



Short communication

Kinetic study of formic acid oxidation on carbon supported Pd electrocatalyst

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ABSTRACT

The oxidation of formic acid at the Pd/C catalyst electrode is a completely irreversible kinetic process with the reaction order of 1.0. The oxidation rate of formic acid is increased with increasing the concentration of formic acid and is decreased with increasing H⁺ concentration. The apparent negative reaction order with respect to H⁺ is about -0.18 or -0.04 in H₂SO₄ or HClO₄ solution respectively, because bisulfate anions would inhibit formic acid oxidation at some extent. The kinetic parameters, charge transfer coefficient and the diffusion coefficient of formic acid were obtained under the quasi steady-state conditions.

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1. Introduction

Recently the electrochemical oxidation of formic acid has been attracting more attention [1–3] because the direct formic acid fuel cell (DFAFC) has some advantages over the direct methanol fuel cell. For example, formic acid is non-toxic and nonflammable. Formic acid has low crossover effect through the Nafion membrane because of the anodic repulsion between the Nafion membrane and the partially dissociated form of formic acid [4,5]. Initially, Pt was used as the anodic catalyst in DFAFC [6,7]. The mechanism for the electrooxidation of formic acid at Pt and Pt based catalyst electrode has been deeply investigated [8–12]. It was found that the electrooxidation of formic acid at the Pt catalyst electrode is through the indirect pathway. In the indirect pathway, the intermediate, CO would be formed. CO can be strongly adsorbed on the surface of the Pt catalyst and could poison the Pt catalyst. Therefore, the main oxidation peak of formic acid at the Pt catalyst electrode is at rather positive potential, about 0.7 V (vs. Ag/AgCl). Recently, it was reported that the Pd and Pd based catalysts have the high electrocatalytic activity for formic acid oxidation [13–16]. However, there are only very few reports about the kinetic study for formic acid oxidation on carbon supported Pd (Pd/C) catalyst electrode. We have obtained and reported the kinetic parameters by the normal pulse voltammetry technique and the dependence of temperature for formic acid oxidation at a Pd/C electrode [17]. In this paper, reaction orders with

respect to the concentration of formic acid and H⁺ were studied. The kinetic parameters obtained under the quasi steady-state conditions at the Pd/C catalyst electrode was also investigated and the result was compared with the data obtained by the normal pulse voltammetry technique.

2. Experimental

The preparation of the Pd/C catalyst was briefly described as follows: 1 g carbon black (Vulcan XC-72R) was mixed with the mixed solution of H₂SO₄ and HNO₃ (volume ratio of sulfuric acid to nitric acid is 3:1). The slurry obtained was ultrasonicated for 5 min and then stirred for half an hour at the room temperature. After that, the carbon black was filtered, washed and dried in vacuum condition at 80 °C for an hour.

The preparation of carbon supported Pd catalysts was briefly described as follows: 10 mL ethylene alcohol and 0.04 g the carbon black of pretreatment above were mixed and ultrasonicated for 1.5 h, followed by adding palladium chloride solution (4.00 g L⁻¹) 4.2 mL drop by drop at 70 °C within 30 min and then add excessive amount of HCOONa in the solution and maintained the temperature at 70 °C for 5 min. After that solution above was heated in the microwave oven for 30 s each time with 20 s intervals for eight cycles. Finally, the slurry was filtered and dried under vacuum at 100 °C for 10 h. The catalyst was designated as Pd/C. The Pd/C catalyst prepared contained 20 wt.% Pd.

The preparation of Pd/C catalyst electrode was as follows. A fixed amount of catalyst was mixed with 5% Nafion solution, 20% PTFE and ethanol was ultrasonicated for 5 min. Then the slurry obtained was spread on a carbon paper and dried at the room temperature.

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The Pd loading of the electrode was 1 mg cm^{-2} . A glass carbon disk electrode covered with a thin film of Pd/C was used as rotating disk electrode. The surface area of the electrode was 0.126 cm^2 .

