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Electrochemical Synthesis of Succinic Acid at a TiO_2 Film Electrode Prepared by *In-Situ* Anodic Oxidation

Fengming Zhao, Fei Yan, Yang Qian, Youqun Chu, Chun'an Ma[*]

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou 310032, P.R. China
[*]E-mail: science@zjut.edu.cn; zhaofm@zjut.edu.cn

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TiO_2 film was prepared by *in-situ* anodic oxidation on a polished titanium sheet in a mixed acid solution containing 1.0 mol/l sulfuric acid and 1.0 mol/l maleic acid. By means of polar conversion technology, succinic acid was synthesized using a TiO_2 film as cathode in the original solution. The reduction yield and current efficiency of succinic acid were 99.36% and 97.52%, respectively. The elemental composition, valence state analysis and superficial morphology of TiO_2 film cathode before and after electrolysis were characterized by XPS and SEM. The electrocatalytic properties of TiO_2 film electrode towards the electrocatalytic reduction of maleic acid to succinic acid were evaluated by CV and galvanostatic electrolysis experiments. Experimental evidence was presented that porous TiO_2 film cathode exhibited powerful electrocatalytic activity for the reduction of maleic acid. Furthermore, a synergistic effect of low valent titanium of Ti(III) and chemisorbed hydrogen (H)Ti was proposed for probable reductive mechanism of malaeic acid to succinic acid.

Keywords: TiO_2 film, anodic oxidation, polar conversion technology, succinic acid, synergistic effect

1. INTRODUCTION

Succinic acid ($C_4H_6O_4$), also known as amber acid or butanedioic acid, is a constituent of plant and animal tissues. The preparation of succinic acid is of great commercial importance, since as an important chemical material or intermediate, it finds extensive applications in areas ranging from radiation dosimetry to surfactant, agriculture, electroplating, foods, medicine, textiles, photography, waste-gas scrubbing, cosmetics and so on [1-5].

Maleic acid can be reduced to succinic acid both chemically and electrochemically. Generally, the production and process methods for succinic acid can be divided into two categories: petrochemical method from maleic acid and fermentation process from corn. Chemical synthesis method has been already eliminated owing to its heavy pollution, low yield and high cost [6].

Fermentation process of succinic acid from corn has attracted more interests in recent decades [7-9]. Rich raw materials are the most attractions [10], but its disadvantage is also very obvious, that is, longer fermentation time, complicated separation and difficult to purify the final product [6]. Therefore, all of these problems make it more difficult for large-scale production. Apart from the above mentioned methods, electrochemical synthesis considerably avoids environmental pollution for industrial production of succinic acid. It has numerous advantages such as high yield, high purity, mild reaction conditions and zero-emission process via filtrate recycle [11-14]. Electrolytic reduction of maleic acid in acidic medium has been reported at conventional cathodes such as lead, graphite and mercury [15-17]. However, lead contamination is a serious problem in the preparation of food grade products in industrial application. Hence, it is desirable to look for alternative cathode materials for the production of succinic acid.

Titanium dioxide (TiO_2) is one of the most widely used and promising materials in electrocatalytic application due to its redox selectivity, high stability, easy preparation, manufacturable at atmospheric conditions and environmental safety [18-23]. The advantages of TiO_2 cathode over conventional cathodes have been discussed. The effect of various operating and process parameters at titanium cathode for the reduction of maleic acid has been studied [24]. Reduction of maleic acid at a Ti/ceramic TiO_2 cathode under galvanostatic and cyclic voltametric conditions has been investigated [25]. The thermally coated Ti/TiO_2 cathode has been found to be useful in the electrochemical process of succinic acid [11]. Moreover, a sol-gel method to prepare nanocrystalline TiO_2 modified cathodes which exhibit excellent performance for the reduction of maleic acid has been reported [26-28]. In our early works, a novel and simple method to fabricate bundles of TiO_2 film prepared by anodic oxidation has been studied. The prepared electrode was used as cathode for the electrocatalytic reduction of maleic acid to succinic acid.

This paper reports a simple and promising method for electrochemical synthesis of succinic acid at a TiO_2 film electrode prepared by *in-situ* anodic oxidation in a mixed acid solution containing 1.0 mol/l sulfuric acid and 1.0 mol/l maleic acid. Polar conversion technology was employed for the electrode preparation and succinic acid synthesis in the original solution. In addition, the probable mechanism of the electrocatalytic reduction of maleic acid was also discussed.

