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Electrolytic synthesis of succinic acid in a flow reactor with solid polymer electrolyte membrane

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Abstract

This paper describes the galvanostatic synthesis of succinic acid from maleic acid in an ion exchange membrane flow cell. The electrolysis was carried out at stainless steel, lead and copper cathodes under variable conditions of current density and substrate concentration. Depending upon the experimental conditions, the yield of succinic acid varied from 95 and 99% with a coulombic efficiency of 80–99%. The product was characterized by various physicochemical techniques, viz. ^{1}H-NMR, IR and UV–Visible spectroscopy and elemental analysis. The operational conditions giving maximum yield of product were identified. The mechanism of electrochemical reduction of maleic acid and advantages of using a catholyte without supporting electrolyte are discussed.

1. Introduction

Succinic acid or butanedioic acid ($C_4H_6O_4$) is a constituent of plant and animal tissues. It is found in beer, molasses, meat, eggs, peat, coal, fruits, honey and urine [1]. It has wide applications ranging from radiation dosimetry to agriculture, food, medicine, plastics, cosmetics, textiles, plating, photography and waste-gas scrubbing [2].

The hydrogenation of maleic acid in aqueous cobalt chloride and potassium chloride solutions has been reported to give 41% succinic acid in the presence of Zn/Hg and 22% in its absence [3]. Succinic acid has also been prepared chemically by treating maleic acid with 50% H_3PO_2 at room temperature in aqueous NaOH/EtOH with an average yield of 83% [4]. It has been reported to be obtained in 99.5% yield when a mixture of maleic acid, water and Pd/C is autoclaved at 100 °C with hydrogen bubbling [5]. Succinic acid may also be obtained at high yields by the hydration of succinic anhydride in an autoclave at 200 °C. Ryuichi and Akira [6] have patented a vapour-phase catalytic process in which 2-butene is oxidized to give a mixture of 45% fumaric acid and 55% succinic acid in the condensed state, followed by a hydrogenation step [7] that yields succinic acid exclusively.

The electrolytic reduction of maleic acid in aqueous or aqueous–alcoholic sulfuric acid/benzene sulfonic acid/hydrochloric acid media [8] has been reported on spongy nickel [9], lead [10] (yield 90%), and Ti/ceramic TiO_2 cathodes [11] (yield 97%).

Although the yield in some of the above processes are good, their practicability is limited by several factors: the requirement of adding a supporting electrolyte in the electrochemical cell, saturation of the medium with succinic acid before electrolysis, need for costly catalysts or reagents, and separation of supporting electrolyte, catalyst and/or unreacted reagents from the reaction mixture/product.

Recently, ion exchange membranes (mainly Nafion) have been used as solid polymer electrolytes (SPEs) in electrochemical reactors and have shown promise for a few electro-organic transformations [12–19]. Advantages with the SPE methods include simplification of the system, higher product selectivity, non-use of solvent, reduced pollution, and easy product separation.

The present paper reports a novel and simple method of electrochemical preparation of succinic acid from maleic acid using an ion conducting polymer electrolyte flow cell. The effect of current density and the nature of the electrode material on the product yield and current efficiency (CE) have been investigated. The effect of different electrolytes in the anode compartment has also been studied.

2. Experimental details

2.1. *Reagents*

Maleic acid (S.D. Fine Chemicals Ltd., India) used was of high purity. All the other chemicals were of AR grade and were used as received. Double distilled water was used to prepare the solutions.

2.2. *Membrane flow cell and galvanostatic electrolysis*

A rectangular Teflon cell (15 cm × 10 cm) fitted with a stainless steel (SS), copper or lead cathode (area 40 cm^2) and a dimensionally stable anode (DSA) [12] or lead anode was used as the flow cell (Figure 1). An interpolymer of polyethylene and styrene divinyl benzene copolymer attached with sulfonic acid to function as a cation exchanger (Nuchem Weir Ltd., India), was used as the conducting SPE. It had a dry resistance of $1.5\ \Omega\ cm^{-2}$, an ion exchange capacity of $1.8\ meq\ g^{-1}$ and a moisture content of 29.8% after drying [20]. The membrane, measuring about 66 cm^2 in exposed geometric area, was placed between the cathode and the anode at a distance of 2 mm, thus dividing the cell into two compartments each having an inlet and an outlet [12]. The catholyte was a 100 ml solution of maleic acid in the desired concentration; 100 ml of a 0.1 M solution of H_2SO_4, Na_2SO_4 or NaOH was used as anolyte. The quantity of current consumed was 2 faradays mol^{-1}. Both solutions were recirculated at 10 ml min^{-1} through the respective compartments until the end of electrolysis. Cathodic current densities in the range 18.7–31.2 mA cm^{-2} were used. The cell voltage between the anode and the cathode at a given current density was noted. The progress of the reaction was followed by recording ^{1}H-NMR spectra of 1 ml aliquots of the electrolyte withdrawn periodically during electrolysis. The electrolysis was continued beyond the theoretically required duration, and was halted once the maximum yield of the product was reached (as deduced by analysis of aliquots withdrawn every minute after the completion of the theoretical duration). After completion of electrolysis, the solution was concentrated and allowed to crystallize as white prisms (MP 187 °C).

