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Short communication

Thermally coated Ti/TiO$_2$ as cathode material for the synthesis of succinic and dihydrophthalic acids

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1. Introduction

Electrochemical reduction of maleic/fumaric acid to produce succinic acid and phthalic acid to produce dihydrophthalic acid is one of the few electroorganic processes that have been commercialized [1–3]. A lead cathode is used for this purpose. However, lead contamination is a serious problem in the preparation of food grade high purity succinic and dihydrophthalic acids. Hence, it is desirable to look for alternative cathode materials for the reduction of these compounds.

The thermally coated Ti/TiO$_2$ electrode has been found to be very useful in the reduction of aromatic nitro compounds [4, 5]. The reduction of carbonyl group was also reported [6]. The application potential of this electrode for the reduction of a number of aromatic nitro compounds such as nitro naphthalene [7], nitro salicylic acid [8], nitro aniline [9], nitro benzene [10] and dinitro benzene [11] has been studied extensively in this laboratory. The pH dependent redox behaviour of this electrode has also been studied [12, 13]. As is well known, aromatic nitro compounds can be easily reduced at less negative potentials. However, polarographic and voltammetric studies of fumaric [14–17] and phthalic acids [3, 18–22] indicate that these compounds undergo reduction only at more negative potentials and hence demand the use of high overvoltage cathodes like lead. In this paper, we report the electrochemical process for the preparation of succinic and dihydrophthalic acids using Ti/TiO$_2$ electrodes. Constant current electrolysis and cyclic voltammetry were used.

2. Experimental studies

Titanium dioxide coated titanium electrodes were prepared according to the method described by Beck and Gabriel [4].

AR grade phthalic and succinic acid were used for cyclic voltammetric and preparative scale experiments. AR grade fumaric acid was recrystallized before use. All solutions were prepared from doubly distilled water. Electrolytic hydrogen was purified and passed through the solvent supporting electrolyte for 20 min for deaeration. All the experiments were performed at a constant temperature of 35 °C and all potentials were determined against the SCE. Potentials were applied using a potential scan generator through a potentiostat and the current output was recorded using a fast response X-Y recorder.

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 G4 sintered glass disc (dia. 25 mm). The Ti/TiO$_2$ working electrode was connected to a saturated calomel electrode by a capillary containing agar–agar and KCl. All the other details of the cell and instrumentation were the same as reported earlier [23]. Only a 0.196 cm^2 area of the Ti/TiO$_2$ electrode was exposed for the voltammetric measurements by insulating the other portions using Araldite.

2.2. *Constant current electrolysis*

For galvanostatic electrolysis, a Ti/TiO$_2$ electrode of area 84 cm^2 was employed as cathode, lead as anode and 1 M H_2SO_4 as the electrolyte (catholyte and anolyte). The anode compartment was separated from the cathode by a porous pot diaphram. The catholyte was stirred mechanically using a glass stirrer. The temperature of the cell was controlled using a water bath. After completion of the electrolysis the succinic acid produced was crystallized out by cooling the electrolyte to 15 °C. The melting point of the product was found to be 186 °C. Likewise, the dihydrophthalic acid was obtained by evaporation of the electrolyte followed by cooling. The unreduced phthalic acid was separated out prior to product separation by cooling the electrolyte, after electrolysis. The melting point of the recrystalized product was found to be 175 °C, which corresponds to that of dihydrophthalic acid.

3. Results and discussion

3.1. *Voltammetric studies*

The cyclic voltammograms obtained for the thermally coated Ti/TiO_2 electrode in 1 M H_2SO_4 at different sweep rates are shown in Figure 1. The cathodic and anodic peaks obtained in the potential range −600 to −500 mV vs SCE are well defined. The peak currents increase linearly with increase in sweep rate. The peak potential difference also increases slightly with increasing sweep rate. More detailed analysis of the cyclic voltammetric behaviour of the thermally coated Ti/TiO_2 electrode in Sulphuric acid [7] and other pH media [12, 13] have been reported elsewhere. In strong acidic media the cathodic and anodic peaks corresponds to the following redox reaction:

$$TiO_2 + H^+ + e^- \rightleftharpoons TiOOH$$

The movement of a proton into the lattice during reduction and into the solution during oxidation is essentially responsible for the quasi reversible nature of the redox peaks.

