Short communication

Study of carbon-supported Au catalyst as the cathodic catalyst in a direct formic acid fuel cell prepared using a polyvinyl alcohol protection method

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Abstract

In this paper, it is reported for the first time that a carbon-supported Au (Au/C) catalyst for the cathodic catalyst in a direct formic acid fuel cell (DFAFC) was prepared using a polyvinyl alcohol (PVA) protection method. The results indicated that for oxygen reduction, the electrocatalytic activity of the Au/C catalyst prepared with the PVA protection method is much better than that of a Au/C catalyst prepared with the pre-precipitation method. This is due to the small average size and low relative crystallinity of the Au particles in the Au/C catalyst prepared by the PVA protection method, compared to that of the Au/C catalyst prepared by the pre-precipitation method, illustrating that the average size and the relative crystallinity of the Au particles has an effect on the electrocatalytic activity of the Au/C catalyst for oxygen reduction. In addition, because Au has no electrocatalytic activity for the oxidation of formic acid, the Au/C catalyst possesses a high formic acid tolerance. After the electrocatalytic activity of the Au/C catalyst for the oxygen reduction is improved, it is suitable to be used as the cathodic catalyst in DFAFC.
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The direct formic acid fuel cell (DFAFC) has many advantages [1–11]. For example, formic acid is non-toxic and is not easily burned. Thus, its storage and transportation are safe. The electrooxidation performance of formic acid is better than that of methanol because the activation energy for the oxidation of formic acid is lower than that of methanol [7]. Especially, formic acid can be oxidized through two parallel routes [12]. Similar to methanol, at some catalysts, such as the Pt catalyst, formic acid would be oxidized through the CO intermediate. However, when some catalysts, such as the Pd catalyst are used, formic acid would be directly oxidized to CO_2 through the "direct way" [7]. Thus, the catalysts are not easily poisoned by CO. In DFAFC, the optimal operating concentration of formic acid can be as high as 20 M [3], while the best concentration of methanol in a

DMFC is only about 2 M. Thus, the energy density of DFAFC can be higher than that of DMFC. In addition, due to the repulsion between $CHOO^-$ and SO_3^- ions in the Nafion membrane, the penetration efficiency of formic acid through the Nafion membrane is much lower than that of methanol [3].

Although, formic acid has two orders of magnitude smaller crossover flux through the Nafion membrane than methanol [3], a certain amount of formic acid enters the cathode. Pt is usually used as the cathodic catalyst in proton exchange membrane fuel cells because Pt possesses high electrocatalytic activity for oxygen reduction. However, the cathodic Pt catalyst is easily poisoned with formic acid because formic acid would be oxidized through the CO intermediate. Therefore, study of the cathodic catalysts with high electrocatalytic activity and formic acid tolerance ability is necessary for DFAFC. In this paper, it is reported for the first time that a Au/C catalyst was used as the cathodic catalyst in a DFAFC. The elelctrocatalytic activity of the Au catalyst is obviously dependent on the sizes of the Au particles and

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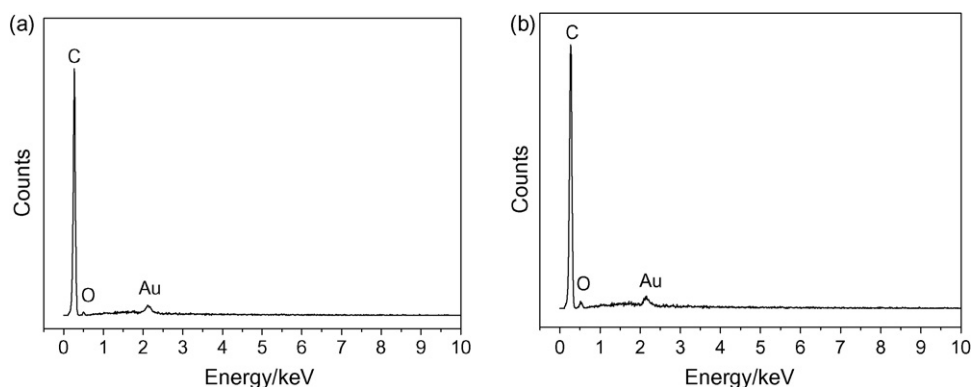*E-mail address:* tianhonglu@263.net (T. Lu).

Fig. 1. The EDS spectra of (a) the Au/C-1 and (b) Au/C-2 catalysts.

the Au/C catalyst with small average size of the Au particles is not easily prepared [13–16]. Thus, the PVA protection method [17–19] was used to prepare the Au/C catalyst with small average size of the Au particles. The results showed that the average size of the Au particles in the Au/C catalyst prepared with the PVA protection method is as small as 5.3 nm. Especially, it was found that the Au catalyst has no electrocatalytic activity for the oxidation of formic acid. Thus, the Au catalyst possesses high formic acid tolerance ability and is suitable to be used as the cathodic catalyst in a DFAFC.

