

Short communication

Carbon-supported Pd–Ir catalyst as anodic catalyst in direct formic acid fuel cell

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Abstract

It was reported for the first time that the electrocatalytic activity of the Carbon-supported Pd–Ir (Pd–Ir/C) catalyst with the suitable atomic ratio of Pd and Ir for the oxidation of formic acid in the direct formic acid fuel cell (DFAFC) is better than that of the Carbon-supported Pd (Pd/C) catalyst, although Ir has no electrocatalytic activity for the oxidation of formic acid. The potential of the anodic peak of formic acid at the Pd–Ir/C catalyst electrode with the atomic ratio of Pd and Ir = 5:1 is 50 mV more negative than that and the peak current density is 13% higher than that at the Pd/C catalyst electrode. This is attributed to that Ir can promote the oxidation of formic acid at Pd through the direct pathway because Ir can decrease the adsorption strength of CO on Pd. However, when the content of Ir in the Pd–Ir/C catalyst is too high the electrocatalytic activity of the Pd–Ir/C catalyst would be decreased because Ir has no electrocatalytic activity for the oxidation of formic acid.

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Keywords: Direct formic acid fuel cell; Carbon-supported Pd–Ir catalyst; Palladium; Iridium

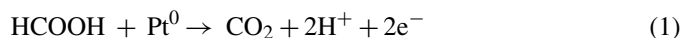
1. Introduction

In the recent years, it has been recognized that the direct methanol fuel cell (DMFC) has some serious disadvantages [1]. Firstly, methanol is easy to penetrate through the Nafion membrane, causing the waste of methanol and the decrease in the DMFC performance. Secondly, the electrocatalytic activity of Pt usually used as the anodic catalyst in DMFC is low and Pt is easy to be poisoned with CO, an intermediate of the methanol oxidation. Thirdly, the use of methanol is not safe because methanol is a toxic, evaporable and burnable compound.

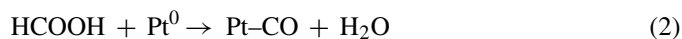
Recently, many advantages of DFAFC have been recognized [2–5]. For example, formic acid is non-toxic. The dilute formic acid is on the US Food and Drug Administration list of food additives [6]. It is not inflammable and thus its storage and transportation are safe. It has two orders of magnitude smaller crossover flux through a Nafion membrane than methanol [7].

When formic acid is used as the fuel in DFAFC the operation concentration can be as high as 20 M, while the best concentration of methanol in DMFC is only about 2 M [2,3]. Thus, the power density of DFAFC can be higher than that of DMFC, although the energy density of formic acid is only one-third that of methanol. Usually, the performance of DFAFC should be better than that of DMFC because the active energy of the oxidation of formic acid is smaller than that of the methanol oxidation. The electrooxidation performance of formic acid is better than that of methanol, because formic acid has the electronic motive force calculated from the Gibbs free energy higher than methanol [2].

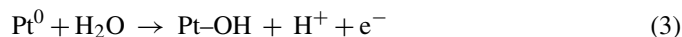
It was reported that the electrooxidation of formic acid could undergo through two parallel pathways, the direct pathway and CO pathway [8–14]. In the direct pathway, formic acid is directly oxidized to CO₂.



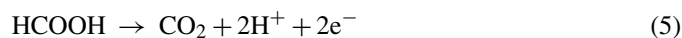
In the CO pathway, formic acid is firstly oxidized to form CO, an intermediate and then CO is oxidized to CO₂.



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The overall reaction:



The previous studies have shown that the electrooxidation rate of formic acid at the Pt catalyst is insufficient for the practical application, because the electrooxidation of formic acid at the Pt catalyst is mainly through the CO pathway and thus Pt is easy to be poisoned by CO [15–19]. Recently, Masel and coworkers. [20,21] have discovered that the Pd and Pd/C catalysts can overcome the CO poisoning effect because the electrooxidation of formic acid at the Pd and Pd/C catalysts is mainly through the direct pathway. In order to further improve the electrocatalytic performance of the Pd and Pd/C catalysts, the Pd-based binary metallic catalysts have been investigated [22]. Until now, the mechanism of the increase in electrocatalytic performance of the Pd-based binary metallic catalysts is not very clear. Two hypotheses have been suggested [23]. It was considered that the second atom can increase the adsorption ability of the active oxygen and then the oxidation rate of formic acid or it can prevent from the formation of strongly adsorbed CO. The Pd-based binary metallic catalysts studied include Pd–Ni [24], Pd–Au [25], Pd–Pt [26], etc.

In this work, it was reported for the first time that the Pd–Ir/C catalyst showed the electrocatalytic activity for the oxidation of formic acid better than that of the Pd/C catalyst, although Ir has no electrocatalytic activity for the oxidation of formic acid. The reason for that Ir can increase the electrocatalytic activity of Pd for the oxidation of formic acid was discussed.

