

Ethanol electrooxidation on Pt/ZSM-5 zeolite-C catalyst

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Abstract The electrooxidation of ethanol on Pt/ZSM-5 zeolite-C catalyst was investigated in sulfuric acid aqueous solution. Because of high stability in general acidic solution, ZSM-5 zeolite particles were selected as the support and the second catalyst. The micrograph and elemental composition of Pt/ZSM-5 zeolite particles were characterized by scanning electron microscopy and energy disperse X-ray spectroscopy. The electrocatalytic properties of Pt/ZSM-5 zeolite-C catalyst for ethanol oxidation have been investigated by cyclic voltammetry. Under the same Pt-loading mass and experimental conditions for ethanol oxidation, Pt/ZSM-5 zeolite-C catalyst shows higher activity than Pt/C catalyst. Additionally, Pt/ZSM-5 zeolite-C catalyst possesses good long-term cycle stability. The results indicate that Pt/ZSM-5 zeolite-C catalyst may have good potential application in direct ethanol fuel cell.

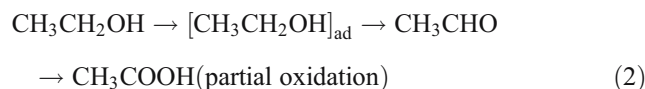
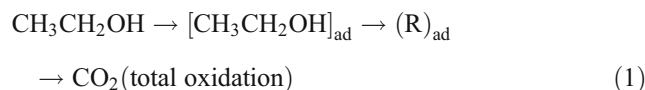
Keywords Ethanol electrooxidation · ZSM-5 zeolite · Electrochemical properties · Electrocatalyst

Introduction

In the past two decades, great attention has been paid to the fuel cell because of its high energy conversion efficiency and environmental affinity. Generally, methanol is considered the most promising as alternative fuels for electrochemical energy conversion [1]. And much effort is being devoted to the study of direct methanol fuel cell [2, 3].

However, some disadvantages of methanol, such as toxicity and an easier crossover through proton exchange membranes, cannot be avoided [4, 5]. Compared with methanol, ethanol has many merits: less toxic, better stability, lower permeability across proton exchange membrane, and higher energy density ($1,325.31 \text{ kJ mol}^{-1}$) at room temperature than that of methanol ($702.32 \text{ kJ mol}^{-1}$) [4, 6]. Several papers have been addressed on the electrooxidation of ethanol [7–9].

In view of its added complexity and application prospects, fundamental study for the electrooxidation of ethanol is important. The investigation for anodic catalyst in direct ethanol fuel cell (DEFC) is focused on the development of a catalyst system, which is able to break C–C bond and oxidize the poisoning intermediates (such as CO_{ads}) from ethanol oxidation at lower temperature and overpotential. Based on the foregoing work, the oxidation mechanism of ethanol in acidic solution may be summarized in the following scheme of parallel reactions:



in which $(\text{R})_{\text{ad}}$ represents the adsorbed intermediate on the electrode. It is reported that only CO_2 was detected during the oxidation of preadsorbed ethanol [4, 10]. This observation suggests that CO_2 is formed through a strong chemisorbed intermediate $[(\text{R})_{\text{ad}}]$, whereas acetaldehyde, ect. is formed through a weakly adsorbed ethanol intermediate.

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Platinum is usually considered as the best single metal to adsorb organic molecules and break intermolecular bond [11–13] and has been used as anode electrocatalysts [14, 15]. However, the process of ethanol oxidation shows slow dynamics and Pt electrocatalyst will be poisoned by the intermediates produced during the oxidation processes of ethanol oxidation, such as CO_{ads} [9, 16]. The development of new catalysts is particularly important for DEFC. Nowadays, it has been proven that the addition of a second catalyst is an effective way to promote the cleavage of the C–C bond and accelerate the ethanol oxidation [17, 18]. Other metals in Pt-based alloy (such as PtRu [9], PtSn [16], PtRh [7], and PtSnNi [19]) and oxides (such as PtMgO [20], PtCeO₂ [21, 22], AuFe₂O₃ [23], PdAl₂O₃ [24], and PtSiO₂ [6]) were reported as the second catalyst. Besides, to investigate newer support material rather than Vulcan XC carbon or acetylene black is also very important for DEFC. Thus, carbon nanotubes have been investigated as catalyst supports for Pt–Ru catalysts and excellent electrocatalytic properties for anodic oxidation of ethanol have been reported [25].