According to the literature [17–19], the Au/C catalyst with the PVA protection method was prepared as follows. The $NaBH_4$ solution was dropwise added to a solution of 1.6×10^{-3} M 15 mL $HAuCl_4$ + 2 wt.% 11.65 mL PVA under vigorous stirring. Then, 90 mg Vulcan XC-7carbon was added into the above solution with vigorously stirring for 4 h. Then it was filtered, washed with triply distilled water and dried in a vacuum oven at 55 °C. A 5 wt.% Au/C catalyst was obtained and is termed the Au/C-1 catalyst.

For comparison, a Au/C catalyst was prepared with the pre-precipitation method [20]. The pH of 1.6×10^{-3} M 15 mL $HAuCl_4$ solution was adjusted to 7 with Na_2CO_3 solution. Then, the solution was mixed with 90 mg Vulcan XC-7carbon and heated to 70 °C with vigorously stirring for 2 h. Finally, 1 wt.% 11.65 mL $Na_3C_6H_5O_7$ solution was dropwise added into the suspension to reduce the $HAuCl_4$. Then it was filtered, washed with the triply distilled water and dried in a vacuum oven at 55 °C. A 5 wt.% Au/C catalyst was obtained and was noted as the Au/C-2 catalyst.

The composition of the catalyst was determined using energy dispersive spectrometer (EDS) with Vantage Digital Acquisition Engine (Thermo Noran, USA). The X-ray diffraction (XRD) measurements were performed on Model D/max-rC diffractometer using Cu Kα radiation ($k = 0.15406$ nm) operating at 45 kV and 100 mA. The electrochemical measurements were performed using a CHI 600 electrochemical analyzer and a conventional three-electrode electrochemical cell at 30 °C. The scan rate was 5 mV s^{-1} and the rotation rate was 2000 rpm.

A Pt plate and a Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. All potentials were quoted with respect to the Ag/AgCl electrode. The working electrode was prepared as described previously [10,11,21]. A

10 mg 5 wt.% Au/C catalysts, 0.332 mL 5 wt.% Nafion solution (Aldrich), 0.83 mL ethanol and 0.83 mL water were mixed ultrasonically. 2.8 μL ink obtained was transferred onto the glassy carbon electrode. After drying overnight at the room temperature, the working electrode was obtained. The specific loading of Au on the electrode surface was about 10 μg cm^{-2}. The electrolyte solution was 0.5 M H_2SO_4 solution with or without 0.5 M HCOOH.

The typical EDS spectra for the Au/C catalysts is shown in Fig. 1. It was obtained from Fig. 1 that both Au/C catalysts contain 4.78 wt.% Au, which is in good agreement with that calculated from the amount of $HAuCl_4$ used.

Fig. 2 shows the XRD patterns of the two Au/C catalysts. It was found from Fig. 2 that except for the carbon peak at 24.7°, the 2θ values of other five peaks are 38.18°, 44.39°, 64.57°, 77.54° and 81.72°, respectively, which correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of the face centered cubic crystalline of Au (JCPDS card 04-0784). This indicated that the Au particles in both Au/C catalysts are face centered cubic and crystalline. The relative crystallinities of the Au particles in the Au/C-1 and Au/C-2 catalysts are 1.05 and 2.78, respectively. The average sizes of the Au particles of the Au/C-1 and Au/C-2 catalysts are 5.3 and 29 nm, respectively, calculated with the Debye-Scherrer formula [22,23].
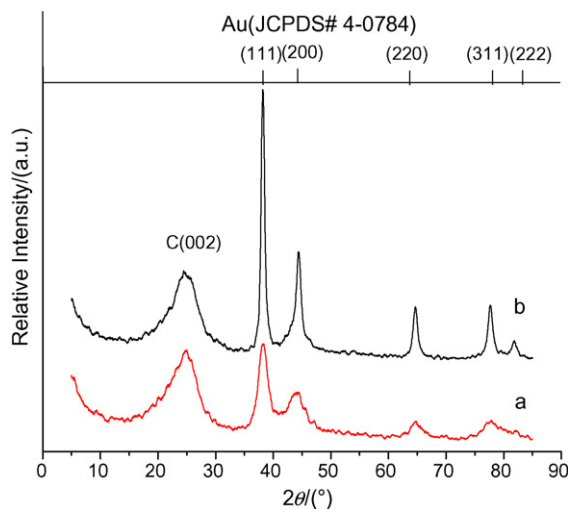

