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Electrocatalytic Oxidation of Methanol and Formaldehyde on Platinum-Modified Poly(o-methoxyaniline)-Multiwalled Carbon Nanotube Composites

Qizhi Dong[*]*,Yanan Li,Liying Zhu,Tian Ma,Cancheng Guo*

School of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P.R.China
[*]E-mail: qzhdong67@163.com

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Poly(o-methoxyaniline)-multiwalled carbon nanotube (POMAN-MCNT) films are deposited onto Platinum (Pt) electrodesusing cyclic voltammetry (CV) methods. Pt nanoparticles are deposited onto the POMAN-MCNT film to form a Pt/POMAN-MCNTs coating under galvanostatic conditions. The morphology of the Pt/POMAN-MCNT composite film is characterized by scanning electron microscopy (SEM) and its electrocatalytic activity toward methanol and formaldehyde oxidation is investigated using CV techniques. Pt/POMAN-MCNTs composite film shows a much higher catalytic activity than Pt/POMAN film. The high activity is attributed to the unique self-crosslinked structure of the POMAN-MCNTs which shows high surface area and uniform distribution of Pt nanoparticles.

Keywords: poly (o-methoxyaniline): multi-walled carbon nanotubes; composite catalyst; electrocatalysis

1. INTRODUCTION

Proton exchange membrane fuel cells have been under intense development in the last decade for power generation and fuel conversion [1]. Among the different types of devices, direct methanol (CH_3OH) fuel cells (DMFCs) have attracted wide attention because of the abundant natural gas discovered recently. The key problem in DMFCs is the understanding and control of the methanol oxidation process[2]. Methanol can produce carboxyl species (such as carbon monoxide, CO) that strongly absorb on the active sites of the electrode surfaces of Pt electrode in the oxidation process, thus poisoning the electrode and decreasing the electrode conductivity [3]. In short, methanol oxidation is a complex process which involves multiple steps of dehydrogenation. Therefore, it is very important to find suitable catalysts for DMFCs[4]. In addition, formaldehyde (HCHO) is the intermediate product of methanol oxidation process[5]. Formaldehyde can be efficiently decomposed into small molecules and ions, such as proton and carbon dioxide. Therefore, the study of electric catalysis of formaldehyde is also important for the development of DMFCs.

The electrocatalytic properties are not only related to the catalyst itself, but also to the structures and chemistry of the support [6-8]. Pt particles supported on porous and high surface area conductive polymers have shown good catalytic properties [9]. Among these conductive polymers, polyaniline is attractive because of low cost, easy synthesis, high temperature stability, good oxidation resistance and high conductivity [10]. Polyaniline has been used as catalyst supports for platinum, palladium, ruthenium and other noble metal particles to obtain good catalytic performance. However, polyaniline also has some limitations, including large intermolecular resistance and poor conductivity. As a result, polyaniline derivatives are now studied to improve the conductivity and charge transport property.

In this paper, electrochemical polymerization is used to prepare a new poly o-methoxyaniline polymer support and its electrocatalytic properties are studied for methanol and formaldehyde oxidation. Multiwalled carbon nanotubes (MCNTs) are used to further improve the electronic conductivity[11-12]. Pt nanoparticles have unique electronic properties and high catalytic activity.In order to take advantage of their unique properties, porous poly(o-methoxyaniline) is combined with multiwalled carbon nanotubes as catalyst support to disperse Pt nanoparticles. The high surface area and good conductivity has significantly improved the electrocatalytic activity of the composite electrode[12-20].

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instruments

Chloroplatinic acid(H_2PtCl_6), o-methoxyaniline, methanol and formaldehyde were purchased from Sinopharm Chemical Reagent Co (China). Multiwalled carbon nanotubes (MCNTs) were obtained from Chengdu Organic Research Institute (China). All chemicals used in this paper were of analytical grade. Scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was used to characterize the morphology of the samples. Electrochemical workstation (Ingsens-3030, China) was from Smart instruments Guangzhou Co. A disk platinum electrode (working area $0.38cm^2$) was used as the working electrode. A large platinum mesh was used as the auxiliary electrode, and a saturated calomei electrode(SCE) as the reference electrode. All electrochemical measurements were carried out at room temperature. High purity nitrogen was introduced to the solutions for 20 minutes to remove oxygen from the solutions.