Typical cyclic voltammogram of 1.7 and 106.7 mM fumaric acid on thermally coated Ti/TiO_2 in 1 M H_2SO_4 are shown in Figure 2. The reduction peak in the presence of fumaric acid is observed in the same peak potential range which corresponds to that of the electroreduction of Ti/TiO_2 electrode (between −600 and −500 mV vs SCE). At slow sweep rates (Figure 2(a) and (b)) no anodic peak corresponding to the reoxidation of surface bound TiOOH species is noticed. These observations confirm that the fumaric acid is essentially reduced by the electro generated TiOOH species. However, the catalytic current in the presence of fumaric acid is not significantly higher than that observed at the bare Ti/TiO_2 electrode (cf. Figure 1(a) and Figure 2(a) and (b)). The cathodic current also does not increase significantly with increasing fumaric acid concentration (Figure 2(a) and(b)). At higher sweep rates, the difference in the cathodic peak currents for 1.7 and 106.7 mM fumaric acid is lower (Figure 2(c) and(d)). The reoxidation peak due to TiOOH oxidation is also clearly noticed at higher sweep rates (Figure 2(c) and(d)). All

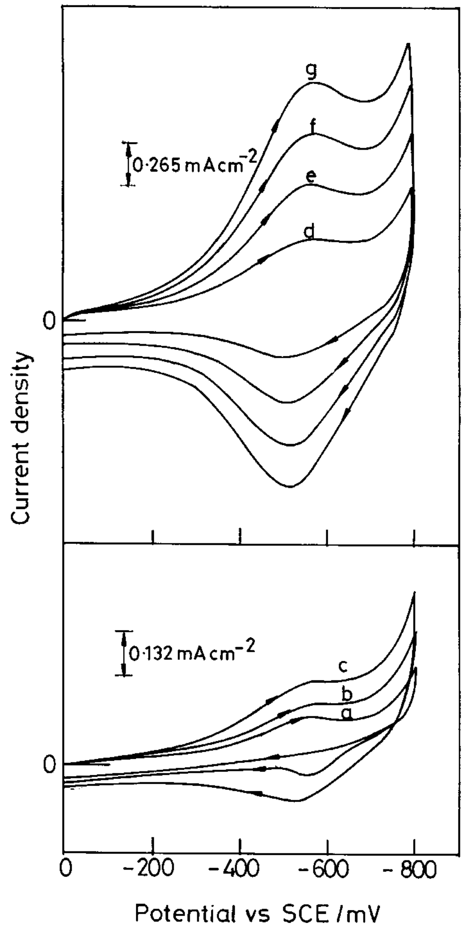


Fig. 1. Cyclic voltametric behaviour of Ti/TiO_2 electrode in 1 M H_2SO_4 at different sweep rates. Sweep rates: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

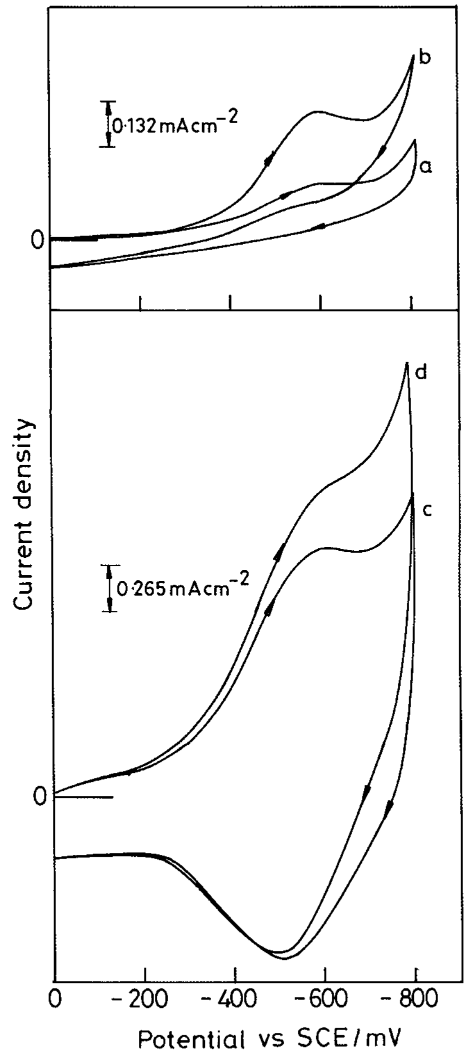


Fig. 2. Effect of concentration 1.7 mM (a,c) and 106.7 mM (b,d) fumaric acid on Ti/TiO_2 electrode in 1 M H_2SO_4 at sweep rates 5 mV s^{-1} (a,b) and 200 mV s^{-1} (c,d).

