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Reduction of Maleic Acid to Succinic Acid on Titanium Cathode

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Abstract:

Electrochemical reduction of maleic acid to succinic acid has been studied. The effect of (i) temperature, (ii) current density, (iii) concentration of H_2SO_4, and (iv) hydrodynamic conditions on conversion of maleic acid and current efficiency has been studied. The reaction was best carried out electrochemically at 40 °C at a current density of 625 A m^{-2}. The effect of recycling the electrolyte, on conversion and current efficiency, has been reported. Conversion of maleic acid and current efficiency are affected marginally up to the fifth reuse. A material balance has been presented for these recycle studies.

Introduction

The preparation of succinic acid (SA) is of great commercial importance, since it finds extensive application in the synthesis of succinc sulphathiazole, rhodamin S, and also as an intermediate for the synthesis of a wide variety of organic compounds.[1] Maleic acid is easily reduced to succinic acid both chemically and electrochemically. Electrolytic reduction of maleic acid in H_2SO_4 medium at conventional cathodes such as rotating lead, platinized platinum, graphite, mercury, and a zinc single crystal has been reported.[2−11]

The electrolytic reduction of maleic acid in acidic media at a Pb cathode in the presence of metal citrate complexes of Co, Ni, Cu, and Mn has been studied.[12] Reduction of maleic acid at Ti/ceramicTiO_2 under galvanostatic and cyclic voltametric conditions has been examined.[13] Reduction of maleic acid on copper electrode and on copper chelate electrode in DMF containing 1 M $NaClO_4$ has been reported. With the Cu electrode, only succinic acid was formed selectively, but, with the copper chelate electrode, formation of many byproducts has been reported.[14]

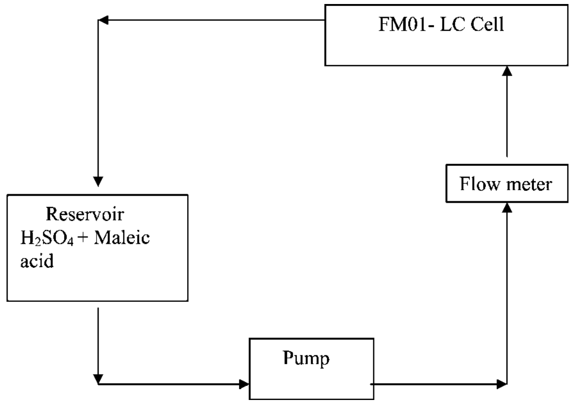

Figure 1. **FM01-LC experimental setup.**

However, reports are not available on the mass transfer limitations and effect of batch time on conversion and current efficiency for this reaction, when it is carried out electrochemically. In the present work the effect of a titanium cathode on current efficiency and conversion of maleic acid is reported after a detailed study of the various operating and process parameters. Recycling of the electrolyte was attempted to improve the economy of the process. The effect of increased loading of maleic acid and charge passed on conversion and current efficiency is also studied.

Experimental Section

Materials and Methods. Analytical grade maleic acid, succinic acid, H_2SO_4, potassium bromate, potassium bromide, potassium iodide, sodium thiosulphate, sodium chloride, starch, and mercuric sulphate were procured by s.d. finechem. Ltd Mumbai, India.

Experimental. The FM01-LC laboratory process package supplied by ICI Chemicals and Polymers, UK was used (Figure 1).[15,16] All experiments were carried out with a titanium cathode (0.0064 m^2) and a lead anode (0.0064 m^2) with an interelectrode gap maintained at 6 mm. Experiments were carried out galvanostatically. The electrolysis was carried out using 0.25−2 M H_2SO_4 and the current density in the range of 312.5−781.25 A m^{-2}. The voltage applied was in the range of 2−5 V. The temperature in the range of 20−40 °C was employed. The flask was kept in a water bath, which was used for temperature variation. The reaction mixture from the flask was pumped through the electrolyser with a magnetically driven PTFE pump. The flow rate was monitored using a rotameter.