2.2 Functionalized Multiwalled Carbon Nanotubes

2.0g multiwalled carbon nanotubes was placed into 100ml mixture of concentrated nitric acid and sulfuric acid (1:3) and heated in a 60^oC water bath for 4 hours with stirring. The above black solution was diluted with de-ionized water, then filtered. The powders from above steps were washed with de-ionized water until the pH value of the washing water was about 7.0. Finally the functionalized multiwalled carbon nanotubes were obtained by drying above washed powders[22].

2.3 Synthesis of POMAN-MCNTs film and Pt/POMAN-MCNTs composite films

20 mg functionalized multiwalled carbon nanotubes and 5ml o-methoxyaniline were placed into a 25ml round bottom flask, which was covered from light and refluxed at 225°C for 4 hours. When the color of the mixture changed from light red to black, the solution was cooled to room temperature. Then the powder was separated from the solution by centrifugation. 1.5ml supernatant was removed and placed into a 50ml flask and diluted with H_2SO_4 solution (0.5mol/L) to 50ml. The above prepared solution was placed into a three electrode reaction tank. Poly-o-methoxyaniline/multi-walled carbon nanotube (POMAM-MCNT) composite film was produced by scanning CV over 10 cycles from -0.2 to -0.9 V with scanning rate of 10mV/s. The composite film was placed into a mixture of chlorophatinic acid(0.002mol/L(H_2PtCl_6) and 0.5mol/L(H_2SO_4)) solution for 15 minutes. Platinum ions could be uniformly absorbed onto the POMAN-MCNTs film. Pt-/POMAM-MCNTs were synthesized by a galvanostatic CV method using -0.25V deposition potential and 800 seconds deposition time. Assuming 100%columbic efficiency, the amount of Pt deposited was estimated to be 110 mg/cm^2[23]. The electrocatalytic activities were studied in a 1mol/L methanol and 0.5mol/L sulfuric acid solution and a 1mol/L formaldehyde and 0.5mol/L sulfuric acid solution respectively using CV methods (0 to -1V potential range, 10mV/s scanning rate).

3. RESULTS AND DISCUSSION

3.1 Synthesis of POMAM-MCNTs

In order for the Pt particles to have good catalytic properties, the polymer support needs to have good conductivity for fast charge transport, as well as stable porosity to disperse the Pt particles. It has been shown that the same polymer can have different surface structures under different synthetic conditions [24]. The POMAN-MCNT composite film studied in this paper is prepared using CV method after 10 cycles. Figure 1 shows the CV curve of the composite in a 0.325 mol/L o-methoxyaniline and 0.5 mol/L H_2SO_4 mixed solution from -0.2 to -0.9 V using a 10 mV/s scanning rate. As illustrated in Figure 1, the first positive scan from -0.2 V only shows a broad oxidation peak around -0.7 V. This is consistent with the polymerization of o-methoxyaniline and suggests that formation of the free o-methoxyaniline cations and the onset of the polymerization process. Three pairs of well-defined redox peaks are observed during the second scan. The first oxidation peak appears at 0.22 V, corresponding to the oxidized radical cations of the completely reduced polymer. The third oxidation peak appears at 0.6 V, corresponding to the completely oxidized polymer. The 0.4 V peak in-between gradually increases with cycle number due to the self-catalyzed reaction once the film is formed. This suggests that the POMAN film is electrochemically active. The final POMAN-MCNTs have a dark-green color [25, 26]. The CV curves show that the three redox peaks increase uniformly with cycling, suggesting that the film has good conductivity and activity, as well as homogeneous structure [27]. The film thickness is determined by the number of cycles and is estimated to be 0.25 μm by integrating the first peak intensity [28].

