

# Electrooxidation of CO<sub>ad</sub> Intermediated from Methanol Oxidation on Polycrystalline Pt Electrode

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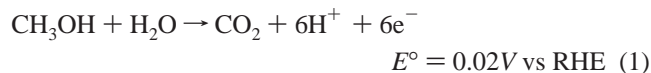
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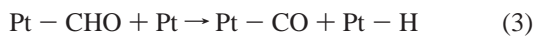
The poisonous intermediate of methanol oxidation on a Pt electrode was validated to be CO<sub>ad</sub> by electrochemical method. An approximate treatment to bimolecular elementary reactions on an electrode was advanced and then was applied to the stripping normal pulse voltammetry (NPV) for complex multistep multielectron transfer processes on plane electrodes to study the kinetics of completely irreversible process of CO<sub>ad</sub> oxidation to CO<sub>2</sub>. The kinetic parameters for this process, such as standard rate constant ( $k^0$ ) and anodic transfer coefficient ( $\alpha$ ) for this irreversible heterogeneous electron-transfer process at electrode/solution interface and apparent diffusion coefficient ( $D_{app}$ ) for charge-transfer process within the monolayer of CO<sub>ad</sub> on electrode surface, were obtained with stripping NPV method. The effect of the approximate treatment on the kinetic parameters was also analyzed.

## Introduction

The oxidation of methanol on Pt-related electrodes has been investigated extensively,<sup>1–3</sup> because of the interest in direct methanol fuel cells (DMFCs). It is well known that there is a complex reaction mechanism in the electrocatalysis of methanol oxidation.<sup>3,4</sup> The overall reaction for irreversible electrochemical oxidation of methanol in aqueous media is



The understanding of the mechanism of adsorption and subsequent oxidation of methanol on Pt electrodes is of importance to the development of DMFCs. According to previous results, in low potential regions, the following reactions are representative:<sup>2,5–7</sup>

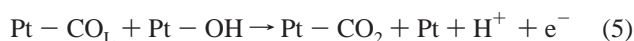


The CO<sub>ad</sub> poisons the electrode and impedes the further oxidation of methanol on electrode surface.

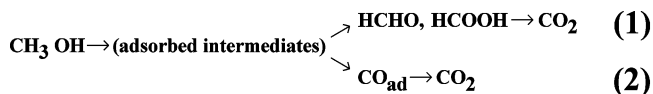
At potentials higher than 0.2 V vs Ag/AgCl, water molecules are adsorbed at the sites neighboring CO<sub>L</sub>, when  $E > 0.4$  V vs Ag/AgCl, Pt–OH is formed,<sup>2</sup>



Then

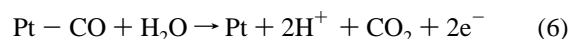


As shown the above, the total oxidation process consists of a pattern of parallel reactions, which can be formulated as follows:<sup>8</sup>