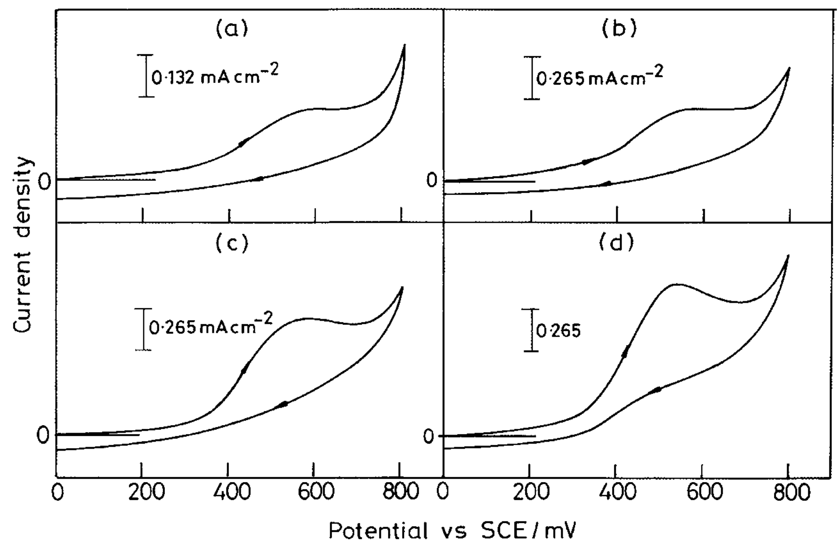
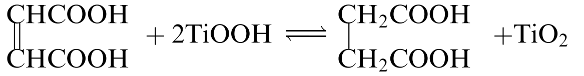


Fig. 3. Effect of concentration on the cyclic voltammograms for the reduction of phthallic acid on Ti/TiO_2 electrode in 1 M H_2SO_4 at a sweep rate of 5 mV s^{-1}. Concentrations: (a) 1.7, (b) 6.7, (c) 26.7 and (d) 106.7 mM.

these observations suggest that the chemical reaction rate constant for the following reaction is much smaller.



$$\begin{matrix}CHCOOH\\ \|\\ CHCOOH\end{matrix} + 2TiOOH \rightleftharpoons \begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix} + TiO_2$$

However, as shown in Section 3.2, this electrode can still be used effectively at low current densities to produce succinic acid from fumaric acid.

Similar observations are also made during the voltammetric study of phthalic acid on thermally coated Ti/TiO_2. Typical cyclic voltammograms presented in Figure 3 indicate that the cathodic peak currents increase slightly with increasing phthalic acid concentration.

At slow sweep rates, the anodic peak current is absent at all concentrations. Even at substantially higher phthalic acid concentration, the anodic peak is absent only at slow sweep rates. At higher sweep rate, the anodic peak due to the reoxidation of surface bound TiOOH species again reappears (Figure 4). The catalytic behaviour of the thermally coated Ti/TiO_2 electrode towards phthalic acid is thus similar to that for fumaric acid.

3.2. *Constant current electrolysis*

Typical experimental results obtained during the preparative electrolysis of fumaric acid under galvanostatic condition using the thermally coated Ti/TiO_2 cathode material are summarized in Table 1.

In 1 M H_2SO_4 fairly high yields of succinic acid (above 90%) were achieved at low current densities (Table 1, expts. 1–3). At a current density of 20 mA cm^{-2} a high yield of 97% was obtained at 60 °C (Table 1; expt. 2). 60 °C was also found to be the optimum temperature for preparative electrolysis (Table 1, expts. 2, 7 and 8). Under identical experimental conditions, the thermally coated Ti/TiO_2 electrode was found to be significantly more efficient than the conventional lead cathode (Table 1, expts. 2 and 9).

