

Short communication

A carbon-supported Pd-P catalyst as the anodic catalyst in a direct formic acid fuel cell

Lingling Zhang^a, Yawen Tang^a, Jianchun Bao^a, Tianhong Lu^{a,b,*}, Cun Li^{a,*}

^a College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing 210097, PR China

^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renming Road, Changchun, Jilin Province 130022, PR China

Received 29 June 2006; received in revised form 1 July 2006; accepted 3 July 2006

Available online 17 August 2006

Abstract

In this paper, it is reported for the first time that a carbon-supported Pd-P (Pd-P/C) catalyst for the anodic catalyst in the direct formic acid fuel cell (DFAFC) can be prepared. The Pd-P/C catalyst shows that its electrocatalytic activity and especially its stability for the oxidation of formic acid are much higher than that of a Pd/C catalyst. Therefore, the Pd-P/C catalyst may have practical applications in DFAFCs.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Direct formic acid fuel cell; Carbon-supported Pd catalyst; Carbon-supported Pd-P catalyst

1. Introduction

Recently, the advantages of a direct formic acid fuel cell (DFAFC) have been progressively recognized compared to a direct methanol fuel cell [1]. For example, formic acid is non-toxic and has two orders of magnitude smaller crossover flux through a Nafion membrane than methanol [2]. Consequently, the optimal operating concentration of formic acid in a DFAFC can be as high as 15 M [3,4]. Thus, the power density of a DFAFC can be higher than that of DMFC although the energy density of methanol is higher than that of formic acid.

In recent years, Ha et al. [1–6] investigated the Pd/C catalyst as an anodic catalyst for the DFAFC and found that Pd possesses good electrocatalytic activity for the oxidation of formic acid [7–10]. However, the Pd catalyst has some drawbacks. Especially, Pd is easily oxidized compared with Pt. Thus, one of the disadvantages of Pd as an anodic catalyst is its instability [11]. A very slow deactivation was found to reduce the oxidation current in the process of the oxidation of formic acid on a Pd catalyst [7]. It was reported that Pd initially shows electrocatalytic activity for the oxidation of formic acid much higher than that of a Pt or a Pt/Pd catalyst, but the steady-state activities

are in the order of Pt/Pd > Pd > Pt [12]. The electrocatalytic stability of Pd for the oxidation of formic acid may be related to impurities in the solution because it was reported that after formic acid was purified, the electrocatalytic stability was in the order of Pd > Pt/Pd > Pt [3,9]. Thus, there may be several factors affecting the electrocatalytic stability of Pd-based catalysts. This should be studied further.

In order to improve the stability of the Pd catalyst, the Pd-based composite catalysts were investigated. Most of the reported Pd-based composite catalysts are composed of Pd and other metal elements, such as Pd-Pt [12,13] and Pd-Au [14]. In the present work, a carbon-supported composite catalyst composed of Pd and a nonmetal element, P, was prepared. Its electrochemical activity and especially the stability for the oxidation of formic acid are better than that of a Pd/C catalyst.

The preparation procedure of the 20 wt.% Pd/C and Pd-P catalysts is as follows. 25.0 mg of NH₄F, 125 mg H₃BO₃ and 3.13 mL 0.045 M PdCl₂ solution were added to 10 mL water. Sixty milligrams Vulcan XC-72 carbon was added to the solution and the suspension obtained was sonicated for 30 min at room temperature. The pH of the suspension was adjusted to 8–9 using concentrated ammonia. Then 10 mL NaBH₄ solution was added slowly into the suspension and sonicated for 30 min. After it was filtered, washed with the triply distilled water and dried in a vacuum oven at 60 °C, a 20 wt.% Pd/C catalyst was obtained.

* Corresponding authors. Tel.: +86 25 83598031; fax: +86 431 5685653.

E-mail addresses: tianhonglu@263.net, tianhonglu_1999@yahoo.com (T. Lu).

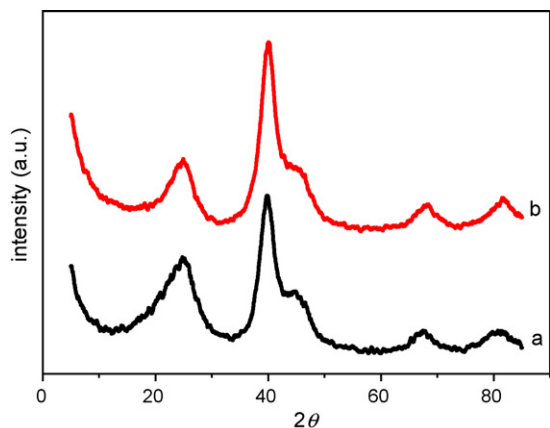


Fig. 1. The XRD patterns of: (a) the Pd/C and (b) Pd-P/C catalysts.

A similar method was used to prepare a Pd-P/C catalyst. The only difference was that after the above suspension was obtained, 10 mL 0.1 M NaH_2PO_2 solution was added to the suspension with stirring and the reductant, NaBH_4 was not added.