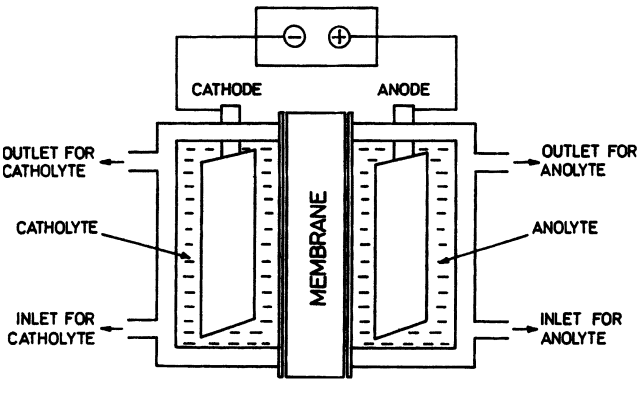

Fig. 1. A sketch of conducting SPE flow cell.

2.3. *Cyclic voltammetric studies*

Cyclic voltammetric studies were carried out in a conventional three electrode cell with provision for introducing the working, reference and counter electrodes. A hanging/static mercury drop electrode (HMDE/SMDE) (0.017 cm^2), a saturated calomel electrode (SCE) and a platinum wire served as the working, reference and counter electrodes, respectively [21]. Cyclic voltammograms for maleic acid (1 mM) were recorded in 1 M H_2SO_4, or 0.1 M CH_3COONa–H_2SO_4 and 0.1 M KH_2PO_4–Na_2HPO_4 solutions in the pH range 1.0–8.1.

2.4. *Instrumentation*

A regulated d.c. power supply (Model L 1288SR, Aplab, India) was employed as the constant current source. Cyclic voltammograms were recorded with an EG&G PAR model 175 Universal Programmer in conjunction with a 174A Polarographic Analyzer coupled with a three-electrode assembly EG&G PAR Model 303 SMDE/HMDE [21].

The ^{1}H-NMR spectra of the partially or completely electrolyzed solution, were recorded in D_2O by a Bruker Advance DPX-200 FT-NMR-200 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer spectrometer (GX FT-IR system) while for elemental analysis a Perkin-Elmer elemental analyser (CHNS/O 2400) was used.

3. Results and discussion

3.1. *Galvanostatic synthesis*

Excellent yields (95–99%) of succinic acid were obtained for the galvanostatic reduction of maleic acid at SS, Cu and Pb cathodes in the membrane cell. The corresponding data obtained under different conditions of cathode and anode material, anolyte medium, and current density are presented in Table 1. It can be seen from the table (S.Nos. 1–3) that in the membrane flow cell, the yield of succinic acid at a given current density was higher at a Pb cathode (by 0.4–3.3%) than at the other two cathodes, indicating the specificity of Pb cathode for this process. On the basis of the yields, the CE may be seen to improve marginally in the order SS < Cu < Pb. However, the use of an SS cathode is preferable as it is stable and introduces no harmful impurities. The yield of succinic acid in all the cases was found to decrease as the current density increased from 18.75 to 31.25 mA cm^{-2}, which may be accounted for by com-

Table 1. Data on the galvanostatic synthesis of succinic acid at different cathodes in a membrane flow cell