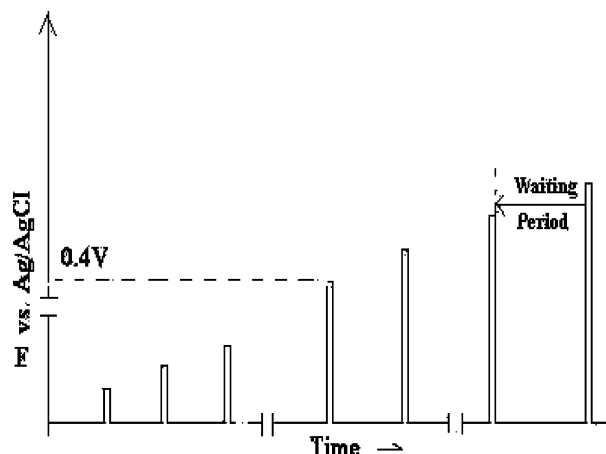


The kinetics for these processes has very important characteristics, which can help to prepare effective electrocatalysts for methanol oxidation in the development of DMFCs. As for the process 1, the electrode kinetics for the step from methanol to formate had been studied with normal pulse voltammetry (NPV) from methanol to formate.<sup>8</sup> For the process 2, Jusys had observed the existence of CO<sub>ad</sub> in methanol oxidation at low potential;<sup>9</sup> Chen also found with in situ surface-enhanced IR absorption spectroscopy (SEIRAS) that the output of CO<sub>ad</sub> in methanol oxidation is higher than 90% in low potential region ( $<0.5$  V vs RHE).<sup>10</sup> So in this work, we use a “stripping” NPV method to study the kinetics for the oxidation of CO<sub>ad</sub> to CO<sub>2</sub>. During the waiting time at base potential ( $E_b$ ) the poisoning species CO<sub>ad</sub> is formed and accumulated gradually and finally oxidized to CO<sub>2</sub> at high potential pulses. This method, which was called as “stripping” NPV, is somewhat different from the usual NPV experiments. Generally, in NPV experiments, the usual practice is to select a base potential  $E_b$  in a region where the electroactive species of interest does not react at the electrode or where there is no Faradic process. In the present work, we choose  $E_b$  at which CO<sub>ad</sub> of interest is formed on the electrode surface from methanol oxidation and wait for different times at fixed  $E_b$  before each pulse. During this time the surface of the electrode is poisoned by CO<sub>ad</sub> gradually. Then scan is made by allowing pulses in successive cycles to reach first into the potential range surrounding  $E^0$  and eventually into the diffusion-limited region, at which the CO<sub>ad</sub> on the electrode surface is almost oxidized completely in pulses. This method is similar to stripping voltammetry,<sup>14c</sup> so we call this experiment as “stripping” NPV.

In the present experiment, the total reaction of interest is the following:



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**Figure 1.** The principle of stripping normal pulse voltammetry for the oxidation of CO<sub>ad</sub> on Pt electrode.

According to previous work,<sup>9,12–13</sup> eq 6 contains two elementary reactions: eq 4 and eq 5. During this multistep process, the rate-determining step for CO<sub>ad</sub> oxidation on Pt surface is an electrochemical or chemical reaction between adsorbed CO and –OH particles as shown in eq 5.<sup>12,13</sup> Therefore,  $n = 2$ , which is the number of electrons for the total reaction of CO<sub>ad</sub> oxidation to CO<sub>2</sub> and  $n_a = 1$ , which is the number of electrons for the rate-determining step.

Operationally, to obtain good NPV response there are three different means to renew the circumstance near the electrode surface.<sup>14c</sup> Two of them involve waiting for a long enough period of time and with convective renewal, respectively. In the previous work the long waiting time is applied to renew the circumstance of the electrode surface.<sup>8,15–20</sup> In the present work we use a rotating disk platinum electrode to study the oxidation of the poison CO<sub>ad</sub>. The role of the rotation is to ensure the supply of methanol and remove the product CO<sub>2</sub>.

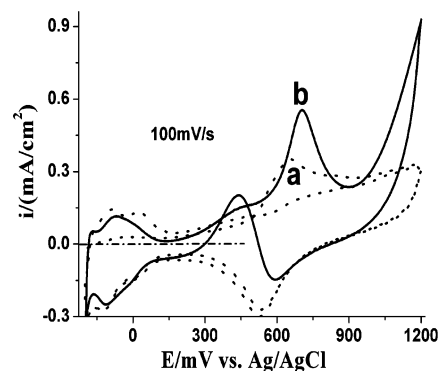
## Experimental Section

**Materials.** All solutions were prepared with Millipore water (>18 MΩ). Sulfuric acid (>98%), high purity argon, and high purity CO were obtained from Shen Yang, China and used as received. Methanol (Beijing, China) was washed over alumina, filtered, distilled, and stored under refrigeration. Argon (99.998%) was used to deaerate the solution. Solutions were deaerated by bubbling argon for 30 min and experiments were conducted at ambient temperature.

**Apparatus and Procedure.** Cyclic voltammetry (CV) and normal pulse voltammetry (NPV) were performed with a Princeton Applied Research model 273A potentiostat at ambient temperature. A polycrystalline platinum working electrode (geometric area: 0.1256 cm<sup>2</sup>) was polished with successively finer grades of alumina and then sonicated in pure water for 5 min. All electrochemical operations were carried out in a three-electrode two-compartment cell using a Pt foil as counter electrode and Ag/AgCl (222 mV vs RHE) as reference electrode. Figure 1 is the principle for the stripping NPV experiment. In these experiments, the pulse width of 16–36 ms was employed with constant rotation rate of 600 rpm. It can be safely considered that the depletion layer of reactants produced during the precedent pulse completely disappears before the following pulse starts.

