



Short communication

Improvement of electrocatalytic performance of carbon supported Pd anodic catalyst in direct formic acid fuel cell by ethylenediamine-tetramethylene phosphonic acid

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ABSTRACT

The direct formic acid fuel cell (DFAFC) has two major shortcomings that limit its lifespan and performance: (i) the poor electrocatalytic stability of the carbon supported Pd (Pd/C) catalyst for the oxidation of formic acid and (ii) rapid decomposition of formic acid over the Pd/C catalyst. To solve the problems, the Pd/C catalyst is modified with ethylenediamine-tetramethylene phosphonic acid (EDTMP). The resulting catalyst is designated as Pd/C-E catalyst. It is found that the Pd/C-E catalyst can inhibit the decomposition of formic acid and promote the oxidation of formic acid through the direct pathway. Consistently, the Pd/C-E catalyst is significantly protected from CO poisoning. As compared to the Pd/C catalyst, the electrocatalytic performance of the Pd/C-E catalyst is significantly superior. These results provide the first proof of the concept that DFAFC can be significantly improved by Pd/C-E catalyst.

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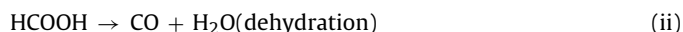
1. Introduction

DFAFC has become an attractive alternative of direct methanol fuel cell (DMFC) for several obvious reasons [1]. DFAFC is not a biohazard. When used at dilute concentrations formic acid is considered a non-toxic food additive [2]. Formic acid is also not inflammable, and does not require special device for storage and transportation. Moreover, DFAFC has the potential to achieve better performance than DMFC, for formic acid has two orders of magnitude smaller crossover flux through the Nafion membrane than methanol [3]. Consequently, the energy consumption in the oxidation of formic acid is lower than that of the oxidation of methanol [4]. However, the efficiency of the oxidation of formic acid is highly dependent on the catalyst. Theoretically, the electrooxidation of formic acid can proceed through two parallel pathways, i.e., the direct pathway and the CO pathway [5–9]. In the direct pathway, formic acid is completely oxidized to generate CO₂. In the CO pathway, incomplete oxidation of formic acid firstly generates CO, which is further oxidized to CO₂. It has been demonstrated that the oxidation of formic acid at the Pd catalyst occurs mainly through the direct pathway [10,11].

It is important to note that although Pd anodic catalyst in DFAFC is a catalyst of choice for its superior electrocatalytic activity [12], its low electrocatalytic stability renders Pd-based DFAFC unsat-

isfactory [13,14]. Therefore, various attempts have been made to improve the electrocatalytic stability of the Pd catalyst with the electronic effect, ensemble effect or the bifunctional effect through the addition of a second element (Pt, P, Co, Ir, Au, Pb, Sn) [15–22]. However, the deactivation problem of the Pd catalyst has not been solved.

Further studies have revealed that Pd catalyst is bifunctional. It can simultaneously catalyze the oxidation and decomposition of formic acid. The decomposition of formic acid over the Pd catalyst could undergo through the following two parallel pathways [23,24]:



The decomposition of formic acid over the Pd catalyst could produce CO in dehydration reaction (ii) CO produced would poison the Pd catalyst and decreases its electrocatalytic performance.

It is known that EDTMP has a strong coordinating capability to chelate divalent metal ions (e.g., Mg^{II}, Ca^{II}, Sr^{II}, Pd^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Cu^{II} and Pb^{II} [25–27]). In this paper, we describe a procedure to modify the Pd/C catalyst with EDTMP. The resulting Pd/C-E catalyst displayed the improved electrocatalytic stability and decreased the decomposition of formic acid, as compared to the Pd/C catalyst. Our results suggest that the Pd/C-E catalyst may significantly improve the lifespan and the performance of DFAFC.