S.No.	MA /g	Anolyte /M	Cathode	Cathode current density /mA cm^{-2}	Cell current /A	Cell voltage /V	Yield of SA[c] /%	CE[d] /%
1	5	H_2SO_4(0.10)	SS[a]	18.7	0.75	4	96.4	96.6
				25.0	1.00	5	95.3	95.5
				31.2	1.25	6	95.2	96.2
2	5	H_2SO_4(0.10)	Cu[a]	18.7	0.75	4	98.4	98.6
				25.0	1.00	5	96.1	96.3
				31.2	1.25	6	95.4	95.5
3	5	H_2SO_4(0.10)	Pb[a]	18.7	0.75	4	98.8	98.9
				25.0	1.00	5	98.6	98.9
				31.2	1.25	6	95.3	95.5
4	5	Na_2SO_4(0.10)	SS[a]	25.0	1.00	9–13	95.5	95.7
5	5	NaOH(0.10)	SS[a]	25.0	1.00	16–24	96.5	96.7
6	5	H_2SO_4(0.10)	SS[b]	25.0	1.00	5–6	93.8	93.9
7	5	Na_2SO_4(0.10)	SS[b]	25.0	1.00	9–13	96.6	96.9
8	5	NaOH(0.10)	SS[b]	25.0	1.00	15–20	80.4	80.5

[a] With DSA as anode.
[b] With Pb as anode.
[c] Isolated yield of succinic acid at the end of electrolysis.
[d] Calculated on the basis of the maximum yield of product obtained.

peting hydrogen evolution reaction. The yield and CE values were high when 0.1 M Na_2SO_4 and 0.1 M NaOH were used as anolytes as compared to those when 0.1 M H_2SO_4 was used. However, the use of H_2SO_4 medium in the anode compartment is desirable as the cell voltage remains low. In the above cases, the flow of counter ions (Na^+ or H^+) from the anode compartment through the membrane to the cathode compartment is responsible for the cell current.

With H_2SO_4 or Na_2SO_4 as the anolyte, the % yield of succinic acid at an SS cathode and the CE for its formation were unaffected by the nature of the anode used (i.e., DSA or lead) (S.No. 1, 4, 6, 7 Table 1). This is understandable because the reaction under consideration is a cathodic one. However, when NaOH was used as the anolyte, the yield and CE were considerably reduced with a Pb anode as compared to those at the DSA (S.No. 5, 8 Table 1). This surprising observation may be attributed to a drastic increase in the cell voltage. A weak electrodissolution of the lead anode under these conditions and the migration of Pb^{2+} to the cathodic compartment are likely to cause a decrease in the yield and CE.

3.2. *Product analysis*

The maleic acid solution exhibited a single sharp peak at 6.33 δ in its ^{1}H-NMR spectrum corresponding to —CH=CH— (ethylenic) protons. The intensity of this peak was reduced as the electrolysis progressed. Simultaneously, a new peak at 2.56 δ corresponding to the four protons of two methylene groups (—CH_2—CH_2—) was observed whose intensity increased with the progress of the reaction. The ^{1}H-NMR spectrum of the solid isolated in D_2O (containing initially 5% maleic acid), after 138 min of electrolysis is depicted in Figure 2. The low intensity peak at 6.33 δ and the high intensity peak at 2.57 δ correspond to the unconverted maleic acid (1.4%) and the generated succinic acid (98.6%), respectively. The product isolated at the completion of electrolysis showed a single peak at 2.57 δ, confirming the formation of succinic acid as the exclusive product.

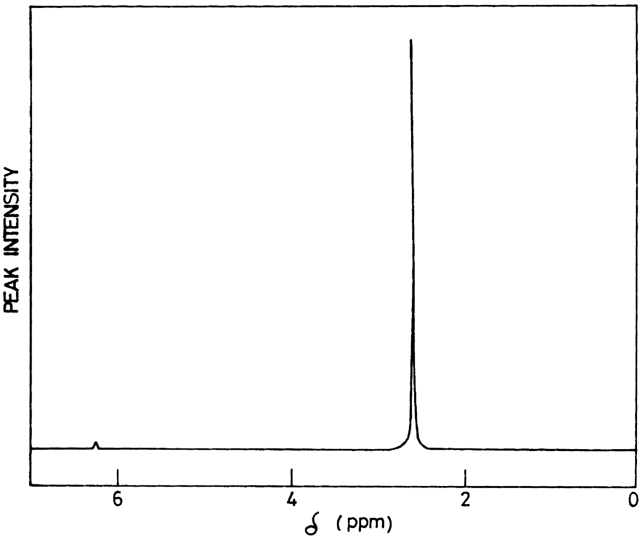

Fig. 2. ^{1}H-NMR spectrum of the solid isolated after 138 min of electrolysis of 5% maleic acid at a lead cathode (current density 25 mA cm^{-2}).

The FT-IR spectrum of the isolated product exhibited a strong absorption band at 1695 cm^{-1} for $>C{=}O$ apart from other absorptions, which matched with that of an authentic sample of succinic acid. The strong band of $>C{=}C<$ observed at 1640 cm^{-1} for maleic acid, was absent in the corresponding FT-IR spectrum of the product.