It is well known that a large number of oxides can promote Pt for oxidation of methanol. Hamnett et al. [26] reported that the addition of metal oxides was an effective way to accelerate the methanol oxidation. Zeolite, which is mainly composed of silicon–aluminum oxides, is found to be an efficient support in methanol oxidation when incorporated with metal groups that consist of Pt, Pd, Ru, Au, Rh, and Ir [27]. The zeolite material contains acidic protonic entities on its surface, which makes it more hydrophilic than carbon. When used as a catalyst support in fuel cell electrode, it results in lower resistance and less ohmic power losses than are found in electrodes that employ the use of carbon, exclusively as the support material [28]. Furthermore, these zeolite materials contain an array of channels which allow relatively high permeability [28]. Also, zeolite, as the adsorption materials, may be beneficial to strongly chemisorbing intermediates produced during ethanol electrooxidation, which results in the total oxidation of ethanol.

In this study, Pt/ZSM-5 zeolite-C particles were prepared and their electrocatalytic properties for ethanol electrooxidation in acid electrolytes were investigated for the first time. The morphology and elemental composition of Pt/ZSM-5 zeolite-C particles were characterized by scanning electron microscopy (SEM) and energy disperse X-ray spectroscopy (EDS), respectively. The electrocatalytic properties of Pt/ZSM-5 zeolite-C particles for ethanol electrooxidation have been investigated by cyclic voltammetry (CV).

Experimental

All chemicals used were of analytical grade. Fresh double-distilled water was used throughout. All experiments were

carried out at 30 °C. ZSM-5 (silica/alumina>300) zeolite powder was purchased from Shanghai Fuxu molecular sieve (Shanghai, China).

Preparation of Pt/ZSM-5 zeolite-C catalyst

After washing with double-distilled water and drying at 353 K for 3 h, 1.3 mg of the zeolite powder was dispersed in 5 ml of double-distilled water. After ultrasonic treatment for 5 min, the ZSM-5 zeolite particles were mixed with 67 μl of 38 mM H_2PtCl_6 aqueous solution. Then the excess sodium borohydride (NaBH_4 , as reducing agent) solution was added drop-wise to the mixture, the color of the solution was changed from yellow to black. This suggests that Pt/ZSM-5 hybrid catalyst was formed. After ultrasonic treatment for 30 min to complete the reduction of H_2PtCl_6 to Pt nanoparticles and the decomposition of the residual NaBH_4 , 1.3 mg of activated Vulcan XC carbon was added into the above solution under ultrasonic stirring for 3 h to obtain Pt/ZSM-5 zeolite-C catalyst. The Pt/ZSM-5 zeolite-C catalyst was washed with double-distilled water, dried under vacuum, and then dispersed in water. A definite volume of the catalyst ink was transferred to the surface of graphite electrode by a microsyringe. The quantity of Pt in Pt/ZSM-5 zeolite-C catalyst loaded on the graphite electrode is 18 μg . After drying in air, the surface of the catalyst was coated with 20 μl of 0.05% Nafion ethanol solution. The morphology and elemental composition of Pt/ZSM-5 zeolite-C catalyst was investigated by scanning electron microscopy (SEM, JSM-6700F) and energy dispersive X-ray spectroscopy (EDS, Vantage 4105, NORAN).

For comparison, Pt/C catalyst was prepared and transferred to the surface of graphite electrode according to the same procedure mentioned above and the mass of Pt in Pt/C catalyst supported on the electrode is also 18 μg .

