

Detection limit and electrochemical behavior of maleic acid on a platinum electrode

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The electrochemical behavior of maleic acid (MA) on a platinum electrode was studied using cyclic voltammetric, linear sweep voltammetric and chronoamperometric techniques. The results showed that the reduction of MA on a Pt electrode is a quasi-reversible process as a result of the diffusion and the reductive potential of MA at -0.62 V (vs. Ag/AgCl). The detection limit of MA on a Pt electrode was calculated to be 1.6×10^{-5} M. The anodic and cathodic current peaks of MA increased with increasing the concentration of MA from 5.00×10^{-3} to 8.89×10^{-3} M at a scan rate ranging from 20-200 mV/s. The diffusion coefficient of MA was determined to be 0.815×10^{-7} cm².s⁻¹. The mechanism of the produced succinic acid by electrochemical reduction of MA was discussed.

Keywords: Maleic acid; Succinic acid; Cyclic voltammetry; Linear sweep voltammetry; Chronoamperometric measurements.

INTRODUCTION

The electrochemical behavior of maleic acid (HOOC-CH=CH-COOH) in oxidation is of great interest because this molecule is the hinge between cyclic and linear structures. So the oxidation of MA on born doped diamond electrode (BDDE) has been studied. The reduction of MA in acidic media on a Pb cathode in electrolytic solution of Co, Ni, Cu, and Mn citrate complexes has been also studied [1]. Reduction of MA on Ti/ceramicTiO₂ under galvanostatic and cyclic voltammetric conditions has been examined [2]. Also, the behavior of MA had previously been studied using Au, (BDD), glassy carbon (GC) and lead electrodes [3-5].

Maleic acid can be easily reduced to succinic acid, both chemically and electrochemically, the electrochemical synthesis having numerous advantages such as high yield, high purity, mild reaction conditions, low environmental pollution and zero-emission process *via* filtrate recycling [6-9].

Succinic acid as a product of the electrochemical reduction of MA is of great marketable rank as an important chemical material. It finds extensive applications in different areas such as radiation dosimetry, agriculture, electroplating, medicine, photography, waste-gas scrubbing, surfactants, foods, textiles, cosmetics and is used in the food and drink industry, mainly as acidity regulator [10-15].

The current study targets to inspect the electrochemical behavior of MA on a Pt electrode by

using cyclic voltammetry to elucidate the mechanism of the reduction process. The effects of concentration of MA and scan rate on the current peaks were studied as well. The electrochemical synthesis of succinic acid from MA using linear sweep voltammetry was studied. The detection limit of MA on a Pt electrode was a part in this work.

EXPERIMENTAL

Reagents and solutions

All solutions used in the present investigation were freshly prepared from Analar grade chemicals used without further purification. 0.1M Sodium phosphate monohydrate Na₂HPO₄ used as a supporting electrolyte was prepared by dissolving 3.55 g in 250 mL of double-distilled water. A stock solution of 0.01M MA (dihydrate) was prepared by dissolving 0.315 g in 250 mL of double-distilled water. Other concentrations of MA were obtained by dilution from the stock solution.

Electrochemical equipment

The device used in these experiments was EG&G Princeton Applied Research potentiostat/galvanostat model 263. The cell contains three electrodes (model K0264 micro-cell), an Ag/AgCl (saturated KCl) -model K0265 electrode was used as the reference electrode, while the working and counter-model K0266-electrodes were of high purity platinum wire. All measurements were carried out at room temperature in duplicate and the reproducibility of these measurements was found to be satisfactory.

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Techniques used

The electrochemical behavior of maleic acid was studied in Na_2HPO_4 solutions on a platinum electrode using cyclic voltammetry (CV). The voltammetric parameters were as follows: initial potential was 1 V; vertex potential was -1 V and final potential was 1 V vs. Ag/AgCl in presence of different concentrations of maleic acid at different scan rates. Another technique used was cathodic linear sweep voltammetry (CLSV) of 8.57×10^{-3} M maleic acid in 0.1 M Na_2HPO_4 from 1 V to -1 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. The third technique used was chronoamperometry (CA) of 3.33 mM to 8.33 mM of MA in 0.1 M Na_2HPO_4 as a supporting electrolyte, setting the working electrode at 0.00 mV (first potential step) and at -1.00 mV (second potential step) at time 5 s.

RESULTS AND DISCUSSION

Supporting electrolyte selection

In the current study, many supporting electrolytes (e. g.: sodium sulfate, silver nitrate, sodium chloride and phosphate monohydrate) have been used to test the behaviour of the MA on a Pt electrode. It has been found that the phosphate monohydrate is the most appropriate.

