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Electrochemistry

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Cyclic voltammetry, electrochemical impedance spectroscopy and potential oscillation during methanol electro-oxidation

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ABSTRACT

In this article the methanol electro-oxidation has been investigated in detail. The electrochemical oxidation reaction mechanism has been analyzed and discussed based on the cyclic voltammetries (CV), electrochemical impedance spectroscopies (EIS) and galvanostatic potential oscillation measurements that were conducted in $0.1M\ H_2SO_4+x\ M\ CH_3OH$ (x=0.05, 0.5 and 3.0) solutions. The hidden oxidation peak appearing at about 0.0V vs. Hg_2SO_4 in positive and negative sweeping potential directions should be contributed to the adsorption/desorption process of some organics on the electrode surface. There is a controversy on the origin of the first main oxidation peak in positive sweeping potential direction. From our analysis, this oxidation peak formation should be related to the formation of adsorbed OH species, not to the formation of adsorbed CO species. The origin of other peaks has been also discussed. It was also found that the real impedance becomes negative for the finite range of non-zero frequencies when the applied potential was just the potential where the first main oxidation peak appears. The galvanostatic test has also explored that during oscillating the average potential does also fall into this potential range.
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INTRODUCTION

As direct alcohol fuel cells (DAFC) emerged as one of the most promising future clean power sources for alternative means to convert chemical energy into electric energy during the past decades, intensive investigation has been done on electro-catalytic activity of Pt-based electro-catalysts that are well-known to have a good catalytic behavior for methanol[1-14]. For improving the performance of Pt-based electro-catalysts, the main strategy is to increase its tolerance to some poisonous intermediates, such as some oxygen-containing adsorbents (CO[2-5,8,9,14]), aldehydes and alcohol acids etc incomplete oxidation products, Pt oxides or hydroxides[4,15-17], that are able to deactivate the Pt-based electrode.

To improve the methanol electro-oxidation reaction kinetics at Pt electrode and to get a satisfied output power of DAFC anode as well as DAFC, it is very crucial to understand the electro-oxidation reaction

mechanism and to explore the elementary reaction steps during charge-transfer process, as well as to determine the rate-limiting reaction step. There are lots of literatures[2-5,17-20] reporting the reaction mechanism. However there exists a discrepancy about the details of the electro-oxidation reaction. According to Scott[4], the first step that represents the loss of the first electron is the slowest reaction step,

Pt+CH₃OH→Pt-CH₂OH+H⁺+e

In methanol molecule, there are two kinds of protons, one is bonded into oxygen atom and another is connected to carbon atom. Until now one can not conclude the sequence of proton losing. It is likely that, the proton in hydroxyl group will be lost preferentially in alkaline medium[18], while the proton in alkyl group will be lost preferentially in acidic medium[4,10,21]. The oxidation products of alcohols have an uncertainty, especially for the long-train alcohols[16,18,20,22]. In addition, the reported shapes of cyclic voltammetries are very different each to other. For instance, in 0.5M H_2SO_4+0.5M CH_3OH solution there is only one oxidation peak in the positive sweeping direction up to 1.4V vs. RHE[16]. Huang[23] reported one shoulder peak that positions at 0.1V vs Hg/Hg_2SO_4 in 0.5M H_2SO_4+1M CH_3OH. According to Chen's report[24], there exist three oxidation peaks in the positive sweeping direction during methanol electro-oxidation; one is a shoulder peak at 0.65V vs. RHE, the second is at 0.95V and the third is at about 1.32V.

Our final purpose is to explore the electro-oxidation activity of different kinds of alcohols. In our previous literature[25] we have reported the electro-oxidation reaction of ethanol. In this article, we have intensively studied the methanol electro-oxidation. It was found that the shape of cyclic voltammetries depends upon the alcohol concentration. The CVs and the oscillatory potential were also analyzed according to the electro-oxidation reaction mechanism.

EXPERIMENTAL

All the electrolyte used in this work were prepared by dissolving the corresponding chemicals (CH_3OH p.a., H_2SO_4 p.a.) in ultra-pure water (18.2MΩ, Hitech ultra-pure water system). The working electrode is a

Pt electrode with an area of 24mm^2 and the purity is 99.99%. The counter electrode is Pt electrode with a much larger working area than the working electrode. The reference electrode is Hg/Hg_2SO_4. The distance between the working electrode and reference electrode is set up at 20mm. The electrochemical measurements were conducted with PE Parc 2273 or CHI660C electrochemical workstations. The electrochemical impedance spectroscopy was performed under potentiostatic mode. The applied frequency ranged from 100k to 0.01 Hz and the applied ac signal amplitude is 5mV. For galvanostatic experiment, the current was stepped from 0 to a series of final current values and at same time the time-evolution of the response potential has been captured. In order to remove the possible organic impurities, the Pt working electrode was pre-treated by sweeping its electrode potential between-in -0.65V and 0.8V in 0.5M H_2SO_4 solution before electrochemical test, until the standard cyclic voltammogram (Figure 1) was obtained.
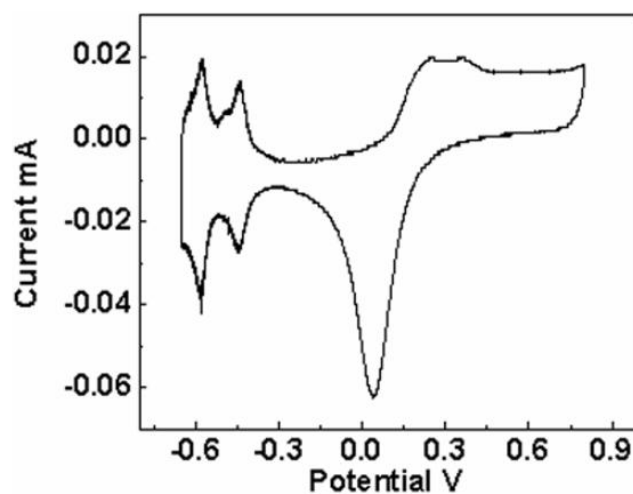

Figure 1 : The CV pattern of Pt electrode in 0.5M H_2SO_4 solution, scanning rate is 50mV s⁻¹.

