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Promoting Influence of Activated Carbon used in Carbon Paste Electrode on Platinum Nanoparticles Efficiency in Methanol Electrooxidation

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ABSTRACT

Direct methanol fuel cell (DMFC) have the advantages of low emissions of carbon dioxide, high power density and high energy density, so they have a great potential to replace fossil fuels. It is well known that Pt with high activity is an ideal catalyst for methanol oxidation in an acidic medium. However, it is an expensive material, and cost of the DMFC containing Pt is prohibitively high and it becomes poisoned by CO_{ads} which is formed during the methanol oxidation. In this work, for the first time, the preparation of activated carbon(YBC) doped carbon paste electrode (YBCPE) and carbon paste electrode (CPE) were carried out for comparison. The electrochemical properties of YBCPE and CPE were investigated by electrochemical impedance spectroscopy. The electrodes of Pt/YBCPE and Pt/CPE were prepared by electrodeposition of platinum on YBCPE and CPE, respectively, at a constant potential (−0.1 V vs. Ag|AgCl (sat)) in 0.5 M H_2SO_4 containing 3 mM H_2PtCl_6. The behavior of electrodeposition of platinum on YBCPE and CPE was studied through the application of theoretical models, and the morphology of Pt/YBCPE and Pt/CPE were characterized by SEM. The electrochemical activities of these catalysts towards methanol electrooxidation were examined by cyclic voltammetry. The influence of YBC mass percentage in YBCPE on both the electrode activity and long-term stability of electrodes in methanol electrooxidation was studied. It was shown that the addition of activated carbon improved the electrocatalytic activity of Pt catalysts on corresponding YBCPE toward methanol electrooxidation.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted more and more attention due to their high energy-conversion efficiency, low pollution emission, and safe fuel handling, low operating temperature, simplicity of design and low cost [1]. In an acidic medium, platinum and its alloys have been considered as the most efficient catalyst for the electrooxidation of methanol at the anode of DMFCs [2–5]. However, there have been two important problems to greatly limit the development of DMFCs. One is that many intermediates and poisoning species during electrooxidation of methanol are produced to make catalyst deactivated [6], the other is that Pt and its alloys are expensive materials and limited supply [7]. Because the electrooxidation of methanol is a very complex reaction, it is well known the electrocatalytic activity of platinum particles for methanol oxidation depends on numerous factors [8,9]. Among these, the supporting materials and their surface conditions are essential for the Pt catalyst to produce high catalytic activity [10,11]. Therefore, it is one of the most simply and effective routes of overcoming above mentioned problems to explore the supporting materials with high surface area to reduce the noble metal loading under the condition of keeping the high catalytic activity. Up to now, a great deal of interests exists in the development of less expensive materials used as substrates for dispersing platinum nanoparticles.

In recent years, carbon materials are very favorable supports for Pt and its alloys catalysts because of their large specific surface area, good electricity and relative stability. Many carbon materials as supports have been reported such as carbon nanotube [12], graphene [13–15], mesoporous carbon [16], carbon black [17], etc. Among many solid electrodes involved carbon materials, carbon paste electrodes (CPEs) are widely used in electrochemical investigations because CPEs have some advantages of over all other carbon electrodes such as renewability of the electrode surface, low residual current, porous surface, versatility of

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chemical modification, compatibility with various electron mediators and low cost [18,19]. The CPEs are both cheaper and suitable for preparing the electrode material with desired composition and pre-determined properties for supports of platinum toward the electrooxidation of methanol. So, many authors have prepared some new CPEs doped with carbon nanotube, zeolite, carbon aerogel and conducting polymer as supports of platinum [2,3,20,21]. The new CPEs were used as supports to prepare platinum based electrodes for electrooxidation of small organic molecules. The platinum based electrodes using the new CPEs have shown better electro catalytic activity.

In the present work, we tried to prepare novel low cost and high performance CPEs doped by an activated carbon that is often used for making lead-acid battery and lithium battery due to its high accessible surface area and low price. To our knowledge, there have been no similar reports on the carbon paste electrode made from graphite powder and the activated carbon and on its supporting platinum for electrooxidation of methanol. So, firstly, the pure carbon paste electrode(CPE) and the carbon paste electrode doped with different mass percentages of activated carbon(YBCPE) were fabricated. Then, the platinum was electrochemical deposited on both the CPE and YBCPEs to get two composite electrodes, Pt/CPE and Pt/YBCPEs, respectively, for the electrooxidation of methanol. The results indicate that Pt/YBCPE offers more excellent electrocatalytic activity than Pt/CPE. Furthermore, Pt/YBCPE also shows quite good electrocatalytic activity for electroxidation of methanol in comparison with the results published in some literature.

2. Experimental

2.1. Reagents and materials

Garphite powder (8000 mesh, Aladdin Co., Ltd), activated carbon (Fuzhou Yihuan Carbon Co., Ltd., China), Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) (Sinopharm Chemical Reagent Co., Ltd., China) and paraffin oil (density: 0.88 g/cm^3, Sinopharm Chemical Reagent Co., Ltd) were used for preparing various electrodes. $K_4[Fe(CN)]_6$, $K_3[Fe(CN)]_6$ and KCl (Sinopharm Chemical Reagent Co., Ltd., China) were used in EIS measurement. Sulfuric acid and methanol were analytical grade used as received. Doubly distilled water was used throughout the work.