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2. Experimental

2.1. Reagents and chemicals

Vulcan XC-72 carbon was obtained from Cabot Company (Boston, USA). Analytical grade EDTMP was purchased from Shandong Taihe Water Treatment Co., Ltd. (Shandong, China) and was recrystallized twice in the ethanol solution prior to use [28]. PdCl₂ was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and used without further purification. All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 MΩ (Purelab Classic Corp., USA).

2.2. Preparation of Pd/C and Pd/C-E catalysts

Pd/C catalyst with 20.0 wt% Pd was prepared with the following procedure: A total of 3.13 mL of 0.04504 M PdCl₂ and 60 mg Vulcan XC-72 carbon were mixed with water to a final volume of 10 mL. The resulting suspension was sonicated for 30 min and stirred mechanically for 4 h. After the pH of the suspension was adjusted to 8–9 with the Na₂CO₃ solution, NaBH₄ solution was added to the suspension to the indicated final concentrations and stirred for an additional 1 h. Finally, the mixture was washed, filtered and dried in a vacuum oven at 50 °C for 12 h.

The Pd/C-E catalyst was prepared as follows. A total of 50 mg of Pd/C catalyst was immersed in 5 × 10⁻⁴ M EDTMP solution and was continuously stirred for 4 h. Finally, the mixture was washed, filtered and dried in a vacuum oven at 50 °C for 12 h.

2.3. Characterizations of Pd/C and Pd/C-E catalysts

The catalyst composition was determined using the energy dispersive spectrometer (EDS) with Vantage Digital Acquisition Engine (Thermo Noran, USA). X-ray diffraction (XRD) patterns were obtained on a Model D/max-rC X-ray diffractometer with the Cu Kα (λ = 1.5406 Å) radiation source operating at 40 kV and 100 mA. The nitrogen element content was obtained using vario ELIII Element Analyzer.

2.4. Electrochemical measurements

The electrochemical measurements were carried out at 30 ± 1 °C with a CHI600 electrochemical analyzer (CHI instruments Co., USA) and a conventional three electrode electrochemical cell.

The working electrodes were prepared as follows. A glassy carbon electrode was polished sequentially with 0.3 and 0.05 μm Al₂O₃, followed by a wash. A total of 8 mg catalyst and 4 mL C₂H₅OH were mixed to obtain the catalyst slurry. Then, a total of 8.9 μL slurry was spread on the surface of the glassy carbon electrode. After drying, 4.5 μL Nafion (5% (wt)) solution was used to cover the surface of the catalyst layer. The diameter of the resulting glassy carbon electrode was 4 mm with an apparent surface area of 0.1256 cm². The specific loading of the catalyst on the electrode surface was 28 μg cm⁻². The Pd/C and Pd/C-E catalyst electrodes were cleaned electrochemically before use. In order to clean the electrode, the cyclic voltammetric measurement was firstly taken from -0.2 V to 0.8 V in 0.5 M H₂SO₄ solution at the Pd/C and Pd/C-E catalyst electrodes.

For electrochemical measurements, a Pt plate was used as the auxiliary electrode. The saturated calomel electrode (SCE) was used as the reference electrode. All the potentials were quoted with respect to SCE. The electrolyte was 0.5 M H₂SO₄ solution with or without 0.5 M formic acid. Prior to the measurements, a steady stream of N₂ was bubbled into the solution for 10 min to remove O₂ in the electrolyte.