RESULTS

The study of electrochemical behavior of Pt metal in sulfuric acid solution is helpful to understand and analyze the electro-oxidation reaction mechanism of methanol at Pt electrode. Figure 1 shows the CV pattern of Pt working electrode in 0.5M H_2SO_4 solution. The two oxidation peaks at 0.25V and 0.36V represent the formation of Pt oxides or hydroxides. If the electrode po-

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tential is swept up to more than 0.8V, the oxygen evolution will start. The reduction peak at 0.02V corresponds to the reduction of Pt oxides or hydroxides to metallic state Pt. The two couples of redox peaks at -0.44v and -0.59V have a typical characteristic, i.e., the oxidation peak potential is almost same with the reduction peak potential. They represent the under-potential deposition and adsorption of hydrogen. The obtained CV pattern of Pt working electrode in 0.5M H_2SO_4 solution is same as the reports[1,25-28], which has confirmed our experimental quality; there is not any impurity in the solution and on the electrode surface.
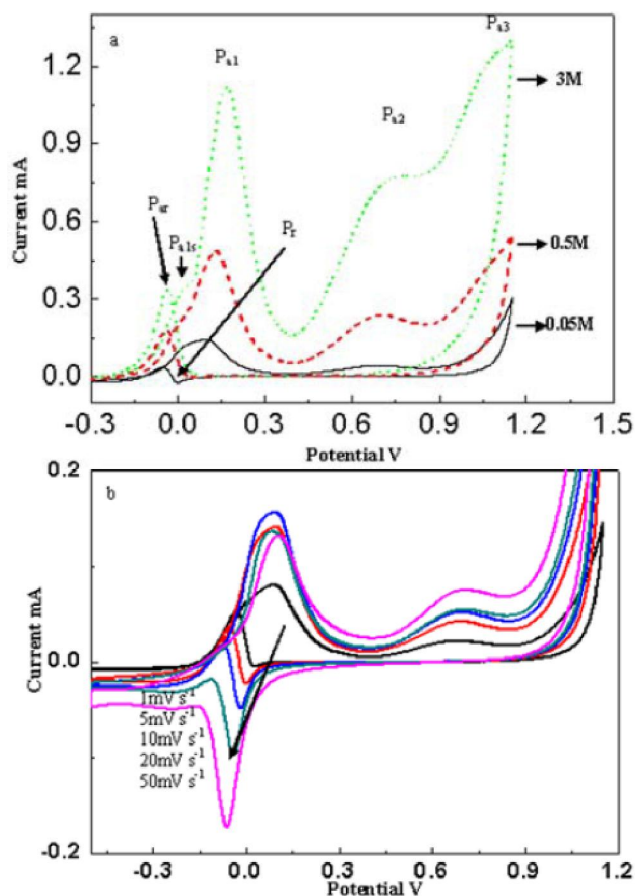

Figure 2 : (a) The cyclic voltammetries of Pt electrode in 0.1M H_2SO_4+xM CH_3OH solution (x=0.05, 0.5 and 3), the scanning rate is 5mV s⁻¹; (b) The CV pattern of Pt electrode in 0.05M CH_3OH+0.1M H_2SO_4 solution.

The cyclic voltammagrams of methanol electro-oxidation on Pt electrode in 0.1M H_2SO_4+xM CH_3OH (x=0.05, 0.5 and 3.0) solutions was showed in Figure 2a. The scanning rate is 5mV/s. In the positive sweeping potential direction, one shoulder peak followed by three oxidation peaks can be captured. The first main

oxidation peak (P_{a1}) positioned at 0.1~0.18V. The peak potential increased as the methanol concentration increased. The oxidation peak (P_{a2}) potential is in the range of 0.65~0.70V. In lower methanol concentration the oxidation peak P_{a3} does not appear. When the potential is more than 1.10V, oxygen gas evolution reaction becomes clearer. The oxidation peak P_{a3} becomes more obvious when the potential-scanning rate decreased down to 1mV/s, as showed in Figure 9, the supplementary figure, for x=3.0. It can be concluded from the Figure 2a that the potential and current of the oxidation peaks Pa1, Pa2 and Pa3 are dependent of the methanol concentration. In higher methanol concentration the oxidation peak potential becomes more positive, the peak current becomes larger and the shoulder peak becomes clearer. But for Pa1s, its peak potential seems to be independent of the scanning rates and the methanol concentrations.

The reduction peak (P_r) is somewhat clear for the 0.1M H_2SO_4+0.05M CH_3OH solution, while the increase in the methanol concentration leads to the disappearance of the reduction peak. Figure 2b shows the CV patterns of methanol electro-oxidation at Pt electrode in the solution containing 0.05M CH_3OH under a series of potential-scanning rates. It can be found that the reduction peak is hardly to see for the 1mV/s scanning rate. When the potential-scanning rate increased, the reduction peak current becomes larger and the corresponding peak potential moved towards more negative potential, which implies that the reduction peak represents an electrochemical process in which a charge transfer step is involved. However, the reduction peak disappears in higher methanol concentration. The electro-reduction reaction rate is very fast for the oxidized Pt electrode surface.

Figure 3a shows the CV patterns of Pt working electrode in 3M CH_3OH+0.1M H_2SO_4 solution under a series of potential-scanning rates. It is clear that the potential of the oxidation peaks P_{a1}, P_{a2} and P_{a3} moved into more positive potential direction, and the corresponding peak current increased as the scanning rate increased. In the reverse potential-scanning process, the oxidation peak P_{ar} exhibits a more negative peak potential in the increased scanning rate. There exists another phenomenon being found in the Figure 3a. As the scanning rate increased, the potential at which the

oxidation reaction starts in the negative sweeping potential direction becomes more negative. But if the upper potential limit in CV measurement was set up at 0.87V or 0.7V, the potential between-in the oxidation peaks P_{a2} and P_{a3}, the potential at which the oxidation current starts to appear in the negative sweeping potential direction keeps unchanged as the potential scanning rate increased, as showed in Figure 10 and 11, the supplementary figures. In the negative potential sweeping direction, the potential the oxidation reaction starts at is dependent of the potential scanning rate when the upper potential limit was set up at 0.387V, as showed in Figure 12. It is guessed that the oxidation peaks Pa2 and Pa3 may correlate with the two-step electro-oxidation process of Pt surface.
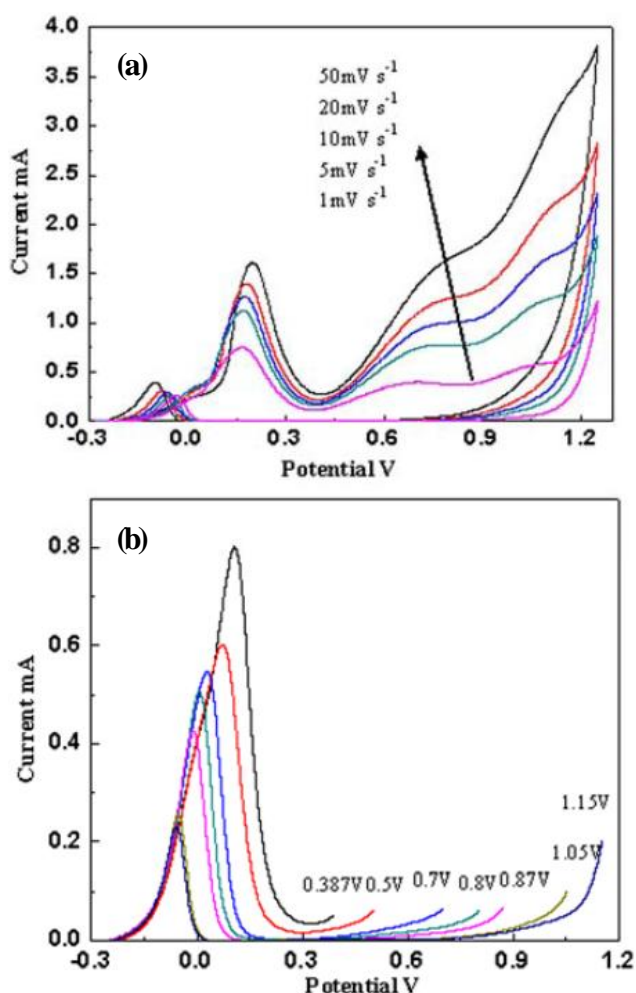
The electrode potential of the Pt working electrode kept for 600s at various constant outer-applied potentials, and then the potential was swept in the negative potential direction. The obtained linear sweeping potential-current curves were showed in Figure 3b. The current and potential of the peak P_{ar} is about 0.8mA and 0.11V, respectively, when the electrode was kept for 600s at 0.387V, while the peak current and potential moved to 0.23mA and -0.16V, respectively after the electrode was kept at 1.15V for 600 seconds. The increase in the outer-applied constant potential makes the peak current declined and makes the peak potential to be more negative.
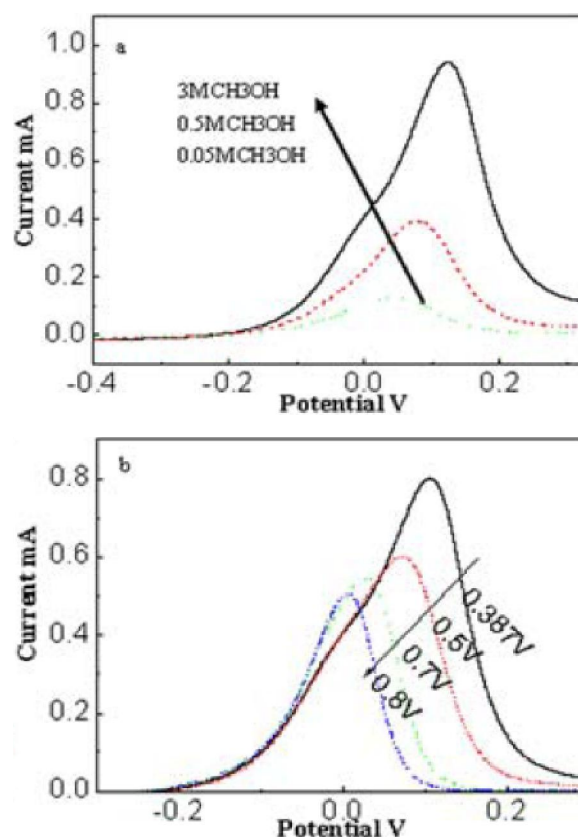