2. Experimental

The preparation method of the catalysts is as follows: 60 mg Vulcan XC-72 carbon, 1.10 mL 0.04504 M PdCl₂ and 2.3 mL 0.067 M (NH₄)₂IrCl₆ were added to 10 mL H₂O. Then, the suspension obtained was sonicated for 30 min and stirred mechanically for 4 h. After the pH of the suspension was adjusted to 8–9 with the NaOH solution, 10 mL 1.0 mg/mL NaBH₄ solution was added dropwise into the suspension to reduce PdCl₂ and (NH₄)₂IrCl₆. After the suspension was sonicated for 20 min, it was stirred for 1 h at 10 °C in order to make sure that PdCl₂ and (NH₄)₂IrCl₆ were completely reduced to Pd and Ir. Then, it was filtered and washed with triply distilled water and ethanol sequentially. Finally, it was dried in a vacuum oven at 60 °C for 12 h. The catalyst obtained is the Pd–Ir/C catalyst with 20 wt.% Pd–Ir and the atomic ratio of Pd:Ir = 1:1 and was noted as the Pd–Ir/C-1 catalyst.

The preparation method of other catalysts is similar to that mentioned above. Only the components of the initial suspension were different. For the Pd–Ir/C catalyst with 20 wt.% Pd–Ir and the atomic ratio of Pd:Ir = 3:1 noted as the Pd–Ir/C-3 catalyst, the components of the initial suspension were 60 mg Vulcan XC-72 carbon, 2.00 mL 0.04504 M PdCl₂ and 1.3 mL 0.067 M (NH₄)₂IrCl₆ in 10 mL H₂O. For the Pd–Ir/C catalyst

with 20 wt.% Pd–Ir and the atomic ratio of Pd:Ir = 5:1 noted as the Pd–Ir/C-5 catalyst, the initial components of the suspension were 60 mg Vulcan XC-72 carbon, 2.30 mL 0.04504 M PdCl₂ and 1.00 mL 0.067 M (NH₄)₂IrCl₆ in 10 mL H₂O. For the Pd/C catalyst with 20 wt.% Pd, the initial components of the suspension were 60 mg Vulcan XC-72 carbon, 3.13 mL 0.04504 M PdCl₂ in 10 mL H₂O. For the Ir/C catalyst with 20 wt.% Ir, the initial components of the suspension were 60 mg Vulcan XC-72 carbon and 3.80 mL 0.067 M (NH₄)₂IrCl₆ in 10 mL H₂O.

The electrochemical measurements were performed with a CHI600 electrochemical analyzer and a conventional three-electrode electrochemical cell. A Pt plate was used as the auxiliary electrode. The saturated calomel electrode (SCE) electrode was used as the reference electrode. All the potentials were quoted with respect to SCE. The working electrode was prepared as follows. A glassy carbon electrode was polished with 0.3 and 0.05 μm Al₂O₃ sequentially and washed. Eight milligrams catalyst and 4 mL C₂H₅OH were mixed to obtain the catalyst slurry. Then, 8.9 μL slurry was spread on the surface of the glassy carbon electrode. After drying, 4.5 μL Nafion (5 wt.%) solution was covered on the surface of the catalyst layer and the working electrode was obtained. The diameter of the glassy carbon electrode is 4 mm and its apparent surface area was 0.1256 cm². The specific loading of Pd–Ir, Pd or Ir on the electrode surface was 28 μg cm⁻².

The solution for the electrochemical measurement was 0.5 M H₂SO₄ solution with or without 0.5 M HCOOH. N₂ was bubbled into the solution for 10 min to remove O₂ dissolved in the solution prior to the electrochemical measurements. In the process of the measurement, N₂ was flowed above the solution. For the electrochemical measurement of the adsorbed CO, when the electrode potential was fixed at 0 V CO was bubbled into the solution for 15 min until CO was fully adsorbed on the electrode. Then, N₂ was bubbled into the solution for 10 min to remove CO in the solution. All the electrochemical measurements were carried out at 30 ± 1 °C.

The composition of catalysts was determined using the energy dispersive spectrometer (EDS) with Vantage Digital Acquisition Engine (Thermo Noran, USA). The X-ray diffraction (XRD) measurements of catalysts were performed on Model D/max-rC diffractometer using Cu Kα radiation (λ = 0.15406 nm) and operating at 45 kV and 100 mA.

3. Results and discussion

Fig. 1 displays the EDS spectrum of the Pd–Ir/C-5 catalyst. The Pd and Ir peaks were observed except the carbon peak. The atomic ratio of Pd and Ir in the catalyst is 5.0:0.95, indicating that both PdCl₂ and (NH₄)₂IrCl₆ added have been completely reduced to Pd and Ir in the Pd–Ir-5 catalyst.

Fig. 2 shows the XRD patterns of the Pd/C and the different Pd–Ir/C catalysts. It was observed from Fig. 2, curve d that except the characteristic peak of carbon at 24.5°, the 2θ values of other four peaks are 40.07°, 46.53°, 68.19° and 82.02°. They correspond to the 2θ values of Pd (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal faces of the face centered cubic crystalline of the Pd particles in the Pd/C catalyst, respectively, (ASTM standard 5-

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