## Results and Discussions

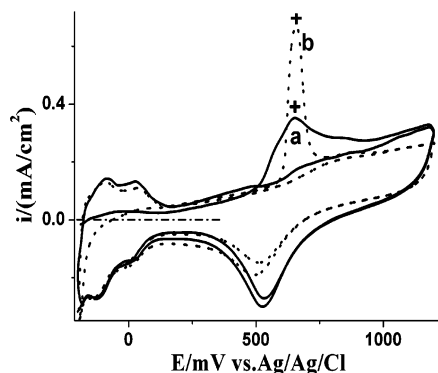
Jusys et al.<sup>9</sup> found with differential electrochemical mass spectrometry (DEMS) that methanol adsorption on Pt/C catalysts



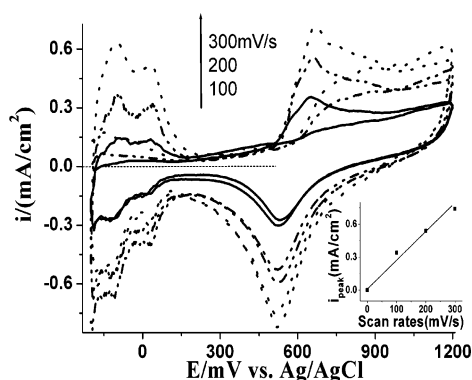
**Figure 2.** (a) The first two cycles of CV for smooth Pt electrode in 0.5 M sulfuric acid after the potential fixed at  $-0.2$  V vs Ag/AgCl for 200 s in 1.0 M methanol + 0.5 M sulfuric acid solution (dotted line). (b) The first cycle of CV for smooth Pt electrode in 1.0 M methanol + 0.5 M sulfuric acid solution (solid line). All electrolyte solutions were deoxygenated by bubbling high pure argon for 30 min.

at potentials in or close to the hydrogen absorption/desorption region leads to CO<sub>ad</sub> as a stable adsorbed product of the instantaneous dehydrogenation process. Chen et al.<sup>10</sup> also studied the dependence of IR intensity of linearly bonded CO, formate, and anodic current on the electrode potential in situ surface-enhanced IR absorption spectroscopy (SEIRAS) with the Kretschmann ATR configuration. It was found that in the low potential region ( $<0.25$  V vs RHE) the surface of Pt electrode was poisoned by CO<sub>ad</sub> gradually. From 0.25 to 0.4 V the intensity of CO<sub>ad</sub> no longer increased, which indicated that the adsorption of CO<sub>ad</sub> on the electrode was saturated. So in the present experiment the base potential is selected as  $-0.2$  V vs Ag/AgCl.

Figure 2a is the CV result of the Pt electrode obtained as follows. First the clear smooth Pt electrode was fixed at  $-0.2$  V vs Ag/AgCl for 200 s in 1.0 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. Then the electrode was taken out and dipped into deionized and deoxygenated water for 1 s to remove the residual methanol molecules on the electrode and then put in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution to carry out the first two cycles of CV. Curve b in Figure 2 is the CV result of the Pt electrode in 1.0 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution with the same scan rate of 100 mV/s. Obviously their peak-potentials and outlines are different. So it can be deduced they are two different species to be oxidized. To validate whether the intermediate of the methanol oxidation was CO<sub>ad</sub> or not under this condition, the following experiment was carried out: the clear Pt electrode was dipped in 0.5 M H<sub>2</sub>SO<sub>4</sub> with high pure CO bubbling for 10 min to adsorb CO molecules on its surface. The electrode was then taken out, dipped into deionized and deoxygenated water for 1 s and at last put in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution to carry out the first two cycles of CV as shown in Figure 3b. The potential and outline of the CO oxidation peak coincide with those of the intermediate as shown in Figure 3a. So combined with the previous work,<sup>9,10</sup> it can be concluded safely that the intermediate is really the adsorbed CO (CO<sub>ad</sub>) produced from the methanol oxidation. On the other hand, for both curve a and b in Figure 3, there is no oxidation-peak of methanol or CO in the reversed scan or second cycle of CV. So it can be concluded that the methanol had been washed away and hypothesized approximately that it was a monolayer of CO<sub>ad</sub> on the electrode surface and CO<sub>ad</sub> had been oxidized to CO<sub>2</sub> completely in the first positive scan.<sup>9,10</sup> Figure 4 is the CV results at different scan rates with waiting time of 200 s. The inset shows the dependence of peak currents on the scan rates. Obviously the peak-current varied linearly with scan rate,