Figure 3 : (a) The CV patterns of Pt in 3.0M CH$_3$OH+0.1M H$_2$SO$_4$ solution; (b) The linear scanning polarization curves of Pt electrode in 0.1M H$_2$SO$_4$+3M CH$_3$OH solution, after the electrode was kept for 600s at an outer-applied potential, the scanning rate is 5mV s^{-1}.

Figure 4 : (a) The dependence of the shape of the oxidation peak (P$_{ar}$) in negative sweeping potential direction on the methanol concentration; (b) The dependence of the oxidation peak in negative sweeping potential direction on the upper potential limit, the electrolyte is 0.1M H$_2$SO$_4$+3M CH$_3$OH solution, the scanning rate is 5mV s^{-1}.

The dependence of the shape of the oxidation peak (P$_{ar}$) on the methanol concentration was also analyzed. The upper potential limit is 0.36V and the scanning rate is 5mV/s. The obtained CV patterns were showed in Figure 4a. For the 3M methanol concentration, the main

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oxidation peak is at about 0.12V. The oxidation peak is not left-to-right symmetric. An obvious shoulder peak can be found in the left side of the main oxidation peak. For the lower methanol concentration, the symmetry of the peak shape becomes better and the shoulder peak is hardly to be found. The shape of the oxidation peak (P_{ar}) is also influenced by the upper potential limit. From Figure 4b, the shoulder peak is clear for the curve obtained at an upper potential of 0.387V, while the shoulder peak becomes unclear for the curves that were obtained at an upper potential of 0.5V and 0.7V. It is difficult to say that there exists a shoulder peak, when the upper potential limit is 0.8V. It could be plausibly concluded that the main oxidation reaction is influenced by the upper potential limit, but the hidden shoulder oxidation peak is independent of the upper potential limit. These results is helpful to determine the origin of the oxidation peaks.

Impedance techniques are extensively used to analyze the kinetic behavior and the stability of electrochemical systems[1,29-31]. In literature[1], the impedance spectra at different potentials were obtained by measuring the alternative-current voltammogram in $H_2SO_4+CH_3CH_2OH$ solution by varying the applied frequency. The reliability of the re-constructed Nyquist diagrams in it is in doubt, especially in low-frequencies, because the potential-scanning rate is not enough fast to ensure the stability which is necessary for EIS measurement reliability. Figure 5a shows the electrochemical impedance spectroscopies of Pt working electrode at various potentials in 3M $CH_3OH+0.1M$ H_2SO_4 solution. The real impedance is positive for all frequency range except for that obtained at 0.165V. In the Nyquist's plot, the real impedance becomes negative for the finite range of non-zero frequency value but becomes positive for the lowest frequency. Such a kind of impedance spectrum should imply the de-stabilization of electrochemical system when it operates in the potentiostatic/galvanostatic mode[30]. For the 0.05V outer-applied potential, the inductive response appears for the finite range of non-zero frequencies. It is commonly accepted that the induction arc in the low frequency range is related with the adsorption/desorption process of the surface intermediates.

Figure 5b shows the electrochemical impedance spectroscopies in 0.5M $CH_3OH+0.1M$ H_2SO_4 solu-

tion. At 0.12V, the real impedance is negative for the finite range of non-zero frequency. As the applied frequency decreased the total impedance has a tendency to reach an infinite value. For the outer-applied potential of 0.13V, the impedance spectrum is similar as that obtained at 0.165V in the solution containing 3M CH_3OH. For other potential values, the real impedance is always positive regardless of the applied potentials and the applied frequencies. The unique difference is that the semicircle radius varies with the applied potentials. At 0.1V, the transition from negative imaginary impedance to positive imaginary impedance is very fast as the frequency decreased from 0.67Hz to 0.42Hz which implies the sensitivity of adsorption process.
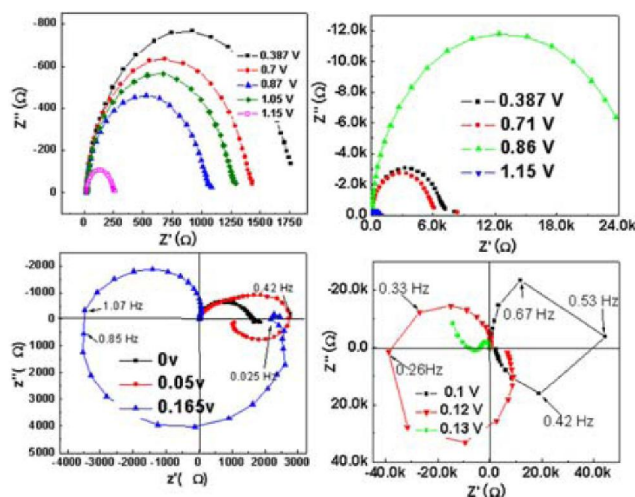

Figure 5 : (a) The electrochemical impedance spectroscopies obtained at various potentials in 3M $CH_3OH+0.1M$ H_2SO_4 solution; (b) The electrochemical impedance spectroscopies obtained at various potentials in 0.5M $CH_3OH+0.1M$ H_2SO_4 solution.

