Short communication

Application of normal pulse voltammetry to the kinetic study of formic acid oxidation on a carbon supported Pd electrocatalyst

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ABSTRACT

The kinetic parameters of formic acid oxidation on a carbon supported Pd electrode, such as the charge transfer coefficient (α) and apparent diffusion coefficient (D) are obtained by applying the technique of normal pulse voltammetry. The standard rate constant (k_0) of formic acid oxidation on a Pd/C electrode is estimated. The results show that formic acid oxidation is more sensitive to temperature at relatively high potential because the activation energy is significantly increased as the potential rose above 0.6 V.

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1. Introduction

In recent years, the electrochemical oxidation of formic acid has attracted much attention [1–3] because of the interest in direct formic acid fuel cells. Pt and Pd metals are the most frequently employed catalyst materials for formic acid electro-oxidation. The mechanism for formic acid oxidation at a Pt electrode has been widely accepted as taking place via a dual path, which involves a reactive intermediate path and adsorbed CO as a poisoning species [4–6]. The adsorbed CO path is the main path for formic acid oxidation on carbon supported Pt catalysts and the catalysts are poisoned severely by the adsorbed CO intermediate of the reaction. Research has shown that Pd catalysts have much higher catalytic activity for formic acid oxidation than Pt [7,8]. A Pd and Pd-based catalysts exhibited no CO poisoning effect and yield high performances in the direct formic acid fuel cells [9–13,2]. However the mechanisms for formic acid oxidation at the Pd electrode have been rarely reported. Zhou [14] suggested that the mechanism for formic acid oxidation at Pd is via a dual path similar to the Pt electrode. But Nishimura and Iwasaki's research did not support the above mechanism [15,16]. Since there have been even fewer reports concerned with the kinetic parameters for formic acid oxidation on Pd, the aim of this paper is to obtain the kinetic parameters using the normal pulse voltammetry technique. The kinetic parameters of the heterogeneous electron transfer process of formic acid oxidation at the carbon supported

Pd electrode/solution interface are basic and important data for characterizing this electrochemistry process. The dependence of temperature for formic acid oxidation at a Pd/C electrode was also investigated.

2. Experimental

For the pretreatment of the carbon black (Vulcan XC-72R), 1 g of carbon black was mixed with a mixture of sulfuric acid and nitric acid (volume ratio 3:1). This slurry was ultrasonicated for 5 min and then stirred for half an hour at room temperature. After that, the carbon black was filtered and dried in a vacuum 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 the Pd/C electrode to be used in the linear sweep voltammograms was as follows. A fixed amount of catalyst was mixed with 5% Nafion solution, 20% PTFE and ethanol and was ultrasonicated for 5 min. Then this slurry was spread on carbon paper and dried at room temperature. The Pd loading for the electrodes used in the experiment was 1 mg cm^{-2} and the surface area of the electrode was 0.5 cm^2. A glass carbon disk electrode covered

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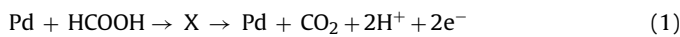E-mail addresses: yinggao99@126.com, yinggao9999@163.com (Y. Gao).

with a thin film of Pd/C was used for normal pulse voltammetry experiment. The surface area of the electrode was 0.126 cm^2.

The experiments were performed in a dual electrochemical cell operating in an anaerobic environment. The electrochemical measurements were carried out with a CHI650A electrochemical analyzer. The Ag/AgCl electrode and Pt gauze were used as the reference and the counter electrode, respectively. In the normal pulse voltammetry experiments, a sampling time of 40–80 ms was used, with intervals of 2 sec between successive pulses. It is supposed that cyclic renewal of the diffusion layer can be obtained simply by waiting long enough (2 s) at the base potential (−0.1 V vs. Ag/AgCl) for diffusion to replace the electroreactant that has been consumed.
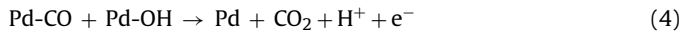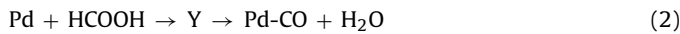
3. Theory, results and discussion