**Figure 3.** (a) The first two cycles of CV for smooth Pt electrode in 0.5 M sulfuric acid after the potential fixed at  $-0.2$  V vs Ag/AgCl for 200 s in 1.0 M methanol + 0.5 M sulfuric acid solution. (b) CV results of smooth Pt electrode in 0.5 M sulfuric acid after adsorbing high pure CO for 10 min in 0.5 M sulfuric acid solution in another cell. Scan rates all are 100 mV/s. All electrolyte solutions were deoxygenated by bubbling high pure argon for 30 min.



**Figure 4.** CVs of Pt electrode in 0.5 M sulfuric acid solution with different scan rates after the potential fixed at  $-0.2$  V vs Ag/AgCl for 200 s in 1.0 M methanol + 0.5 M sulfuric acid solution. The inset is the relationship between peak currents of  $\text{CO}_{\text{ad}}$  oxidation and the scan rates. All electrolyte solutions were deoxygenated by bubbling high pure argon for 30 min.

indicating that the oxidation of intermediate ( $\text{CO}_{\text{ad}}$ ) was really a surface process.

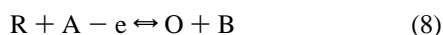
The normal pulse voltammetry (NPV) is an effective method to study the electron transfer (ET) kinetics of electrode reactions. Early on, the NPV theory was applied only to the ET processes on dropping mercury electrode (DME);<sup>15,21–24</sup> later this theory was extended to the ET processes on plane electrodes.<sup>15–20</sup> But these processes had a common ground: they were all based on simple one-step, one-electron transfer reversible or irreversible rate-determining steps (or first-order elementary reactions):



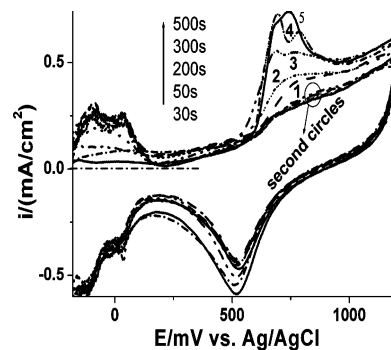
where R and O are the redox centers of interest.

Recently this theory had been extended to complex multistep, multielectron transfer process.<sup>8</sup> It had been successfully applied to study the electrode kinetics of the complex reaction of methanol oxidation on platinum electrode.<sup>8</sup>

The elementary reaction 7, however, is too simple or utopian to be satisfied in practice. In fact there are many ET reactions, in which the rate-determining step (an elementary reaction) shows the following type:



where A and B are assistant molecules or ions, such as  $\text{H}_2\text{O}$ ,  $\text{H}^+$ , or  $\text{OH}^-$ , etc.



**Figure 5.** The first two cycles of CV for smooth Pt electrode in 0.5 M sulfuric acid after the potential fixed at  $-0.2$  V vs Ag/AgCl for different times in 1.0 M methanol + 0.5 M sulfuric acid solution. All electrolyte solutions were deoxygenated by bubbling high pure argon for 30 min. Scan rate: 200 mV/s.

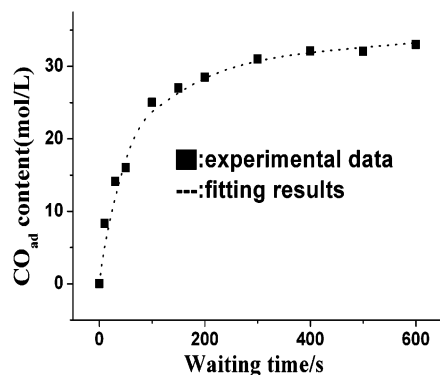
The existing electrochemistry theories for the NPV method, however, were based on simple unimolecular first order elementary reactions, such as reaction 7. To study the kinetics of other typical ET reactions on the electrode, such as reaction 8, there are two ways to settle this problem: one is to develop a new theory based on reaction 8, the other is to use previous theory based reaction 7 to study the systems based on reaction 8 approximately. The first way is too complex to be used in short time. Only the second way probably is a feasible method in temporary, especially for some quasi-quantitative or qualitative studies. So herein we made the following approximate treatment between unimolecular elementary reactions and bimolecular elementary reactions. If the bimolecular or the second-order elementary reaction 8 satisfies the condition where the concentration of A or B keeps approximately constant during the whole experimental process or is very much higher than that of O or R, the concentration of A or B can be treated as a constant and the elementary reaction 8 can be regarded approximately as a pseudo first order elementary reaction, such as reaction 7. Then simple basic theories can be applied to study this kind of complex reaction. Based on the above principle or hypothesis, the electrode kinetics of many more valuable electrochemical systems can be studied now in approximation. In the present work we applied it first to the oxidation of  $\text{CO}_{\text{ad}}$  intermediated from methanol oxidation on platinum.