2. EXPERIMENTAL

2.1. Preparation and characterization of TiO_2 film electrode

Titanium sheets were polished with $6^{\#}$ metallographic abrasive paper and followed by ultrasonic cleaning in acetone and ethanol for 30 minutes, respectively. Then titanium sheets were washed using ultra-pure water with a resistivity of 18.2 MΩ obtained from Millipore-Q system to get a clean surface prior to anodization. Anodic oxidation was carried out in an undivided cell, in which a polished titanium sheet served as anode and a DSA as cathode. A mixed acid solution containing 1.0 mol/l sulfuric acid and 1.0 mol/l maleic acid was used as the electrolyte. The electrolyte temperature maintained at 45 ℃ using a water bath. The voltage remained at 10 V for 80 minutes. A magnetic stirrer was used during electrolysis. The elemental composition and valence state of TiO_2 film surface were determined by XPS (Kratos Axis Ultra DLD spectrometer (England), Al Kα X-ray as excitatonsource, 45W). Superficial morphology and microcosmic structure were characterized by SEM using a Hitachi S-4700 II electron microscope (America).

2.2. Cyclic voltammetry

Cyclic voltammetry measurements were carried out in a conventional three-electrode glass cell controlled by a CHI660D electrochemical workstation (Shanghai, China). A TiO_2 film electrode (10 mm × 10 mm) was used as the working electrode, A platinum foil and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. All potentials were recorded with respect to SCE. All experiments were performed at 45 ℃.

2.3. Galvanostatic electrolysis

Galvanostatic electrolysis experiments were performed in a 1 dm^3 beaker. A TiO_2 film (30 mm×30 mm) prepared by the method described above and a polished titanium sheet (30 mm×30 mm) served as cathodes and DSA served as anode. A mixed acid solution containing 1.0 mol/l sulfuric acid and 1.0 mol/l maleic acid was used as the electrolyte. The electrolyte was stirred magnetically. Current density in the range of 5 ~ 10 $A\cdot dm^{-2}$ was employed. The temperature was controlled at 45 ℃ using a water bath during the electrolysis. Succinic acid produced was crystallized out by cooling the electrolyte to 15 ℃ after completion of the electrolysis. And then the products were filtered and dried. It was identified from its melting point and IR spectrum (Thermo Nicolet Nexus6700).

2.4 Reductive ability of Ti (III) for maleic acid

Reductive ability of Ti(III) for maleic acid was evaluated by chemical synthesis of succinic acid with Ti(III). $Ti_2(SO_4)_3$ solution of 228 ml was put into the flask and deaerated for 15 minutes using pure nitrogen in advance. Maleic anhydride of 9.8 g was added into the solution, condensing reflux for 5 hours at 80 ℃. Then the mixture was cooled to make the product separate out and then the product was identified from IR spectrum. UV-vis spectrophotometry (VARYAN CARY100) was used to analyze whether Ti(III) existed or not in the electrolyte after electrolysis.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Figure 1 shows the cyclic voltammograms of the TiO_2 film electrode in 1.0 mol/l H_2SO_4 and 1.0 mol/l H_2SO_4 +1.0 mol/l maleic acid at a sweep rate of 0.05 Vs^{-1}. It was seen that there were no any redox peaks except for hydrogen evolution on Fig.1 (a). Fig.1 (b) showed that a strong cathodic peak was observed at around -0.65 V ~ -1.1 V in the presence of maleic acid. The peak current was high enough and indicated an excellent eletrocatalytic catalytic activity for maleic acid. During the reverse scan, there was no anodic peak but an absorption peak occurred, which illustrated the eletrocatalytic reduction of maleic acid to succinic acid was irreversible [13, 14].

