JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 60–63

Indirect electroreduction of o-nitrophenol to o-aminophenol on titanium dioxide coated titanium electrodes

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Received 6 November 1989; 2 April 1990

The heterogeneous catalytic redox behaviour of a titanium dioxide coated titanium electrode surface was investigated with and without o-nitrophenol using cyclic voltammetry. A comparison of the cyclic voltammograms recorded in the absence and in the presence of o-nitrophenol confirmed the catalytic reduction of o-nitrophenol by the surface Ti^{4+}/Ti^{3+} redox system present on the electrode surface. Preparative scale experiments were also carried out using a Ti/TiO_2 electrode of large surface area and the redox behaviour of the electrode was confirmed by the isolation of o-aminophenol with high current efficiency and yield.

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1. Introduction

Since electrochemical methods are simple and considerably avoid environmental pollution, many organic compounds are synthesized by such methods. Nitro compounds are reduced to amines on a number of electrodes in dilute sulphuric acid electrolyte [1–3]. But the reduction efficiency and product yield are reported to be low. To increase the current efficiency and product yield, an indirect electrochemical method has been applied. Metal ionic redox couples such as Ti^{4+}/Ti^{3+}, Sn^{4+}/Sn^{2+} were used as mediator or electron carrier, particularly for the reduction of nitro compounds [4–6]. The metal ions were reduced from the higher oxidation state to the lower oxidation state on the electrode surface and then reacted with the organic substrates. A series of nitro compounds were reduced to amines by indirect electrochemical reduction using the titanous titanic redox system within the cell [7]. Though the reduction of nitro compounds occurs with very high efficiency as a homogeneous catalytic reaction, in certain cases amines form complexes with the redox species and product isolation is difficult.

Beck and co-workers [8–10] have developed a titanium dioxide coated titanium electrode which functions as a stable Ti^{4+}/Ti^{3+} redox electron carrier and the electrode has been used in the reduction of nitro compounds [8, 9, 11]. In the present work the catalytic redox behaviour of the titanium dioxide coated titanium electrode was investigated in the absence and in the presence of o-nitro phenol using cyclic voltammetry and preparative scale experimental techniques. The heterogeneous catalytic redox reaction was confirmed and optimum conditions for the conversion of o-nitro phenol to o-amino phenol were determined and reported.

2. Experimental details

2.1. *Cyclic voltammetry*

Voltammetric measurements were carried out in a three electrode H-form glass cell. The cathode and anode compartments were separated by a No. 4 sintered glass disc 25 mm in diameter. The working electrode was connected to a saturated calomel electrode (SCE) by a capillary containing agar and KCl. All the other details of the cell and instrumentation are the same as reported earlier [12].

The TiO_2 coated titanium electrode was prepared by the following standard procedure [8, 9]. Titanium metal strip was treated with 50% hydrochloric acid at 90° C for ~1 h to obtain a rough surface for good aherence of the oxide coating and then the metal strip was dipped in a solution of 0.05 M titanyl acetyl acetonate in isopropanol and the adherant film was dried in an oven at 100–110° C. The metal strip was placed in a muffle furnace at 500° C for 25 min. The above method of coating was repeated at least five times to get a good coating of TiO_2 over the titanium. A 0.385 cm^2 area of the electrode was exposed for the voltammetric measurements by protecting the other portions by araldite coating. The electrode was attached to a copper rod for electrical contact and positioned in the cell containing solvent supporting electrolyte.

Laboratory grade o-nitro phenol was purified twice and used in these studies. Analar grade sulphuric acid was used. All solutions were prepared from double distilled water. Electrolytic hydrogen was purified and passed through the solvent supporting electrolyte for 20 min for deaeration. Both catholyte and anolyte were the same. All experiments were performed at a constant temperature of 35° C and all

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potentials referred to herein were measured against SCE.

Potentials were applied from a potential Scan generator through a potentiostat and the current output was recorded using a fast response X–Y recorder. A few cyclic potential sweeps were applied between 0 to −0.7 V before actual recording of the voltammograms.

