnace at 550°C for 15 min. After a total of five activation cycles, a TiO₂ concentration of 5 μmol cm⁻² is present on the electrode surface.

The electrolytic cell consisted of a glass beaker of one litre capacity provided with a lead cover for introducing the cathode, anode (placed inside a porous pot diaphragm) and an overhead stirrer. A stationary Ti/ceramic TiO₂ cathode (area 0.35 dm²) or a GCE (area 0.40 dm²) served as the cathode and a lead sheet served as the anode. 200 ml of 50% (v/v) ethanolic

* Current address and address for communication: D. Vasudevan, c/o Prof. Dr H. Wendt, Institut für Chemische Technologie, Technische Hochschule Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany.

H₂SO₄ (10%) or Na₂SO₄ (5%) or NaOH (10%). (These electrolyte media would also be quoted as acid, neutral and basic media in subsequent discussions.) Along with 25 g of NN served as the catholyte and 25 ml of one of the above solutions without NN served as the anolyte. The quantity of electricity consumed was 4 faraday mol⁻¹ of NN. A current density of 5 A dm⁻² was employed. The temperature was maintained at 30° C. The amine in solution was estimated by the standard method [13]. The electrolysed solution was neutralized after the completion of electrolysis and the resulting solid obtained was dried, weighed and stored in an amber coloured bottle. Its structure was confirmed from its melting point and i.r. spectra.

3. Results and discussion

3.1. Cyclic voltammetric behaviour of Ti/ceramic TiO₂ cathode in different media

The cyclic voltammetric behaviour for the first and repeated cycles of the Ti/ceramic TiO₂ cathode in acid, neutral and basic media is shown in Fig. 1(a),

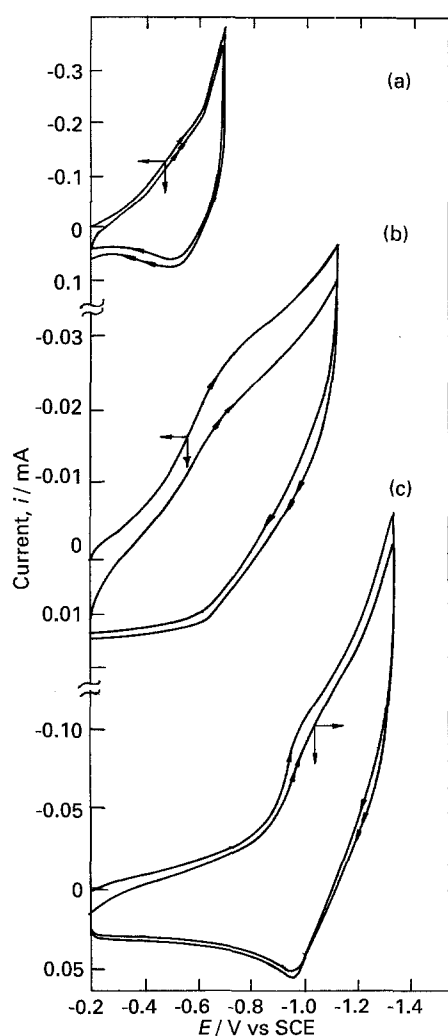
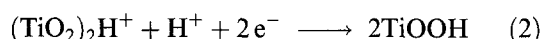
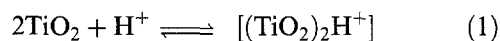
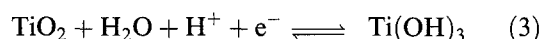


Fig. 1. Cyclic voltammetric response of Ti/ceramic TiO₂ cathode for the first and repeated cycles in acid(a), neutral(b) and basic(c) media at a sweep rate of 0.100 V s⁻¹.

(b) and (c). The high reversibility of the cathode in acid media was previously reported [1–4]. The cathodic peak in this medium appears at around –0.55––0.58 V depending on the sweep rate employed, with the peak potentials (not corrected for *iR*) shifting cathodically with increase in sweep rate. The shift of peak potential with pH is in the range 0.030–0.050 V. The value of 0.030 V observed at lower sweep rates suggests the occurrence of a preprotonation reaction involving a dimeric TiO₂ species [4] which undergoes a two-electron reduction in a rate determining step as shown below:



The preprotonation has been reported previously [14, 15] for the ceramic oxide electrodes by Beck *et al.* Alternatively, the value of 0.050 V suggests the following redox reaction:



It can be seen from Fig. 1(c) that the cathode shows considerable reversibility in basic medium. Both the cathodic and anodic peaks are well defined. The cathodic peak appears in the potential range –0.99––1.02 V in the sweep rate range of 0.05 to 0.3 V s⁻¹, with the peak potential values shifting negatively with increase in the sweep rate. The negative shift in the peak potentials on going from acid to basic medium is understandable since surface protonation becomes more and more difficult with increasing pH. The peak separation was around 55–60 mV in the sweep rate range 0.05–0.3 V s⁻¹ in basic medium. At sweep rates less than 0.05 V s⁻¹, the peaks are not well defined due to higher background current. The possible redox reaction in this medium is



In neutral medium, the cathodic peak is observed at –0.70––0.80 V depending on the sweep rate employed. A cathodic shift of peak potentials with increase in sweep rate is observed. The peak separation is around 100 mV in the sweep rate range 0.05–0.3 V s⁻¹. The peak is less well defined as compared to those in acid and basic media. A redox reaction similar to Reaction 3 above may be operative.

3.2. Cyclic voltammetric reduction of NN in different media at a Ti/ceramic TiO₂ cathode and a GCE

Cyclic voltammograms for the first and repeated cycles of NN (5 × 10⁻³ M) at a GCE(a) and a Ti/ceramic TiO₂ cathode(b) in acid, neutral and basic media are shown in Figs 2(a) and (b), 3(a) and (b) and 4(a) and (b), respectively. A single cathodic peak is seen for the reduction of NN at a GCE in acid and basic media (Figs 2(a) and 4(a)). However, in neutral medium (Fig. 3(a)), the main peak is pre-

The plot of peak current density (I_p) against the square root of sweep rate (v) for the reduction of NN ($5 \times 10^{-3} \text{M}$) in acid, neutral and basic media at both GCE and Ti/ceramic TiO_2 cathode are shown in Fig. 5. It can be seen that a straight line passing through origin is obtained in general indicating diffusion limited reduction of NN. In neutral media, however, at a Ti/ceramic TiO_2 cathode, the current density corresponding to the second peak is seen to increase continuously and that of the third peak decrease continuously with decrease in sweep rate. This is probably due to an equilibria between the protonated and unprotonated forms of the depolariser molecule, and the protonation being predominant in the time scale of lower sweep rates. The peak potentials were found to be more negative at a Ti/ceramic TiO_2 cathode as compared to that at a GCE and the values were found to shift negatively with increase in sweep rate in both the cases.

The above results indicate that the reduction of NN in acid, neutral and basic media at a Ti/ceramic TiO_2

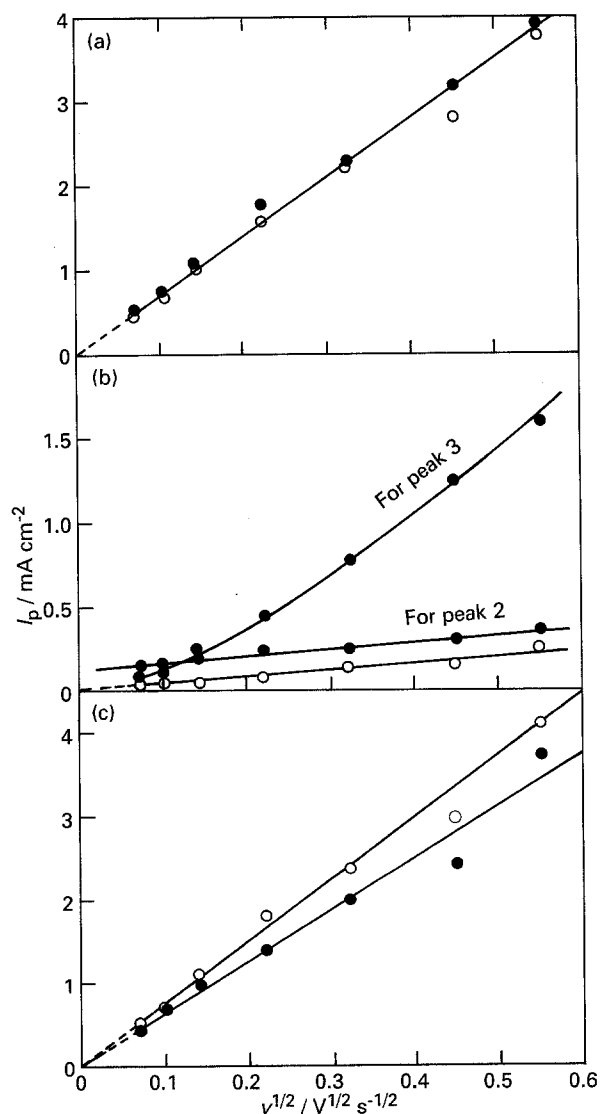


Fig. 5. $I_p/v^{1/2}$ plots of the cyclic voltammetric peaks for the reduction of NN ($5 \times 10^{-3} \text{M}$) at a GCE (○—○) and at a Ti/ceramic TiO_2 cathode (●—●) in acid (a), neutral (b) and basic (c) media.

cathode occurs by a chemical reaction of the electro-generated Ti^{3+} species with NN. Though the reversibility of the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox species is considerably lower in neutral medium, mechanism involving the reduction with the electrogenerated Ti^{3+} species is still operative.