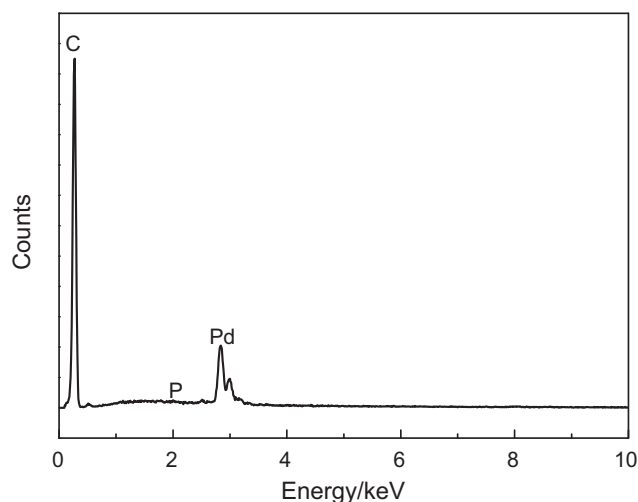


Fig. 1. The EDS spectrum of the Pd/C-E catalyst.

During the measurement, N₂ was flowed above the solution. For the electrochemical measurement of the adsorbed CO, the electrode potential was fixed at 0V, and CO was bubbled into the electrolyte 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.

2.5. Measurement of decomposition of formic acid

A total of 20 mg Pd/C or Pd/C-E catalyst, 30 mL 0.5 M formic acid and 0.5 M H₂SO₄ solution were added into a three-necked flask. The gases produced can be collected between 28 °C and 29 °C from the water bath under continuous stirring condition. Then, the volume of gas produced from decomposition of formic acid over the catalyst was recorded every 5 min for 2 h.

3. Results and discussion

As shown by the EDS spectrum of the Pd/C-E catalyst (Fig. 1). The P peak was observed except the carbon and Pd peaks. The atomic ratio of Pd and P in the catalyst is 50:1. Since only EDTMP molecule contained P element, this result indicates that the Pd/C catalyst was indeed modified by EDTMP.

To further confirm that EDTMP had been adsorbed on the Pd/C-E catalyst, the nitrogen element content of the Pd/C-E catalyst was examined. The nitrogen element content is 0.88% (wt), indicating that one compound containing nitrogen element had been adsorbed onto the surface of Pd. Since the only nitrogen-containing compound in Pd/C-E preparation was EDTMP, this result supports the incorporation of EDTMP.

Fig. 2 shows the XRD patterns of the Pd/C and Pd/C-E catalysts. It was observed from Fig. 2, except the characteristic peak of C (002) at 24.8°, the observed other diffraction peaks at 39.8°, 44.9°, 67.6°, and 81.2° can be indexed to Pd (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face-centered cubic crystalline of Pd, respectively (JCPDS standard 05-0681(Pd)). The average size of the Pd nanoparticles can be calculated from the half peak width of the Pd (2 2 0) peak according to Scherrer equation [29,30]. The average sizes of the Pd nanoparticles in the Pd/C and Pd/C-E catalysts are calculated to be both 4.8 nm. These results demonstrate that EDTMP adsorbed on the Pd/C catalyst has no effect on the structure of the Pd/C catalyst.

Fig. 3 shows the cyclic voltammograms of 0.5 M formic acid in 0.5 M H₂SO₄ solution at the Pd/C and Pd/C-E catalyst electrodes. It was observed from Fig. 3, the potentials of the main anodic peaks of the oxidation of formic acid at the Pd/C and Pd/C-E catalyst

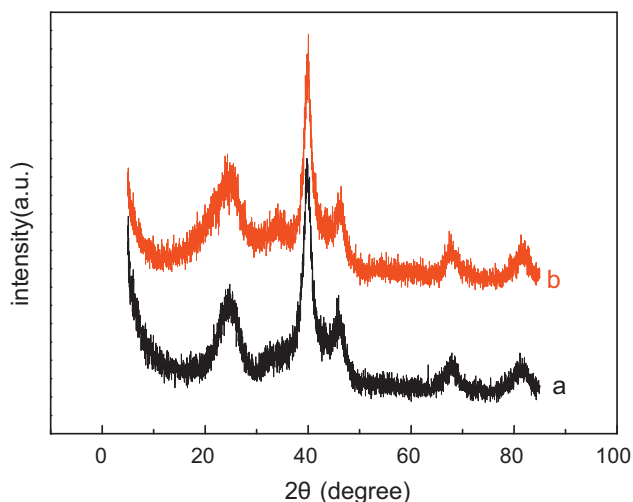


Fig. 2. The XRD patterns of the (a) Pd/C and (b) Pd/C-E catalysts.