Figure 1 shows the cyclic voltammogram of 0.1M Na_2HPO_4 as supporting electrolyte from 1 V to -1 V at a scan rate 50 mV/s on a Pt electrode. It is seen that there is one reduction peak at -0.9 V and one oxidation peak at -0.6 V.

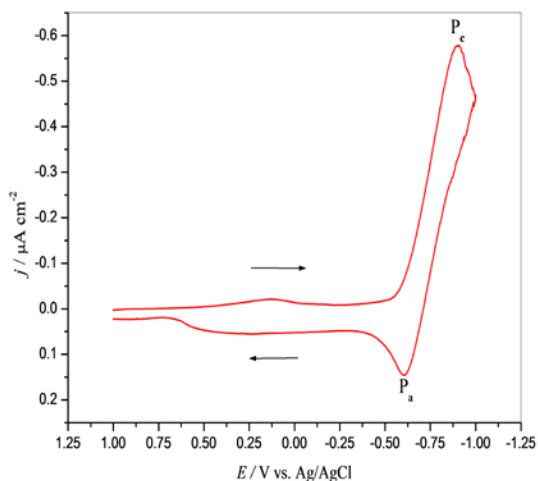


Fig. 1. Cyclic voltammogram of a Pt electrode in 0.1M Na_2HPO_4 at a scan rate of 50 mV/s.

Different volumes of 0.01M maleic acid were added to other different volumes of 0.1M sodium phosphate monohydrate to study the cyclic voltammetry of MA in this supporting electrolyte.

But there are no peaks of MA observed from concentrations 5.00×10^{-5} M to 3.33×10^{-3} M, as illustrated in Figure 2.

Also the cathodic and anodic current peaks of supporting electrolyte (Na_2HPO_4) decreased with increasing in the concentration of MA, as observed in Figure 2.

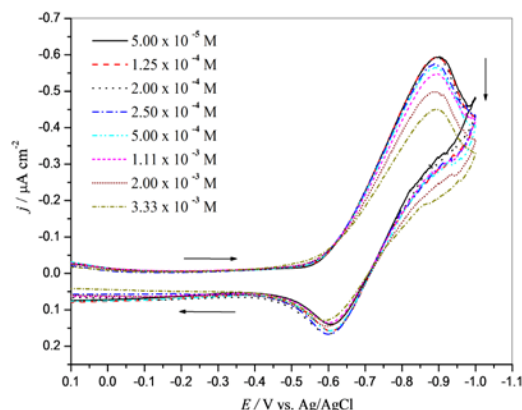


Fig. 2. Cyclic voltammograms of different concentrations of maleic acid in 0.1 M Na_2HPO_4 , at a scan rate 50 mV/s.

At a concentration of 8.57×10^{-3} M, the best cathodic peak (P_{C1}) at -0.62 V appears which corresponds to the reduction of MA to succinic acid and the anodic peak (P_{A1}) at -0.33 V. P_{C2} and P_{A2} belong to Na_2HPO_4 , as follows from Figure 3.

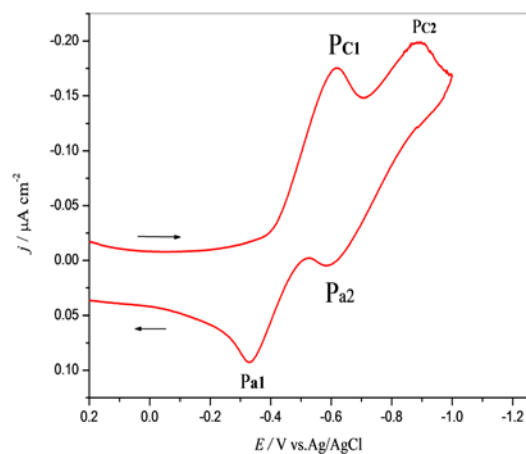


Fig. 3. Cyclic voltammograms of 8.57×10^{-3} M maleic acid in 0.1 M Na_2HPO_4 , at a scan rate of 50 mV/s.

From the anodic and cathodic peaks the potential difference was calculated as equation (1):

$$\Delta E = E_c - E_a = -0.62 - (-0.33) = -0.29V \quad (1)$$

A quasi-reversible process controlled by diffusion represents the electrochemical reduction of maleic acid on a Pt electrode [16,17], where the

potential difference (-0.29 V) refers to a quasi-reversible process controlled by diffusion.