In the present experiments for the oxidation of  $\text{CO}_{\text{ad}}$  the rate-determining step is the elementary reaction 5. In the reactants there is a radical  $-\text{OH}$  from the decomposition of water. The radical  $-\text{OH}$  is always sufficient and then its content can be treated as a constant. Thus according to the above approximate correspondence principle, this system can be treated with NPV theory based on the simple first-order elementary reaction.

In the “stripping” experiments, the longer the waiting time at the fixed “stripping” or base potential, the higher the  $\text{CO}_{\text{ad}}$  content on the electrode surface. Figure 5 is the CV results of Pt electrode covered with  $\text{CO}_{\text{ad}}$ , which were obtained after the electrode was fixed at  $-0.2$  V vs Ag/AgCl for different times in 1.0 M  $\text{CH}_3\text{OH}$  and 0.5 M  $\text{H}_2\text{SO}_4$ . To calculate the  $\text{CO}_{\text{ad}}$  contents on the electrode surface at different waiting times, the waiting time dependence of  $\text{CO}_{\text{ad}}$  content on Pt electrode surface was hypothesized to be the following Langmuir monolayer model:

$$C = C_0\theta = C_0 \frac{bt}{1 + bt}$$

where  $\theta$  is the coverage percent and  $b$  is a constant related with time ( $\text{s}^{-1}$ );  $C_0$  is saturated  $\text{CO}_{\text{ad}}$  concentration (mol/L) on the electrode surface, and  $t$  is adsorption or waiting time (s).



**Figure 6.** Fitting result of the Langmuir monolayer model based on experimental results at different waiting times.

The values of  $b$  and  $C_0$  obviously depend both on methanol concentration in electrolyte solution and the fixed electrode potential. The CO<sub>ad</sub> contents at different waiting times were calculated approximately based on the peak-area of CO<sub>ad</sub> oxidation. Then we used these data to fit the above Langmuir monolayer model and the values of  $b$  ( $= 0.02 \text{ s}^{-1}$ ) and  $C_0$  ( $= 36 \text{ mol/L}$ ) were obtained approximately and the results are shown in Figure 6.

In NPV experiments as shown in Figure 1, during the waiting time at base potential, CO<sub>ad</sub> was formed at the electrode surface from methanol oxidation. At high potential pulses over 0.4 V vs Ag/AgCl, the CO<sub>ad</sub> accumulated on the electrode then is oxidized to CO<sub>2</sub> with the cooperation of Pt–OH.<sup>3,4</sup> In the potential region ( $E < 0.1 \text{ V}$  vs Ag/AgCl), only CO<sub>ad</sub> could be formed from methanol oxidation,<sup>10</sup> so at the pulses below 0.1 V the poison of CO<sub>ad</sub> accumulated gradually on the electrode surface. In the present experiments there were about 100 pulses with scan increment of 3 mV. So the total waiting time before the starting of CO<sub>ad</sub> oxidation should be expended 100 times. Combined with the above Langmuir model, the initial contents of CO<sub>ad</sub> at different waiting times were obtained.

According to previous results,<sup>8,14c</sup> the current–potential relationship for the multistep electron-transfer reactions could be given by the following Butler–Volmer equation

$$i = nFAk^0 \left\{ C_{\text{Red}}^s \exp \left[ -\alpha n_{\alpha} \frac{F}{RT} (E - E^0) \right] - C_{\text{Ox}}^s \exp \left[ (1 - \alpha) n_{\alpha} \frac{F}{RT} (E - E^0) \right] \right\} \quad (9)$$

where  $k^0$  (standard rate constant),  $\alpha$  (anodic transfer coefficient), and  $E^0$  (formal standard potential) apply to the rate-determining step (eq 5).  $A$  is the electrode area and  $C^s$  the surface concentration of Ox or Red.  $E$  is the electrode potential, and  $i$  is the normal pulse voltammetric current. The terms  $n$  and  $n_{\alpha}$  have their usual meanings.