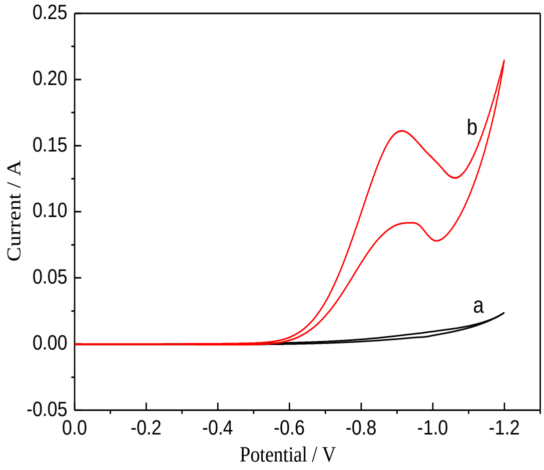


Figure 1. CV voltammograms of the TiO_2 film electrode in (a) 1.0 mol/l H_2SO_4; (b) 1.0 mol/l H_2SO_4+1.0 mol/l maleic acid; T = 45℃; Scan Rate: 0.05 Vs^{-1}.

The effect of various sweep rates on the electrochemical behavior of the TiO_2 film electrode was studied by linear sweep voltammograms. Fig.2 showed the effect of sweep rate on i_p in the presence of maleic acid. It was found that the cathodic peak current increased with the sweep rate and the plot of i_p *vs*. the square root of scan rate was linear (Fig.2B). The peak potential also moved slightly with increasing the sweep rate. It revealed that the TiO_2 film electrode behaved as a very good heterogeneous redox catalytic electrode and the reduction of maleic acid was fast and irreversible [13, 14, 26, 29].

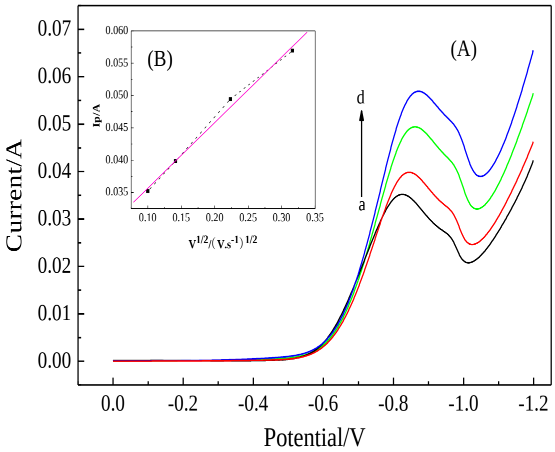


Figure 2. LSV curves of the TiO_2 flim electrode; Scan rate: Vs^{-1}: a-0.01; b-0.02; c-0.05; d-0.10.

3.2. Galvanostatic electrolysis at the TiO_2 film electrode

The results of galvanostatic electrolysis at the TiO_2 film electrode were listed in Table 1. It can be seen that excellent yields and current efficiencies of succinic acid were obtained. Recycling of the electrolyte (experimental cycle 1~10) showed that the average reduction yield and current efficiency were 99.36% and 97.52%, respectively. The reduction yield and current efficiency are higher than any other electrodes reported before, such as the thermally coated Ti/TiO_2 electrode [11], the Ti/ceramic TiO_2 electrode [25] and nanocrystalline TiO_2 modified electrode [26-28]. And the technique of filtrate recycle could substantially reduce production cost as well as the waste disposal when it will be carried out at a larger scale level.

Table 1. Galvanostatic electrolysis data on the reduction of maleic acid at the TiO_2 film electrode.

Cycle number	Inventory /g	Output /g	Quantity yield^{*1} /%	Reduction yield^{*2} /%	Current efficiency /%
0	9.80	9.38	95.71	79.49	79.39
Cycle 1	9.80	11.55	117.86	97.88	97.76
Cycle 2	7.50	9.05	120.67	100.21	97.88
Cycle 3	7.50	9.10	121.33	100.77	98.42
Cycle 4	7.50	8.92	118.93	98.78	96.71
Cycle 5	7.50	9.80	130.67	108.52	105.99
Cycle 6	7.50	9.01	120.13	98.77	97.44
Cycle 7	7.50	9.75	130.00	107.97	105.45
Cycle 8	7.50	9.35	124.67	103.54	101.12
Cycle 9	7.50	9.39	125.2	103.98	101.55
Cycle 10	7.50	8.91	118.8	98.66	96.36
Total	87.10	104.20	119.63	99.36	97.52

$*^1$: Quantity yield= $\frac{m_{output}}{m_{inventory}}$; $*^2$: Reduction yield= $\frac{n_{output}}{n_{inventory}} = \frac{m_{output}/118}{m_{inventory}/98}$