Electrochemical measurements

The electrochemical properties of Pt/ZSM-5 catalyst were investigated in 0.1 M H_2SO_4 +1.0 M $\text{CH}_3\text{CH}_2\text{OH}$ aqueous solution by cyclic voltammetry (CV) in the potential range from -0.15 to 1.3 V at a sweep rate of 50 mV s^{-1} . All CV measurements were performed with a conventional three-electrode cell linked to a CHI 660A electrochemical working station (CH Instrument). The graphite electrode (12 mm in length, 6 mm in width, and 4 mm in height) with an exposure area of 0.70 cm^2 was sealed using silicone sealant and used as the working electrode after loading a definite mass of catalyst. Before catalyst loading, the graphite electrode was pretreated in nitric acid aqueous solution (30 wt.%) for 2 h. A platinum wire and a saturated calomel electrode (SCE) was employed as counter electrode and reference electrode, respectively, all the potentials in

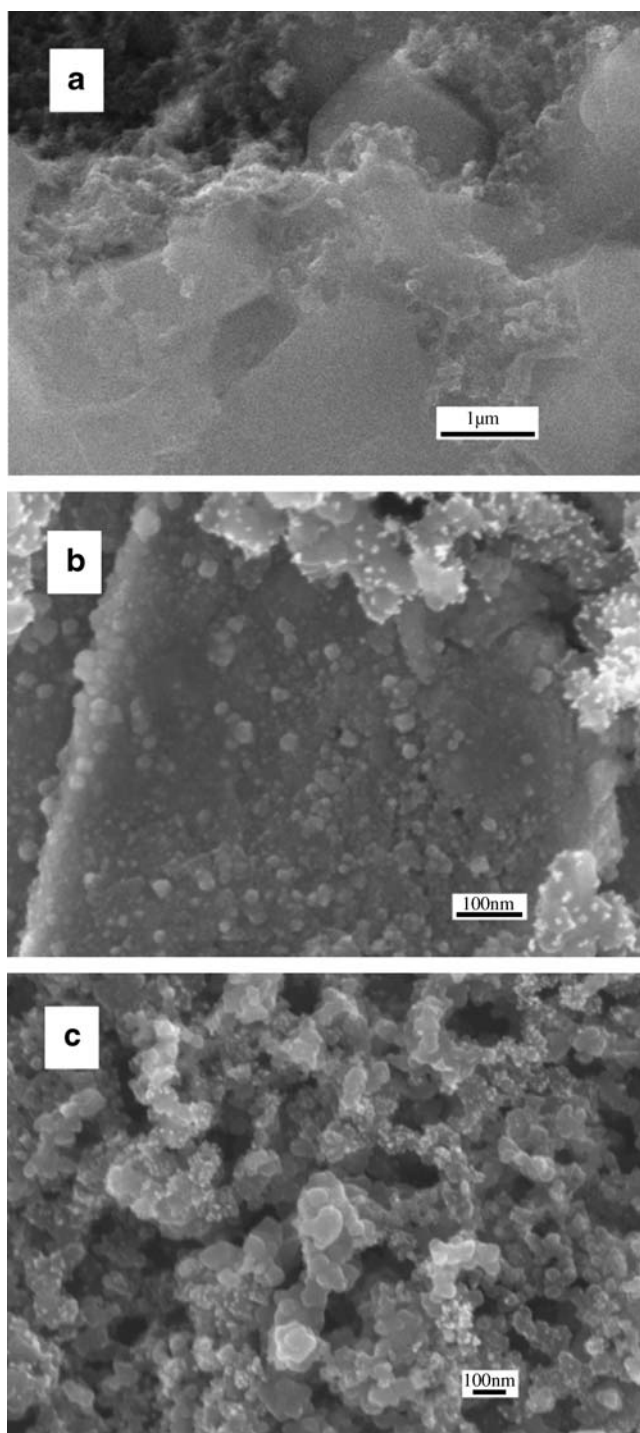


Fig. 1 SEM images of Pt/ZSM-5 zeolite-C and Pt/C catalysts supported on graphite electrodes. The loading mass of Pt is $25.7 \mu\text{g cm}^{-2}$

this paper are given relative to SCE. For comparison, the electrochemical properties of Pt/C (the quantity of Pt in Pt/C catalyst is the same as that in Pt/ZSM-5 zeolite-C catalyst) supported on the graphite electrode were investigated, too.