Fig. 2. The XRD patterns of (a) the Au/C-1 and (b) Au/C-2 catalysts.
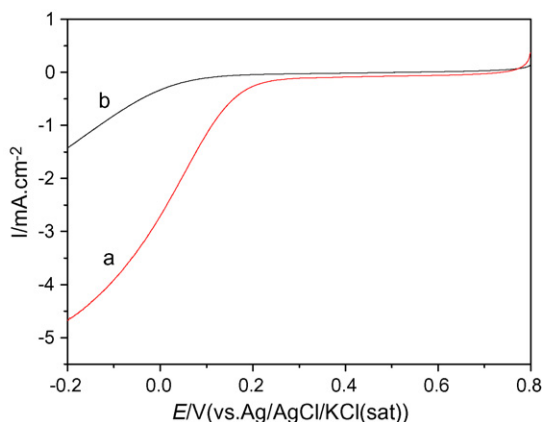
Fig. 3. The linear sweeping voltammograms of (a) the Au/C-1 and (b) Au/C-2 catalyst electrodes in 0.5 M H_2SO_4 solution saturated with O_2.

Fig. 3 displays the linear sweeping voltammograms of the Au/C-1 and Au/C-2 catalyst electrodes in 0.5 M H_2SO_4 solution saturated with O_2. It can be observed from Fig. 3 that the onset potentials of oxygen reduction at the Au/C-1 catalyst electrode is 100 mV more positive than that at the Au/C-2 catalyst electrode and the current density of the oxygen reduction at the Au/C-1 catalyst electrode is 218% larger than that at the Au/C-2 catalyst electrode, demonstrating that the electrocatalytic activity of the Au/C-1 catalyst for the oxygen reduction is higher than that of the Au/C-2 catalyst. This is due to the small average size and the low relative crystallinity of the Au particles in the Au/C-1 catalyst, comparing with that in the Au/C-2 catalyst [13–16,24]. Usually, the catalyst with a small average size and low relative crystallinity would show the large electrochemical active surface [25]. Thus, the Au/C-1 catalyst showed the electrocatalytic activity higher than that of the Au/C-2 catalyst.

Fig. 4 shows the linear sweeping voltammograms of the Au/C-1 catalyst electrode in O_2-saturated 0.5 M H_2SO_4 solution without and with 0.5 M HCOOH. It can be observed from Fig. 4 that two curves are similar and no oxidation peaks of HCOOH were observed in curve b [9,10]. The above results demonstrated that the Au/C catalyst has no electrocatalytic activity for the oxidation of formic acid. Thus, the Au/C catalyst possesses high formic acid tolerance and is suitable to be used as the cathodic
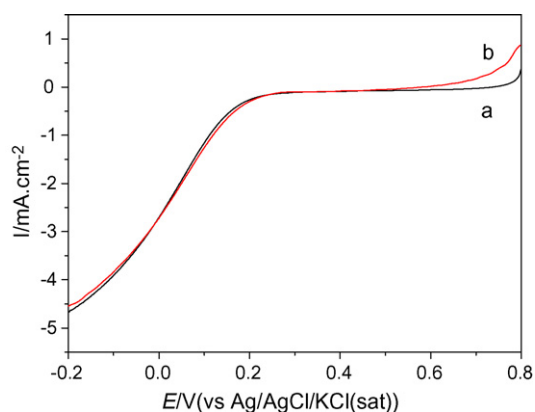
catalyst in a DFAFC. Usually, Pt is used as the cathodic catalyst in DMFC. However, in order to obtain the cathodic catalysts with high methanol tolerance in DMFC, Pd based cathodic catalysts were investigated although the electrocatalytic activity of the Pd catalyst is lower than that of the Pt catalyst [26,27]. Similarly, although the electrocatalytic activity of the Au/C catalyst for the oxygen reduction is lower than that of the Pt/C catalysts, the Au/C catalyst could be used as the cathodic catalyst due to its high formic acid tolerance in DFAFC. The electrocatalytic activity of the Au/C catalyst for the oxygen reduction would be significantly increased using the Au-based composite catalysts. In addition, the electrocatalytic activity of the Au/C catalyst can be improved with further decrease in the average size of the Au particles. Further study is in progress.

In conclusion, the electrocatalytic activity of the Au/C-1 catalyst for the oxygen reduction is better than that of the Au/C-2 catalyst because the average size and the relative crystallinity of the Au particles in the Au/C-1 catalyst are much smaller than that in the Au/C-2 catalyst. In addition, it was found that the Au/C catalyst possesses high formic acid tolerance because Au has no electrocatalytic activity for the oxidation of formic acid. After the performance of the Au/C catalyst for the oxygen reduction is improved, it could be suitable for use as the cathodic catalyst in a DFAFC.

Acknowledgements

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Fig. 4. The linear sweeping voltammograms of the Au/C-1 catalyst electrode in O_2-saturated 0.5 M H_2SO_4 solution (a) without and (b) with 0.5 M HCOOH.

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