Effect of maleic acid concentration

Figure 4 shows the effect of various concentrations of MA on the cathodic and the anodic peaks. The cathodic peak of MA increases with the increase in MA concentrations from 5.00×10^{-3} M to 8.89×10^{-3} M, and also the cathodic peak potential shifted to more negative values.

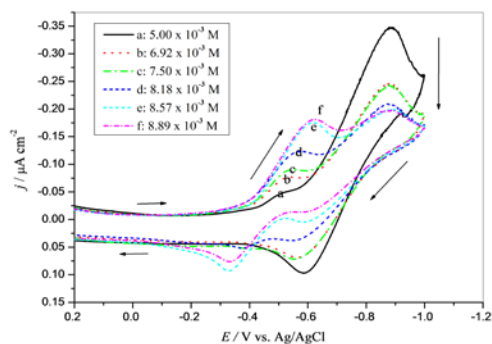


Fig. 4. Cyclic voltammograms of different concentrations of maleic acid in 0.1 M Na_2HPO_4 , at a scan rate of 50 mV/s.

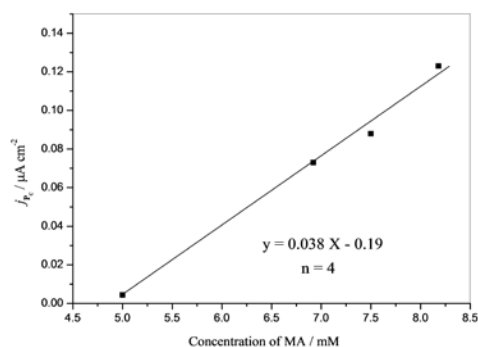


Fig. 5. Calibration graph of maleic acid in 0.1 M Na_2HPO_4 using a Pt electrode at a scan rate of 50 mV/s.

On the other side, the anodic peak started to appear at a concentration of 8.18 mM of MA and its oxidation current increased with the increase in the concentration of maleic acid up to 8.57×10^{-3} M and then decreased with the increase in concentration (8.89×10^{-3} M). This supports the idea that the electrochemical reduction of maleic acid on a Pt electrode is a quasi-reversible process controlled by diffusion.

The calibration graph of MA in different concentrations was obtained by using a Pt electrode, as shown in Figure 5. A linear response was achieved in the concentration range (5.00 - 8.18 mM) of MA at a sensitivity response of 0.19 $\mu\text{A}/\text{mM}$. Table 1 displays the data used to estimate the value of SD (standard deviation) of the mean current applying on Figure 5.

Table 1. Data used to calculate the value of SD taken from figure 5

I_j	i_j	X
0.00	0.002	5.00
0.073	0.074	6.92
0.095	0.093	7.50
0.121	0.123	8.18

The SD value can be calculated according to Miller equation (2):

$$SD = 1/(n-2) \sum (i_j - I_j)^2 \quad (2)$$

where, n is the number of MA concentrations used ($n = 4$), i_j is the experimental value of the experiment number j and I_j is the corresponding recalculated value, at the same concentration using the regression line equation (3):

$$j_{pc} (\mu\text{A}/\text{cm}^2) = 0.038C (\text{mM}) - 0.190 \quad (3)$$

The calculated SD was used to determine the detection limit of MA at the platinum electrode [17] (DL, $3 \times SD / \text{slope}$), which was calculated as 1.6×10^{-5} M.

Effect of scan rate

The effect of a varying scan rate of the oxidation-reduction process of MA was studied. Cyclic voltammograms of 8.57×10^{-3} M MA in 0.1M Na_2HPO_4 supporting electrolyte using a Pt electrode were obtained for a scan rate ranging from 20-200 mV/s (Figure 6).

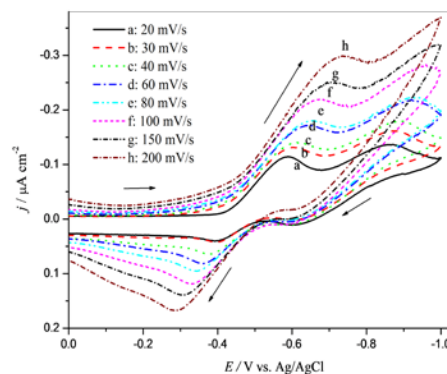


Fig. 6. Cyclic voltammograms of 8.57×10^{-3} M maleic acid in 0.1M Na_2HPO_4 , at different scan rates.

As shown in Figure 6, the cathodic and anodic peak currents of MA increased with increasing the scan rate at the Pt electrode. Furthermore, the cathodic peak potential shifted to lower negative values and the anodic peak potential shifted to higher positive values with increasing the scan rate. This is because of the accumulation of the MA molecules on the Pt electrode.