The electrochemical measurements were carried out with a CHI650A electrochemical analyzer and a conventional three-electrode electrochemical cell at $25 \pm 1^\circ \text{C}$. The working electrodes are the Pd/C catalyst electrode and Pd/C catalyst rotating disk electrode. The Ag/AgCl electrode and Pt gauze were used as the reference and the counter electrode, respectively. All the potentials were quoted with respect to the Ag/AgCl electrode. The electrolyte solution for the electrochemical measurement was different concentrations of H_2SO_4 or HClO_4 solution with different concentrations of HCOOH. The scan rate of the potential is 2 mV s^{-1} . 99.999% N_2 was bubbled into the solution for 10 min to remove O_2 dissolved in the solution prior to the electrochemical measurements.

3. Results and discussion

Fig. 1 shows the Tafel plot of $\log i$ vs. E for the oxidation of 0.5 M HCOOH in $0.5 \text{ M H}_2\text{SO}_4$ solution at Pd/C catalyst electrode at 2 mV s^{-1} scan rate. It can be seen that the very good linear Tafel region stretches from 0.06 to 0.18 V . The Tafel slope is 180 mV dec^{-1} . When the potential exceeds 0.18 V the slope increases and the reaction rate reaches a limiting value (Fig. 1, inset).

In Fig. 2 Curve a displays the dependence of $\log j$ of the oxidation of 1.0 M HCOOH at the Pd/C catalyst electrode on the $\log C$ of H_2SO_4 solution. It can be seen from Fig. 2, Curve a that $\log j$ largely increases with increasing the pH of H_2SO_4 solution up to pH 4. However, The linear relationship of $\log j$ and pH is between pH value of 0.3 – 2.0 . The apparent negative reaction order with respect to H^+ in H_2SO_4 solution is about -0.18 at the pH range of 0.3 – 2.0 . The data about pH dependence of $\log j$ of formic acid oxidation are scarce in the literature. Only Tripkovic [11,12] reported the reaction order with respect to H^+ concentration is -0.15 at the $\text{Pt}_2\text{Ru}_3/\text{C}$ catalyst electrode in H_2SO_4 solution and -0.8 at the Pt/C catalyst electrode in HClO_4 solution.

The effect of pH dependence is not only caused by H^+ , the adsorption of bisulfate anions, which increases with increasing the concentration of H_2SO_4 , also inhibits the reaction [12,18]. In order to avoid the effect of bisulfate anions, the pH dependence of formic acid oxidation was studied in HClO_4 solutions with the different concentrations (Fig. 2, Curve b). It can be observed from Fig. 2, Curve

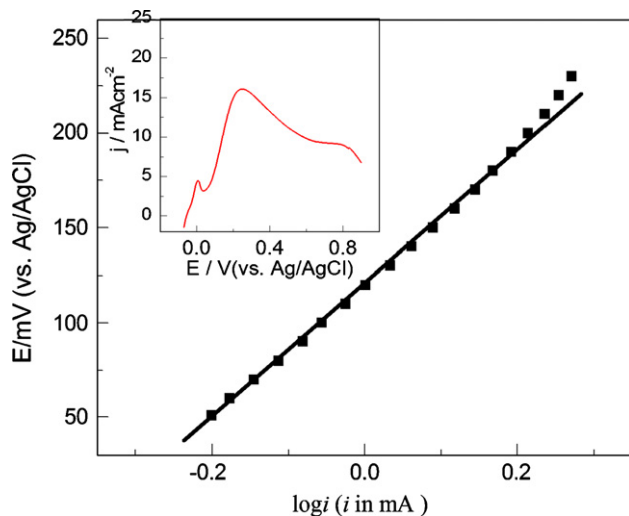


Fig. 1. Tafel plot of $\log i$ vs. E for the oxidation of 0.5 M HCOOH in $0.5 \text{ M H}_2\text{SO}_4$ solution at the Pd/C catalyst electrode. Scan rate 2 mV s^{-1} . Inset: the linear sweeping voltammograms of 0.5 M HCOOH in $0.5 \text{ M H}_2\text{SO}_4$ solution at the Pd/C catalyst electrode. Scan rate: 2 mV s^{-1} .