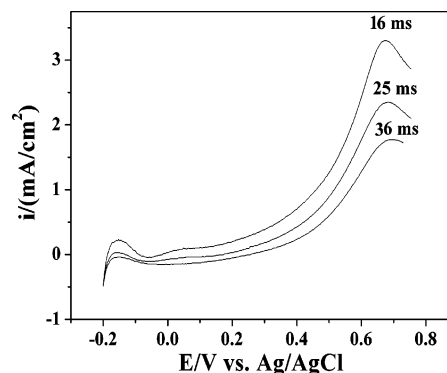
In the case of normal pulse voltammetry at the expanding plane electrode for completely irreversible multistep processes, the solution of eq 9 should be the following:<sup>25–29</sup>

$$E = E^* + \frac{RT}{\alpha n_{\alpha} F} \ln \left\{ x \left( \frac{1.75 + x^2}{1 - x} \right)^{1/2} \right\} \quad (9^*)$$

$$x = i/(i_d)_{\text{Cott}} \quad (9a)$$

where  $E^*$  is the half-wave potential of the irreversible wave. According to the results of Oldham and Parry,<sup>29</sup>

$$E^* = E^0 - \frac{RT}{\alpha n_{\alpha} F} \ln \left[ \frac{4}{\sqrt{3}} \frac{k^0 \sqrt{\tau}}{\sqrt{D_{\text{app}}}} \right] \quad (9b)$$



**Figure 7.** Normal pulse voltammograms for the oxidation of CO<sub>ad</sub> in 1.0 M methanol and 0.5 M sulfuric acid solution with different sampling times and waiting time of 2 s before each pulse. Scan rate: 1 mV/s.

where  $\tau$  is the sampling time,  $D_{\text{app}}$  is apparent diffusion coefficient of Ox or Red. In the case of adsorbed reactants, the CO<sub>ad</sub> content was estimated based on the diameter of CO<sub>ad</sub> ( $\approx 150 \times 10^{-10} \text{ cm}$ ). The term  $(i_d)_{\text{Cott}}$  denotes the diffusion current expressed by the Cottrell equation in the following:<sup>30</sup>

$$(i_d)_{\text{Cott}} = \frac{nFAC\sqrt{D_{\text{app}}}}{\sqrt{\pi\tau}} \quad (10)$$

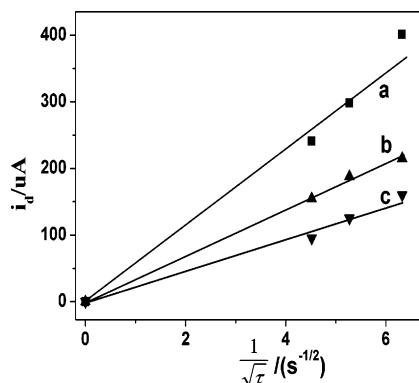
where  $C = C^s$ . In the present experiments, the limiting current was reached at pulses where the CO<sub>ad</sub> content consumed at the pulse was approximately equal to the content of CO<sub>ad</sub> produced at previous waiting times. In the following, the above equations were used to study the kinetics of CO<sub>ad</sub> oxidation on a polycrystalline Pt electrode.

Figure 7 shows the typical normal pulse voltammograms for CO<sub>ad</sub> oxidation in 1.0 M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution on the polycrystalline Pt electrode with waiting time of 2 s before each pulse at various sampling times ( $\tau$ ). The S-shaped waves were similar to those predicated previously.<sup>6–7,30</sup> The anodic limiting currents increase and the half-wave potentials of the NPVs for CO<sub>ad</sub> oxidation shifted in positive directions with the decrease in  $\tau$ . The diffusion-like electron-transfer process is consistent with previous results.<sup>6–7,30</sup> Thus, the above conventional analysis for normal pulse voltammograms was applicable to the irreversible CO<sub>ad</sub> electrooxidation.<sup>6</sup> Furthermore, after the limiting currents the currents decrease once more; obviously the reason was that the consuming content of CO<sub>ad</sub> at high potential is more than the CO<sub>ad</sub> content produced at previous waiting times.