The mechanism of formic acid oxidation on Pd reported by Zhou was a dual path similar to that for a Pt electrode [9]:

Direct path:

$$Pd + HCOOH \rightarrow X \rightarrow Pd + CO_2 + 2H^+ + 2e^- \qquad (1)$$

Indirect path:

$$Pd + HCOOH \rightarrow Y \rightarrow Pd\text{-}CO + H_2O \qquad (2)$$

$$Pd + H_2O \rightarrow Pd\text{-}OH + H^+ + e^- \qquad (3)$$

$$Pd\text{-}CO + Pd\text{-}OH \rightarrow Pd + CO_2 + H^+ + e^- \qquad (4)$$

However, no adsorbed CO is produced during the formic acid oxidation on the Pd electrode, according to an IRAS study [15], but formate ions were detected [16]. Therefore the formic acid oxidation does not appear to proceed by a CO-like intermediate path, but is more likely to take place via an active-intermediate path (or direct path) as follows [17]:

$$HCOOH + Pd \rightarrow Pd\text{-}(COOH)_{ads} + H^+ + e \qquad (5)$$

$$Pd\text{-}(COOH)_{ads} \rightarrow CO_2 + H^+ + e \qquad (6)$$
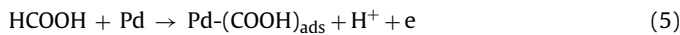
Reaction (5) might be regarded as the rate-determining step (RDS), so the two reaction processes can be simplified as follows:

$$R \rightarrow R' + n'e \quad (RDS) \qquad (7)$$

$$R' \rightarrow O + n''e \qquad (8)$$
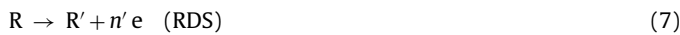
$$n' = n'' = 1$$

$$n = n' + n'' = 2$$

If the diffusion layer can be effectively renewed at the electrode the current–potential characteristic for the rate-determining oxidation process in the irreversible system can be written as [18,19]:

$$E = E_{1/2} - 0.0542(\alpha n')^{-1} \log \left[\frac{i_d - i}{i} \right] \qquad (9)$$

with $\quad E_{1/2} = E^0 - 2.303 RT(\alpha n'F)^{-1} \log[1.349 k_0 \tau^{1/2} D^{-1/2}] \quad (10)$

where E is the electrode potential, $E_{1/2}$ is the half-wave potential, E^0 is the formal potential, D is the apparent diffusion coefficient, k_0 is the standard rate constant, α is the anodic transfer coefficient, n' is the number of electrons for the rate-determining step, i is the normal pulse voltammetric current, i_d is the limiting current which is expressed by the Cottrell equation in the following [18]:

$$i_d(\tau) = nFAD^{1/2}C\pi^{-1/2}\tau^{-1/2} \qquad (11)$$

where C is the concentration of formic acid in the solution, A is electrode area and τ is the sampling time. Normal pulse voltammetry consists of a series of pulses of increasing amplitude applied to the electrode. Because of the short pulse duration and sufficiently long
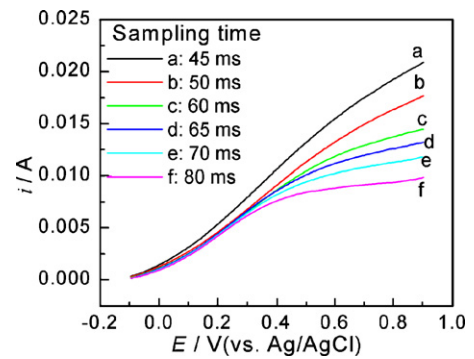

Fig. 1. Normal pulse voltammograms for the oxidation of formic acid on a Pd/C electrode in 0.5 M HCOOH and 0.5 M H$_2$SO$_4$ with different sampling times, at 25 °C.

waiting time (2 s) at base potential, cyclic renewal of the diffusion layer can be achieved.