2.2. *Preparative scale experiments*

Preparative scale experiments were carried out in a 1 dm^3 (one litre) capacity glass cell. The cell cover was equipped with openings for introducing the porous diaphragm, thermometer, condenser and electrodes. About 500 cm^3 of 2 M sulphuric acid was used as catholyte and the same sulphuric acid solution was used as anolyte. A 84 cm^2 area of TiO_2 coated titanium electrode was prepared by the method described above and used as cathode and a lead sheet, which was placed inside the porous pot, was used as anode. The glass cell was placed in an electric water bath for maintaining the required temperature. The catholyte was stirred by means of a glass stirrer. Current density, temperature, concentration of the supporting electrolyte and concentration of o-nitro phenol were varied. The experimental conditions are given in Table 2. After the completion of the electrolysis, the o-amino phenol content of the catholyte was estimated by the nitrous acid method [13]. The catholyte pH was increased to pH 4–6 by adding ammonium carbonate and the precipitated o-amino phenol was isolated.

3. Results and Discussion

3.1 *Cyclic voltammetric studies*

3.1.1. Voltammetric behaviour of the Ti/TiO_2 electrode in 2 M H_2SO_4. Figure 1 shows the typical cyclic voltammograms recorded for the redox behaviour of the species present on the electrode surface in 2 M H_2SO_4 at different sweep rates. Two cathodic waves C_1 and C_2 were observed within −600 mV (SCE) beyond which hydrogen evolution occurred. In the reverse scan two anodic waves, A_1 and A_2, were also observed. In earlier reports [8–11] it was suggested that the first cathodic wave, C_1, is due to the reduction

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

and the second cathodic wave, C_2, which occurs at slightly more negative potential, is due to the following reaction

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

or due to the reaction

$$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}. \quad (3)$$

But it has been observed under the same experimental conditions [8–10] that Ti^{2+} species in the oxide form TiO is reactive and dissolves spontaneously. As the TiO_2 coated electrode is stable under the present experimental conditions, it may be concluded that Reaction (2) rather than Reaction (3) is responsible for the second cathodic wave. The two anodic waves are due to the corresponding reverse reactions.

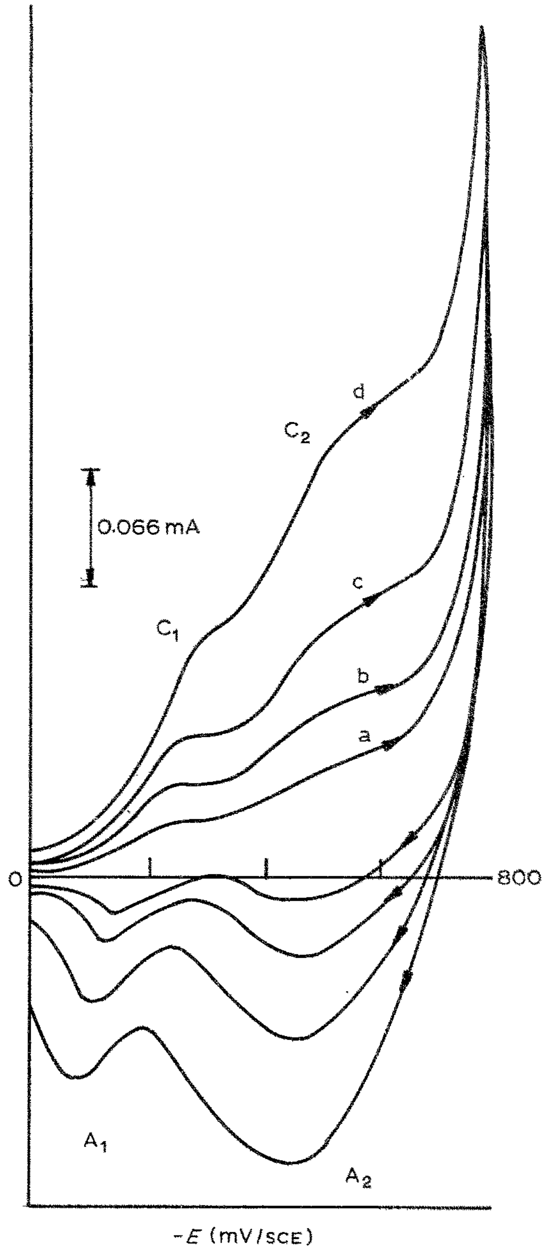

Fig. 1. Typical cyclic voltammograms recorded for the redox behaviour of TiO_2 coated titanium electrodes in 2 M H_2SO_4. Sweep rate: (a) 20, (b) 40 and (c) 80 mV s^{-1}, (d) 160 mV s^{-1}.