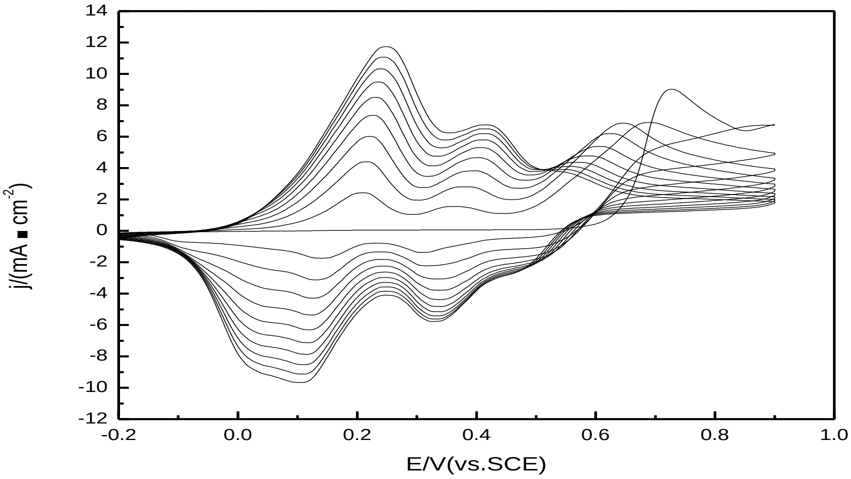
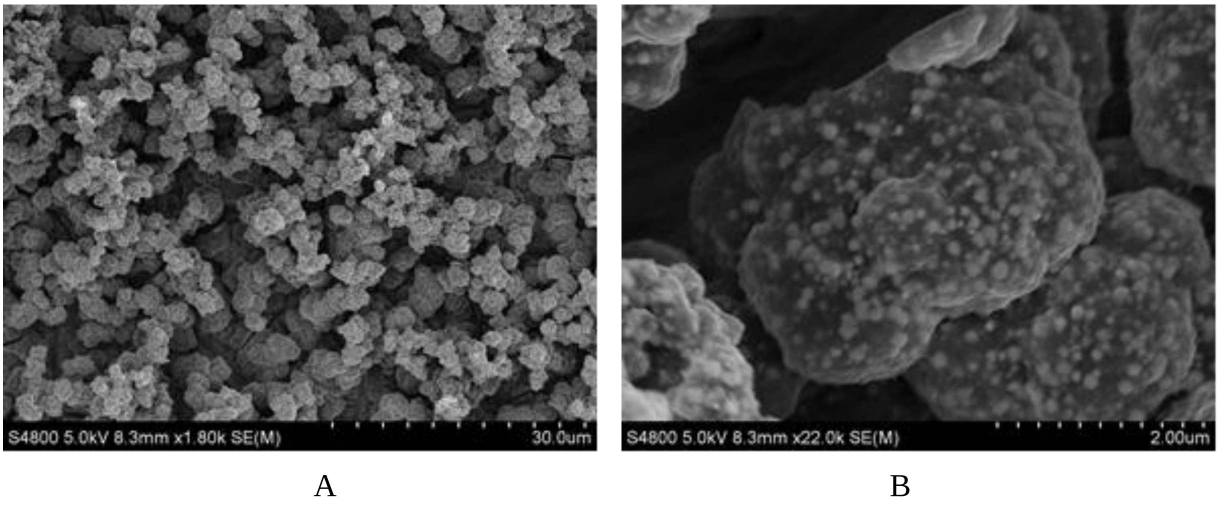


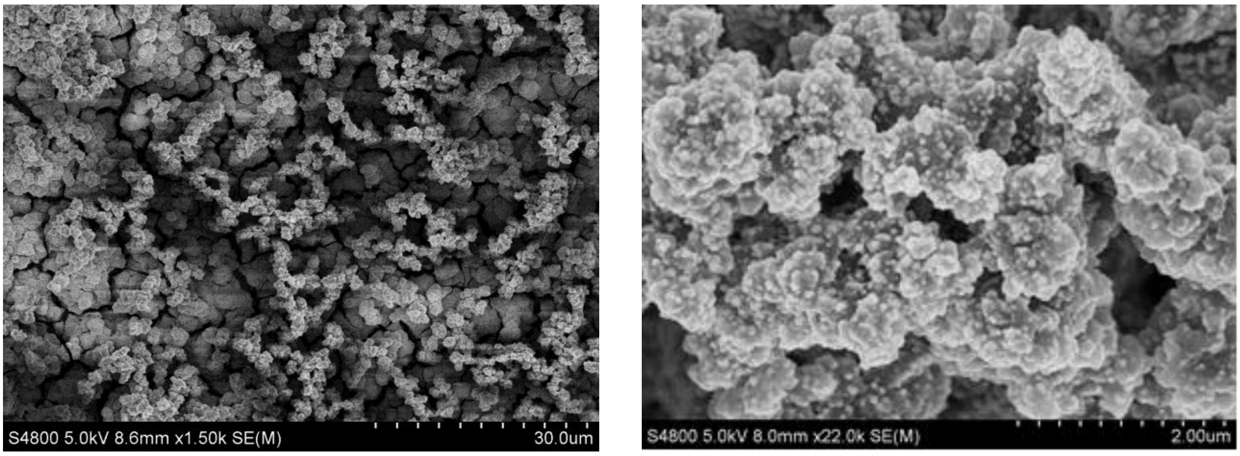
Figure 1. Cyclic voltammograms of 2-methoxyaniline（MCNTs）electrochemical polymerization on Pt electrode