Results and discussion

The micrograph and element composition of Pt/ZSM-5 zeolite-C catalyst

The micrograph of Pt/ZSM-5 zeolite-C catalyst has been investigated by SEM and the corresponding results are shown in Fig. 1. From Fig. 1a and b, it can be observed that ZSM-5 zeolite and activated Vulcan XC carbon are mixed well and Pt nanoparticles with diameter of about 6–7 nm are supported on ZSM-5 zeolite and activated Vulcan XC carbon. Figure 1c is the SEM image of Pt/C catalyst and Pt nanoparticles with diameter of about 12–13 nm can be observed on the surface of activated Vulcan XC carbon. Under the same Pt loading mass, the surface area of Pt in the Pt/ZSM-5 zeolite-C catalyst should be larger than that in Pt/C catalyst because the diameter of the Pt nanoparticles in the Pt/ZSM-5 zeolite-C catalyst is smaller than that in Pt/C catalyst. This implies that the electrocatalytic activity of the Pt/ZSM-5 zeolite-C catalyst for ethanol oxidation may be better than that of the Pt/C catalyst.

On the other hand, to identify the element composition of Pt/ZSM-5 zeolite-C catalyst, EDS measurement was carried out. The corresponding result is shown in Fig. 2. It can be obtained from Fig. 2 that the major elements in Pt/ZSM-5 zeolite-C catalyst are Pt, Si, Al, and C.

Electrocatalytic properties of Pt/ZSM-5 zeolite-C catalyst for ethanol oxidation

Cyclic voltammetric studies

The electrochemical properties of the Pt/ZSM-5 zeolite-C catalyst for ethanol oxidation were investigated by cyclic voltammetry in 0.1 M $\text{H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{CH}_2\text{OH}$ aqueous

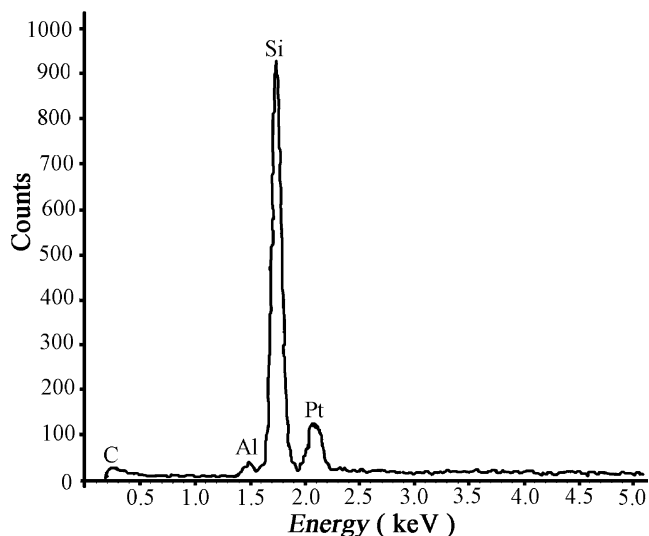


Fig. 2 EDS pattern of Pt/ZSM-5 zeolite-C catalyst supported on graphite electrode

