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Effect of surface activation treatment on Pt/C catalyst for electrooxidation of ethylene glycol and adsorbed CO

Bing Wu[a,b], Ying Gao[b], Guichun Li[b], Weili Qu[b], and Zhaohua Jiang[a,*]

[a]*Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, P. R. China*
[b]*Department of Chemistry, Harbin Normal University, Harbin 150080, P. R. China*

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It was reported for the first time that the electrocatalytic activity of the Pt/C electrode for the oxidation of ethylene glycol (EG) could be dramatically improved after the new surface treatment of the Pt/C electrode. It was also found that the surface treatment of the Pt/C electrode could greatly promote the electrooxidation of CO adsorbed on the Pt/C electrode. Promoting the electrooxidation of CO would lead to the acceleration of the electrooxidation of EG because CO is an intermediate product of the oxidation of EG and it would be strongly adsorbed on the Pt catalyst, leading the poison of the Pt/C catalyst.

1. Introduction

Usually, methanol is used as the fuel in the direct methanol fuel cell (DMFC). However, methanol as the fuel in DMFC has some disadvantages. For example, it is toxic and inflammable. In addition, it is easy to permeate the proton exchange membrane causing a decrease in the cathode performance. Therefore, ethanol [1–3], acetaldehyde [4], EG [5,6] and other alcohols [7] have been considered and investigated as alternative fuels. However, the electrooxidation performances of these possible alternative fuels are lower than that of methanol. Among these alternative fuels, EG is an interesting candidate mainly because both the toxicity and permeableness through the membrane for EG are much less than methanol.

Pt is a good catalyst for the alcohol electrooxidation, but it is very easy to be poisoned by an intermediate product of alcohol oxidation, CO [8]. In order to solve this problem, the Pt based complex catalysts, such as Pt–Ru [9,10], Pt–Sn [11], Pt–WO_x [12] and Pt–TiO_2 [13] are used as the anodic catalysts because they possess a high electrocatalytic activity for the alcohol oxidation and high CO tolerant ability. This paper reported a new way to solve the CO poisoning problem and thus to increase the electrocatalytic activity for the oxidation of EG at the Pt/C electrode. It was found in this paper that after the Pt/C electrode is pretreated with the mixture solution containing tetrahydrofuran(THF) and acetone, the electrocatalytic activity for EG oxidation and the CO tolerant ability of the Pt/C electrode could be greatly increased.

* To whom correspondence should be addressed.
E-mail: jiangzhaohua@hit.edu.cn

2. Experimental

The carbon supporter is Vulcan XC-72 carbon black (Cabot Co.). Teflon suspension was supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. CO (99.99%) and N_2 (99.99%) were purchased from Northeast Special Gas Co and Nanya Gas Co., respectively. All the other chemicals were analytical grade. All the solutions were prepared with triply distilled water.

The 20 wt% Pt/C catalyst was prepared according to reference [14]. The Pt/C electrode was prepared as follows. The Pt/C catalyst prepared was dispersed into ethanol and the slurry obtained was sonicated for 5 min. Then, a certain amount of 5 wt% of Teflon suspension and Nafion solution was added to the slurry. Finally, the slurry was spread on the carbon paper, followed by drying at the room temperature in the air. The apparent surface area of the Pt/C electrode obtained was 0.5 cm^2. The Pt loading in the catalyst layer was about 1 mg/cm^2.

The Pt/C electrode was treated with the mixture solutions of THF and acetone (1:4 in volume) for 5 min and then the electrode was washed with triply distilled water in order to clean the organic solvent. After the treatment, the Pt/C electrode was activated with cyclic voltammetric method in the 0.5 M H_2SO_4 solution for five cycles between −0.1 and 1.3 V.

All the electrochemical measurements were carried out with a Model PARC 273A Potentiostat/Galvonostat and a three-electrode electrochemical cell. The working electrode was the Pt/C electrode prepared. A Pt mesh and a KCl-saturated Ag–AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrolyte was the 0.5 M H_2SO_4 solution with 1.0 M EG or the 0.5 M Na_2SO_4 with 1.0 M EG.

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Oxygen was purged with bubbling the highly purified N_2 for 20 min before the electrochemical measurements. In order to measure the electrochemical behavior of the adsorbed CO (CO_{ads}, CO was bubbled into the solution for 10 min to allow complete adsorption of CO onto the Pt/C catalyst. CO dissolved in the electrolyte was purged out with highly purified N_2 for at least 10 min. All the experiments were carried out at the room temperature and the potential sweep rate is 10 mV/s.