3.3 Characterization of the TiO_2 film electrode

Fig.3 and Fig.4 showed SEM images and XPS of the TiO_2 film electrode before and after galvanostatic electrolysis. The surface of the TiO_2 film electrode prepared by anodic oxidation is covered with a smooth, compact film compared with polished titanium sheet. The film is composed of three elements Ti, O and C (correction element), Ti and O exist as TiO_2 according to the XPS data (Fig.4A and B), which confirms the prepared film electrode is TiO_2 [30]. After electrolysis, the TiO_2 film became sparse and numerous pores (Fig.3 B and E), the composed elements also are Ti, O and C (correction element), but Ti and O exist as a mixture of Ti and TiO_2 (Fig. 4 C and D). It indicated that TiO_2 dissolved possibly into the electrolyte as lower valent titanium element.

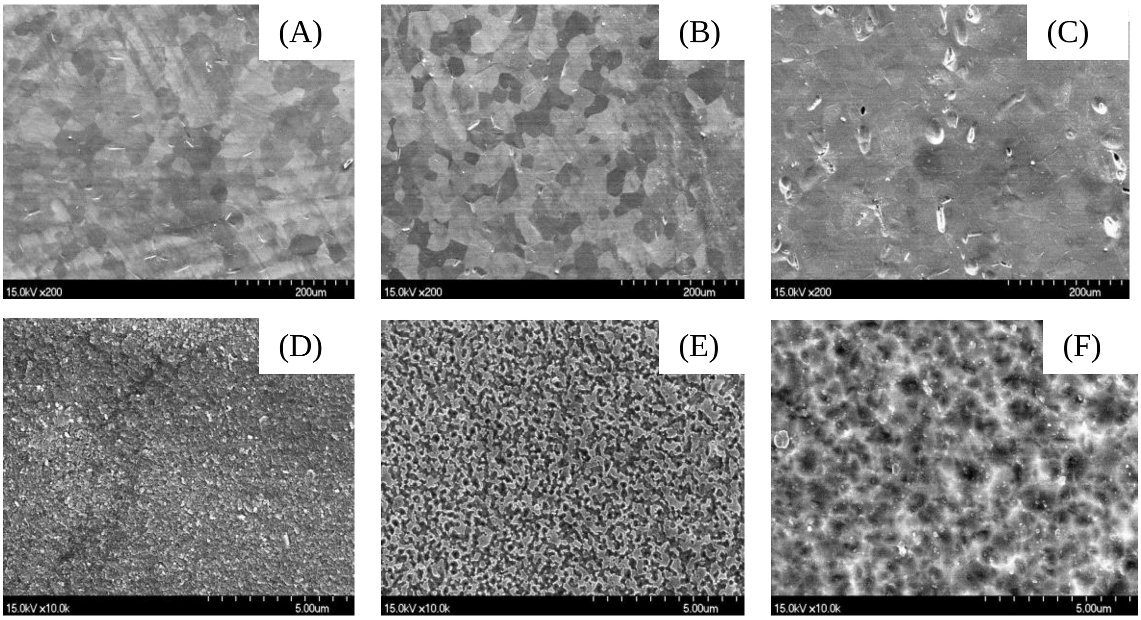


Figure 3. SEM images of (A) and (D): TiO_2 film electrode before electrolysis; (B) and (E): TiO_2 film electrode after electrolysis; (C) and (F): Ti electrode.