The electrochemical measurements were performed using a CHI 600 electrochemical analyzer and a conventional three-electrode electrochemical cell at $30 \pm 1^\circ\text{C}$. A Pt plate was used as the auxiliary electrode. A saturated calomel electrode (SCE) electrode was used as the reference electrode. A catalyst modified glassy carbon (GC) electrode was used as the working electrode. Nine microliters slurry obtained was laid on the surface of the glassy carbon electrode. The specific loading of Pd on the electrode surface was about $28 \mu\text{g cm}^{-2}$. The solution for the measurement was 0.5 M H_2SO_4 solution with or without 0.5 M HCOOH.

Energy dispersive spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques were used to characterize the catalysts.

The measurement of the energy dispersive spectrum of the Pd-P/C catalyst indicated that the Pd-P/C catalyst contained about 20.0 wt.% Pd, 0.52 wt.% P and the atomic ratio of Pd and P in the catalyst was 1.0:0.09.

Fig. 1 shows XRD patterns of the Pd/C and Pd-P/C catalysts. It was found from Fig. 2, curve 'a', that the 2θ values of four

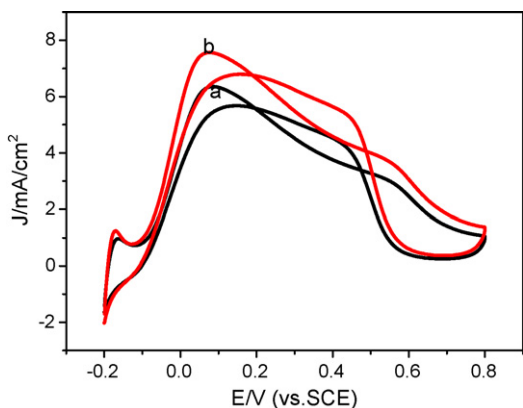


Fig. 2. The cyclic voltammograms of 0.5 M HCOOH in the 0.5 M H_2SO_4 solution at: (a) the Pd/C and (b) Pd-P/C catalyst electrodes at 50 mV s^{-1} .

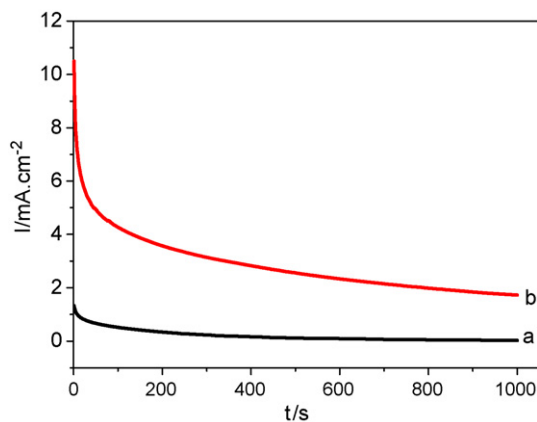


Fig. 3. The chronoamperometric curves of 0.5 M HCOOH in 0.5 M H_2SO_4 solution at: (a) the Pd/C and (b) Pd-P/C catalyst electrodes for 1000 s. Fixed potential: 0.3 V.

peaks corresponded to that of the 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/C catalyst, respectively (ASTM standard 5-681(Pd)), illustrating that Pd in the Pd/C catalyst possesses the structure of a face centered cubic crystal. The 2θ values of the characteristic peaks for the Pd-P/C catalyst (Fig. 1, curve 'b') shifted to the high 2θ direction comparing the peak positions of Pd (Fig. 1, curve 'a'), revealing that P has entered into the Pd lattice and an alloy of Pd and P was formed. The average sizes of the Pd and Pd-P particles in the Pd/C and Pd-P/C catalysts were measured to be 3.2 and 3.0, respectively, according to the procedure in the literature [15,16]. The results indicated that the Pd and Pd-P particles in the Pd/C and Pd-P/C catalysts were similar. The average sizes of the Pd and Pd-P particles obtained from TEM measurements are in agreement with that from the above XRD measurements.

Fig. 2 shows the cyclic voltammograms of 0.5 M HCOOH in the 0.5 M H_2SO_4 solution at the Pd/C and Pd-P/C catalyst electrodes at 50 mV s^{-1} . It can be observed from Fig. 2, curve 'a', that in the positive scan direction, a main peak at 0.085 V and a small peak at about 0.546 V were observed. Their peak currents are 6.34 and 3.00 mA cm^{-2} , respectively. The corresponding peaks are located at 0.072 and 0.543 V and the peak currents are 7.57 and 3.72 mA cm^{-2} at the Pd-P/C catalyst in Fig. 2, curve 'b'.