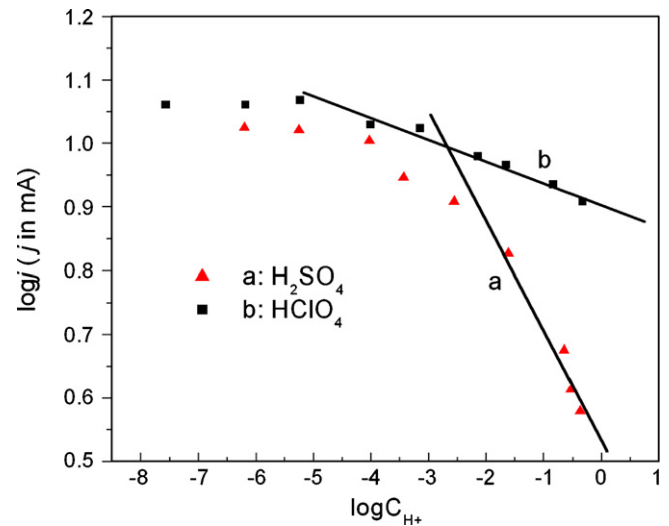


Fig. 2. The plots of $\log j$ vs. $\log C_{\text{H}^+}$ for the oxidation of 1.0 M HCOOH at the Pd/C catalyst rotating disk electrode at sweep rate 50 mV s^{-1} with the rotation rate of 500 rpm in (a) H_2SO_4 and (b) HClO_4 solution.

b that $\log j$ increases linearly with increasing the pH of HClO_4 solution in the pH range of 0.3 – 5.0 . When the pH further increases $\log j$ decrease slightly and become constant at last. The apparent negative reaction order with respect to H^+ in HClO_4 solution is about -0.04 in the pH range of 0.3 – 5.0 , which is smaller than that in H_2SO_4 solution. This result indicated that bisulfate anions influence formic acid reaction at some extent except that H^+ would affect on formic acid oxidation at Pd/C catalyst electrode, which is disagreement with that at $\text{Pt}_2\text{Ru}_3/\text{C}$ catalyst electrode [11].

Fig. 3 displays the linear sweeping voltammograms of different concentrations of HCOOH in $0.5 \text{ M H}_2\text{SO}_4$ solution at the Pd/C catalyst electrode. The apparent peak current density of formic acid increases with increasing the formic acid concentration from 0.1 to 3.0 M . The slope of the curve of $\log j$ vs. $\log C_{\text{HCOOH}}$ (Fig. 4) was about 1.01 . Therefore, the reaction order of formic acid is 1.0 at the Pd/C catalyst electrode.

The effect of scan rate on the behavior of formic acid oxidation at Pd/C electrode was investigated (Fig. 5). It can be clearly seen in Fig. 5 that the peak potential shift positively with the increase in the scan rate, which indicated that the electrocatalytic oxidation of

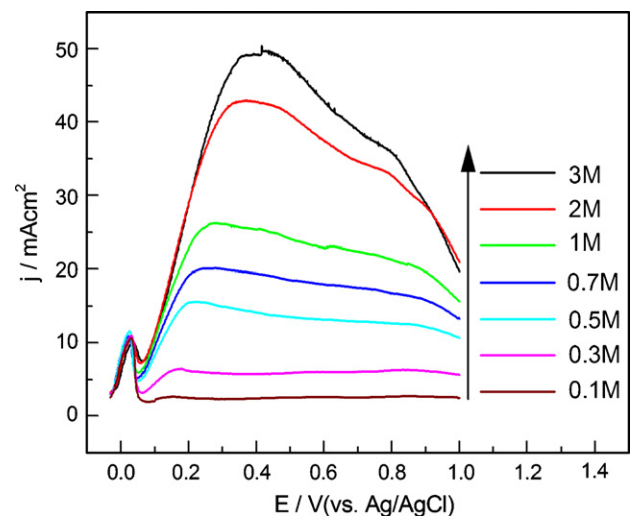


Fig. 3. The linear sweep voltammograms for different concentrations of formic acid in $0.5 \text{ M H}_2\text{SO}_4$ on a Pd/C electrode at 25°C . Scan rate: 2 mV s^{-1} .