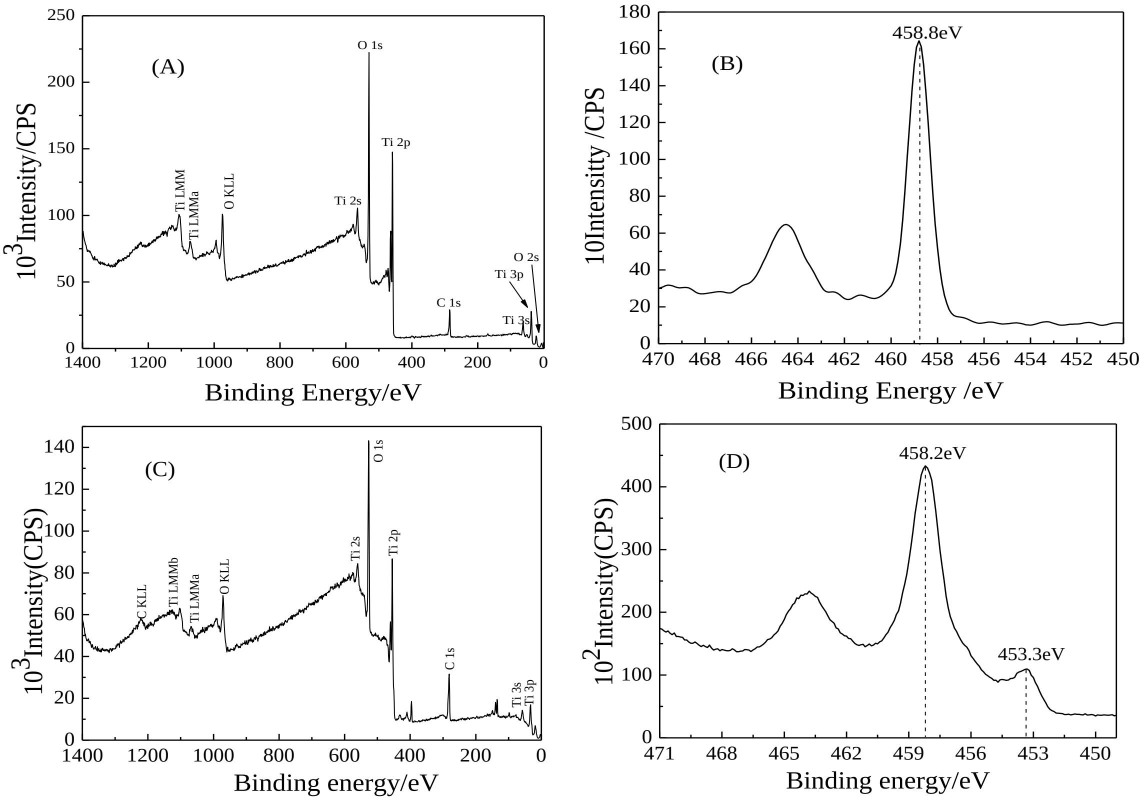


Figure 4. XPS of (A) and (B): TiO_2 film electrode before electrolysis; (C) and (D): TiO_2 film electrode after electrolysis.

3.4 Analysis of Ti (III) and its reductive ability for maleic acid

The UV-vis spectrum of various electrolytes was shown in Fig.5. It can be seen that $Ti_2(SO_4)_3$ standard solution had a strong absorption peak at 198 nm approximately (Fig.5 (a)). Fig.5 (b) showed the absorption of electrolyte with TiO_2 film electrode after galvanostatic electrolysis. The absorption peak occurred at the same wave number of 198 nm. It indicated that Ti(III) existed in the electrolyte because the surface of TiO_2 film dissolved possibly into the electrolyte.

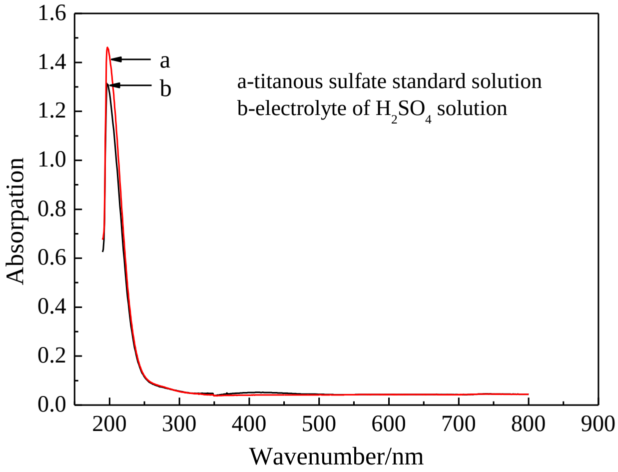


Figure 5. UV-vis spectrum of (a) $Ti_2(SO_4)_3$ standard solution; (b) electrolyte after electrolysis.

The IR spectrum of succinic acid prepared by chemical synthesis with $Ti_2(SO_4)_3$ solution was shown in Fig.6(a). The strong band of C=C for maleic anhydride (1640 cm^{-1}) was absent. It was identical from IR spectrum to the product of succinic acid by galvanostatic electrolysis (Fig.6 (b)). All the above experimental results revealed that Ti(III) has the ability to reduce maleic acid to succinic acid.