3.2 SEM Images of Pt/POMAN Film and Pt/POMAN-MCNT Film

Figure 2 gives the SEM images of the Pt/POMAN film and the Pt/POMAN-MCNT film at different magnifications. The Pt/POMAN-MCNT film contains fine features and smaller particles. In particularly the Pt/POMAN film shows a smooth surface and the Pt/POMAN-MCNT film has a rough surface. The rough surface and fine features suggest a more porous and open structure. This unique structure can effectively increase the interfacial area between the Pt and the polymer, and more Pt nanoparticles can be deposited, therefore increasing the deposition density of Pt nanoparticles.



A B



C D

Figure 2. SEM images of the Pt-modified POMAN film(a)、（b）and the Pt-modified POMAN-MCNT film（c）、（d）

The high interfacial area also facilitates the charge transfer between the Pt particles and the electrodes, making electrochemical reactions more feasible. Therefore, Pt/POMAN-MCNT film has a better conductivity and a higher surface area for Pt nanoparticles deposition due to addition of multiwalled carbon nanotubes.

3.3 Electrocatalytic Oxidation of Methanol

Figure 3 shows the CV curves of POMAN (a), Pt/POMAN (b) and Pt/POMAN-MCNT (c)electrodes in 1mol/L CH_3OH and 0.5 mol/L H_2SO_4 electrolytes. The curves for POMAN in the electrolytes with and without methanol are similar, indicating that POMAN has no catalytic activity. From (b) and (c), the methanol oxidation peaks for Pt/POMAN-MCNTs appeared at 0.63V and 0.47V, which shifted by -30mV and -20mV respectively compared with those of the Pt/POMAN electrode. In addition, the peak current density of Pt/POMAN-MCNTs electrode is about 6 times larger than that of Pt/POMAN electrode. We suggest that methanol molecules absorbed on the electrode surface is first dehydrogenated at a low potential. The proton and water molecules incorporated in POMAN-MCNT film at a low potential greatly accelerated the complete dehydrogenation of formaldehyde on the Pt surface. At the same time, the proton and water molecules in the film increase the absorption of the oxygen containing species. The carboxyls react with the oxygen containing species to produce CO_2. As a result, POMAN/MCNTs accelerate the CO to CO2 reaction, mitigate the poisoning of the electrode surfaces, and cause the negative shift of the redox potentials.

According to previous studies [29,30], the methanol oxidation reaction is a multi-step dehydrogenation complex reaction. The possible reaction mechanism is:

$$Pt+(CH_3OH)_{sol} \rightarrow Pt\text{-}(CH_3OH)_{ads} \qquad (1)$$

$$Pt\text{-}(CH_3OH)_{ads} \rightarrow Pt\text{-}(CH_2OH)_{ads}+H^{+}+ e \qquad (2)$$

$Pt\text{-}(CH_2OH)_{ads} \rightarrow Pt\text{-}(CHOH)_{ads} + H^+ + e$ (3)

$Pt\text{-}(CHOH)_{ads} \rightarrow Pt\text{-}(COH)_{ads} + H^+ + e$ (4)

$Pt\text{-}(COH)_{ads} \rightarrow Pt\text{-}(CO)_{ads} + H^+ + e$ (5)

$Pt + H_2O \rightarrow Pt\text{-}(OH)_{ads} + H^+ + e$ (6)

$Pt\text{-}(CO)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow CO_2 + 2Pt + H^+ + e$ (7)

The overall reaction is： $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$ (8)