Figure 6 shows the electrochemical impedance spectroscopies in 0.05M $CH_3OH+0.1M$ H_2SO_4 solution. The dependence of the shape of the Nyquist's plot upon the applied potentials becomes more complicated. At 0.02V, the real impedance is always positive in despite of the applied frequencies, but the imaginary impedance becomes positive in the lower frequency range. The transition from negative to positive imaginary impedance is fast. At 0.05V, the impedance data point appears in a counterclockwise rotation around the origin of coordinate and cross the x-axis when the frequency is 0.26~0.21Hz. The further decrease in the applied frequency leads to a positive real impedance. The impedance spectrum at 0.09V is similar as that

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obtained at 0.13V in 0.5M CH3OH. The impedance has a negative real part and a zero imaginary part for a finite range of non-zero frequency but has a further decreasing real part and decreasing imaginary part. As the frequency decreased, the impedance response transited from the counterclockwise rotation to clockwise rotation. In the range of 0.12~0.21V and in the same range of signal frequencies, the obtained semicircle positioned in the fourth quadrant. The semicircle positioned in the first quadrant when the potential is more than 0.36V. For the potential of 0.24V, the semicircle is hard to see and the impedance response is similar as a pure capacitance in the low frequency range. The potential region at which the negative real impedance appears is almost same to the report by Palmore[12,13].
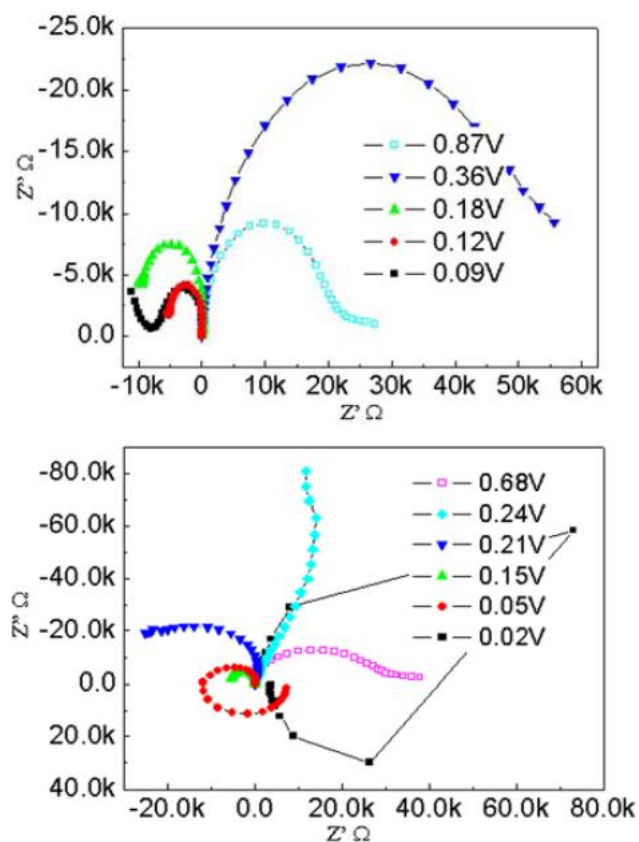

Figure 6 : The electrochemical impedance spectroscopies obtained at various potentials in 0.05M CH3OH+0.1M H2SO4 solution.

Usually, the potential oscillation phenomena can be found when an anodic current was applied to the electrooxidation system of small organic molecule[5,14,23]. The oscillatory behavior is influenced by the applied potential/current. When the methanol concentration is 3.0M,

the induction period is about 13.4hours for the applied current of 0.02mA and decreased as the applied current get increased. The potential oscillation appears immediately just after 0.3mA current was applied to the working electrode. For 0.02mA, there is only one kind of oscillation mode and the oscillation amplitude is about 0.29V (from -0.05V to 0.24V). The oscillation becomes faster when the current is 0.3 or 0.5mA. At last the electrode potential reached more than 0.5V after the oscillation disappears. The oscillation has a characteristic of high frequency (about 0.42Hz) and small amplitude (about 200mV) at the early stage. The oscillation amplitude has an increased tendency as the applied current increased. The average potential is about 0.0V in the oscillatory potential range. The potential does slowly increase after the oscillation stops and a new kind of oscillation manifests itself when the potential reached about 0.18V. Here we call the oscillation that appears at the beginning of the constant current polarization as the 1st oscillation and denote the oscillation after which an obvious potential transition occurs as the 2nd oscillation, for convenient discussion. It should be pointed out that the potential at which the second kind of oscillation starts to appear is almost same in all cases of applied currents and seems to be independent of the applied current. At 0.7mA the first oscillation disappears. The second oscillation becomes faster as the applied current increased. No oscillation was found when the applied current is more than 0.95mA.

Figure 7 shows the oscillation behavior in 0.5M CH3OH+0.1M H2SO4 solution. The scenario is similar as that in 3M CH3OH+0.1M H2SO4 solution. The first oscillation is influenced by the applied current. As the current increased from 1.0 mA to 4.5 mA, the oscillation amplitude increases and the oscillation frequency becomes slightly faster (from about 0.375Hz to about 0.4Hz). The amplitude of the second oscillation increased and the corresponding oscillation frequency increased with the applied current. There exists an interested phenomenon that the effect of the applied current on the first and second oscillations is very different. In the small current (1mA) there exists only the first oscillation. As the current becomes larger the second oscillation appears, but the further increase in the applied current leads to the disappearance of the first oscillation. At last, the second oscillation does also disap-

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pear, when the applied current reaches some or other critical value.

The further decrease in the methanol concentration causes the first oscillation to disappear.
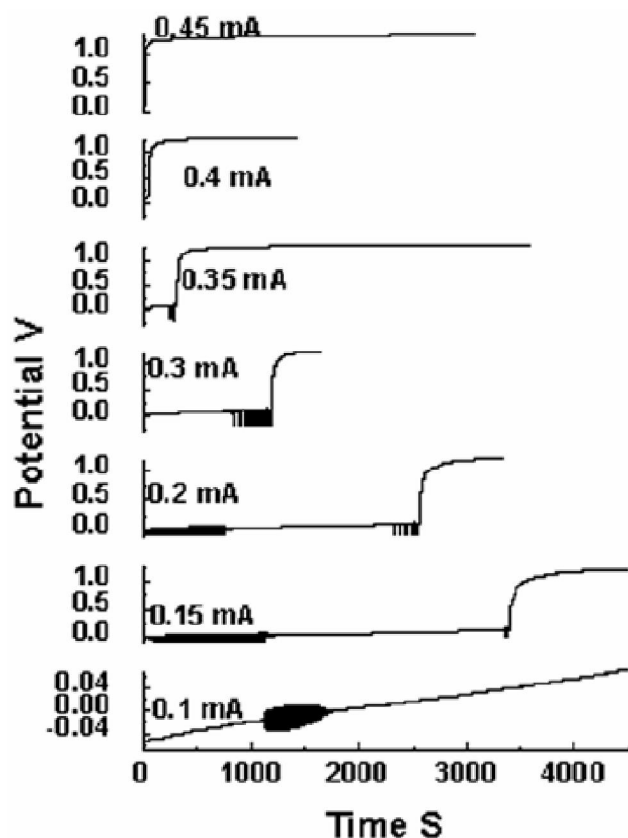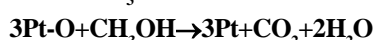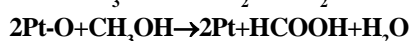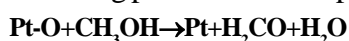

Figure 7 : The galvanostatic potential oscillation in 0.5M CH₃OH+0.1M H₂SO₄ solution.

