



## Short communication

## Pd oxides/hydrous oxides as highly efficient catalyst for formic acid electrooxidation

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## HIGHLIGHTS

- Annealing of Pd/C catalyst under the O<sub>2</sub> atmosphere produces POHOs.
- Improved mass activity and stability was obtained for FAEO.
- The introduction of POHOs significantly improves the performance of the DFAFCs.

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## ABSTRACT

A novel Pd-based catalyst for formic acid electrooxidation (FAEO) was prepared by annealing commercial Pd/C catalyst under the O<sub>2</sub> atmosphere at 100 °C, which exhibits excellent catalytic activity and stability for FAEO due to introduction of Pd oxides/hydrous oxides (POHOs). The catalytic activity of the as-prepared catalyst towards FAEO is 1.86 times of the commercial Pd/C catalyst in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M HCOOH solution. Chronoamperometric curves show obvious improvement of the as-prepared catalyst electrocatalytic stability for FAEO. It is confirmed that POHOs can provide the required oxygen species for intermediate CO oxidation during the oxidation process of formic acid.

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## 1. Introduction

Direct formic acid fuel cells (DFAFCs) have been attracting much attention as clean and high-efficiency energy conversion devices for portable electronic apparatus due to several attractive features, such as faster oxidation kinetics, less toxicity and lower crossover of formic acid through Nafion membrane than methanol etc. [1–3]. For the DFAFCs, Pd-based catalysts have commonly been used as the anode because of their higher catalytic activity for FAEO, lower cost, and greater abundance compared with Pt-based catalysts [2,4]. Although the Pd has been widely studied as the catalyst for FAEO, the limited durability of Pd-based catalysts for FAEO is still unsolved and hinders the practical application of DFAFCs [5,6]. The performance degradation of the DFAFCs is resulted from the agglomeration of Pd nanoparticles due to dissolution and

redeposition process during DFAFC operation [6–8] and the poisoning of the anode. Possible adsorbed species, such as CO<sub>ad</sub> [9] and –COOH [10], were considered as the reaction intermediates or the side products for FAEO, which causes the poisoning of the electrode and therefore performance loss of the DFAFCs.

Pd-based catalysts have been extensively employed for the FAEO, oxygen reduction reaction and alcohol electrooxidation [11–13]. Although Pd-based catalysts have better catalytic activity than Pt-based, the limited durability of Pd-based catalysts for FAEO is still the major challenges for the practical application of DFAFCs. Recently, improved catalytic activity for electrocatalysts by heat-treated in oxygen atmosphere has been investigated by many groups [14–19]. Huang et al. [14] found that the activity of the fresh PtRu/C catalyst was significantly improved by oxidation treatment. The variation in activity may be caused by changes in catalyst structure during oxidation treatment. The enhancement was attributed to the segregation of Ru and the formation of Ru<sup>2+</sup>O<sub>2</sub>. Ren et al. [19] found that POHOs play a crucial role in increasing cell performance and minimizing performance degradation of the Pd-

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based catalysts. The introduction of POHOs during electrocatalysis of FAEO is found to promote elimination of poisoning species, thereby leading to a better performance of the Pd-based catalysts. However, the Pd-based catalyst needs exposure in the air for ca. six months, which seems to be rather time consuming according to the report in the literature.

In present work, in order to obtain a high POHOs content in Pd/C catalysts in a short period of time for practical application, the commercial Pd/C catalysts were applied by an annealing treatment at a certain temperature in a tubular oven. The as-prepared catalysts exhibited much higher catalytic activity and much higher stability for FAEO than the commercial catalysts; the passive DFAFCs with the as-prepared catalysts have exhibited much higher cell performance and much better long-term stability than those with the commercial catalysts.

## 2. Experimental

### 2.1. Catalyst treatment

Commercial 30 wt.% Pd/C catalyst (Sigma–Aldrich, USA) denoted as Pd/C–C was used for comparison as a baseline catalyst. It was transferred and heated in a tubular oven at 100 °C under the O<sub>2</sub> atmosphere for 24 h, the temperature was ramped at a rate of 5 °C min<sup>-1</sup> to the final temperature and the flow rate of O<sub>2</sub> was 80 cc min<sup>-1</sup> to obtain the POHOs, the sample was denoted as Pd/C–O. The above-mentioned procedure was applied to fabricate the Pd/C–H catalyst, except that the annealing atmosphere was H<sub>2</sub>.

### 2.2. Electrochemical measurements

All the electrochemical measurements were performed with an EG & G PARC potentiostat/galvanostat (Model 273A Princeton Applied Research Co., USA) and a conventional three-electrode electrochemical cell. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All potentials were referenced to SCE. The working electrode was prepared as follows. First, 5 mg of the catalyst was dispersed ultrasonically in 1000 μL of the alcohol solution containing 50 μL Nafion solution (5 wt.%, Aldrich Co., USA). Second, 5 μL of the above solution was pipetted and spread on a mirror-finished glassy carbon electrode with 4 mm diameter. At last, it was dried at room temperature for 30 min.