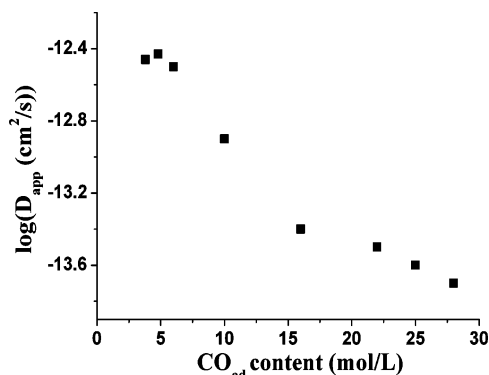
As shown in Figure 8 or in eq 10, plots of the anodic limiting currents of these normal pulse voltammograms against the inverse square roots of the sampling times were found to be linear. This means that the limiting current was controlled by content of CO<sub>ad</sub> produced on the electrode surface and this behavior was similar to semi-infinite.<sup>31–33</sup> The values of diffusion coefficients,  $D_{\text{app}}$ , could be obtained from the slopes of lines in Figure 8 by using eq 10. The  $D_{\text{app}}$  value is a measurement of the charge transport rate within the monolayer of CO<sub>ad</sub> on the electrode surface.<sup>34</sup>

Figure 9 shows the logarithmic plot of  $D_{\text{app}}$  vs CO<sub>ad</sub> content. The apparent diffusion coefficient increased with the decrease in CO<sub>ad</sub> content and then kept constant at lower reactant content. Similar results had also been obtained in previous work.<sup>8,19</sup> The reason for the lower  $D_{\text{app}}$  at higher CO<sub>ad</sub> content probably was the increase in the encounter distances required for efficient electron transfer.<sup>16–19</sup>

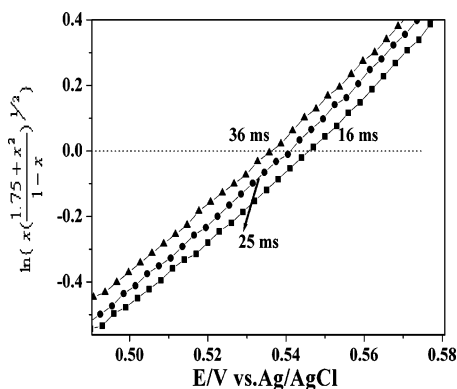




**Figure 8.** Plot of limiting current vs (sampling time)<sup>-1/2</sup> for the oxidation of CO<sub>ad</sub> with waiting time of 2 s (a), 1.2 s (b) and 0.8 s (c) before pulse.

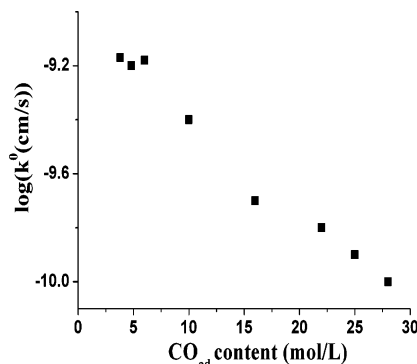


**Figure 9.** Logarithmic plot of  $D_{app}$  vs CO<sub>ad</sub> content for the oxidation of CO<sub>ad</sub>.



**Figure 10.** Modified log plots of normal pulse voltammograms for the oxidation of CO<sub>ad</sub> in 1.0 M methanol and 0.5 M sulfuric acid solution with different sampling times and waiting time of 2 s before each pulse.

Figure 10 shows the typical examples of such log-plots of normal pulse voltammograms with methanol concentration of 1.0 M and waiting time of 2 s, in which the logarithm of second term of eq 9\* was plotted against  $E$  for the oxidation of CO<sub>ad</sub>. These plots gave straight lines, the slopes of which were constant at different sampling times within experimental errors. This fact indicates that the oxidation of CO<sub>ad</sub> on the electrode surfaces obeys the conventional Butler–Volmer equation,<sup>35</sup> which was consistent with that reported by others.<sup>8,15–21</sup> The slopes of the straight lines were equal to  $(\alpha n_{\alpha} F/RT)$ . The anodic transfer coefficient ( $\alpha$ ) could be evaluated from the slopes and its value was in the range of  $0.31 \pm 0.02$  for different CO<sub>ad</sub> concentrations. It indicates that the value of  $\alpha$  was independent of CO<sub>ad</sub> concentration. The value of  $\alpha$  was less than 0.5, which indicates a slow anode kinetic process for the CO<sub>ad</sub> oxidation.<sup>14c</sup>