3. Results and discussion

Figure 1 shows the cyclic voltammograms of 1.0 M EG in the 0.5 M H_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment. It can be observed from figure 1, curve a that in the positive scan direction, an anodic peak for the EG oxidation is located about 0.80 V and the peak current density is 27 mA/cm^2. The onset oxidation potential is at about 0.50 V. After the Pt/C electrode is treated, two anodic peaks at about 0.55 and 0.82 V were observed (figure 1, curve b). Their peak current densities are 32 and 112 mA/cm^2, respectively. The onset oxidation potential is at about 0.40 V, which is 100 mV more negative than that at the untreated Pt/C electrode. The potential of the first peak at 0.55 V is 250 mV more negative than that at the untreated Pt/C electrode. Even the potential of the second peak is only 20 mV more positive than that at the untreated Pt/C electrode. In addition, the current density of the first peak is little bit larger and the current density of the second peak is four times larger than that at the untreated Pt/C electrode. All the above results indicated that the electrocatalytic activity of the Pt/C electrode for EG oxidation in the H_2SO_4 solution is dramatically improved after immersing the Pt/C electrodes in the solution of THF and acetone. The reason for it is not clearly understood. Possibly, immersing the Pt/C electrodes in the solution of THF and acetone can remove the impurity, such as the surfactant from Teflon suspension leading to a decrease in ohmic resistance. It could also be the outcome of the increase in the active sites as the result of the certain change in the Nafion structure during the immersion process.

It was observed from figure 1 that in the negative scan direction, a sharp anodic peak of EG at the untreated Pt/C electrode is located at 0.57 V (figure 1, curve a), but four peaks appear at the treated Pt/C electrode (figure 1, curve b). This phenomenon is usually called as the current oscillations, though the exact reason causing current oscillations in this experiment is unclear. Strasser et al. [15] have emphasized that if there exists some potential interval characterized by a negative differential resistance $Z_F = dI/d\varphi$ and a sufficiently large ohmic resistance, R, which fulfills the condition $R > |Z_F|$, the current oscillations would accrue [9]. The surface treatment of the electrode can remove the impurity, such as the surfactant from Teflon suspension. Thus, it may reduce Z_F and meet the above conditions, leading the occurrence of the current oscillations.

Figure 2 shows the cyclic voltammograms of 1.0 M EG in the 0.5 M Na_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment. In the positive scan direction in figure 2, curve a, an anodic peak for the EG oxidation is at about 0.76 V and the peak current density is 20 mA/cm^2. The onset oxidation potential is at about 0.44 V. After the Pt/C electrode is treated (figure 2, curve b), a main anodic peak is located at 1.0 V and a shoulder peak is at about 0.50 V. Their peak current densities are 90 and 27 mA/cm^2, respectively. The onset oxidation potential is at about 0.22 V, which is 220 mV more negative than that at the untreated Pt/C electrode. The potential of the shoulder peak is 260 mV more negative than that at the untreated

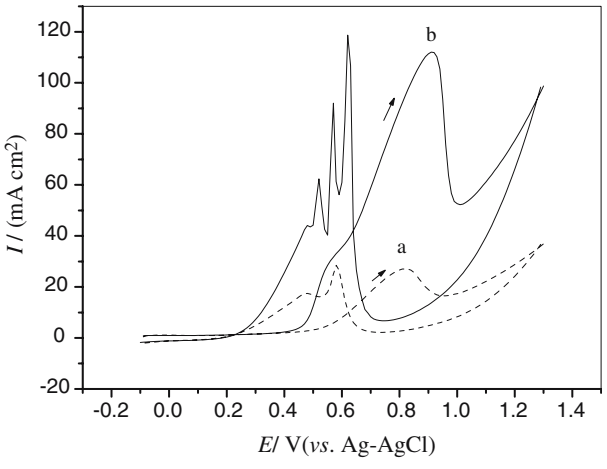

Figure 1. The cyclic voltammograms of 1.0 M EG in the 0.5 M H_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment.

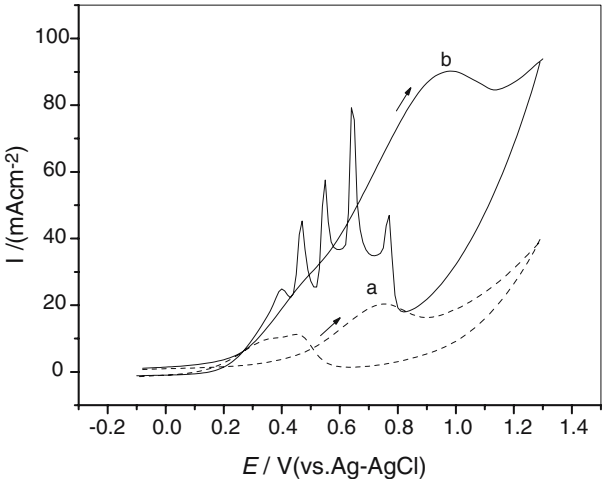

Figure 2. The cyclic voltammograms of 1.0 M EG in the 0.5 M Na_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment

Pt/C electrode. However, the potential of the main peak is 240 mV more positive than that at the untreated Pt/C electrode. Although the current density of the shoulder peak is 7 mA/cm^2 larger than that at the untreated Pt/C electrode, the current density of the main peak is 4.5 times larger than that at the untreated Pt/C electrode. All the above results indicated that the electrocatalytic activity of the Pt/C electrode after the surface treatment for EG oxidation in the Na_2SO_4 solution is also much higher than that of the Pt/C electrode before the surface treatment.

For the untreated Pt/C electrode, no obvious current oscillation was observed (figure 2, curve a). However, the current oscillations also appear in the negative scan direction at the treated Pt/C electrode as in the H_2SO_4 solution.