All electrochemical measurements were carried out in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with or without HCOOH deaerated by pure N<sub>2</sub> for at least 20 min prior to any measurements. For the electrooxidation of formic acid, the scan potential range was from -0.2 to +0.8 V. The CO<sub>ad</sub> stripping voltammograms were measured in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. CO was purged into the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 15 min to allow the complete adsorption of CO onto the catalyst when the working electrode was kept at 0.2 V, and excess CO in the electrolyte was purged out with N<sub>2</sub> for 30 min. All the measurements were carried out at room temperature, unless otherwise noted. The surface area of Pd metal was estimated assuming that the coulombic charge necessary for oxidation of a monolayer of linearly adsorbed H was 210 μC cm<sup>-2</sup> [20] while CO was 420 μC cm<sup>-2</sup> [21,22].

### 2.3. Physical characterization

X-ray diffraction (XRD) measurements were performed with a PW-1700 diffractometer using a Cu K<sub>α</sub> (λ = 1.5405 Å) radiation source (Philips Co.), the obtained XRD patterns were analyzed with Jade 5.0 software to remove the background radiation; X-ray photoelectron spectroscopy (XPS) measurements were carried out

on Mg K<sub>α</sub> radiation source (Kratos XSAM-800 spectrometer), the size and morphology of the catalysts were measured by transmission electron microscope (TEM) operating at 200 kV (Philips TECNAI G2).

### 2.4. MEA preparation

Preparation of membrane electrode assemblies (MEAs) [23]: A slurry consisted of Vulcan XC-72 carbon and PTFE (20 wt.%) was coated onto the carbon paper (TGPH030, 20 wt.% PTFE, Toray) to form the cathode diffusion layer. The Vulcan XC-72 carbon loading was ca. 2 mg cm<sup>-2</sup>.

Commercial 30 wt.% Pd/C black (Sigma–Aldrich, USA) and Pt black (Johnson Matthey, USA) were used as catalysts in the anode and cathode, respectively. The catalyst ink mixed by the catalyst, ultrapure water, isopropyl alcohol and 5 wt.% Nafion<sup>®</sup> ionomer solution was sprayed onto the diffusion layer to fabricate the catalyst layers. The anode catalytic ink was directly sprayed onto the carbon paper (TGPH060, 20 wt.% PTFE, Toray). The noble metal loading was 4.0 mg cm<sup>-2</sup> for both the anode and cathode. The Nafion ionomer loadings were 20 wt.% for anode and 15 wt.% for cathode. Then an additional layer of Nafion<sup>®</sup> ionomer with an amount of 0.1 g cm<sup>-2</sup> was sprayed on the catalyst layer, it acts as an adhesion layer. The MEAs were prepared by hot-pressing both anode and cathode on both sides of a pretreated Nafion 115 proton exchange membrane at 135 °C and 3 MPa for 150 s. The above procedure was applied to fabricate other two MEAs, the difference is that the anode catalysts were heat-treated under the O<sub>2</sub> or H<sub>2</sub> for 24 h, while the former was not heat-treated.

### 2.5. Single cell assembly and measurement

The MEA performance was evaluated in a single cell with an active cross-section area of 4 cm<sup>2</sup>. The single cell was measured at ambient conditions. A 10 M HCOOH solution was injected into a reservoir. The polarization and power density curves of the single cell were measured by a Fuel Cell Test System (Arbin Instruments Co.).

## 3. Results and discussion

### 3.1. Electrochemical analysis

Fig. 1 shows cyclic voltammograms (CVs) of the Pd/C–C, Pd/C–O, Pd/C–H catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at the scan rate of

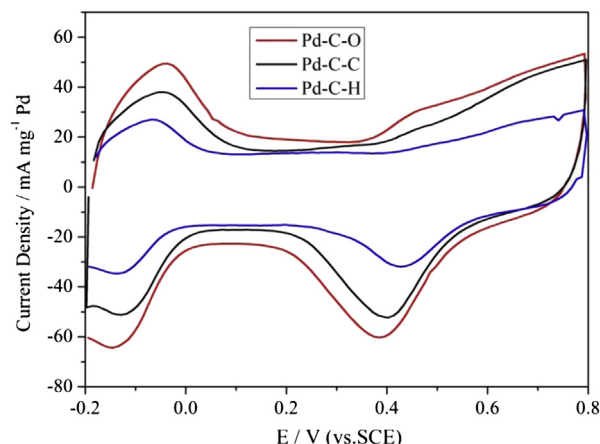


Fig. 1. CVs of different catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a scan rate of 50 mV s<sup>-1</sup>.

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