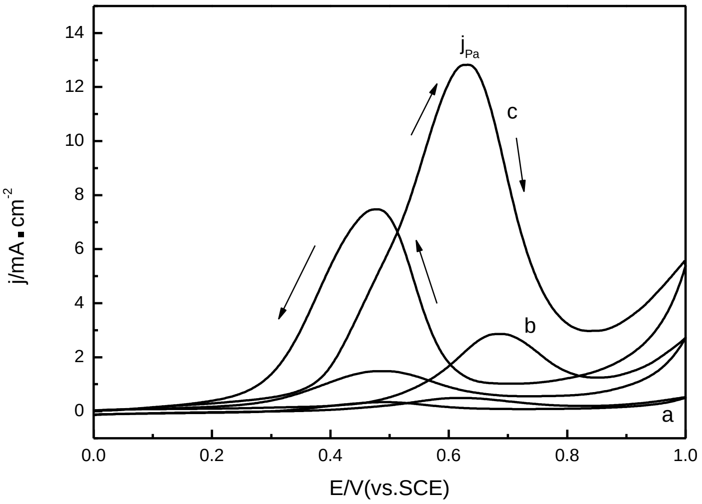


Figure 3. Cyclic voltammograms of methanol oxidation on POMAN(a), Pt/POMAN（b）and Pt/POMAN-MCNT（c）film electrodes

3.4 Effect of Cycle Numbers and POMAN Film Thickness

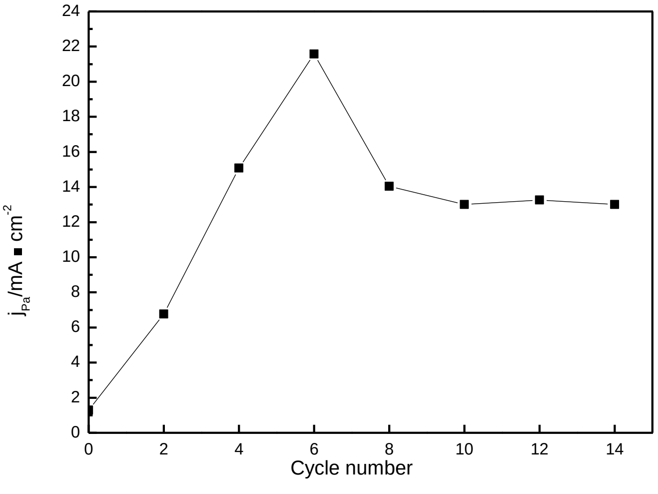


Figure 4. Effect of the thickness of the film on peak current density of methanol oxidation

Figure 4 shows the methanol oxidation peak current density (j_{Pa}) on a Pt/POMAN-MCNT electrode with different POMAN thickness at a fixed potential (-250 mV) in a 1mol·L^{-1} CH_3OH and 0.5 mol·L^{-1} H_2SO_4 electrolyte solution. The POMAN thickness is determined by the cycle number during electrochemical deposition. As illustrated, when thickness of POMAN film increases from 0 to 6 laps, j_{Pa} increases from 1.4 mA/cm^2 to 21.8mA/cm^2; after reaching the maximum value at 21.8mA/cm^2, j_{Pa} decreases rapidly to 14mA/cm2 when thickness of POMAN film increases from 6 to 10 laps, indicating a decrease in electrocatalytic activity. The decrease could be attributed to three factors: (1) an increase in electrical resistance due to the increase of the thickness; (2) a poorer dispersion of the catalyst particles; and (3) a less uniform structure of the POMAN film.

3.5 Effect of Deposition Potential of Pt Particles

The deposition potential directly determines the growth rate and the final morphology of Pt nanoparticles which can give different electrocatalytic activities. Figure 5 shows the relationship between different Pt deposition potential and methanol oxidation peak current density (j_{Pa}) with the same film thickness. j_{Pa} increases when the deposition potential is negatively shifted and reaches the maximum 13mA/cm^2 at around -250mV. After that j_{Pa} decreases rapidly. We suggest first when the deposition potential is shifted negatively, more Pt particles are deposited, so that the total active area of Pt particles also increases quickly, resulting an increase of the total catalytic activity. However, as the particle growth rate increases and more particles are deposited, the particles also begin to agglomerate and overlap, decreasing the specific active area of the catalyst thus the methanol oxidation activity.