3.3. *Cyclic voltammetric studies and reaction mechanism*

Figure 3A shows the cyclic voltammetric response for 1 mM maleic acid in 1 M H_2SO_4 obtained at a HMDE

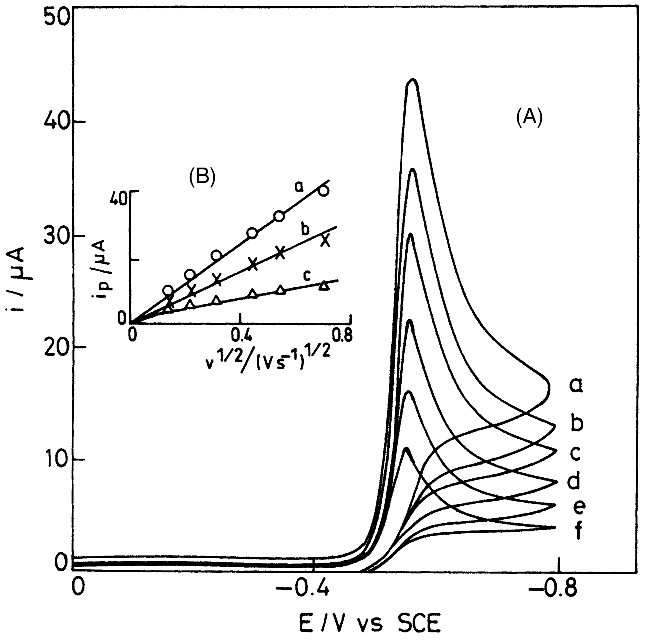

Fig. 3. (A) Cyclic voltammograms of maleic acid (1 mM) in 1 M H_2SO_4 at HMDE. Scan rate (V s^{-1}): (a) 0.50 (b) 0.30 (c) 0.20 (d) 0.10 (e) 0.05 (f) 0.02. (B) Plot of i_p vs. square root of scan rate pH: (a) 0.35 (b) 5.0 (c) 8.1.

in the potential range of 0 to −1.0 V at different scan rates. A sharp peak in the cathodic scan with no response in the reverse scan was observed. At 0.5 V s^{-1} [Figure 3A(a)], the peak ($E_{p/2}-E_p$ = 24 mV) appeared at E_p = −0.570 V which changed negligibly with decrease in the scan rate as seen in Figure 3A(b,c). Also, the $E_{p/2}-E_p$ values varied little in the range 25–35 mV. The plot of i_p vs. the square root of scan rate (Figure 3B) was linear (passing through the origin). The above data indicate that the electroreduction of maleic acid is a two-electron, irreversible, diffusion-limited process as shown below:

$$\begin{aligned}&\mathrm{HOOC{-}CH{=}CH{-}COOH} + 2H^+ + 2e^-\\&\longrightarrow \mathrm{HOOC{-}CH_2{-}CH_2{-}COOH}\end{aligned}$$

As suggested earlier [22, 23], the reduction of maleic acid may occur in three possible ways, viz. (i) direct transfer of electrons from the electrode (ii) reaction of activated hydrogen ions and/or (iii) reaction of adsorbed hydrogen ions with it. Among the three, the reaction (iii) would be the more likely mechanism if a reversible and low hydrogen overpotential cathode is employed. In the case of electrodes possessing high hydrogen overpotential (like mercury), the reduction may take place through (i) or (ii). Direct electron transfer from the electrode seems the most probable mechanism for the reduction of maleic acid, under the present experimental conditions, as may be inferred from the literature [23]. The same mechanism can be extrapolated for the reduction of maleic acid at other working electrodes like SS, Cu and Pb used under galvanostatic electrolysis conditions in the present work. It must be noted that a two-electron, diffusion-limited, irreversible reduction of maleic acid is observed in neutral and alkaline media as well.

4. Conclusion

Succinic acid was prepared in excellent yields by the galvanostatic reduction of maleic acid at SS, Cu and Pb cathodes in an ion exchange membrane flow cell. The present method demonstrates the advantages of using a highly conductive solid ion exchange membrane film between the two electrodes in a flow cell which employs a catholyte without supporting electrolyte for the electroreduction of maleic acid. Hence the requirement of additional separation steps, otherwise required in conventional methods, is made redundant. Cyclic voltammetric studies indicate a two-electron diffusion-limited irreversible reduction of maleic acid to succinic acid.

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