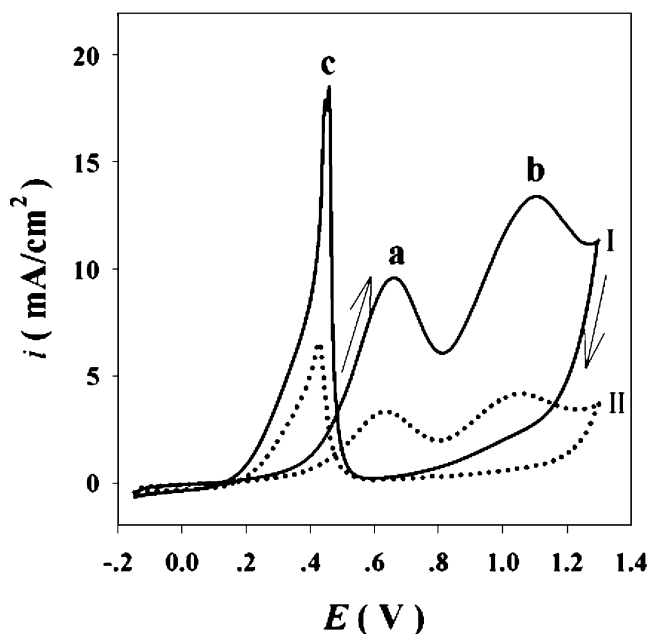


Fig. 3 Cyclic voltammograms of various electrodes at 50 mV s^{-1} in $0.1 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{CH}_2\text{OH}$ aqueous solution. The loading mass of Pt is $25.7 \mu\text{g cm}^{-2}$. Curve I, Pt/ZSM-5 zeolite-C/graphite electrode; Curve II, Pt/C/graphite electrode

solution and the corresponding results are shown in Fig. 3 (curve I). For comparison, the cyclic voltammograms of Pt/C catalyst are also presented in Fig. 3 (curve II). From Fig. 3, the typical cyclic voltammograms of ethanol oxidation can be observed at both Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes (curves I and II). As reported in the literatures [4, 5], three oxidation peaks of ethanol oxidation are observed. Among those, two oxidation peaks are found during the forward sweep. The first oxidation peak (peak a) corresponds mainly to the formation of CO_2 , whereas the second oxidation peak (peak b) corresponds mainly to the formation of CH_3CHO , as has been demonstrated by mass spectrometric CVs (MSCVs). But the exact product of peak c is still unclear. On the other hand, from Fig. 3, it can be observed that the electrocatalytic activity (shown as the current densities at peaks a, b, and c) of Pt/ZSM-5 zeolite-C/graphite electrode is higher than that of Pt/C/graphite electrode. To express more clearly, the mass activity (MA, mA mg^{-1}), defined by peak current density per unit of catalyst loading, is used to evaluate the electrocatalytic activity of the catalyst for ethanol electrooxidation in this paper. The MA can be calculated according to the following equation [1]:

$$\text{MA} = i_p/m_d \times 10^3 \quad (3)$$

where i_p (mA cm^{-2}) is the current density of peak a, and m_d ($\mu\text{g cm}^{-2}$) is the loading mass of Pt. In this paper, supposing that the precursor of Pt catalyst (H_2PtCl_6) has been reduced completely by NaBH_4 , which is actually ten times excessive, the loading mass (m_d) of Pt can be

calculated based on the mass of H_2PtCl_6 . From Fig. 3, the MA value of Pt/ZSM-5 zeolite-C catalyst can be obtained and is 374 mA mg^{-1} , which is about 2.88 times as large as that of Pt/C catalyst (130 mA mg^{-1}). This may be mainly explained as follows: (1) the smaller particles of Pt supported on ZSM-5 zeolite-C have higher specific surface area, which results in higher electrocatalytic activity of Pt/ZSM-5 zeolite-C catalyst; (2) SiO_2 in the framework of ZSM-5 zeolite may provide the function as Ru does in Pt–Ru/C catalysts [6, 29]; (3) Al_2O_3 in the framework of ZSM-5 zeolite is helpful for CO_{ads} oxidation [30]; (4) zeolite material with special porous structure provides relatively high permeability and good micromedia for ethanol oxidation [28]. For Pt/ZSM-5 zeolite-C catalyst, Pt acts as the main catalyst for catalyzing the dehydrogenation of ethanol during the oxidation reaction and the oxygen-containing species can be provided by the framework oxygen sites or surface hydroxyls of the zeolite particles. These oxygen-containing species strongly react with CO-like intermediate species on Pt surface to release the active sites for further ethanol oxidation [28].

