SHORT COMMUNICATION

Reduction of maleic acid at a Ti/ceramic TiO$_2$ cathode*

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1. Introduction

The Ti/ceramic TiO$_2$ cathode, a modified electrode, has been found to be catalytic in the reduction of the nitro group and the galvanostatic reduction of 5-nitrosalicyclic acid [1], isomeric nitroanilines [2, 3] and isomeric chloronitrobenzenes [4] to the corresponding amines has been reported in high yields with high current efficiency (c.e.) values. The advantages of this cathode over conventional cathodes have been discussed. In the present work, use of this cathode has been extended to the reduction of maleic acid (MA) to succinic acid (SA), under galvanostatic and cyclic voltammetric conditions.

Maleic acid is easily reduced to SA both chemically and electrochemically. Electrolytic reduction of MA in H$_2$SO$_4$ medium at conventional cathodes such as platinized platinum, rotating lead, titanium, graphite, mercury and also at zinc single crystals has been reported [5–10]. The yield of SA was 95% with a c.e. of 98% at a rotating lead cathode with a current density of 20 A dm^{-2}. With titanium as cathode, a maximum c.e. of 99% was obtained at 80 °C. With a vertical type mercury cathode, average yields in the range 75–95% were obtained, depending on the MA purity. The reduction rate of MA was the same on a polycrystalline electrode as was on the faces of a single crystal. Polarographic studies on the reduction of MA in 0.5 M H$_2$SO$_4$ at room temperature indicated a single two electron wave with a half wave potential of −0.57 V vs SCE.

Succinic acid finds several scientific applications [11].

2. Experimental details

2.1. Galvanostatic electrolysis studies

The Ti/ceramic TiO$_2$ cathode was prepared as reported earlier [1–4]. The baking temperature was 525 °C and three activation cycles were used. The layer appeared grey in colour. XRD measurements showed the TiO$_2$ to be in the anatase form and SEM studies showed a rippled structure [12]. The cathode area was 1.31 dm^2 or 4.4 dm^2 for the 22 A cell. A lead strip (placed inside the porous pot diaphragm) served as the anode. The electrolysis was carried out in a 2 dm^3 beaker using 1/1.5 dm^3 of 0.94–3.76 M H$_2$SO$_4$, the solution being agitated

mechanically using a glass stirrer. Current density in the range 3–7 A dm^{-2} and temperature in the range 20–50 °C were employed. The electrolyte temperature was adjusted manually using a water bath. The amount of MA employed ranged from 50 to 1000 g. The quantity of current consumed was 2 faraday mole^{-1}. The potential values were noted for every 15 min after the start of electrolysis. The voltage remained almost constant a few minutes after the start of electrolysis and the average value is reported. The solution after electrolysis was concentrated to half the volume and kept overnight, when the product SA separated out. Choosing the optimum conditions from the above, scale up to 22 A was carried out. Studies involving reuse of the catholyte was also carried out to saturate the product. The SA so obtained, was identified from its melting point and IR spectrum which were compared with those of authentic samples.

2.2. Cyclic voltammetry

Cyclic voltammetry (CV) was carried out in an undivided cell. A Ti/ceramic TiO$_2$ strip (area 0.283 cm^2), an aqueous SCE and a platinum foil served as the working, reference and counter electrodes, respectively. 1 M H$_2$SO$_4$ was used as the electrolyte. MA solution in the concentration range 1–200 mM was used. The experimental solution was deaerated using pure nitrogen. The CV experiments were carried out on a BAS 100A analyser. Cyclic voltammograms were recorded in the sweep rate range 0.005 to 5 V s^{-1}.

3. Results and discussion

3.1. Galvanostatic electrolysis

The results of galvanostatic electrolysis carried out on MA under varying conditions of current density, acid strength and temperature are listed in Table 1. It is seen that temperature has a considerable effect on the yield of SA (S. nos 1–3). At a temperature of 35 °C (S. no. 2), the yield of SA is maximum. Increase of temperature from 20 to 35 °C increases the solubility of MA and hence the yield of the product. As the temperature is further increased, reduction in the yield is attributed to a side reaction involving resin formation. A black sticky resinous material could be seen which is likely to be a polymeric condensation product.

Table 1. Galvanostatic electrolysis data on the reduction of maleic acid at a Ti/ceramic TiO_2 cathode

S	Wt. of MA /g	H_2SO_4 /M	c.d. /A dm^{-2}	Current /A	T /°C	Cell voltage /V	Wt. of SA /g	Yield /%	c.e. /%
1	50	1.88	5	6.6	20	2.5	41.0	80.6	96.5
2	50	1.88	5	6.6	35	1.5	49.0	96.3	98.0
3	50	1.88	5	6.6	50	1.5	43.5	85.5	96.0
4	50	1.88	3	3.9	35	2.0	44.5	87.5	97.0
5	50	1.88	7	9.2	35	2.5	43.5	85.5	92.0
6	50	0.94	5	6.6	35	2.5	48.0	94.4	96.0
7	50	3.76	5	6.6	35	1.5	42.5	83.5	97.0
8*	500	1.88	5	6.6	35	1.5	482.0	94.8	97.5
9*	1000	1.88	5	22.0	35	4.5	928.5	91.3	92.0

* The same electrolyte was reused four and eight times and the average values for the yield and c.e. (which are within ±0.5% and ±0.4%) are respectively reported.