2.2. Electrochemical measurements

The electrochemical experiments were carried out in a three electrode electrochemical cell on the CHI660B electrochemical workstation (Shanghai Chenhua Instrument Plant, China). A Ag|AgCl(sat) and a platinum foil were used as the reference and counter electrode, respectively. The different prepared electrodes were used as working electrode. The surface morphology of corresponding electrode was examined by scanning electron microscopy (SEM) (S-4800, Hitachi High Technologies Corporation, Japan). All the experiments were carried out at room temperature.

2.3. Electrode preparation

CPE or YBCPE was prepared by blending a mixture of graphite powders with activated carbon (total 0.5 g) and paraffin oil (0.327 g) with a mortar and pestle. And activated carbon using mass percentages of 0, 4%, 8%, 10%, 12%, 14%, 16%, 18% to yield CPE, YBCPE(4%), YBCPE(8%), YBCPE(10%), YBCPE(12%), YBCPE(14%), YBCPE(16%), YBCPE(18%), respectively. The obtained composite carbon paste was then inserted in a Teflon hollow tube with inner diameter of 3.0 mm. Electrical connection was made by a copper wire fitted into the Teflon hollow tube. The prepared CPE and YBCPE were polished on white paper until a smooth shiny surface was observed.

Prior to electrochemical deposition of Pt on the CPE and YBCPE, cyclic voltammetry was performed on the electrodes between −0.1 V and 0.85 V at a scan rate of 100 mV s^{-1} in 0.5 M H_2SO_4 until one stable voltammogram was seen. Electrochemical deposition of platinum nanoparticles onto the CPE or YBCPE was carried out in the solution containing 3.0 mM H_2PtCl_6 and 0.5 M H_2SO_4 by using potentiostatic electrolysis at −0.1 V. The amount of Pt was obtained by integrating the experimental current-time curve assuming 100% current efficiency [22]. The Pt amount was calculated from the equation (1):

$$m_{pt} = \frac{QM}{FZ} \quad (1)$$

Where m_{pt} is calculated by using the integrated charge (Q/C) during the Pt electrodeposition process. M (195.08 g/mol) is the atomic weight of Pt, F (96485C/mol) is the Faraday constant, Z = 4 is the number of electrons transferred. In this work, the amount of deposited Pt both CPE and YBCPEs was controlled at 0.12 mg/cm^2.

3. Results and discussion

3.1. Electrochemical properties of the working electrode

The properties of CPE and YBCPE mainly depend on the composition of carbon materials in both electrodes. The electrochemical response of the CPE and YBCPEs were investigated by cyclic voltammetry using 1.0 mM potassium hexacyanoferrates (II)/(III) as a model redox systems in 0.1 M KCl solution from −0.1 V to 0.6 V at a scan rate of 50 mV s^{-1}. The voltammograms are shown in Fig. 1. As can be seen in Fig. 1, the background current of YBCPE is higher than that of CPE and better redox peaks are also obtained on YBCPE. The cathodic/anodic peak potential difference (ΔEp) is 175 mV for the YBCPE(14%) while for the CPE, ΔEp is 319 mV. By comparing these results, it is concluded that the reversibility of YBCPE is better than CPE. This may be due to the higher accessible surface area of activated carbon that resulted in easier electric charge transfer at the surface of YBCPE.

3.2. Electrochemical impedance spectra of YBCPE and CPE

Electrochemical impedance spectroscopy is one of the most effective technologies for studying the electrochemical properties of electrodes [23]. The EIS spectra of the electrodes were measured in 1 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ (1:1) + 0.1 M KCl solution at open

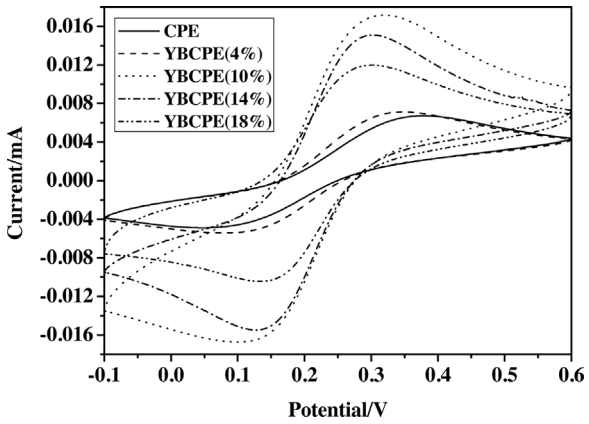

Fig. 1. Cyclic voltammograms of bare CPE and YBCPE with different activated carbon percentages in 0.1 M KCl solution containing 1 mM $K_4[Fe(CN)_6]$. Scan rate: 50 mV s^{-1}.

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