3.1.2. Reduction of o-nitro phenol on the Ti/TiO_2 electrode. Figure 2 shows a typical cyclic voltammogram obtained on the Ti/TiO_2 electrode in the presence of 5×10^{-3} M o-nitro phenol in 2 M H_2SO_4 at 40 mV s^{-1}. In the presence of o-nitro phenol, the anodic waves completely disappeared and the cathodic wave, C_2, was observed in a peak shaped form with a much higher value of current when compared with the cathodic wave C_1 (Fig. 2) as well as with the cathodic wave C_2 (Fig. 1) in the absence of o-nitro phenol at the same sweep rate. The half peak potential, $E_{p1/2}$, of the wave C_2 (Fig. 2) was found to be the same as wave C_2 in the absence of o-nitro phenol (Fig. 1). The increase in the current value of wave C_2 may be either due to

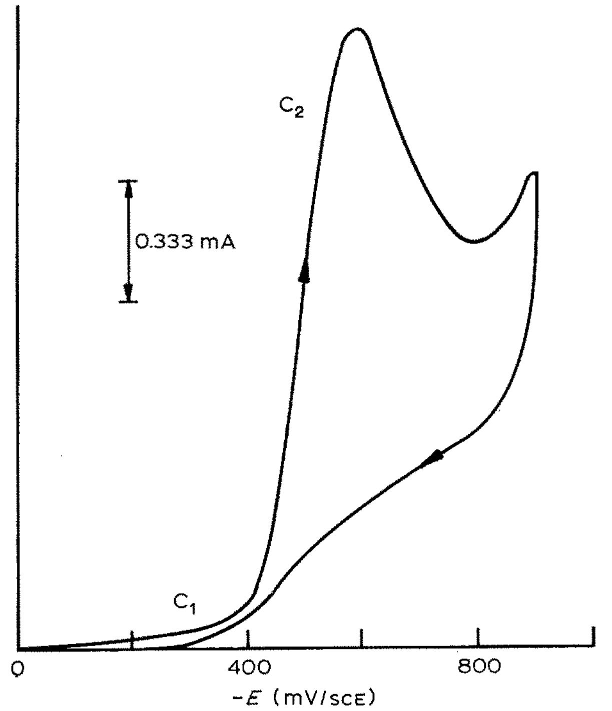

Fig. 2. Typical cyclic voltammogram obtained on Ti/TiO_2 electrode in the presence of 5.0 × 10^{-3} M o-nitrophenol. Sweep rate: 40 mV s^{-1}. Temperature: 35° C.

the combined current for the reduction of Ti^{4+} species and direct reduction of o-nitro phenol or due to the reduction of the large amount of Ti^{4+} species generated instantaneously by the fact chemical reaction

$$6Ti^{3+} + O_2NC_6H_4OH + 6H^+ \longrightarrow 6Ti^{4+} H_2NC_6H_4OH + 2H_2O \qquad (4)$$

The fact that no anodic wave was observed in the presence of o-nitro phenol indicates the absence of Ti^{3+} species for oxidation on the reverse scan. The only possibility for the absence of Ti^{3+} species in the presence of o-nitro phenol is the heterogeneous chemical reaction as shown in Equation (4) and the fast regeneration of Ti^{4+} species in this reaction is responsible for the large increase in current for the reduction in the presence of o-nitro phenol.

The sweep rate was varied from 10 to 160 mV s^{-1}. Figure 3 shows the effect of sweep rate on i_p in the presence of o-nitro phenol. It was found that the wave height of wave C_2 increased with increase in sweep rate and the anodic wave was absent even at 160 mV s^{-1}. This observation shows that the heterogeneous catalytic reduction is a fast reaction. Table 1 shows the cyclic peak parameters obtained on the Ti/TiO_2 electrode surface in the presence of o-nitro phenol.

The concentration of o-nitro phenol also was varied and its effect on i_p and E_p was also recorded. It was found that the increase in i_p was linear with concentration and the peak potential was constant. On the whole the cyclic voltammetric study has revealed that the titanium dioxide coated titanium electrode behaves as a very good heterogeneous redox catalytic electrode and o-nitro phenol undergoes fast chemical reduction.