Chronoamperometric studies

Figure 4 shows the chronoamperograms of Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes at 0.4 V in $0.1 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{CH}_2\text{OH}$ aqueous solutions. From Fig. 4, it can be observed that a gradual decay of current density with time can be observed on both Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes when the

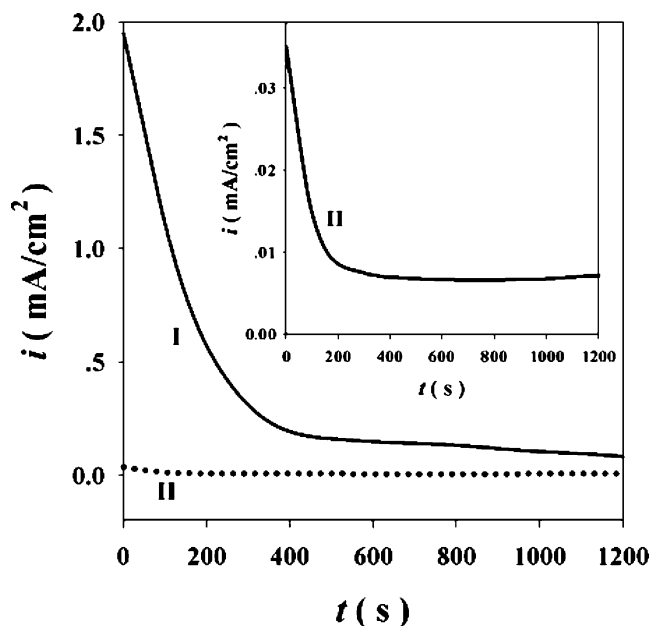


Fig. 4 Chronoamperograms of Pt/ZSM-5 zeolite-C/graphite (curve I) and Pt/C/graphite (curve II) electrodes at 0.4 V in $0.1 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{CH}_2\text{OH}$ aqueous solution. The loading mass of Pt is $25.7 \mu\text{g cm}^{-2}$

potential is fixed at 0.4 V. However, during the whole time, the current density of ethanol oxidation on Pt/ZSM-5 zeolite-C/graphite electrode (curve I in Fig. 4) is higher than that on the Pt/C/graphite electrode (curve II in Fig. 4). This also confirms that the electrocatalytic activity of the Pt/ZSM-5 zeolite-C/graphite electrode is higher than that of the Pt/C/graphite electrode due to the presence of ZSM-5 zeolite and small particle size of Pt.

Tafel plots studies

To further investigate the effect of zeolite on the electrocatalytic activity of Pt catalyst, the exchange current density (i_0) of ethanol oxidation at different electrodes was investigated. The polarization studies on Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes have been carried out and the typical Tafel curves are shown in Fig. 5. According to the Tafel equation [31], the values of i_0 at Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes are calculated and equal to $24.88 \mu\text{A cm}^{-2}$ and $11.79 \mu\text{A cm}^{-2}$, respectively. The i_0 value of the Pt/ZSM-5 zeolite-C/graphite electrode is about 2.11 times higher than that of Pt/C/graphite electrode. It indicates that the existence of ZSM-5 zeolite particles accelerate significantly the process of ethanol electrooxidation. On the other hand, the open-circuit potential of ethanol oxidation is also decreased obviously from 0.287 to 0.159 V, which implies that the electrooxidation of ethanol at Pt/ZSM-5 zeolite-C/graphite electrode is easier than that at Pt/C/graphite electrode because of the assistance of ZSM-5 zeolite particles.

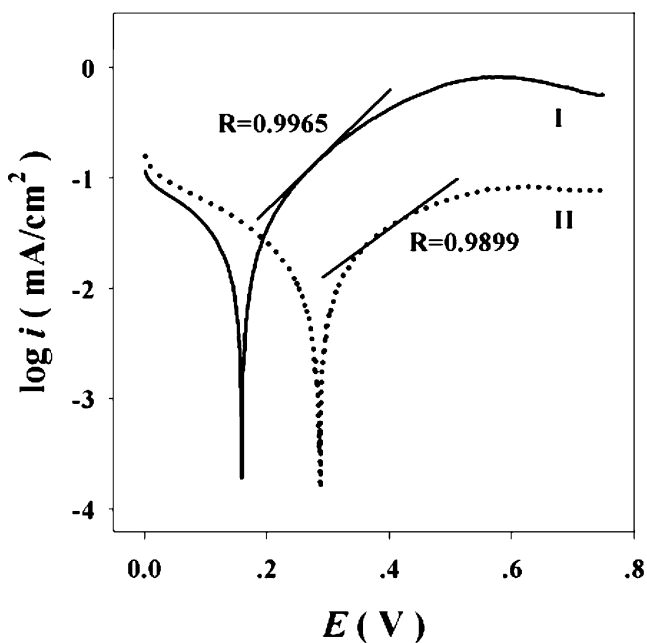


Fig. 5 Tafel plots of Pt/ZSM-5 zeolite-C/graphite (curve I) and Pt/C/graphite (curve II) electrodes in 0.1 M H₂SO₄+1.0 M CH₃CH₂OH aqueous solutions. The loading mass of Pt is 25.7 $\mu\text{g cm}^{-2}$ and scan rate is 2 mVs⁻¹