electrodes are almost the same, at 0.14 V. However, the current densities of the peaks at the Pd/C and Pd/C-E catalyst electrodes are 0.565 and 0.309 A mg^{-1} , respectively. The current density of the peak at the Pd/C-E catalyst electrode is about 1.83 times larger than that at the Pd/C catalyst electrode, illustrating that the electrocatalytic activity of the Pd/C-E catalyst for formic acid oxidation is much higher than that of the Pd/C catalyst.

Fig. 4 displays the chronoamperometric curves of 0.5 M formic acid in 0.5 M H_2SO_4 solution at the Pd/C and Pd/C-E catalyst electrodes at 0.15 V. It is observed that the current densities at the Pd/C and Pd/C-E catalyst electrodes are 0.007 and 0.068 A mg^{-1} at 6000 s. They correspond to 1.4% and 12.8% current densities at 10 s at the Pd/C and Pd/C-E catalyst electrodes, respectively. This clearly illustrates that the electrocatalytic stability of the Pd/C-E catalyst is much better than that of the Pd/C catalyst.

Fig. 5 shows the current density versus cycle numbers curves for the cyclic voltammograms of 0.5 M formic acid in 0.5 M H_2SO_4 solution at the Pd/C and Pd/C-E catalyst electrodes. It was observed from Fig. 5 that although the current densities at the Pd/C and Pd/C-E catalyst electrodes both decreased gradually with successive scans, the current densities at the Pd/C-E catalyst electrode is always higher than that at the Pd/C catalyst electrode in the whole process [31]. This further confirms that the electrocatalytic stability of the

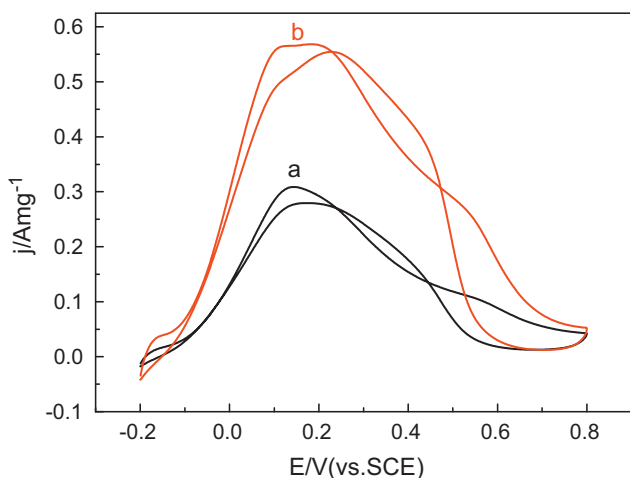


Fig. 3. The cyclic voltammograms of 0.5 M formic acid in 0.5 M H_2SO_4 solution at the (a) Pd/C and (b) Pd/C-E catalyst electrodes.

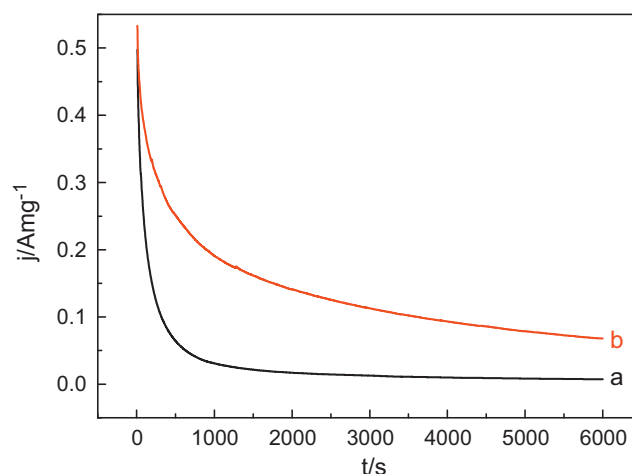


Fig. 4. The chronoamperometric curves of 0.5 M formic acid in 0.5 M H_2SO_4 solution at the (a) Pd/C and (b) Pd/C-E catalyst electrodes at 0.15 V.