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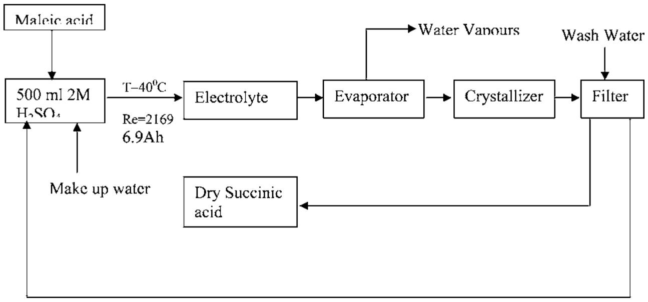
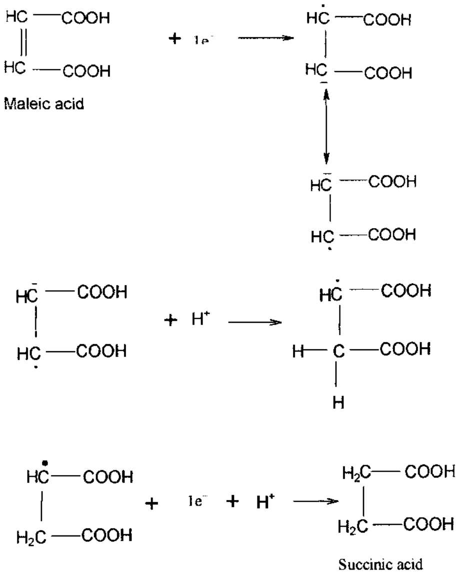


Figure 2. **Scheme of recovery of succinic acid and recycling of the electrolyte.**

The solution after electrolysis was concentrated to half the volume and kept overnight when the product succinic acid separated out. The succinic acid so obtained was filtered, given washings with cold water, and dried (Figure 2). It was identified from its melting point[17] and IR spectrum.[18] The purity of the crystallized succinic acid was determined by HPLC. It was 98.9%. The maleic acid initially added to the electrolyte, and the maleic acid left unreacted in the electrolyte after the electrolysis was determined using the Bromate−Bromide method.[19] The conversion of maleic acid was determined from the amount of maleic acid left unreacted at the end of the electrochemical reaction.

Mechanism of the Reaction. The mechanism for the reduction of maleic acid to succinic acid is as given below.[20]



Results and Discussion

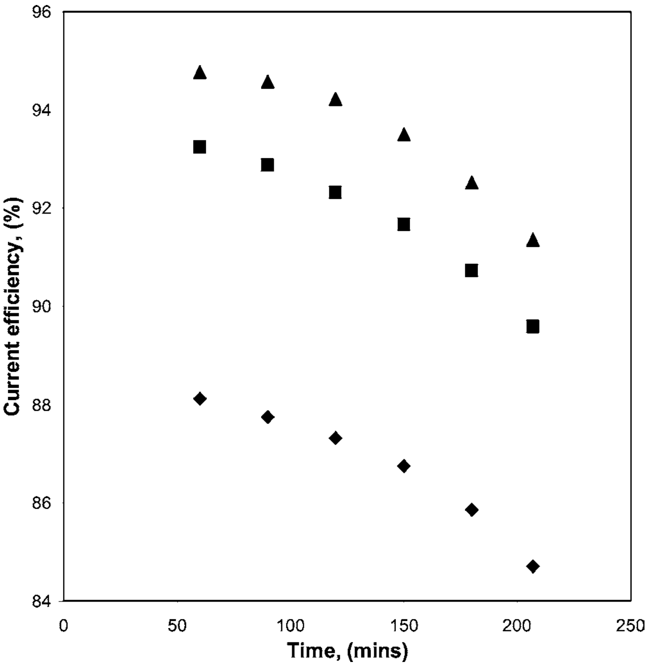


Figure 3. **Effect of batch time on current efficiency at a current density of 312.5 A m^{-2} and molarity of H_2SO_4 as 0.25, 1, and 2 M. (◆) *M* = 0.25 M, (■) *M* = 1 M, (▲) *M* = 2 M.**

Effect of Hydrodynamic Conditions. Experiments were carried out at different velocities of the electrolyte to determine whether the flow rate of the electrolyte has any effect on the rate of the reaction and to ascertain whether the reaction is under a mass transfer controlled regime. The current density was maintained at 625 A m^{-2}, and a charge equivalent to 6.9 A h was passed during the reaction. A 0.124 mol amount of maleic acid was used, and the temperature was maintained at 40 °C. A turbulence promoter in the form of a Teflon mesh was used in all experiments. Current efficiency varies in the range of 96.46% to 96.9% for $1446 < Re < 2900$. Thus the effect of the Reynolds number on current efficiency is negligible. It is therefore evident that there is no mass transfer limitation.