3.3. Galvanostatic electrolysis of NN at a Ti/ceramic TiO_2 cathode

The results of the galvanostatic electrolysis data carried out on the reduction of NN in acid, neutral and basic media at a GCE and a Ti/ceramic TiO_2 cathode are shown in Table 1. It can be seen that good yield of 1-amino-2-naphthol is obtained in acid media with a high current efficiency (CE). The yield of 1-amino-2-naphthol and also the CE value are slightly lower in neutral and basic media. This is because at the end of electrolysis, some tarry material could also be seen in these media which is the likely air oxidation product of 1-amino-2-naphthol. The observation of 1-amino-2-naphthol as almost the exclusive product in neutral and basic media suggests that the dehydration step in the reduction mechanism suggested for NN, is considerably fast and hence the formation of the corresponding azoxy, azo or hydrazo products is avoided. A comparison of the yields obtained at the two cathodes shows that the yields are generally slightly higher at the Ti/ceramic TiO_2 cathode although the reduction potentials for the nitroso group reduction are more negative than those observed at the GCE. However, it was established earlier that for the reduction of nitro compounds to the corresponding amines, Ti/ceramic TiO_2 cathode is much superior in its efficiency as compared to the existing conventional cathodes [1–4].

The amine so isolated melted at 150°C with decomposition in agreement with the literature value [17]. IR spectra of the sample showed absorptions at frequencies (cm^{-1}) of 3260, 3060 and 2800 (apart from other absorptions) which coincide with those obtained with an authentic sample of the amine reported in the literature [17]. These values correspond to the $-\text{N}-\text{H}$ and $-\text{O}-\text{H}$ stretching frequencies, respectively.

Table 1. Galvanostatic electrolysis data on the reduction of NN in acid, neutral and basic media at a GCE and a Ti/ceramic TiO_2 cathode

Medium	GCE		Ti/ceramic TiO_2 cathode	
	Yield* %	CE %	Yield* %	CE %
Acid	83.6	83.0	87.0	85.0
Neutral	74.1	76.5	79.0	78.3
Alkaline	72.9	71.0	74.5	74.5

* Yield refers to the yield of amine isolated at the end of galvanostatic electrolysis.

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 and P. N. Anantharaman, *ibid.* **22** (1992) 1087.
- [4] C. Ravichandran, D. Vasudevan and P. N. Anantharaman, *ibid.* **22** (1992) 1192.
- [5] C. A. Streuli and W. D. Cooke, *Anal. Chem.* **26** (1954) 963.
- [6] R. M. Eloffson and J. G. Atkinson, *Can. J. Chem.* **34** (1956) 4.
- [7] H. P. Cleghorn, *J. Chem. Soc. (B)*, (1970) 1387.
- [8] M. M. Ghoneim, R. M. Issa, I. M. Issa and M. Khattab, *Ind. J. Chem.* **15A** (1977) 19.
- [9] I. M. Kolthoff and A. Langer, *J. Am. Chem. Soc.* **62** (1940) 3172.
- [10] K. S. Tewari, *Ind. J. Chem.* **3** (1965) 204.
- [11] F. Beck and W. Gabriel, *Angew Chem. Int. Ed. Engl.* **24** (1985) 771.
- [12] F. Beck, *Electrochim. Acta* **34** (1989) 811.
- [13] A. R. Day and W. Taggart, *Ind. Eng. Chem.* **29** (1928) 545.
- [14] F. Beck and H. Schulz, *Ber. Bunsenges. Phys. Chem.* **88** (1984) 155.
- [15] F. Beck, W. Gabriel and H. Schulz, *Dechema Monogr.* **102** (1986) 339.
- [16] A. J. Dombroski, L. Meites and K. Rose, *J. Electroanal. Chem.* **137** (1982) 67.
- [17] 'Atlas of Spectral data and Physical constants for Organic compounds', (edited by J. S. Grasselli), CRC Press, USA (1973) p. B666.