Pd/C-E catalyst for the oxidation of formic acid is much better than that of the Pd/C catalyst.

Fig. 6 displays the linear sweeping voltammograms of the adsorbed CO in 0.5 M H_2SO_4 solution at the Pd/C and Pd/C-E catalyst electrodes. The peak potentials of the adsorbed CO at the Pd/C and Pd/C-E catalyst electrodes are nearly the same, at 0.66 V, illustrating the adsorbed EDTMP has no influence on the adsorption strength of CO. The oxidation peak area of the adsorbed CO can be calculated by Origin 7.0 software. Then, the Coulombic amount (Q) of the adsorbed CO is the ratio of the oxidation peak area to a scan rate of 10 mV s^{-1} . The calculated amounts of adsorbed CO at the Pd/C and Pd/C-E catalyst electrodes are 4419 and 3795 $\mu\text{C mg}^{-1}$, respectively. Therefore, the amount of adsorbed CO at the Pd/C-E catalyst electrode is less than that at the Pd/C catalyst electrode. It was widely accepted that the oxidation of formic acid through the CO pathway requires at least three continuous catalyst atoms and the indirect pathway will be inhibited if the catalyst atoms are separated [32]. The modification of EDTMP on Pd causes the separation of Pd active sites. Thus, the adsorbed EDTMP would inhibit the CO pathway for the oxidation of formic acid. Therefore, the electrocatalytic performance of the Pd/C-E catalyst is improved.

Fig. 7 displays the relationship curves between the time and the gas volume produced from the catalytic decomposition of formic

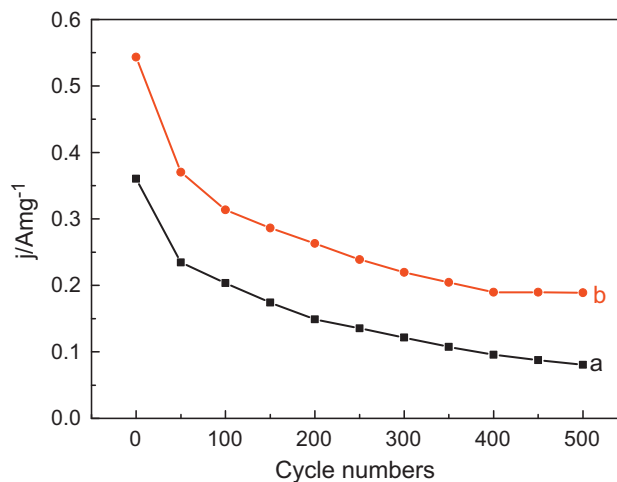


Fig. 5. The current density versus cycle numbers curves for the cyclic voltammograms of 0.5 M formic acid in 0.5 M H_2SO_4 solution at the (a) Pd/C and (b) Pd/C-E catalyst electrodes.