Good linearity between the cathodic and the anodic peak currents with the square root of scan rate (Figures 7, 8) was obtained by:

$$j_{pc}(\mu\text{A}/\text{cm}^2)=0.0189^{0.5}(\text{mV}/\text{s})^{0.5}+0.085 \quad (4)$$

$$j_{pa}(\mu\text{A}/\text{cm}^2)=0.0135^{0.5}(\text{mV}/\text{s})^{0.5}+0.019 \quad (5)$$

This supports the idea that the electrode reactions of maleic acid were under diffusion control, referring to [17].

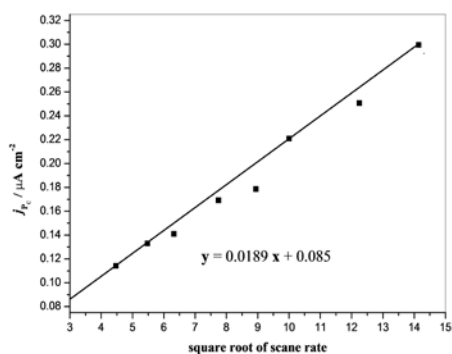


Fig. 7. Plot of cathodic peak current *versus* square root of scan rate of 8.57×10^{-3} M maleic acid in 0.1M Na_2HPO_4 .

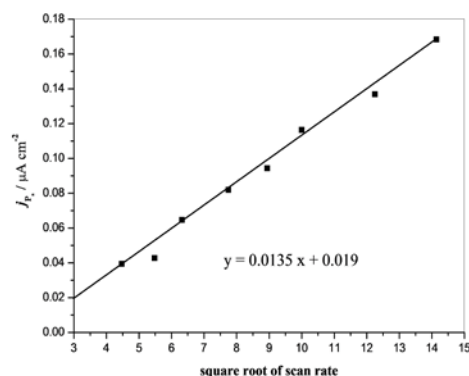


Fig. 8. Plot of anodic peak current *versus* square root of scan rate of 8.57×10^{-3} M maleic acid in 0.1M Na_2HPO_4 .

Cathodic linear sweep voltammetry

Cathodic linear sweep voltammetry can be used as an electrosynthesis process because it is a simple, quick and accurate technique. So succinic acid can be electrosynthesized from maleic acid by this technique.

Cathodic linear sweep voltammetry of 8.57×10^{-3} M MA at a scan rate of 100 mV/s displays two cathodic peaks in a cathodic scan. The P_c at -0.68 V may be referred to the reduction of maleic acid into succinic acid. The second P_c at -0.96 V belongs to Na_2HPO_4 as a supporting electrolyte (Figure 9).

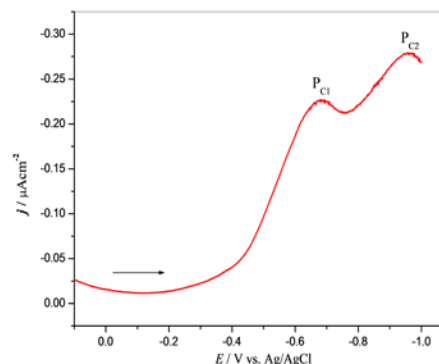


Fig. 9. Cathodic linear sweep voltammogram of 8.57×10^{-3} M maleic acid in 0.1 M Na_2HPO_4 , at a scan rate of 100 mV/s, in cathodic scan.

Chronoamperometric method

Chronoamperometry was used as a revealing method and also to investigate the electrode process [18-22]. Figure 10 displays the chronoamperometric measurements of MA by adjusting the working electrode at 0.00 mV (first potential step) and at -1.00 mV (second potential step) vs. Ag/AgCl which shows increased current when MA concentrations were changed from 3.33 to 8.33 mM in 0.1M Na_2HPO_4 as a supporting electrolyte.

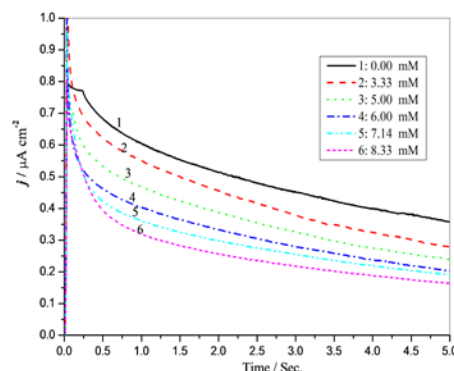


Fig. 10. Chronoamperograms in the absence and presence of different concentrations of maleic acid in 0.1 M Na_2HPO_4 supporting electrolyte; first and second potential steps were 0.00 and -1.00 V vs. Ag/AgCl, respectively.