DISCUSSION

The cyclic voltemmetries, linear scanning polarization, electrochemical impedance and galvanostatic potential oscillation are able to provide some useful information on the methanol electro-oxidation mechanism. Summarizing the literatures, it can be found that there exists an obvious discrepancy on the methanol electro-oxidation mechanism as well as on the explanation about the cyclic voltemmograms. In the literature[18] the authors have concluded that the peak current of the methanol electro-oxidation is not influenced by the adsorbed OH group. In the literature[17] the authors proposed the following possible reaction pathway.
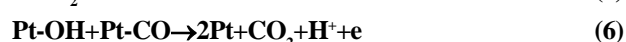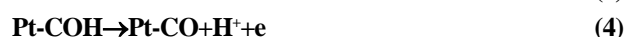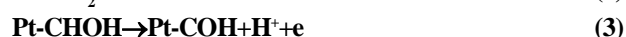
$$Pt-O+CH_3OH \rightarrow Pt+H_2CO+H_2O$$
$$2Pt-O+CH_3OH \rightarrow 2Pt+HCOOH+H_2O$$
$$3Pt-O+CH_3OH \rightarrow 3Pt+CO_2+2H_2O$$
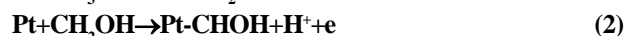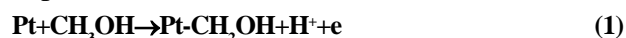
In fact, the reaction pathway and the products including long-live intermediates and by-products must be influenced by the surface chemistry[32]. Otomo etc[6] have also discussed the possibility of the direct decomposition of methanol to hydrogen gas,

$$CH_3OH \rightarrow CO+2H_2$$
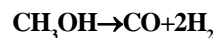
But, the probability for this reaction should be very small. Okamoto[33] has contributed the oxidation peak at about 0.5V in the positive sweeping potential direction to the adsorption of hydroxyl group at the electrode. According to his report, the appearance of this oxidation peak is dependent of the scanning rate. In the slow rate this peak can not be found. To the authors' knowledge, it is more reasonable to contribute this peak[33] to the HCOOH or analogues adsorption.

Summarizing the literatures[2-5], all the possible reactions the methanol electro-oxidation may concern are expressed as follows
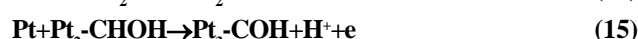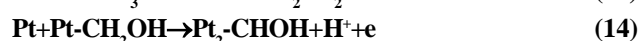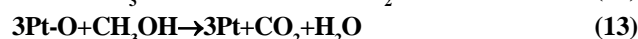
$$Pt+CH_3OH \rightarrow Pt-CH_2OH+H^++e \qquad (1)$$
$$Pt+CH_2OH \rightarrow Pt-CHOH+H^++e \qquad (2)$$
$$Pt-CHOH \rightarrow Pt-COH+H^++e \qquad (3)$$
$$Pt-COH \rightarrow Pt-CO+H^++e \qquad (4)$$
$$Pt+H_2O \rightarrow Pt-OH+H^++e \qquad (5)$$
$$Pt-OH+Pt-CO \rightarrow 2Pt+CO_2+H^++e \qquad (6)$$

The reactions (1)-(6) were summarized by Scott etc[4]. In the literature by Krausa[19], the reaction (1) is considered to be the slowest step. Kadirgan[15] has also proposed some possible reactions, as follows

$$Pt-CHOH+H_2O \rightarrow Pt-HCOOH+2H^++2e \qquad (7)$$
$$Pt-HCOOH \rightarrow Pt+CO_2+2H^++2e \qquad (8)$$
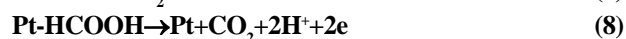
The fate of adsorbed formic acid may be as follows

$$Pt-HCOOH \rightarrow Pt-HCOO+H^++e \qquad (9)$$
$$Pt-HCOO \rightarrow Pt+CO_2+H^++e \qquad (10)$$

In the literature[17] the following reaction steps were mentioned.

$$Pt-O+CH_3OH \rightarrow Pt+HCHO+H_2O \qquad (11)$$
$$2Pt-O+CH_3OH \rightarrow 2Pt+HCOOH+H_2O \qquad (12)$$
$$3Pt-O+CH_3OH \rightarrow 3Pt+CO_2+H_2O \qquad (13)$$
$$Pt+Pt-CH_2OH \rightarrow Pt_2-CHOH+H^++e \qquad (14)$$
$$Pt+Pt_2-CHOH \rightarrow Pt_3-COH+H^++e \qquad (15)$$

The literature[10] supported the reactions (14) and (15).

$$2Pt-CH_2OH+Pt-O \rightarrow 3Pt+2HCHO+H_2O \qquad (16)$$
$$Pt_3-COH \rightarrow 2Pt+Pt-CO+H^++e \qquad (17)$$
$$Pt_3-COH \rightarrow Pt+Pt_2-CO+H^++e \qquad (18)$$
$$Pt_x-CO+Pt-OH \rightarrow (x+1)Pt+CO_2+H^++e \qquad (19)$$

$$Pt_x\text{-}CO+Pt\text{-}O\rightarrow(x+1)Pt+CO_2 \qquad (20)$$

$$Pt\text{-}O+H_2O+2e\rightarrow Pt+2OH^- \qquad (21)$$

$$Pt\text{-}O+2H^++2e\rightarrow Pt+H_2O \qquad (22)$$

$$Pt\text{-}OH+Pt\text{-}CO\rightarrow Pt\text{-}COOH \qquad (23)$$

$$Pt\text{-}CO+H_2O\rightarrow Pt\text{-}COOH+H^++e \qquad (24)$$

$$Pt\text{-}COOH\rightarrow Pt+HCOO \qquad (25)$$

$$Pt\text{-}CH^2OH\rightarrow Pt+HCHO+H^++e \qquad (26)$$

$$Pt_2\text{-}CHOH+PT\text{-}OH\rightarrow3Pt+HCOOH+H^++e \qquad (27)$$

$$Pt_2\text{-}CHOH+H_2O2Pt+HCOOH+2H^++2e \qquad (28)$$

$$Pt_3\text{-}CHOH+Pt\text{-}OH\rightarrow3Pt+Pt\text{-}COOH+H^++e \qquad (29)$$

$$Pt_3\text{-}COH+H_2O\rightarrow2Pt+Pt\text{-}COOH+2H^++2e \qquad (30)$$
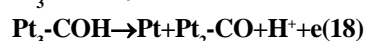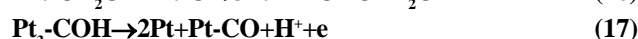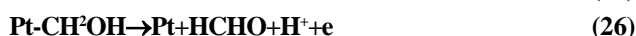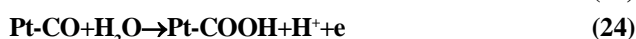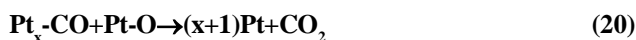
In a relatively low methanol concentration, Pt_3-COH formed preferably[10].