Fig. 1 shows typical normal pulse voltammograms for the oxidation of formic acid at the Pd/C electrode for various sampling times (τ). The resulting voltammograms have a sigmoidal shape, which are similar to those described in the theory of Bard and reported by others [18–20]. This indicated that the diffusion layer is effectively renewed under these conditions. The anodic limiting currents increase with decreasing sampling time. Fig. 2 shows the anodic limiting currents plotted against the inverse square root of the sampling times, showing a linear relationship between them, with the line passing through the origin, indicating that the limiting current is controlled by formic acid diffusion and the behavior of the diffusion process is semi-infinite. The values of the apparent diffusion coefficient can be obtained from the slope of the line (Fig. 2) by using Eq. (11). The calculated value of the apparent diffusion coefficient, D, is 1.47×10^{-7} cm^2 s^{-1}.

Fig. 3 is the plot of E versus log $[(i_d - i)/i]$ which shows a good linear relationship with a slope of −0.20 V and an error of 7.6×10^{-4} V. The slope of the line in Fig. 3 is equal to $-0.0542(\alpha n')^{-1}$ according to Eq. (9) so the anodic transfer coefficient can be evaluated from the slope:

$$-0.0542(\alpha n')^{-1} = -0.20$$

Because $n' = 1$, the value of α is 0.26. This value is lower than 0.5, which reflects the slow anode kinetic process for formic acid oxidation. The standard rate constant k_0 value can be evaluated from the intercept ($E_{1/2}$) of the plot (Fig. 3) by means of Eq. (10). According to the research of Xu [19], E^0 can be estimated since it lies between the potentials of adsorption and oxidation of the reactant. In this
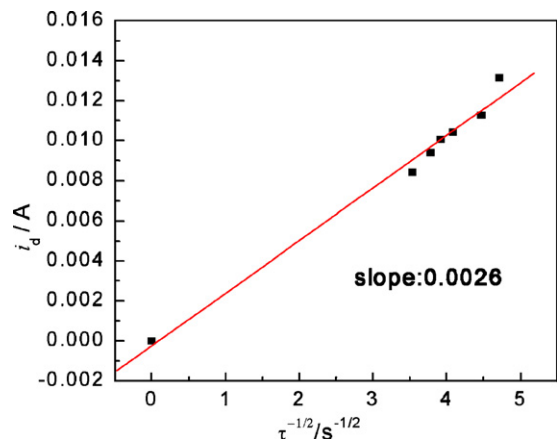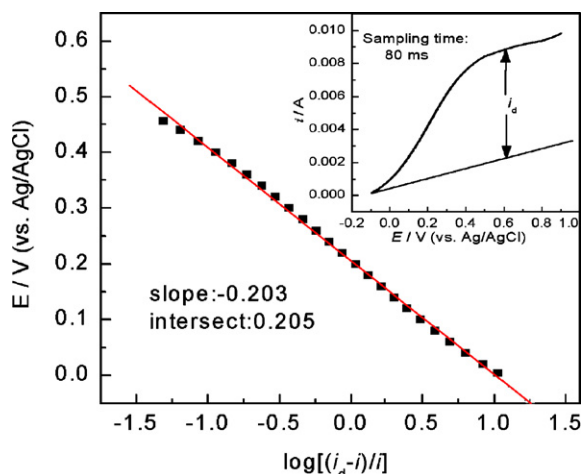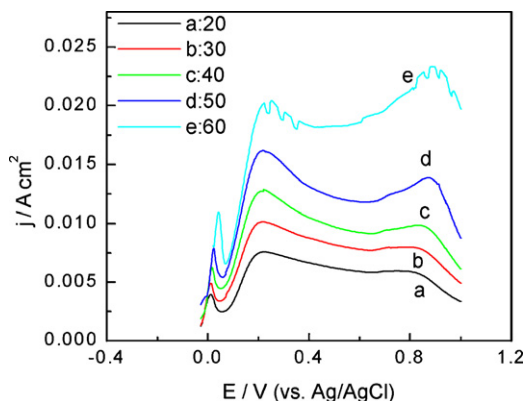