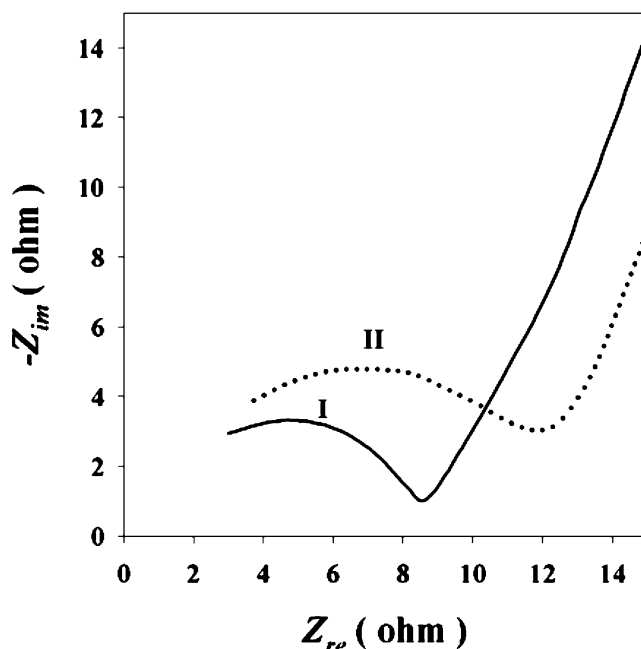


Fig. 6 Electrochemical impedance spectra of Pt/ZSM-5 zeolite-C/graphite (curve I) and Pt/C/graphite (curve II) electrodes in 0.1 M H₂SO₄+1.0 M CH₃CH₂OH aqueous solutions. The loading mass of Pt is 25.7 $\mu\text{g cm}^{-2}$, initial potential is 0 V, and amplitude is 5 mV

Electrochemical impedance spectroscopy studies

It is well known that electrochemical impedance spectroscopy (EIS) technique is a powerful tool to characterize the electrochemical processes occurred at the solution/electrode interface. A typical electrochemical impedance spectrum

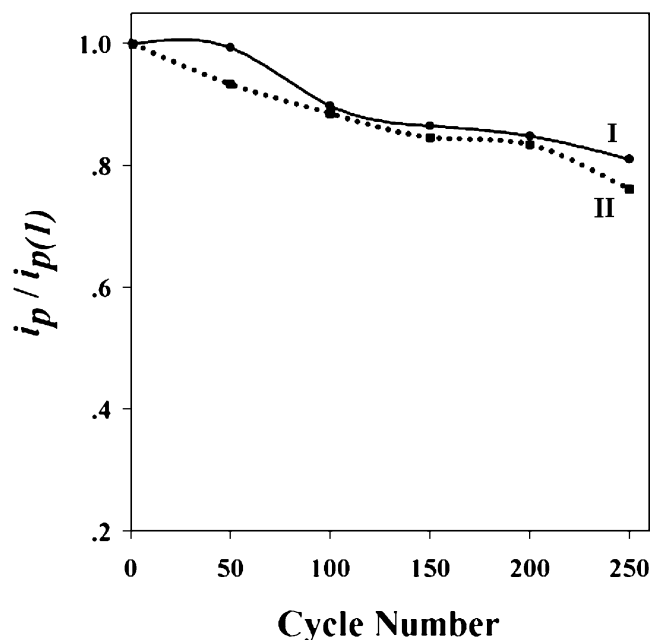


Fig. 7 Long-term cycle stabilities of Pt/ZSM-5 zeolite-C/graphite (curve I) and Pt/C/graphite (curve II) electrodes in 0.1 M H₂SO₄+1.0 M CH₃CH₂OH aqueous solutions at 50 mVs⁻¹. i_p is the peak current density for peak a; $i_{p(1)}$ is the peak current density for peak a at the first cycle