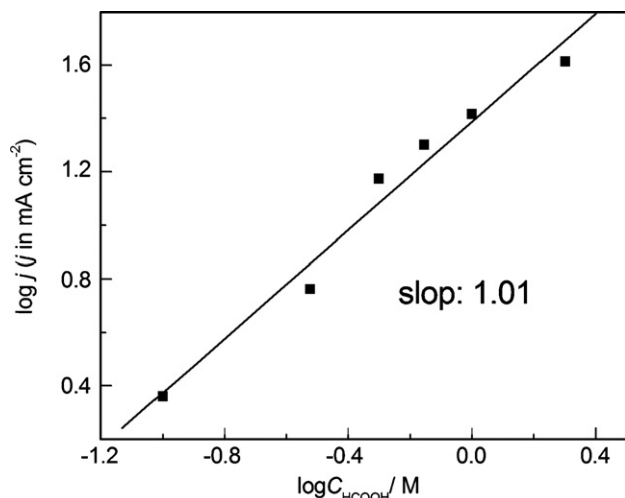


Fig. 4. The plot of $\log j$ vs. $\log C_{\text{HCOOH}}$ at the potential of 0.3 V at the Pd/C catalyst electrode in 0.5 M H_2SO_4 .

formic acid at the Pd/C catalyst electrode is an irreversible electrode process. In the case of an irreversible reaction, the peak current in amperes is [19]

$$j_p = 2.99 \times 10^5 n(\alpha n')^{1/2} C_{\infty} D^{1/2} \nu^{1/2} \quad (1)$$

where n is the electron number for the total reaction, n' is the electron number transferred in the rate-determining step and α is the charge transfer coefficient. The peak current density j_p measured in A cm^{-2} and the diffusion coefficient D is in $\text{cm}^2 \text{s}^{-1}$. The formic acid concentration is in the solution, C_{∞} , is in mol cm^{-3} and the sweep rate, ν , is in V s^{-1} . Fig. 6 shows the curve of peak current density vs. the square root of the scan rate. The peak current density is proportional to the square root of scan rates and the slope is 0.11. According to Brett and Brett [19], for the irreversible system the peak potential values are proportional to the $\log \nu$ as the following equation at 298 K

$$\left| \frac{dE_p}{d \log \nu} \right| = \frac{29.6}{\alpha n'} \quad (\text{mV}) \quad (2)$$

where E_p is the peak potential and ν is the scan rate. The dependence of the peak potential on the $\log \nu$ is shown in Fig. 7. The slope is 133.7 mV. Thus, the value of $\alpha n'$ is 0.22 obtained from Eq. (2). A common concept in electrochemistry is that truly elementary

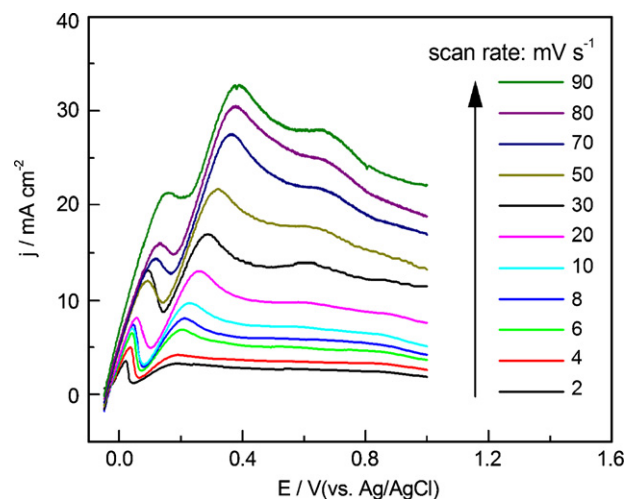


Fig. 5. The linear sweep curves for formic acid oxidation on Pd/C electrode at different scan rate in 0.5 M H_2SO_4 containing 0.5 M HCOOH at 25 °C.