Effect of Concentration of H_2SO_4 on Current Efficiency and Conversion. The reaction was carried out using 0.25 M, 1 M, 2 M, and 3 M H_2SO_4 as an electrolyte. The current densities (i) 625 A m^{-2} and (ii) 312.5 A m^{-2} were used, and the Reynolds number was kept constant at 2169. Charge passed was 6.9 A hr, and 0.124 mol of maleic acid was used in these experiments. Temperature was maintained at 40 °C. As the molarity of H_2SO_4 is increased from 0.25 M to 2 M at a current density of 312.5 A m^{-2}, there is an increase in the current efficiency from 84.71% to 91.36% (Figure 3). For a current density of 625 A m^{-2}, the current efficiency increased from 89.59% to 96.86% (Figure 4). There is also an increase in the conversion as the molarity of H_2SO_4 increases from 0.25 to 2 M. For an H_2SO_4 concentration of 3 M, the reaction had to be terminated due to formation of thick charred mass. Hence 2 M H_2SO_4 was used in subsequent experiments.

Effect of Temperature on Current Efficiency and Conversion. The effect of temperature on the progress of the reaction was investigated at 20, 30, 40, and 50 °C with all other parameters unaltered. The current density was maintained at 625 A m^{-2} at the electrolyte flow Reynolds number of 2169. A charge equivalent to 6.9 A h was passed for 0.124 mol of maleic acid, dissolved in 500 mL of 2 M

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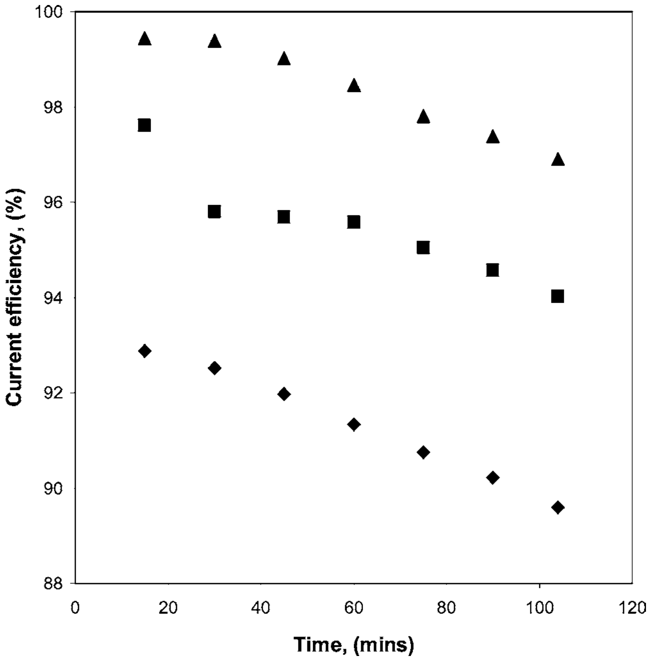

Figure 4. **Effect of batch time on current efficiency at a current density of 625 A m^{-2} and molarity of H_2SO_4 as 0.25, 1, and 2 M. (◆) $M = 0.25$ M, (■) $M = 1$ M, (▲) $M = 2$ M.**

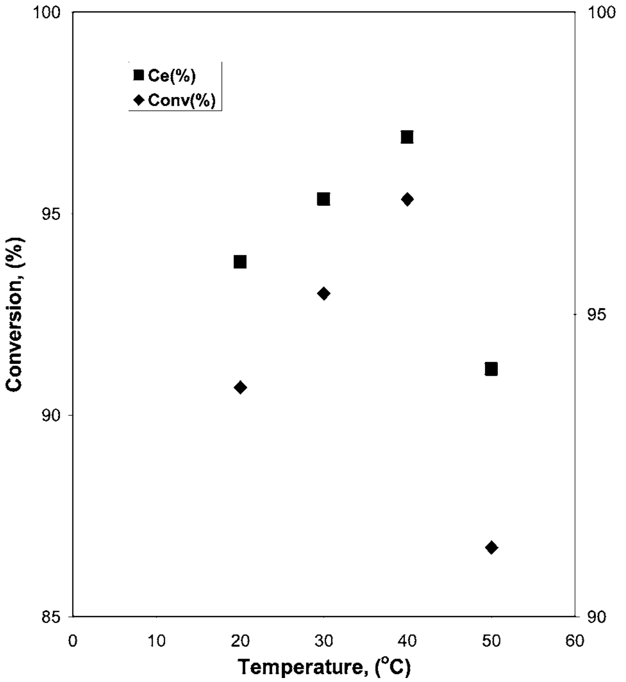

Figure 5. **Effect of temperature on conversion and current efficiency for reduction of maleic acid to succinic acid. (■) Current efficiency (Ce) (%), (◆) conversion (Conv) (%).**