**Figure 11.** Logarithmic plot of  $k^0$  vs CO<sub>ad</sub> content for the oxidation of CO<sub>ad</sub>.

The  $E^0$  for the rate-determining step of eq 5 was estimated approximately based on the standard forming free energy. Thus, the standard rate constant,  $k^0$ , of electron-transfer process for the rate-determining step was evaluated by introducing the experimental values of  $D_{app}$ ,  $\alpha$ ,  $E^*$ , and hypothetical  $E^0$  into eq 9b. Figure 11 shows the dependence of  $k^0$  upon the concentration of CO<sub>ad</sub>. The  $k^0$  also increased with the decrease in reactant concentration and then reached a relative constant value at low concentration region. As  $k^0$  is correlative with  $D_{app}$  according to eq 9b, so the possible reason for the concentration dependence of  $k^0$  is the same as that for  $D_{app}$ .<sup>16–19</sup>

In the following the effect of treating the content of A or B in eq 8 as constant on the kinetic parameters for completely irreversible reactions was analyzed. According to the law of mass action, the rate for an elementary reaction should be proportional with the product of all the reactant concentrations. As for eq 8, the rate for it should be the following:

$$\frac{i_a}{nFA} = k_f C_R C_A, \frac{i_c}{nFA} = k_b C_O C_B$$

So eq 9 should be rewritten as the following:

$$i = nFAk^0 \left\{ C_A C_{Red}^s \exp \left[ -\alpha n_{\alpha} \frac{F}{RT} (E - E^0) \right] - C_B C_{Ox}^s \exp \left[ (1 - \alpha) n_{\alpha} \frac{F}{RT} (E - E^0) \right] \right\}$$

As for the completely irreversible oxidative reactions,

$$i \approx nFA(k^0 C_A) \left\{ C_{Red}^s \exp \left[ -\alpha n_{\alpha} \frac{F}{RT} (E - E^0) \right] \right\} = nFAk_{app}^0 \left\{ C_{Red}^s \exp \left[ -\alpha n_{\alpha} \frac{F}{RT} (E - E^0) \right] \right\}$$

Therefore, when a second order elementary reaction was approximately treated as a first-order reaction, the calculated  $k^0$  on the above was really the apparent standard rate constant  $k_{app}^0 (= k_T^0 C_A)$ ,  $k_T^0$  is the true standard rate constant for the second-order reaction of eq 8 or eq 5 herein. If the value of  $C_A$  was constant or known then the value of  $k_T^0$  for the second-order reaction could be obtained with the dimension of mol s<sup>-1</sup> cm<sup>-2</sup>. In the present experiment Pt–OH from the decomposition of H<sub>2</sub>O is always sufficient and its content was treated as a constant. Although the data in Figure 11 were not so exact quantitatively, they could reflect the qualitative relationship between  $k_T^0$  and CO<sub>ad</sub> content. As for the value of  $\alpha$  or  $D_{app}$ , the calculation of them was independent of standard rate constant, so the approximate treatment had no effect on  $\alpha$  or  $D_{app}$ .

## Conclusions

In the present work the intermediate of methanol oxidation on Pt electrode was validated to be CO<sub>ad</sub> by an electrochemical method. An approximate treatment to bimolecular elementary reactions was advanced first and then applied to the NPV to study the surface process of CO<sub>ad</sub> oxidation. The results obtained in the present study show that the oxidation of CO<sub>ad</sub> on polycrystalline platinum electrode was a slow completely irreversible kinetic process, as the apparent diffusion coefficient ( $D_{app}$ ) was on the order of  $10^{-12}$  cm<sup>2</sup>/s and the anodic transfer coefficient ( $\alpha$ ) was  $0.31 \pm 0.02$ . The analysis of the effect of the approximate treatment on the kinetic parameters showed that the approximate treatment for the bimolecular elementary reactions was reasonable in a certain extent.

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**Supporting Information Available:** Experimental details describing reference electrode in special glassy tube (salt bridge). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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