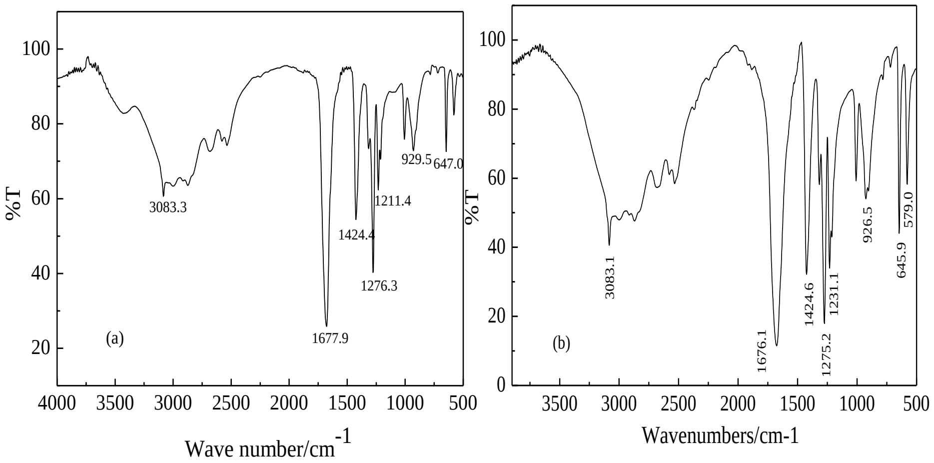


Figure 6. IR spectrum of succinic acid (a) prepared by chemical synthesis with $Ti_2(SO_4)_3$ solution; (b) prepared by electrolysis.

3.5 Galvanostatic electrolysis compared with the polished titanium electrode

The results of galvanostatic electrolysis at the polished titanium electrode were shown in Table 2. The average reduction yield and current efficiency for succinic acid are 89.53% and 89.26%, respectively. It can be seen that the polished titanium electrode also has catalytic activity to the electroreduction of maleic acid [24], but the results of electrolysis at the polished titanium electrode were lower than that at the TiO_2 film electrode. Combined with the above experimental evidence, Ti(III) in the electrolyte could contribute to the reduction of maleic acid to succinic acid.

Table 2. Galvanostatic electrolysis data on the reduction of maleic acid at the polished titanium electrode.

Cycle number	Inventory /g	Output /g	Quantity yield /%	Reduction yield /%	Current efficiency /%
0	9.80	9.26	94.49	77.69	78.38
Cycle 1	7.54	8.01	106.23	87.35	88.60
Cycle 2	7.60	7.65	100.66	82.76	83.67
Cycle 3	7.51	7.10	94.54	77.73	77.65
Cycle 4	7.50	9.07	120.93	99.43	100.32
Cycle 5	7.50	8.70	116.00	95.38	96.23
Cycle 6	7.55	9.06	120.00	98.66	100.21
Cycle 7	7.56	8.39	110.98	91.25	91.76
Cycle 8	7.51	8.80	117.18	96.34	97.34
Total	70.07	76.04	108.52	89.53	89.26

Consequently, a synergistic effect of Ti(III) and chemisorbed hydrogen (H)Ti was described by reactions (1)-(7). $Ti(OH)_3$ reduced by electroreduction of TiO_2 film (reaction (1)) [12, 28, 31, 32], reacts with maleic acid in the electrolyte. Chemisorbed hydrogen, (H)Ti generated in situ by electroreduction of water (reaction (2)), reacts with the adsorbed maleic acid (reaction (3)-(5)). The interaction of both the external and original effects eventually produced the maximum yield and current efficiency for electrochemical synthesis of succinic acid. The detail reaction processes are shown in scheme 1.