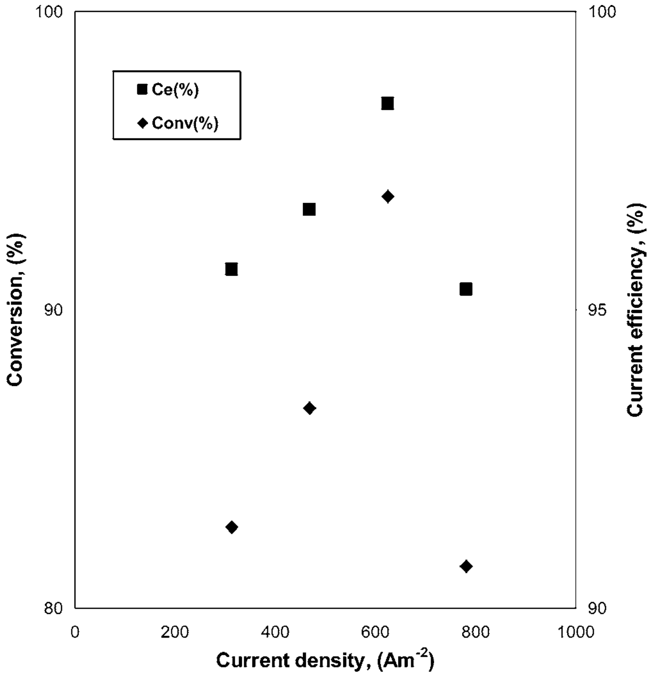

Figure 6. **Effect of current density on conversion and current efficiency for reduction of maleic acid to succinic acid. (■) Current efficiency (Ce) (%), (◆) Conversion (Conv) (%).**

H_2SO_4 for all the experiments. With the increase in the temperature from 20 °C to 40 °C, the current efficiency increased from 93.8% to 96.9% as shown in Figure 5. In this electrochemical reduction of maleic acid to succinic acid, formation of resinous matter was not observed when the temperature was maintained between 20°C to 40°C. The melting point and the IR spectrum of the final product was compared with those of the authentic sample. When the temperature was increased beyond 40 °C, there was apparently a side reaction, which gave rise to formation of a tarry resinous mass. Thus, at 50 °C, the current efficiency decreased sharply to 91.14% as shown in Figure 5.

Effect of Current Density on Current Efficiency and Conversion. The reaction was carried out using a current density in the range of 312.5−781.25 Am^{-2} at 40 °C. The Reynolds number was maintained at 2169, and the charge passed was 6.9 A h. Maleic acid (0.124 mol) was dissolved in 500 mL of 2 M H_2SO_4. At a current density of 625 A m^{-2}, 96% current efficiency was obtained. But when the current density was increased to 781.25 A m^{-2}, formation of resinous matter was observed. Resinous matter may be formed due to polymeric condensation of maleic acid.[6] Consequently the current efficiency dropped sharply to 90.7% as shown in Figure 6.

Effect of Batch Time on Current Efficiency and Conversion. Reactions were carried out at different molarities (H_2SO_4: 0.25 M/1 M/2 M) and at different current densities (312.5 A m^{-2} and 625 A m^{-2}). The Reynolds number was maintained at 2169, and the charge passed was 6.9 A h. In each experiment, 0.124 mol of maleic acid was dissolved in 500 mL of the electrolyte. The reaction temperature was maintained at 40 °C. As the reaction proceeds, the formation of succinic acid increases and the availability of the reactant, i.e., maleic acid, decreases. Thus conversion goes on increasing while the current efficiency decreases with time (Figures 3 and 4). When the current density was maintained at 312.5 A m^{-2} with the molarity of H_2SO_4 as 0.25 M, the conversion increased from 25.42% to 84.71%; at a molarity of 1 M, the conversion increased from 26.9% to 89.59%, and at a molarity of 2 M the conversion increased from 27.34% to 91.36%. For the current density of 625 A m^{-2}, there was a similar increase in the conversion. For 0.25 M H_2SO_4, the conversion increased from 52.33% to 89.59%; for 1 M H_2SO_4, the conversion increased from