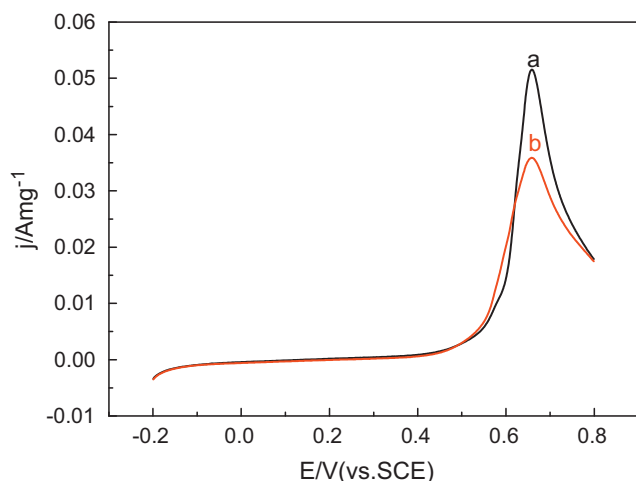


Fig. 6. The linear sweeping voltammograms of the adsorbed CO in 0.5 M H₂SO₄ solution at the (a) Pd/C and (b) Pd/C-E catalyst electrodes.

acid over the Pd/C and Pd/C-E catalysts in 0.5 M formic acid and 0.5 M H₂SO₄ solution. The gas volume produced from the decomposition of formic acid over the Pd/C and Pd/C-E catalysts in 2 h are 22.4 and 9.7 mL, respectively. The gas volume produced from the decomposition of formic acid over the Pd/C-E catalyst is only 43% of that over the Pd/C catalyst.

Previous research has shown that the main products of the decomposition of formic acid over the Pd catalyst are CO₂ and H₂. The products also contain a small amount of CO [33,34]. The catalytic decomposition of formic acid over the Pd catalyst wastes a lot of formic acid. Furthermore, CO from the decomposition of formic acid may poison the Pd catalyst to decrease the electrocatalytic performance of the Pd catalyst. The gas volume produced from the decomposition of formic acid over the Pd/C-E catalyst is much less than that over the Pd/C catalyst, indicating that the Pd/C-E catalyst can inhibit the decomposition of formic acid and then decrease the CO production. Therefore, the electrocatalytic stability of the Pd/C-E catalyst for the oxidation of formic acid is much better than that of the Pd/C catalyst.

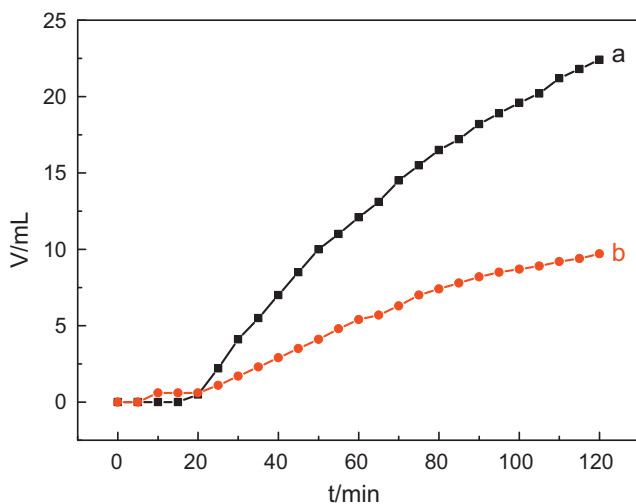


Fig. 7. The relationship between the time and the gas volume produced from the catalytic decomposition of formic acid over the (a) Pd/C and (b) Pd/C-E catalysts in 0.5 M formic acid and 0.5 M H₂SO₄ solution.

4. Conclusions

In order to increase the lifespan and the electrocatalytic performance of the Pd/C anodic catalyst for the oxidation of formic acid in DFAFC, we developed and characterized the Pd/C-E catalyst. We found that Pd/C-E catalyst possessed improved electrocatalytic activity and stability for the oxidation of formic acid. The excellent electrocatalytic performance of the Pd/C-E catalyst may be attributed to inhibiting the decomposition of formic acid and to promoting the oxidation of formic acid through the direct pathway. The preparation of the Pd/C-E catalyst was simple and economic. Based on our results, the Pd/C-E catalyst could solve the two major problems of Pd/C-based DFAFC, with decreased the decomposition of formic acid and improved the electrocatalytic stability. Thus, the Pd/C-E catalyst has the potential application for promoting the industrialization of DFAFC.

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