ELECTROCATALYTIC PERFORMANCES OF PHOSPHORUS DOPED CARBON SUPPORTED PALLADIUM TOWARD FORMIC ACID OXIDATION

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Abstract

A new kind of phosphorus contained carbon support (P–C) was fabricated by calcining the mixture of the carbon and triphenylphosphine under nitrogen. The effects of different calcining temperature on the catalytic activity of the formic acid oxidation were investigated. The Pd/P–C and Pd/C catalysts were synthesized as formic acid oxidation catalyst by liquid reduction method. The catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Well-dispersed Pd nanoparticles were obtained and their particle sizes are in the range of 3.46–4.46 nm. The catalytic activity of the catalysts toward formic acid electro-oxidation was evaluated by cyclic voltammetry, chronoamperometry and CO-stripping voltammetry. The results depicted that when the mixture of carbon and triphenylphosphine were annealed at 800°C, the activity of the corresponding catalyst (Pd/P–C-800) was enhanced as a factor of 3.14 than the Pd/C catalyst. The stability of Pd/P–C–800 catalyst was also improved as compared with the Pd/C catalyst. The ratio of $I_{3600}$ (the current at 3600 s) / $I_{10}$ (the current at 10 s) for Pd/C and Pd/P–C–800 catalysts was found to be 5.9% and 18.4%, respectively. A negative shift (31mV than Pd/C) of formic acid oxidation was observed from the Pd/P–C–800 catalyst. Moreover, faster charge-transfer kinetics of the formic acid oxidation for the Pd/P–C–800 catalyst was determined through electrochemical impedance spectroscopy (EIS) measurements. The better catalytic activity and stability of the Pd/P–C catalyst may be ascribed to the doping of phosphorus, which caused better dispersion of Pd nanoparticles. The modified electronic effect by doping led to more integral of carbon, more negative onset oxidation potential and faster charge-transfer kinetics of the formic acid oxidation.

Keywords
Phosphorus doped carbon; formic acid oxidation; electrocatalytic activity; catalyst.

Introduction

The direct formic acid fuel cell (DFAFC) can be used as the power source due to its several advantages, such as high energy conversion efficiency, low environmental pollution and low toxicity. Recently, researchers find that non-metallic elements doping, such as N, P, S, can not only improve the acid resistance of the catalysts effectively, but also enhance the catalytic activity. The phosphorus element has a multi-electron system and can feasibly change the outer electron structure of metal particle by interacting with them. Our previous work demonstrated that the nitrogen contained composite support (MMT–CNx) loaded Pd catalyst improved the electrocatalytic activity and stability as compared with the Pd/C towards the formic acid electro-oxidation. Since phosphorus and nitrogen

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were both placed in the group VA, it would present similar performances like nitrogen. So the element of phosphorus was selected as the dopant. The Pd catalysts supported on the phosphorus doped carbon for formic acid electro-oxidation were reported in this paper.

**Methodology**

In the synthesis of P-doped activated carbon, 1.0 g of activated carbon was introduced to a 500 mL beaker, and then 200 mL ethanol with 5.0 g triphenylphosphine (TPP) was added to the beaker. The solution was vigorously stirred for 5 h at room temperature. The obtained solution was added to the beaker. The solution was vigorously stirred for 5 h at room temperature. The obtained solution was dried at 80℃. The powder was denoted as C–TPP. The powder was then placed in a quartz tube furnace and heated to 800℃ at the ramp rate of 5 ℃ min⁻¹ under N₂ atmosphere and pyrolyzed at 800℃ for 3 h. After the furnace was cooled down to room temperature, P-doped carbon was obtained. Other P-doped activated carbon supports were also prepared and referred to as P–C–X (X=700, 900, X is calcining temperature, ℃). The powder of P–C–X (80 mg) was added into a 100 mL flask. 3.76 mL of 0.05 mol L⁻¹ PdCl₂ solution and 20 mL of H₂O were added into the flask. The solution was stirred for 12 h and dispersed ultrasonically for 40 min afterwards. The pH of the suspension was adjusted to 8–9 by adding 1 mol L⁻¹ of Na₂CO₃ solution. It was stirred for half an hour before an excess of freshly prepared NaBH₄ solution was added dropwise into the above mixture. Subsequently, an additional 4 h of stirring was performed to complete the reaction. The resulting catalyst (Pd/P–C–X) was filtered and washed with ultrapure water until no Cl⁻ was detected and then dried in a vacuum oven at 60 ℃ for 6 h. For comparison, Pd/C catalyst was prepared in this paper with the same procedure.

**Results and Discussion**

Figure 1(a) depicts the specific activities of the Pd/C, Pd/P–C–700, Pd/P–C–800, Pd/P–C–900 catalysts and the P–C support. The specific oxidative current of Pd/C, Pd/P–C–700, Pd/P–C–800 and Pd/P–C–900 catalyst electrodes were determined as 6.19 A m⁻², 11.83 A m⁻², 16.60 A m⁻² and 19.45 A m⁻², respectively. Apparent improvement of electrocatalytic activity of catalysts was found by P-doped carbon. The formic acid oxidation activity on the P–C–X electrodes of Pd/P–C–700, Pd/P–C–800, and Pd/P–C–900 was found to be 5.9%, 12.5%, 18.4% and 10.7%, respectively. Therefore, the results demonstrated that the phosphorus incorporation can greatly improve the activity and stability of the catalyst for the electro-oxidation of formic acid.

Figure 1(c) demonstrates the Nyquist plots of Pd/P–C–700, Pd/P–C–800, Pd/P–C–900 and Pd/C catalysts obtained in a solution of 0.5 M H₂SO₄ and 0.5 M HCOOH. The diameter of the semicircle in the Nyquist plot represents the charge transfer resistance of the reaction 4. As given in the Figure 1(c), smaller diameter of the catalysts of the Pd/P–C–700, Pd/P–C–800, and Pd/P–C–900 exhibits their faster charge transfer kinetics in comparison with the Pd/C catalyst.

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**References**