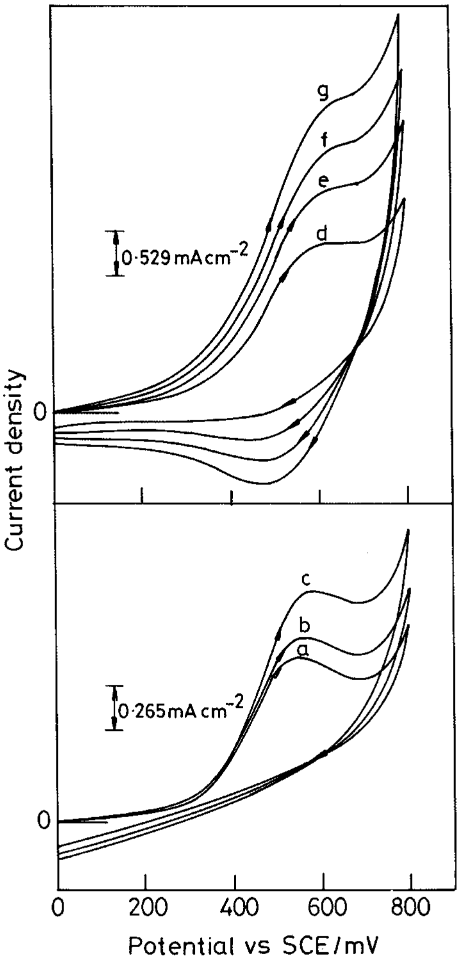


Fig. 4. Effect of sweep rate on the cyclic voltammograms for the reduction of 106.7 mM phthalic acid on Ti/TiO_2 electrode in 1 M H_2SO_4. Sweep rates: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

Table 1. Galvanostatic reduction of fumaric acid to succinic acid at a Ti/TiO_2 electrode
Conditions: fumaric acid taken 10.00 g; anode lead; electrolyte 1 M H_2SO_4.

Experiment	Current density /mA cm^{-2}	Temperature /°C	Yield of succinic acid /g	Yield /%
1	10	60	9.2	90
2	20	60	9.9	97
3	30	60	9.4	92
4	40	60	8.9	88
5	50	60	8.7	86
6	75	60	8.1	80
7	20	40	6.9	68
8	20	50	7.3	72
9	20 (lead cathode)	60	8.0	79

Table 2. Galvanostatic reduction of phthalic acid to 3,5-cyclohexadiene-1,2 dicarboxylic acid (dihydrophthalic acid) at a Ti/TiO_2 electrode
Conditions: phthalic acid taken 7.00 g; anode lead; electrolyte 1 M H_2SO_4.

Experiment	Current density /mA cm^{-2}	Temperature /°C	Yield of dihydrophthalic acid /g	Yield /%
1	10	60	6.4	90
2	20	60	6.0	85
3	30	60	5.5	78
4	40	60	5.1	72
5	50	60	4.8	68
6	75	60	3.7	52
7	10	40	3.9	55
8	10	50	4.5	64
9	10 (lead cathode)	60	5.2	73

Similar results obtained during the electroreduction of phthalic acid under galvanostatic conditions are summarized in Table 2. For this compound, a maximum yield of 90% was achieved at a low current density of 10 mA cm^{-2}. With increase in current density, the overall yield was found to decrease significantly (Table 2, expts. 1–6). The optimum reaction temperature was again 60 °C (Table 2, expts. 1, 7 and 8). For the preparation of dihydrophthalic acid the thermally coated Ti/TiO_2 electrode was also found to give better results when compared to the conventional lead cathode under otherwise identical experimental conditions (Table 2, expts. 1 and 9).

4. Conclusion

Cyclic voltammetry and constant current electrolysis have shown that the thermally coated Ti/TiO_2 electrode can be used for the reduction of fumaric acid to succinic acid and phthalic acid to dihydrophthalic acid, respectively. Fairly high yields were achieved for both these compounds. However, lead contamination in the product is still possible from the dissolution of lead dioxide anode and subsequent migration of lead, from the anode compartment to the cathodic compartment containing the organic reactants and products. Attempts to overcome this problem are in progress.

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