Comparing with the Pd/C catalyst, the potential of the main peak for the oxidation of formic acid at the Pd-P/C catalyst electrode shifted 18 mV in the negative direction and the peak current was increased 1.19 mA cm^{-2} . Thus, it is obvious that the electrocatalytic activity of the Pd-P/C catalyst for the oxidation of formic acid is higher than that of the Pd/C catalyst. Because the average sizes of the Pd and Pd-P particles in the Pd/C and Pd-P/C catalysts are similar, the high electrocatalytic activity of the Pd-P/C catalyst can be only attributed to the P doping.

Fig. 3 shows the chronoamperometric curves of 0.5 M HCOOH in 0.5 M H_2SO_4 solution for two catalyst electrodes at 0.3 V. It can be observed that the current densities at the Pd/C and Pd-P/C catalyst electrodes at 1000 s were 0.33 and 1.72 mA cm^{-2} , respectively. When the potential was fixed at 0.3 V, the current densities at the Pd/C and Pd-P/C catalyst elec-

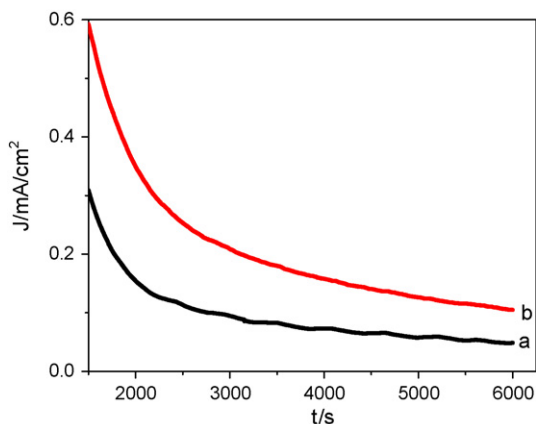


Fig. 4. The chronoamperometric curves of 0.5 M HCOOH in 0.5 M H₂SO₄ solution at: (a) the Pd/C and (b) Pd-P/C catalyst electrodes for 6000 s. Fixed potential: 0.1 V.

trodes at 1000 s were 0.017 and 1.510 mA cm⁻², respectively. At 0.1 V, the corresponding current densities were 1.54 and 2.41 mA cm⁻², respectively. When the fixed potential was 0.1 V and the time was extended to 6000 s, the current densities at the Pd/C and Pd-P/C catalyst electrodes at 6000 s were 0.060 and 0.118 mA cm⁻², respectively (Fig. 4). The above electrochemical results demonstrate that after P is added to the Pd particles, the electrocatalytic performance of the catalyst for the oxidation of formic acid was increased. Especially, the electrocatalytic stability of the Pd-P/C catalyst for the oxidation of formic acid was much better than that of the Pd/C catalyst. Pd is easily oxidized, but after P is added to the Pd particles, Pd may not be so easily oxidized because P is already a nonmetallic element.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20433060, 20473038, 20573057), the Natural Science foundation of Jiangsu Province (BK2006224), the Natural Science Foundation of the Education Committee of Jiangsu Province (05KJB150061, 04KJB150066).

References

- [1] S. Ha, B. Adams, R.I. Masel, *J. Power Sources* 128 (2004) 119.
- [2] Y.W. Rhee, S. Ha, C. Rice, R.I. Masel, *J. Power Sources* 117 (2003) 35.
- [3] C. Rice, S. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *J. Power Sources* 111 (2002) 83.
- [4] C. Rice, S. Ha, R.I. Masel, A. Wieckowski, *J. Power Sources* 115 (2003) 229.
- [5] Y.W. Rhee, S.Y. Ha, R.I. Masel, *J. Power Sources* 117 (2003) 35.
- [6] S.Y. Ha, R. Larsen, R.I. Masel, *J. Power Sources* 144 (2005) 28.
- [7] P.K. Badu, H.S. Kim, J.H. Chung, E. Oldfield, A. Wieckowski, *J. Phys. Chem. B* 108 (2004) 20228.
- [8] X.G. Zhang, A. Toshihide, M. Yasushi, Y. Kiyochika, T. Yoshio, *Electrochim. Acta* (1995) 1889.
- [9] Y.M. Zhu, K. Zakia, R.I. Masel, *J. Power Sources* 139 (2005) 15.
- [10] Y.M. Zhu, S.Y. Ha, R.I. Masel, *J. Power Sources* 130 (2004) 8.
- [11] K. Persson, A. Ersson, K. Jansson, N. Iverlund, S. Jaras, *J. Catal.* 231 (2005) 139.
- [12] F.S. Thomas, R.I. Masel, *Surf. Sci.* 573 (2004) 169.
- [13] M.J. Llorca, J.M. Feliu, A. Aldaz, J. Clavilier, *J. Electroanal. Chem.* 376 (1994) 151.
- [14] M. Baldauf, D.M. Kolb, *J. Phys. Chem.* 100 (1996) 11375.
- [15] E. Antolini, F. Cardellini, *J. Alloys Compd.* 315 (2001) 118.
- [16] V. Radmilovic, H.A. Gasteiger, P.N. Ross, *J. Catal.* 15 (1995) 98.