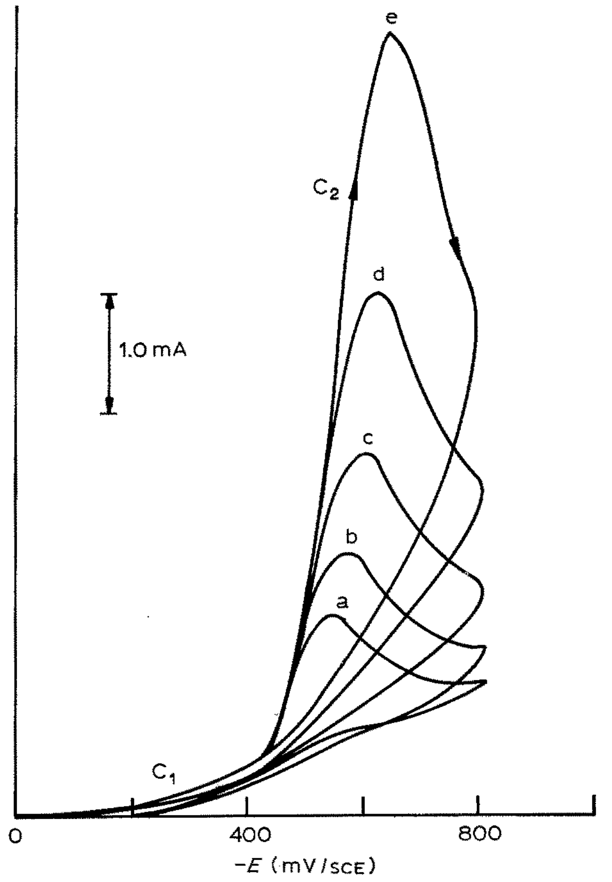

Fig. 3. Effect of sweep rate on the cyclic voltammograms recorded on Ti/TiO_2 electrode in the presence of 1.0 × 10^{-2} M o-nitrophenol. Sweep rates: (a) 10, (b) 20, (c) 40, (d) 80 and (e) 160 mV s^{-1}.

3.2. *Preparative scale studies*

A few experiments on a preparative scale were carried out changing the various experimental parameters such as current density, temperature and concentration of the electrolyte as shown in Table 2. It was found that as the current density was increased above 5 A dm^{-2}, competitive hydrogen evolution along with the redox process occurred and current efficiency was reduced. Higher current efficiency was observed when the temperature of the electrolyte was above 45° C due to the dispersion of the molten o-nitro phenol in the electrolyte at this temperature. Higher concentration of the supporting electrolyte favoured the competitive hydrogen evolution reaction and decreased the current efficiency. Product was isolated and identified as o-amino phenol by infrared spectroscopy and by the acetyl derivative of o-amino phenol. In the reduction of o-nitro phenol to o-amino phenol on a Ti/TiO_2

Table 1. Cyclic voltammetric peak parameters observed on Ti/TiO_2 electrode in the presence of 1.0 × 10^{-2} M *o-nitro phenol (ONP)*

Sweep rate (*mV s^{-1}*)	*Background i_p*		*i_p for ONP* (*mA*)	*E_p for ONP* (*mV*)
	C_1 (*mA*)	*C_2* (*mA*)		
20	0.0297	0.0662	2.2043	−570
40	0.0528	0.0561	2.9982	−600
80	0.0825	0.0825	4.2719	−630
160	0.1386	0.1419	6.333	−660

Table 2. Experimental conditions and results for the electroreduction of o-nitro phenol (ONP) to o-amino phenol (OAP)

Sl. No.	*Weight of ONP taken (g)*	*Concentration of supporting electrolyte H_2SO_4 (M)*	*Temperature (°C)*	*Current density $A\,dm^{-2}$*	*Weight of unreduced ONP (g)*	*Weight of OAP estimated (g)*	*Current efficiency (%)*	*Yield (%)*
1	20	2	30–40	5	18	0.86	5.5	54.5
2	20	2	40–50	5	–	15.4	95	98.2
3	20	2	50–60	5	–	14.8	91.3	94.4
4	20	2	40–50	2.5	7	7.0	42	65.5
5	20	2	40–50	7.5	13.5	4.9	32	31.5
6	20	1	40–50	5	11.5	6.5	40	41.5
7	20	3	40–50	5	4.2	12.3	76	78.6

electrode approximately 98% yield and 95% current efficiency were obtained at a current density of $5\,A\,dm^{-2}$ in 2 M sulphuric acid.

4. Conclusion

The titanium dioxide coated titanium electrode is found to behave as an effective heterogeneous redox electron carrier and nitro compounds can be reduced catalytically on the surface of the electrode with high current efficiency. The above redox electrode can be conveniently used for electro synthesis wherein processing of the electrolyte after electrolysis is simple and product purity is very high.

Acknowledgement

The authors wish to express their sincere thanks to the Director of the Central Electrochemical Research Institute, Karaikudi, for his permission to publish this paper.

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