$$Pt_x+CH_3OH\rightarrow Pt_x\text{-}CH_3OH \qquad (31)$$

$$Pt_x\text{-}CH_3OH+OH^-\rightarrow Pt_x\text{-}CH_3O+H_2O+e \qquad (32)$$

$$Pt_x\text{-}CH_3O+OH^-\rightarrow Pt_x\text{-}CH_2O+H_2O+e \qquad (33)$$

$$Pt_x\text{-}CH_2O+OH^-\rightarrow Pt_x\text{-}CHO+H_2O+e \qquad (34)$$

$$Pt_x\text{-}CHO+OH^-\rightarrow Pt_x\text{-}CO+H_2O+e \qquad (35)$$

$$Pt_x\text{-}CO+OH^-\rightarrow Pt_x\text{-}COOH+e \qquad (36)$$

$$Pt_x\text{-}COOH+OH^-\rightarrow xPt+CO_2+H_2O+e \qquad (37)$$

$$Pt_x\text{-}CHO+3OH^-\rightarrow xPt+CO_2+2H_2O+3e \qquad (38)$$

$$Pt_x\text{-}CO+2OH^-\rightarrow xPt+CO_2+H_2O+e \qquad (39)$$
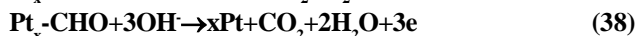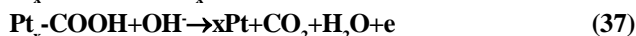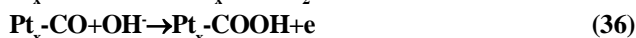
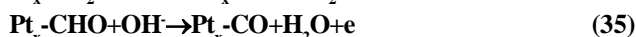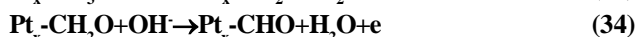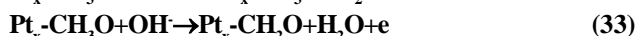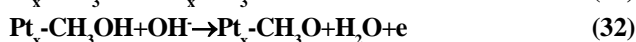It should be pointed out that some adsorbed intermediates may leave the electrode surface into the solution. In such case there exist some incomplete-oxidized by-products, such as HCHO and HCOOH. Based on the above mentioned reactions, the multi-pathway reaction model can be compiled, as showed in Figure 8. Based on the literatures, not considering the details, the electro-oxidation reaction pathways that are widely accepted by the researchers could be divided into two main categories. The first category is widely used in explaining the electrochemical behavior of methanol electro-oxidation in acidic medium[4,22], the reaction pathway can be expressed as follows

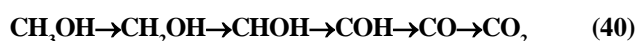$$CH_3OH\rightarrow CH_2OH\rightarrow CHOH\rightarrow COH\rightarrow CO\rightarrow CO_2 \qquad (40)$$

In the second category, the proton that bonded to oxygen atom will be firstly loss and the reaction pathway is as

$$CH_3OH\rightarrow CH_3O\rightarrow CH_2O\rightarrow CHO\rightarrow CO\rightarrow CO_2 \qquad (41)$$

To the authors' intuition, the pathway (40) is more possible in acidic medium and the pathway (41) is more preferable in alkaline medium, although there is no direct evidence. There exist two possible explanations on the phenomenon that the peak P_{a1} current decreased

as the potential was further swept in positive potential direction. In the first explanation, we can contribute this peak current to the direct oxidation of methanol and at higher potential some formed poisoning intermediates, such as CO, poisoned the electrode and caused the reaction current declined. In the literature[34] the authors have contributed the oxidation peak P_{a1} in the positive sweeping potential direction to the direct oxidation of the methanol. In this explanation, the Pt electrode surface is covered by the CO if the electrode was kept at a potential more than 0.2V in 3M $CH_3OH+0.1M$ H_2SO_4. In other words, the electrode is covered by the CO specimen if its potential was kept at 0.4V in Figure 3a.
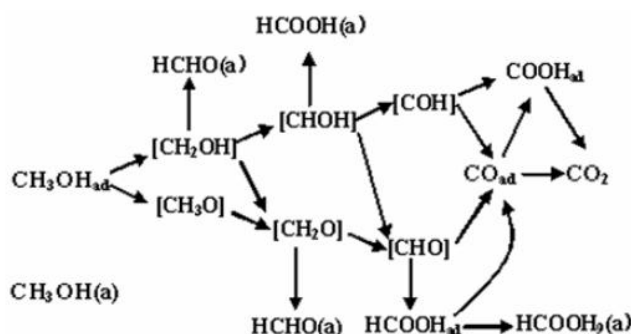

Figure 8 Multi-pathway reaction model of methanol electro-oxidation.

The fact that the current and potential of the main oxidation peak (P_{a1}) are affected by the methanol concentration and the scanning rates supported that this oxidation peak represents an electrochemical process. After immersed into the solution containing CH_3OH, the chemical oxidation reaction of methanol will occur on the Pt electrode and the product should include the adsorbed carbon oxides. Before the oxidation current appears, the Pt electrode surface is covered by the adsorbed CO specimen. So, in the second explanation, the formation of the oxidation peak P_{a1} is related with the absorbed OH specimen. In this case, the oxidation current has been contributed to the direct and indirect reaction pathways and the current decrease is due to the formation of the adsorbed OH specimen. In other words, in the 2nd explanation, the electrode is covered by the OH if its potential was kept at 0.4V in Figure 3a.

In the first explanation, the electrode surface is free of poisonous intermediates before the oxidation reaction occurs. And after the oxidation reaction occurs,

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the CO starts to form due to the reaction (4). In the second explanation, the electrode surface is covered by CO that comes from the (electro) chemical oxidation reaction of methanol. After the occurrence of oxidation reaction, especially after the potential is more than P_{a1} peak potential, the reaction (5) has a relatively high reaction rate and the adsorbed OH species start to cover the electrode surface. The authors prefer the second explanation is correct. In the literature[10], it is believed that the CO_2 starts to form at a potential of more than 0.5V vs. RHE. And the authors concluded that there exists no adsorbed CO on the Pt electrode surface when the potential is more than 0.7V vs. RHE.