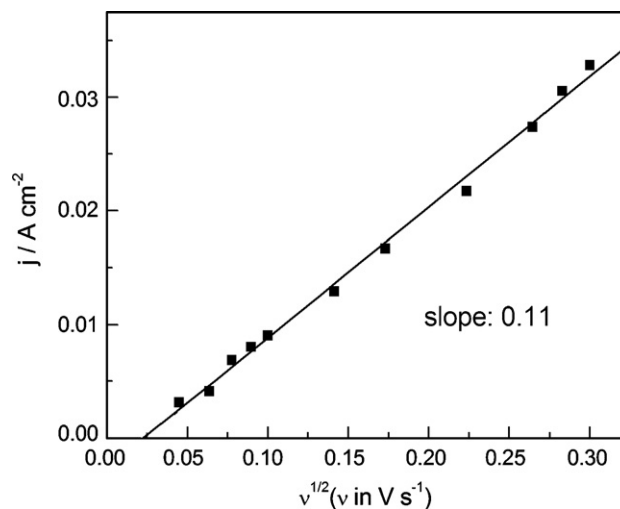


Fig. 6. The plot of the peak current density vs. the square root of scan rates for 0.5 M HCOOH in 0.5 M H_2SO_4 solution at the Pd/C catalyst electrode.

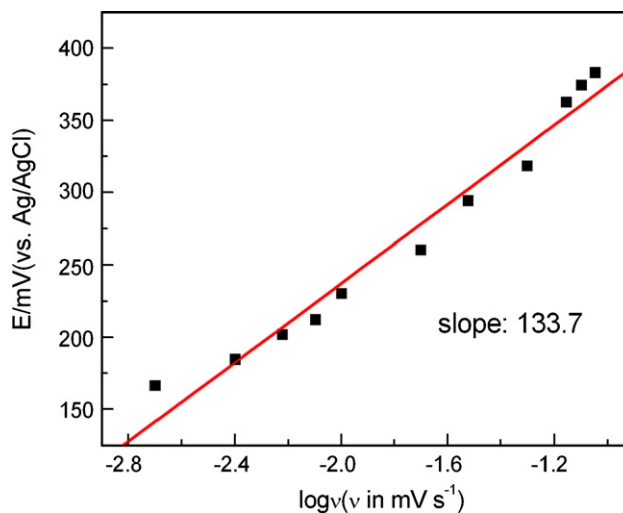


Fig. 7. The plot of the peak potential vs. $\log \nu$ for 0.5 M HCOOH in 0.5 M H_2SO_4 solution at the Pd/C catalyst electrode.

electron-transfer reaction always involves the exchange of one electron, so that an overall process involving a change in n electrons must involve n distinct electron-transfer steps [20]. Within this view, a rate-determining electron transfer is always a one-electron-process. $n' = 1$, $\alpha = 0.22$. The value of diffusion coefficients, D , can be obtained from the slopes of the lines in Fig. 7 using Eq. (1). The D value is a measurement of the charge-transport rate within the liquid film near the electrode surface. In this case, the value of D is $6.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Compared these results with the data obtained by normal pulse voltammetry [17], the charge transfer coefficient is slightly lower than that obtained by normal pulse voltammetry ($\alpha = 0.26$) and the value of the diffusion coefficient is slightly larger but with the same order of magnitude, $1.47 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The small differences of the results by these two methods may be caused by experimental errors.

4. Conclusions

In the present study, it was found that oxidation rate of formic acid increases with increasing the concentration of formic acid and decreases with H^+ concentration in the certain pH range. In addition, bisulfate anions would inhibit formic acid oxidation at some

extent. The oxidation of formic acid at the Pd/C catalyst electrode is a completely irreversible kinetic process. The low values of $\alpha = 0.22$ indicated the slow kinetic process for formic acid oxidation at the Pd/C catalyst electrode. The diffusion coefficient of formic acid, D , obtained in the present work is $6.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

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