presented in the form of a Nyquist plot (Z_{im} vs Z_{re}) includes a semicircle region lying on the Z_{re} -axis observed at higher frequencies (it is related to the electron-transfer-limited process), followed by a linear part at lower frequencies (it is related to the diffusion-limited electron-transfer process). Usually, the electron-transfer kinetics and diffusion characteristics can be extracted from the EIS spectra. The semicircle diameter equals to the electron-transfer resistance, R_{ct} , which is affected obviously by the surface modification of the electrode [32]. Figure 6 shows the electrochemical impedance spectra presented as Nyquist plots (Z_{im} vs Z_{re}) of the Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes recorded in an aqueous solution of 0.1 M H_2SO_4 +1.0 M $\text{CH}_3\text{CH}_2\text{OH}$. As shown in Fig. 6, the electron-transfer resistance (R_{ct}) decreases after the introduction of ZSM-5 zeolite. The values of R_{ct} on Pt/ZSM-5 zeolite-C/graphite and Pt/C/graphite electrodes are 8.49 and 11.80 Ω , respectively. This also implies that the electrooxidation of ethanol molecules is enhanced by the presence of ZSM-5 zeolite particles. The corresponding reason may be the proton conduction properties of the zeolite materials.

Long-term cycle stability studies

In practical application, the long-term cycle stability of the electrode is of great importance. In this paper, the long-term cycle stability of Pt/ZSM-5 zeolite-C/graphite electrode has been investigated in 0.1 M H_2SO_4 +1.0 M $\text{CH}_3\text{CH}_2\text{OH}$ aqueous solution by cyclic voltammetry and the corresponding results are shown in Fig. 7. When the potential is cycled continuously for 250 cycles, 18.9% loss of the peak current density for peak a can be observed. However, for Pt/C/graphite electrode, a larger decrease (23.8%) is obtained. The reasons for the decrease of i_p may be as follows: accumulation of poisonous species (such as CO_{ads}) on the surface of the Pt particles, ethanol consumption during the successive scans, and change of the surface structure of the Pt catalyst. The results from Fig. 7 imply that the presence of zeolite is helpful for the improvement of the long-term cycle stability of Pt catalyst during the electrooxidation process of ethanol.

To understand the main reason to decrease the electrocatalytic activity of the electrode, a control experiment was carried out as follows: after the electrodes were cycled continuously for 250 cycles in 0.1 M H_2SO_4 +1.0 M $\text{CH}_3\text{CH}_2\text{OH}$ aqueous solution, the electrodes were stored in double-distilled water for 30 min, and then the electrocatalytic properties of the electrode for ethanol oxidation were investigated again in fresh aqueous solutions containing 0.1 M H_2SO_4 +1.0 M $\text{CH}_3\text{CH}_2\text{OH}$. The peak current density of peak a at Pt/ZSM-5 zeolite-C/graphite electrode still remains 82.7% value of $i_{p(1)}$ (the peak current density

of peak a at the first cycle). However, for Pt/C/graphite electrode, only 76.2% value of $i_{p(1)}$ remains. This suggests that the main reason for the decrease of current density in the continuous 250 cycles may be the accumulation of poisonous species (such as CO_{ads}) on the surface of the Pt particles.

Conclusion

Because of high stability in general acidic solution, ZSM-5 (silica/alumina>300) zeolite material was selected as both the support and the second catalyst for ethanol oxidation. The electrochemical properties of the Pt/ZSM-5 zeolite-C/graphite electrode have been investigated by cyclic voltammetry, chronoamperometry, polarization method, and electrochemical impedance spectroscopy. Good electrochemical performance of the catalyst (high electrocatalytic activity and good long-term cycle stability) is achieved by the presence of zeolite. The corresponding results imply that ZSM-5 zeolite particles may be a good candidate as the support and the second catalyst for ethanol oxidation in DEFC.

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