Fig. 2. Plot of observed limiting current versus $\tau^{-1/2}$ for the oxidation of formic acid on a Pd/C electrode in 0.5 M HCOOH and 0.5 M H$_2$SO$_4$ at 25 °C.

Fig. 3. The plot of E versus $\log[(i_d - i)/i]$ for formic acid oxidation on a Pd/C electrode from the normal pulsed voltammetry data (the inset) with an 80 ms sampling time and 2 sec measurement intervals at 25 °C.

Fig. 4. Linear sweep voltammograms for 0.5 M formic acid in 0.5 M H_2SO_4 on a Pd/C electrode at different temperatures. Scan rate: 2 mV s^{-1}.
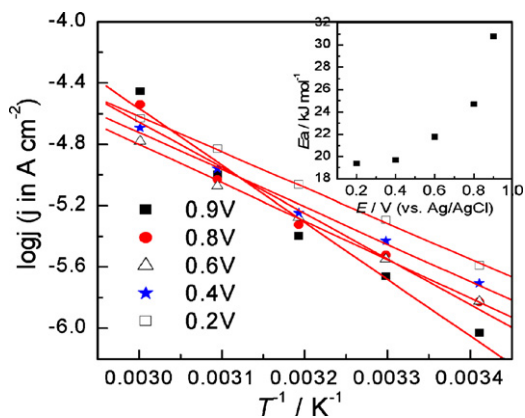
Fig. 5. Arrhenius plots of $\log i$ versus $1/T$ at different potentials for the oxidation of formic acid on a Pd/C electrode; the inset shows the activation energy (E_a) at different values of potential.

case, E^0 is expected to be about 0.1 V. Thus the standard rate constant, k_0, can be obtained by introducing the experimental values of D and α, and the expected value of E^0 into Eq. (10), giving an estimated value of k_0 4.5×10^{-5} cm s^{-1}.

We further investigated the temperature dependence of the formic acid oxidation on a Pd/C electrode in the temperature range of 20–60 °C at very low scan rate (2 mV s^{-1}) which can be thought of as a quasi steady state (Fig. 4). The two oxidations peaks are attributed to the structural effects of formic acid oxidation on Pd [21]. With elevated temperature, the activities are enhanced, as indicated by the increase in oxidation current. It can be clearly seen that the current increased more rapidly at relatively high potential. Fig. 5 shows the Arrhenius plots for the current densities of formic acid oxidation reaction at various potentials. Linear relationships exist between $\log i$ and $1/T$ indicating that the reaction mechanism at each potential does not change with temperature. The apparent activation energies, E_a are calculated to be in the potential range 0.2–0.9 V, as shown in the inset in Fig. 5. The activation energies increased with increasing potential. This result means that the activity of formic acid oxidation on the Pd/C electrode was more sensitive to temperature at higher potential.

4. Conclusion

The experiment results show that the diffusion layer near the surface of Pd/C electrode can be effectively renewed by applying the technique of normal pulse voltammetry. Therefore the theory of A.J. Bard can be used to obtain the kinetic parameters of formic acid oxidation, The values of charge transfer coefficient (α) and diffusion coefficient (D) are 0.26 and 1.47×10^{-7} cm^2 s^{-1}, respectively. The small value of k_0, that is about 4.5×10^{-5} cm s^{-1}, means that the electrode process for formic acid oxidation on Pd electrode is irreversible.

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