(1) $\mathrm{TiO_2 + H_2O + H^+ + \mathit{e} \rightarrow Ti(OH)_3}$

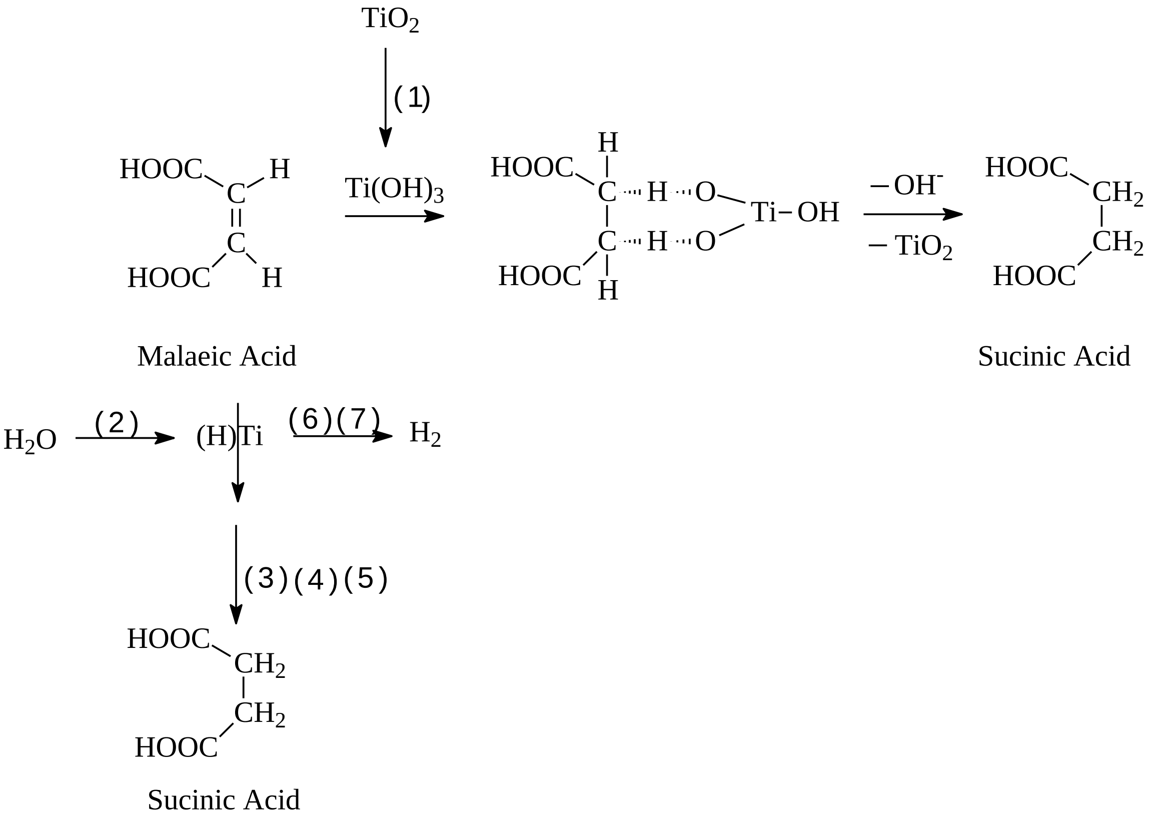
(2) $\mathrm{H_2O + \mathit{e} + Ti \rightarrow (\mathit{H})Ti + OH^-}$

(3) $\mathrm{(R_1C{=}CR_2)Ti + Ti \rightarrow (R_1C = CR_2)Ti}$
(4) $\mathrm{(R_1C{=}CR_2)Ti + 2(\mathit{H})Ti \rightarrow (R_1CH{-}CHR_2)Ti + 2Ti}$

(5) $\mathrm{R_1CH{-}CHR_2)Ti \rightarrow R_1CH{-}CHR_2 + Ti}$

(6) $(H)\mathrm{Ti}+\mathrm{H_2O}+e \rightarrow \mathrm{H_2}+\mathrm{Ti}+\mathrm{OH^-}$

(7) $(H)\mathrm{Ti}+(H)\mathrm{Ti} \rightarrow \mathrm{H_2}+2\mathrm{Ti}$



Scheme 1. Mechanism of electrocatalytic reduction of maleic acid to succinic acid.

4. CONCLUSIONS

In summary, the TiO_2 film electrode prepared by in-situ anodic oxidation appears to be an excellent electrocatalytic material for electrochemical synthesis of succinic acid. Electrocatalytic reduction of maleic acid to succinic acid with excellent reduction yield (99.36%) and current efficiency (97.52%) can be successfully achieved without changing the electrolyte. The extraordinary electrocatalytic activity of the TiO_2 film electrode for the reduction of maleic acid to succinic acid probably originates from the synergistic effect of low valent titanium (Ti(III)) and chemisorbed hydrogen ((H)Ti).

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