One well-known fact is able to confirm that the first explanation is not correct. If this explanation is correct, and then if the potential in methanol electro-oxidation system is kept at the potential of the main oxidation peak P_{a1}, then the response current will decay down to zero as soon as the electrode surface was full of the adsorbed CO. In comparison with the adsorbed O-containing species, the adsorbed CO on Pt electrode surface has a stronger blocking effect for the entrance of other specimen into the Pt surface[35]. The electrode covered by CO adsorbents should have larger impedance than the electrode covered by OH adsorbents. As mentioned above, the electrode is covered by CO adsorbents before the oxidation reaction occurs, and the electrode is covered by the OH adsorbents when the electrode potential is more than the peak P_{a1} potential. The EIS results in Figure 5 and 6 have confirmed our suggestion. It can be found that the semicircle obtained at 0.05V is larger than that obtained at 0.387V for 3M CH_3OH. Comparing the semicircle obtained at 0.1V with that obtained at 0.38V for 0.5M CH_3OH, it can be seen that the suggestion is also effective for the 0.5M CH_3OH. For the 0.05M CH_3OH the situation becomes different. The further intensive study is necessary.

Some literatures[17,23,24] have mentioned the hidden shoulder peak in the left side of the main oxidation peak, P_{a1s}. In 0.5M H_2SO_4+1M CH_3OH solution, a hidden shoulder peak can be found at a potential of about 0.1V vs. Hg/Hg_2SO_4[23]. This shoulder peak is not very clear when the methanol concentration and the scanning rate are relatively low. We contributed this hidden shoulder peak to a non-faradaic adsorption process of some

specimen, such as CH_3OH.

The reduction peak P_r is affected by the scanning rate and the methanol concentration, as showed in Figure 9 and Figure 2b. The peak current increased when the scanning rate increased or the methanol concentration decreased. The faster potential-scanning rate leads to a more negative peak potential. These phenomena imply that this reduction peak should represent an electrochemical process. It can be seen from Figure 1 that the reduction peak at about 0.02V represent the reduction of the formed Pt oxides/hydroxides. When there exists the methanol in the solution, the chemical reaction between Pt oxides/hydroxides and the methanol is not avoided to occur. So, the reduction peak current decreased and at last disappeared with the increased methanol concentration. In addition, the phenomenon that the reduction peak becomes clearer only in lower methanol concentration and at faster scanning rate may support that the (electro) reduction reaction kinetic of Pt oxides/hydroxides is a relatively fast.
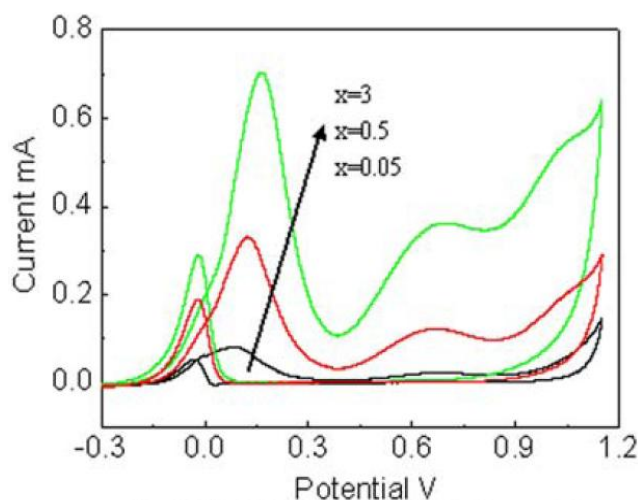

Figure 9 : The CV patterns of Pt electrode in 0.1M H_2SO_4+xM CH_3OH solution, the scanning rate is 1mV s^{-1}.

When the potential is more than 0.45V, the Pt oxides start to form on the Pt electrode surface. The occurring oxidation peaks in the potential range of more than 0.45V should be due to the electro-oxidation of methanol on the oxidized Pt surface[21]. Another possibility would not be excluded that these two oxidation peaks are also related with the two-step electro-oxidation reaction of surface Pt. The oxidation peak at 0.65~0.7V should correspond to the adsorption or electro-adsorption of some specimen, including SO_4^{2-}

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ions on the positively charged surface. The oxidation peak at about 1.05V, P_{a3}, is clear only when the methanol concentration is relatively high. In other words, the peak P_{a3} is related with the methanol concentration. It could be plausibly concluded that this oxidation peak may correspond to the adsorption or electro-adsorption process of some specimen.
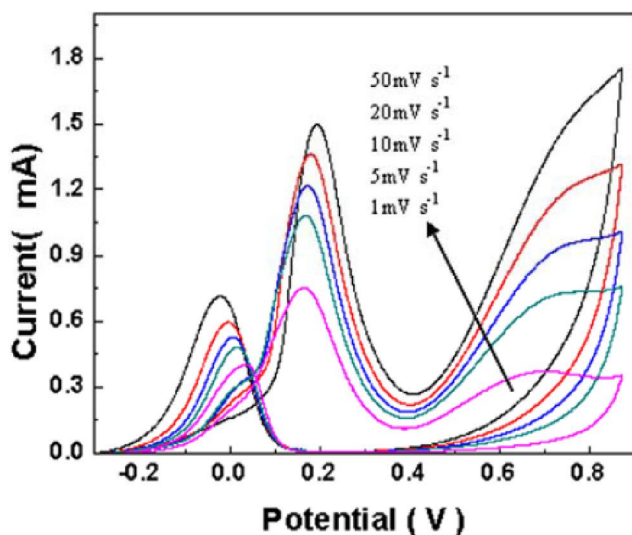

Figure 10 : The CV patterns of Pt in 3M CH₃OH+0.1M H₂SO₄ solution with a upper potential limit of 0.87V.
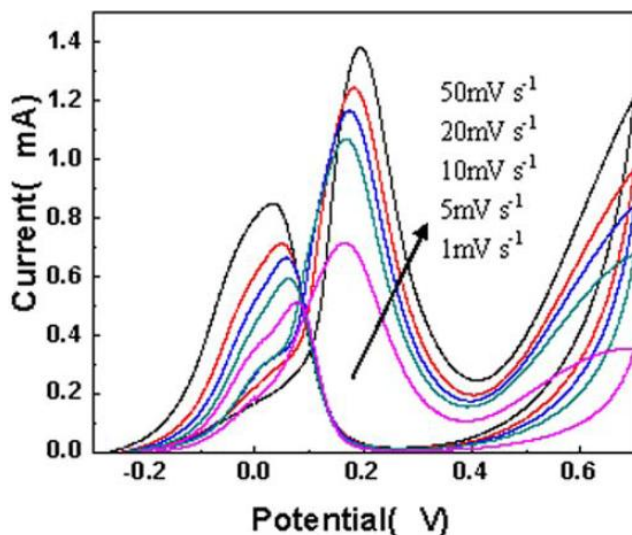
Figure 11 : The CV patterns of Pt in 3M CH₃OH+0.1M H₂SO₄ solution with a upper potential limit of 0.70V.