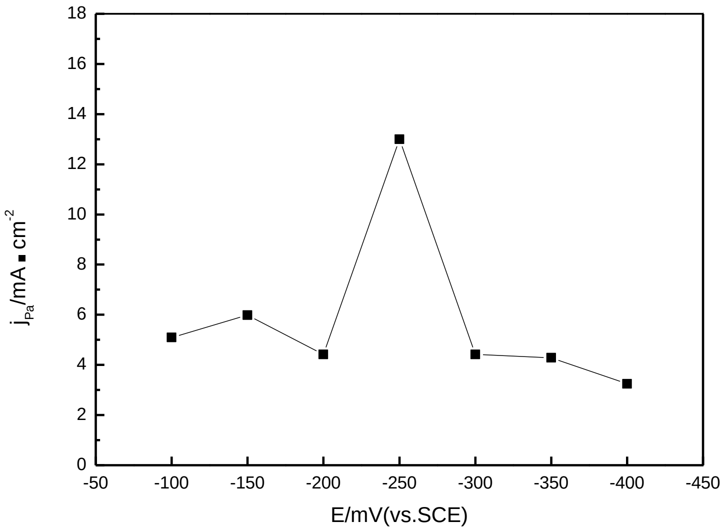


Figure 5. Effect of deposition potential on peak current density of methanol oxidation

3.6 Study of Electrocatalytic Activity of Formaldehyde

Figure 6 shows the CV curves of Pt modified POMAN composite film (a) and Pt modified POMAN-MCNT composite film (b) in a 1mol/L HCHO and 0.5mol/L sulfuric acid electrolytes. As illustrated in curve (a), an anodic peak appears at 0.72V corresponding to the oxidation process of carbon oxide to carbon dioxide on the surface Pt particles in positive scanning. On the other hand, an anodic peak appears at 0.34V corresponding to complete HCHO oxidation to carbon dioxide on Pt particles. The reaction is accomplished through a dehydrogenation reaction ($HCHO + H_2O \rightarrow CO_2 + 4H^+ + 4e$) [31]. Comparing with curve (a), curve (b) shows a slightly higher redox potential and a much higher peak current. An oxidation peak for formaldehyde can be observed at 0.68V in positive scan and a sharp oxidation peak appears at 0.36V in negative scan. In particular, j_{Pa} in curve (b) is 3.5 times bigger than that in curve (a). From above discussion, it can be conclude that formaldehyde is more likely to be oxidized on the Pt modified POMAN-MCNTs composite film. Furthermore, the introduction of MCNTs can benefit the dispersion of Pt particles on POMAN-MCNTs composite film. As a result, Pt modified POMAN-MCNTs composite films has larger surface area and more active sites to catalyze the oxidation of small organic molecules. In addition, the electrocatalytic reaction likely occurs between the substrate and the dispersed Pt particles. MCNTs can greatly promote the electron transfer through the films. In short, the POMAN-MCNT composite film modified by Pt particles has higher electrocatalytic activities.