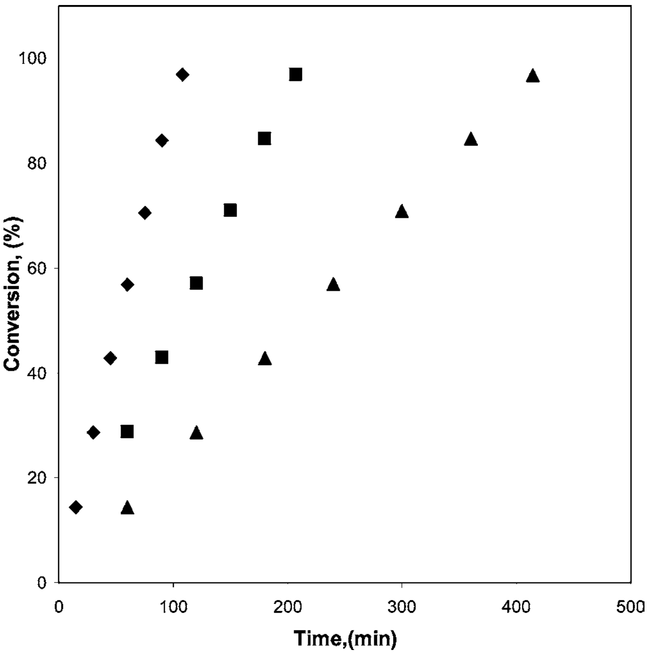

Figure 7. **Effect of loading of maleic acid on conversion and current efficiency. (◆) Conversion (L_1) $L_1 = 0.124$ mol of maleic acid. (■) Conversion (L_2) $L_2 = 0.248$ mol of maleic acid. (▲) Conversion (L_3) $L_3 = 0.497$ mol of maleic acid.**

55.14% to 94.02%; and for 2 M, the conversion increased from 56.8% to 96.9%.

Effect of Loading of Maleic Acid and Charge Passed on Current Efficiency and Conversion. Experiments were carried out at a current density of 625 A m^{-2}, with 2 M H_2SO_4 as the electrolyte, using (i) 0.124 (L_1), (ii) 0.248 (L_2), and (iii) 0.497 (L_3) mol of maleic acid. The charge passed was 6.9, 13.8, and 27.6 A h, respectively. The Reynolds number was maintained at 2169. The temperature was maintained at 40 °C. It was observed that the current efficiency and conversion remain unaffected as the loading of maleic acid and charge passed is increased. For L_1, the current efficiency observed was 96.9%. When the loading is increased to 0.248 mol, the current efficiency remained unaffected, while at L_3 it increased to 98.41%. (Figure 7).

Recycle Studies. Succinic acid formed in the reaction is recovered from the electrolyte by concentration of the electrolyte followed by crystallization. The mother liquor obtained from the filtration and washing of succinic acid crystals contains H_2SO_4, succinic acid, and the unreacted maleic acid. Recycle of this mother liquor as an electrolyte for subsequent batches was investigated to reduce/eliminate the problem of disposal of the mother liquor.

Recycle studies were carried out at the current density 625 A m^{-2} and a molarity of H_2SO_4 of 2 M. The Reynolds number was kept unaltered at 2169. The charge equivalent to 6.9 A h was passed during each reaction cycle with the temperature being maintained at 40 °C.

Table 1. **Effect of electrolyte recycling on conversion and current efficiency**[a]

number of cycles	conversion (%)	current efficiency (%)	maleic acid present in the electrolyte at the start of each cycle (gm)	succinic acid weighed (g)
0	96.78	96.94	29.68	28.40
1	96.69	96.82	29.89	29.22
2	96.40	96.64	29.99	29.32
3	96.20	96.42	30.23	29.41
4	95.90	96.22	30.34	29.50

[a] Conditions: current density = 625 A m^{-2}, 2 M H_2SO_4 is used as the electrolyte, Maleic acid = 0.124 mol (30 g), charge passed = 6.9 A h, temperature = 40 °C, Reynolds number = 2169.

After every cycle, 30 g of maleic acid was added to the recycled electrolyte (500 mL). The amount of maleic acid present in the electrolyte at the beginning and the end of each run was determined titrimetrically using the Bromate–Bromine method. After every run, the electrolyte was concentrated and then cooled to get crystallized succinnic acid. It was filtered, washed with cold water, dried, and weighed (Figure 2). The electrolyte concentration was determined by the acid–base titration. Then it was diluted to the initial concentration with the cold water that was used for washings of the succinic acid crystals from the previous batch. The electrolyte was then recycled after addition of 30 g of maleic acid.

Recycling of the electrolyte showed that the conversion and current efficiency are marginally affected up to the fifth reuse. This reuse of electrolyte can substantially reduce production cost as well as the waste disposal problem when reaction is carried out at a large scale level. The total succinic acid obtained after five cycles was 145.85 g as shown in Table 1. The recovery was 92%.

Conclusions

A study of the effect of various operating variables on the electrochemical reduction of maleic acid to succinic acid has indicated that a current density of 625 A m^{-2} and 2 M H_2SO_4 as an electrolyte in the temperature range around 40 °C are most favorable for high current efficiency and maximum conversion of maleic acid to succinic acid. With further increase in the current density, temperature, and molarity of H_2SO_4, there is a decrease in the current efficiency due to formation of resinous matter. The electrolyte can be successfully recycled 4 times, with 92% overall recovery of SA, without affecting the current efficiency.

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