Gonzalez[34] has contributed the oxidation peak in the negative sweeping potential direction to the oxidation of the intermediates. Okamoto[33] has proposed that the oxidation peak in the negative sweeping potential direction is due to the reduction of the oxides existing on the Pt surface. This peak is dependent of the

potential-scanning rate (Figure 3a), the methanol concentration (see Figure 2a and Figure 9) and the upper potential limit (as seen in Figure 3b). In addition, the shape of this peak is somewhat same with the oxidation peak in the positive sweeping potential direction, P_{a1} and P_{a1s}. If this oxidation peak represents the oxidation of the intermediates or oxides existing on the Pt electrode surface, then its current and potential should be not influenced by the methanol concentration. To our opinion, this peak should represent the electro-oxidation of methanol on the free electrode surface. As the potential swept in negative potential direction from the potential upper limit, some chemical transformations should occur and at same time the OH desorption reaction does also occur, although there is no current peak being detected. At some potential point the electrode surface is free of any adsorbents. The free sites form on the blocked surface. As results, the methanol electro-oxidation reaction occurs on the free surface sites.
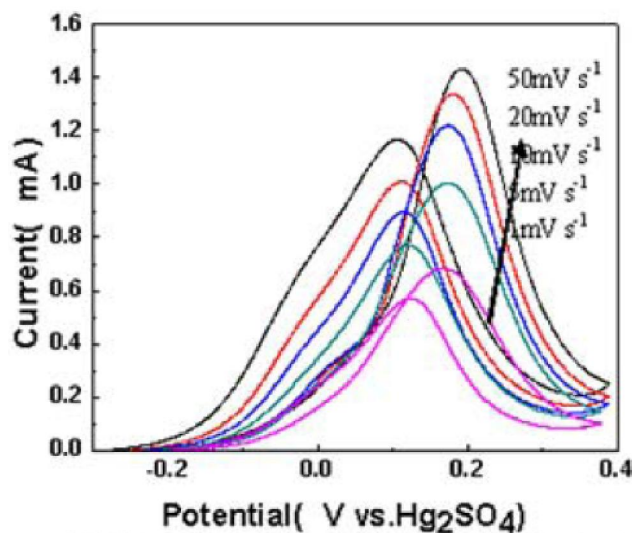
Figure 12 : The CV patterns of Pt in 3M CH₃OH+0.1M H₂SO₄ solution with a upper potential limit of 0.384V.

When the methanol concentration is relatively low (as seen Figure 4a) or the upper potential limit is 0.387V, the oxidation peak P_{ar} is slightly left-to-right symmetric. But when the upper potential limit is set up at more positive potentials or the methanol concentration increased, one obvious hidden shoulder peak appears on the left side of the main oxidation peak P_{ar}. Indeed, we can still find that this oxidation peak is not symmetric even at a lower methanol concentration or at 0.387V upper potential limit. The basement line current on the

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left side is larger than that on the right side. This hidden shoulder peak should have a same nature as the hidden shoulder peak P_{a1s}. Some literatures have mentioned the shoulder peaks and others did mention their existence. To our opinion, it represents an adsorption/desorption process of some organics or anions.

In the majority of literatures concerning the electrochemical impedance spectroscopies during methanol electro-oxidation, the real impedance keeps always a positive. In the literature[36], the negative real impedance has been reported when the potential was kept at a potential at which the first main oxidation peak P_{a1} manifests. In our experiments, the basic situation is same as that in the report[36]. From the Figure 5 and 6, the real negative impedance exists only the potential is near to the potential at which the methanol electro-oxidation reaction occurs. But the shape of the impedance spectrum is very sensitive to the applied potentials. This may be one of the main reasons why there exist plentiful electrochemical spatio-temporal structures in electro-oxidation system of small organic molecules[37,38].

From Figure 7, the average potential of the oscillatory curves is about 0.0V and the varying potentials position in the potential range where the first oxidation peak P_{a1} does also fall into. In addition, in the same potential range the negative real impedance manifest itself in the impedance spectrum. The oscillatory behavior should be directly related to the reaction (6). Before the first oscillation, the electrode is covered by the CO. However, the formation of OH will remove the adsorbed CO and leads to a larger current. But because of the galvanostatic constraint, the removal of CO will lead to the potential movement toward a more negative potential. At the potential maximum, the electrode is covered by the adsorbed OH species and at the potential minimum the electrode is covered by CO. After the first oscillation, the potential increased slowly up to about 0.2V for 3M CH_3OH (for the lower methanol concentration this value becomes slightly smaller), the second oscillation appears. The potential oscillates toward to more negative potential direction. In this case, the oscillation should be caused by the removal of the adsorbed OH by the CO species. The basic characteristic of the impedance spectrum is very sensitive to the applied potential. Such a phenomenon implies a more complicated oscillatory behavior. We contributed the

first oscillation to the removal of adsorbed CO by formed OH species and the second oscillation to the removal of adsorbed OH by formed CO species. The formation of the induction period, may be, can be explained as follows. After immerses into the solution, the CO adsorbent that formed via (electro) chemical reaction poisoned the electrode. After the anodic current was applied, the OH species starts to form, and the formed OH will react with the CO. in such case, the electrode surface is alternatively covered by CO or OH. As results, the oscillation starts to appear. The induction period depends on the formation rate of OH species.

CONCLUSION

In this article the methanol electro-oxidation reaction has been investigated in detail. One hidden shoulder peak followed by other three oxidation peaks has been detected in the positive sweeping potential direction and the corresponding peak potential is about 0.0V, 0.1~0.18V, 0.65~0.70V and about 1.05V vs. Hg/Hg_2SO_4 in 0.1M H_2SO_4+3.0M CH_3OH solution. The hidden shoulder peak at 0.0V is likely not to vary with the potential-scanning rates and contributed to the adsorption/desorption process of some organics. The formation of the main oxidation peak at 0.1~0.18V must be due to the formation of adsorbed OH species that formed at the increased potential. Other two oxidation peaks might represent the electro-oxidation processes occurring at the oxidized Pt surface, and might also correlate with th electro-oxidation reaction of metallic Pt. There exists an oxidation peak followed by a hidden shoulder peak in the negative sweeping potential direction. The existence of this hidden shoulder peak is influenced by the scanning rates, the upper potential limits and the methanol concentration. Lower methanol concentration, lower potential-sweeping rate and more positive potential upper limit leads to a disappeared shoulder peak. But the oxidation peak in negative sweeping potential direction is asymmetric.

The impedance obtained at the potentials where the first oxidation peak and the hidden shoulder peak appear in the positive sweeping potential direction has a negative real part. The impedance spectrum obtained in 0.05M CH_3OH solution is very sensitive to the outer-

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applied potentials. The galvanostatic potential oscillation has a frequency of 0.3~0.5Hz. The increase in the methanol concentration leads to larger oscillation amplitude, slightly increased frequency. It is also found that the increased current leads to the disappearance the first oscillation and appearance of the second oscillation. At too much larger or smaller currents the oscillatory behavior disappears. The parameter space in which the system may exhibit the unstable behavior is relatively small.

ACKNOWLEDGEMENTS

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