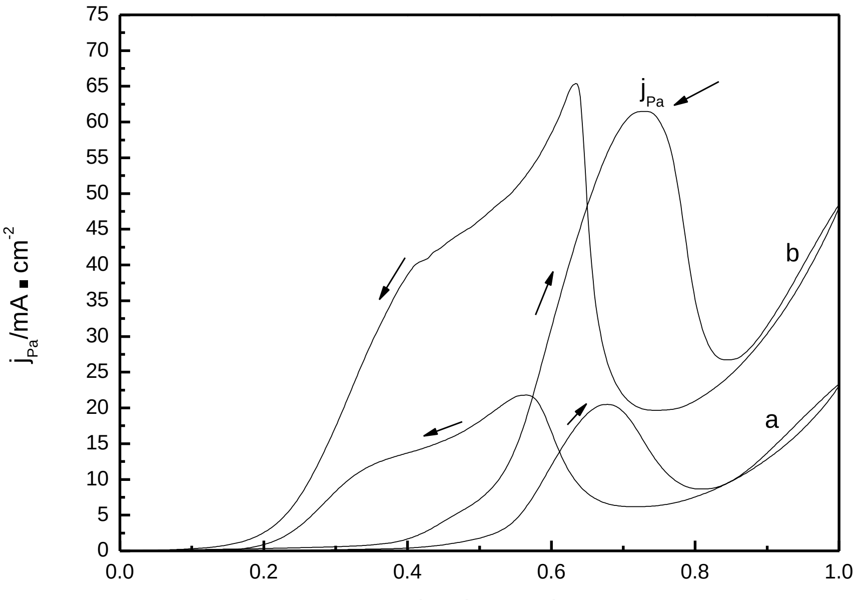


Figure 6. The potential cyclic voltammograms of electrooxidation of formaldehyde at (a) Pt-modified POMAN film electrode and(b) Pt-modified POMAN-MCNTs composite film electrode in 1 mol/L HCHO and 0.5 mol/L H_2SO_4(vs.SCE)

3.7 Long Term Stability Study of Electrocatalytic Oxidation of Formaldehyde

For practical application, the electrode stability is important. The long-term stability of Pt modified POMAN composite films and Pt modified POMAN-MCNTs composite films are investigated in 1 mol/L HCHO and 0.5mol/L sulfuric acid electrolyte. As shown in Figure 7, the positive peak current density j_{Pa} of Pt modified POMAN films gradually decrease with continuous scanning with more than 80% degradation after 1800 cycles. This is likely due to the Pt surface poisoning by small organic molecules generated during the electrochemical reaction or due to POMAN degradation in the electrolyte. On the other hand, the Pt/POMAN-MCNTs film has much higher activity and better long-term stability after addition of MCNTs with only 20% degradation after 1800 cycles. In addition, after the long cycling and subsequent storage in pure water for more than two weeks, Pt/POMAN-MCNT electrode retains high catalytic activity for formaldehyde oxidation. As we all know, during formaldehyde oxidation, some carbon oxide intermediate reaction products can be strongly absorbed on the electrode and poisoning the catalyst. However, the specific surface architecture of Pt/POMAN-MCNTs composite film reduces the formation of such surface poisoning species, therefore improves the catalytic properties.

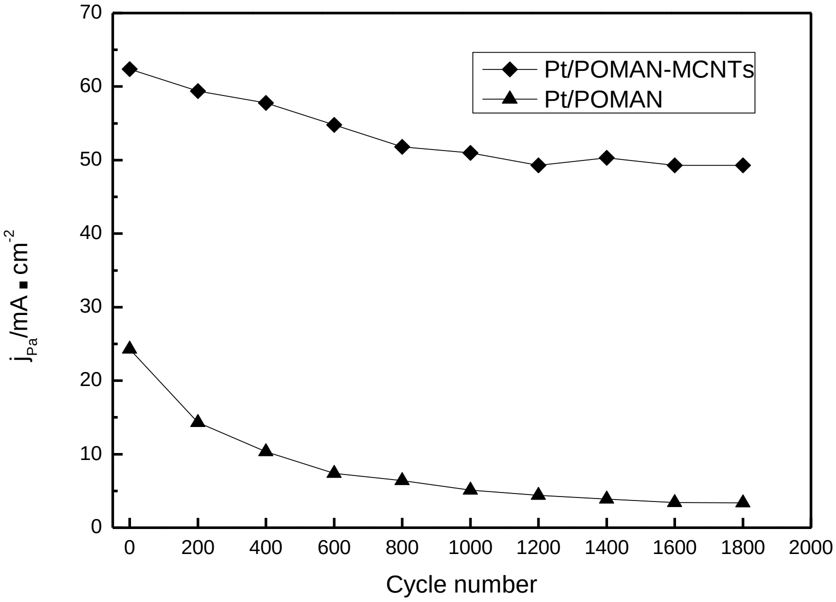


Figure 7. Long-term stability of the electrodes in 1mol/LHCHO and 0.5mol/LH_2SO_4 (Scan rate: 10mV/s)

4. CONCLUSION

In this paper, Pt modified POMAN-MCNT composite films are synthesized through electrochemical polymerization from o-methoxyanilline solution containing multi-walled carbon nanotubes. Pt nanoparticles are deposited on the Pt-modified POMAN-MCNT composite films. SEM results show that POMAN-MCNT composite films have a more open structure and the large surface area facilitated the uniform dispersion of platinum nanoparticles. Pt/POMAN-MCNT composite films have much higher electrocatalytic activity and better long term stability for methanol and formaldehyde oxidation.

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