Figure 3 shows the linear sweeping curves of CO_{ads} in the 0.5 M H_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment. It is found from figure 3, curve a that the potential of the anodic peak of CO_{ads} is at 0.62 V and the onset potential of the CO_{ads} oxidation is about 0.54 V at the untreated Pt/C electrode. While the potential of the anodic peak of CO_{ads} and the onset potential of the CO_{ads} oxidation are 0.53 V and 0.43 V, respectively, at the treated Pt/C electrode (figure 3, curve b). It means that the potential of the anodic peak of CO_{ads} and the onset potential of the CO_{ads} oxidation at the treated Pt/C electrode are negatively shifted to 90 and 110 mV comparing with that at the untreated Pt/C electrode. It indicated that the surface treatment could promote the electrooxidation of CO_{ads} at the Pt/C electrode in the H_2SO_4 solution.

Figure 4 shows the linear sweeping curves of the adsorbed CO in the 0.5 M Na_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment. The potential of the anodic peak of CO_{ads} and the onset potential of the CO_{ads} oxidation are 0.64 V and 0.35 V, respectively, at the untreated Pt/C electrode in the Na_2SO_4 solution (figure 4, curve a), while they are negatively shifted to 0.49 and 0.10 V, respectively, at the treated Pt/C electrode (figure 4, curve b). These results illustrated that the surface treatment could also promote the electrooxidation of CO_{ads} at the Pt/C electrode in the Na_2SO_4 solution.

The above results indicated that electrooxidation of CO_{ads} at the treated Pt/C electrode is easier than that at the untreated Pt/C electrode either in acidic or in neutral solution. It illustrated that the surface treatment could create some new active centers at the Pt/C electrode to weaken the absorption strength of CO. CO is an intermediate product of the oxidation of EG and can be strongly adsorbed on Pt, leading to the poisoning of the Pt catalyst [16]. Therefore, the surface treatment can increase the electrocatalytic activity of the Pt/C catalyst for the EG oxidation mainly due to the surface treatment that could promote the electrooxidation of CO_{ad}.

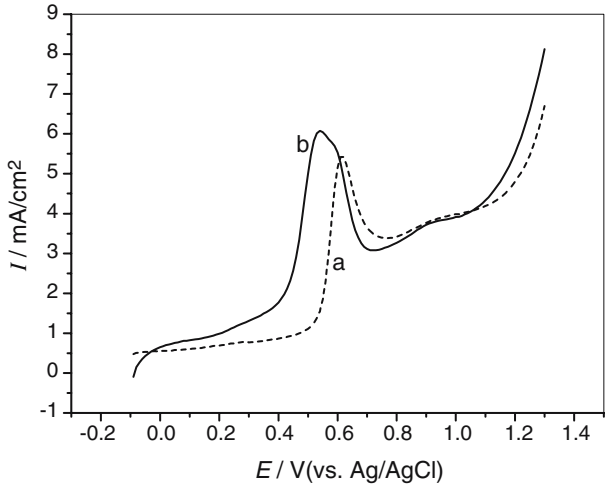

Figure 3. The linear sweeping curves of the adsorbed CO in the 0.5 M H_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment.

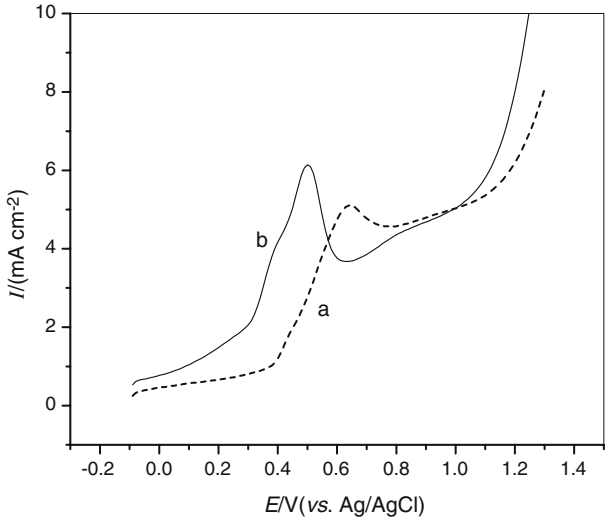

Figure 4. The linear sweeping curves of the adsorbed CO in the 0.5 M Na_2SO_4 solution at the Pt/C electrode (a) before and (b) after the surface treatment.

4. Conclusions

The above results showed that after the Pt/C electrode is immersed in the solutions of THF and acetone, the electrocatalytic activity of the Pt/C catalyst for the EG oxidation can be increased in the acidic and neutral solution. It is mainly due to that the surface treatment can promote the electrooxidation of CO_{ad}, which is an intermediate product of the oxidation of EG and can be strongly adsorbed on Pt, leading to the poisoning of the Pt catalyst. The above results are caused by the surface treatment that could remove the impurity, such as the surfactant from Teflon suspension leading to a decrease in ohmic resistance. In addition, it could also be the outcome of an increase in the active sites as a result of a

certain change in the Nafion structure during the immersion process.

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