The results of experiments 2, 4 and 5 show that a current density of 5 A dm^{-2} gave the best yield of SA. At a higher current density, the yield and c.e. decrease due to competitive hydrogen evolution. The results of the experiments 2, 6 and 7 show that with 1.88 M H_2SO_4 , the yield of SA is maximum (S. no. 2). As the acid strength is increased from 0.94 to 1.88 M, the solubility of MA is increased and hence the yield. With further increase in H_2SO_4 strength, a side reaction involving resin formation occurs, thus lowering the yield and c.e. Maximum product yield is observed at a current density of 5 A dm^{-2} with an acid strength of 1.88 M and a temperature of 35 °C (S. no. 2). Reuse of the electrolyte carried out with 500 g of MA (S. no. 8) showed that the yield and c.e. for SA formation are little affected up to the fourth reuse (the variation being ±0.5 and ±0.4 for the yield and c.e. values respectively). Also on scaling up to 22 A (S. no. 9), under the above condition, the yield and c.e. were little affected. The energy efficiency was found to be 2.2 kWh (kg of SA)$^{-1}$. The c.e. was, in general, found to be in the range 91–98% and was lower at higher current densities, where competitive hydrogen evolution occurs.

The cell voltages are generally low (Table 1), indicating low power consumption, a favourable situation for electrochemical scale-up. The voltage values decrease with either increase in temperature, decrease in current density and increase in acid strength (with other conditions remaining the same) as expected (S. nos. 1–7). The cell voltage is not affected during reuse of the electrolyte for a 6.6 A cell (S. no. 8). However, on scale-up to 22 A scale (S. no. 9), the cell voltage increases to 4.5 V. This occurs due to the higher inter-electrode distance maintained in this case.

Under galvanostatic conditions, the same electrode when reused for several runs, was found to have good reproducibility and no chemical or electrochemical deterioration occurred. In the literature, a high turn over factor of the order of 10^6 is reported for this electrode in the reduction of nitroaromatics [13].

The SA melted at 187 °C (literature value 185–187 °C [14]). Also the i.r. spectra of the SA matched that for an authentic sample [15] with the carbonyl stretch at 1695 cm^{-1} apart from other absorptions.

The strong absorption of $>C=C<$ at 1640 cm^{-1} observed for MA was absent in the i.r. spectra of the product.

3.2. Cyclic voltammetry

The cyclic voltammetric behaviour of the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at a sweep rate of 0.02 V s^{-1} is shown in Fig. 1(a). The redox peaks [12] are seen, the cathodic at around −0.58 V and the anodic at around −0.52 V and can be attributed to the following redox reaction:

$$TiO_2 + H_2O + H^+ + e^- \rightleftharpoons Ti(OH)_3 \qquad (1)$$
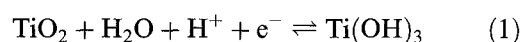
The redox peaks are highly reproducible indicating good stability of the Ti^{4+}/Ti^{3+} species at the electrode surface in acid media. The effect of added MA $(1 \times 10^{-1}$ M) on the cyclic voltammetric response is shown in Fig. 1(b). It is seen that on addition of MA, the cathodic peak height is enhanced with simultaneous disappearance of the anodic peak indicating
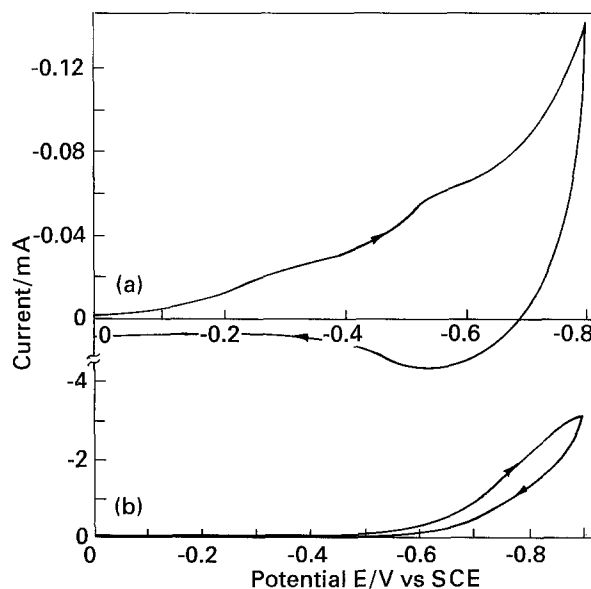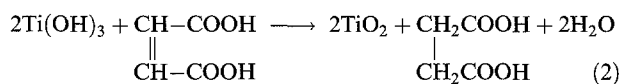

Fig. 1. Cyclic voltammetric behaviour of Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at 0.02 V s^{-1} sweep rate (a) in the absence and (b) in the presence of MA $(1 \times 10^{-1}$ M).

heterogeneous redox catalysis; the electrogenerated Ti^{3+} species (i.e. $Ti(OH)_3$ as shown above in Reaction 1 reduces the MA to SA and in this process, Ti^{4+} (i.e. TiO_2) is regenerated, as shown below, and a cyclic process occurs:

$$2Ti(OH)_3 + \underset{\underset{\text{CH--COOH}}{\|}}{\text{CH--COOH}} \longrightarrow 2TiO_2 + \underset{\underset{\text{CH}_2\text{COOH}}{|}}{\text{CH}_2\text{COOH}} + 2H_2O \qquad (2)$$

For higher concentrations of MA and for higher sweep rates, the voltammetric peak was not clearly defined and was found to merge with the current rise due to hydrogen evolution.

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