The current of the electrochemical reaction (Figure 11, under mass transport control) of an electroactive material with a diffusion coefficient is expressed by Cottrell equation (6) [21-23]:

$$I(t) = nFAC(D/\pi t)^{1/2} \quad (6)$$

where, D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C - bulk concentration (mM), n - number of electrons, F - Faraday's constant and A - electrode surface area.

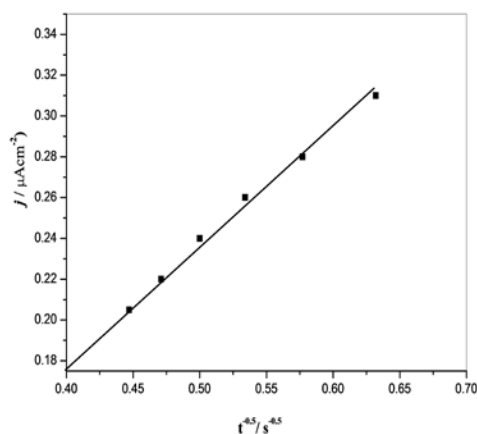


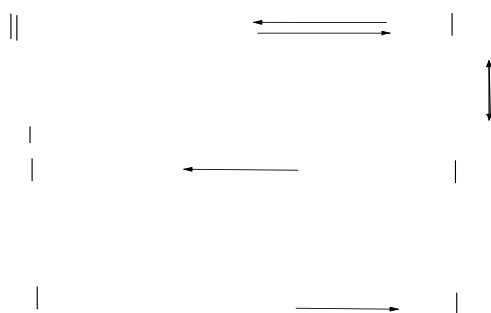
Fig. 11. Cottrell plot for potential step chronoamperometry of 6 mM maleic acid in 0.1 M Na_2HPO_4 .

Figure 11 reveals that the plot of I vs. $t^{-0.5}$ is a linear relationship from which we can obtain the value of D . According to the Cottrell equation, the diffusion coefficient of MA (D) was found to be $0.815 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The obtained value is comparable with the relevant previous studies [17].

Mechanism of the reduction reaction

From the results it is known that during the electroreduction process of MA the gain of electron leads to the formation of an anion-radical intermediate. Then this intermediate accepted one proton from the aqueous media and formed succinic radical. At the end, the succinic radical accepted one electron and one proton to form succinic acid.

The reduction mechanism of MA to succinic acid may be expressed as follows [24-26]:



CONCLUSION

The results indicated that the reduction of MA on a Pt electrode is a quasi-reversible process controlled by diffusion. The cathodic and anodic peak currents of MA increased with an increase in concentration of MA from $5.00 \times 10^{-3} \text{ M}$ to $8.89 \times 10^{-3} \text{ M}$ at a scan rate ranging from 20-200 mV/s vs. Ag/AgCl. From chronoamperometric measurements, the diffusion

coefficient of maleic acid was found to be $0.815 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$. Maleic acid can be electrochemically reduced to succinic acid using cathodic linear voltammetry using a simple, quick, accurate, and sensitive technique.

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ГРАНИЦА НА ОТКРИВАНЕ И ЕЛЕКТРОХИМИЧНО ОТНАСЯНЕ НА МАЛЕИНОВА КИСЕЛИНА ВЪРХУ ПЛАТИНОВ ЕЛЕКТРОД

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(Резюме)

Електрохимичното отнасяне на малеинова киселина (МК) върху платинов електрод е изучено чрез циклична волтамметрия, линейна волтамметрия и хроноамперометрия. Установено е, че редукцията на МК върху Pt електрод е квазиобратим процес в резултат на дифузията и на редукционния потенциал на МК при -0.62 V (спрямо Ag/AgCl). Изчислената граница на откриване на МК върху Pt електрод е $1.6 \times 10^{-5}\text{ M}$. Анодните и катодните токови пикове на МК нарастват с увеличаване на концентрацията на малеинова киселина от 5.00×10^{-3} to $8.89 \times 10^{-3}\text{ M}$ при скорост на сканиране в интервала от 20 до 200 mV/s. Дифузионният коефициент на МК е $0.815 \times 10^{-7}\text{ cm}^2\cdot\text{s}^{-1}$. Дискутиран е механизъмът на получаване на сукцинова киселина чрез електрохимична редукция на МК.