



# Based on a new support for synthesis of highly efficient palladium/hydroxyapatite catalyst for ethanol electrooxidation



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## ABSTRACT

Based on a new support, hydroxyapatite (HAP), a facile and low-cost preparation of palladium/hydroxyapatite catalyst for ethanol electrooxidation is introduced in this paper through a solvothermal reaction without additives. HAP was employed as the catalyst support for its hydroxyl-rich surface in order to increase the stability and utilization ratio of catalyst. According to transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) measurements, the as-prepared Pd nanoparticles with face-centered cubic crystal structure were evenly deposited on the surface of HAP. Cyclic voltammetry and chronoamperometry tests demonstrated that the Pd/HAP catalyst possessed a much higher current density ( $246 \text{ mA cm}^{-2}$ ) than the Pd/C catalyst ( $109 \text{ mA cm}^{-2}$ ) towards ethanol electrooxidation, and better stability as well. In the direct ethanol fuel cell (DEFC) test, Pd/HAP catalyst gives better performance than that with Pd/C in terms of both open-circuit voltage (OCV) and power density. These results indicate that the HAP is a better support and the catalyst developed in this study may be a better candidate for DEFCs. A possible mechanism consistent with the experimental is also proposed.

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## 1. Introduction

DEFCs are widely investigated and considered as a possible power source for electric vehicles owing to their advantages such as low toxicity, high volumetric energy density and relatively low operating temperature [1–4]. Among the anodic organic molecules of DEFCs, ethanol as a kind of major renewable biofuel is thought to be very promising for the development of fuel cells because it is less toxic than methanol and can be produced from the fermentation of biomass [5]. But it is crucial to design and synthesize an efficient anode catalyst with a high ability to break the C–C bond of the ethanol molecule at low overpotential and a high tolerance to the partially oxidized products such as CO. At present, platinum (Pt) and Pt-based materials are widely used as catalysts for low temperature fuel cells [6–8]. However, the high price and the toxic intermediate products of the ethanol electrooxidation in alkaline solution restrict the commercial application of Pt in DEFCs. Consequently, a large number of investigations have been made to develop non-platinum electrocatalysts. Recently, various Pd and

Pd-based catalysts have aroused increasing interests owing to their outstanding electrocatalytic activities towards ethanol electrooxidation in alkaline media, more abundant storage and lower cost than Pt [9–12].

It is well-accepted that fabricating catalyst nanoparticles immobilized on a suitable support is an ideal goal for maximizing the utilization rate of catalyst, and thereby, the choice of a suitable support is one of the key factors affecting the performance of the catalysts [6]. At present, XC-72 [13] and carbon nanotubes (CNTs) [14] are widely used as supports due to their high specific surface area, electrical conductivity, and good thermal and chemical stability. However, pristine CNTs are chemically inert and not enough to anchor and deposit catalyst nanoparticles. In order to solve the problem, some new strategies are carried out, which have involved the utilization of surface modification with additives [14], surfactants [15] and polymers [16] to link the metal nanoparticles to the XC-72 or CNTs surface. However, the additive materials may not be readily removed from the system, and might cover up the active crystal face of the catalyst, which result in the reduction of the catalytical activity. To address these issues, we attempt to find a new support to increase the metal loading. Recently, layered double hydroxides (LDHs) were used as new supports for the synthesis of Pd/LDH and the combined DFT calculation study indicates that

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the LDHs support stabilize the Pd nanoparticles via the formation of Pd–HO bond, which improved the catalytic behavior towards ethanol electrooxidation [17]. In this regard, Pd nanoparticles without any additive materials anchor the supports with the ability of supplying adequate OH species, which may eliminate the bad impact of additives and significantly enhance the electrocatalytic property in the DEFCs.

As the main component of bones and teeth, HAP is particularly rich in hydroxyl, nontoxic and abundantly available in nature [18,19], which has received considerable interests in many areas because of adsorption capacity, ion–exchange ability and acid–base properties [20–22]. Recently, Wang et al. have reported that Pd or Ru supported on HAP displayed high performance of selective oxidation of alcohols to the corresponding carbonyl compounds by use of molecular oxygen under solvent-free conditions [23,24]. However, to the best of our knowledge, no attention has been paid to the investigation of HAP as catalyst support for DEFCs. Herein, we used HAP as support to synthesize Pd/HAP catalyst without any additives for ethanol electrooxidation. The results indicate that HAP is a better support. The obtained Pd nanoparticles had small size and good distribution. Meanwhile, the Pd/HAP catalyst possessed a much higher current density ( $246 \text{ mA cm}^{-2}$ ) towards ethanol electrooxidation than the Pd/C catalyst ( $109 \text{ mA cm}^{-2}$ ) and better stability.

## 2. Experimental

### 2.1. Materials

Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), ammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ), ethylene glycol, ethanol and potassium hydroxide (KOH) were purchased from China National Pharmaceutical Group Corp., commercial Pt/C (40%) catalyst and  $\text{PdCl}_2$  were obtained from Alfa Aesar. Vulcan XC-72 (carbon black) was obtained from Cabot. All of the chemical reagents used in the experiments were analytical grade and were used as received without further purification. Double distilled water (DD water) was used in all of the experiments.

### 2.2. Catalyst preparation

HAP was synthesized according to a previous literature from  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  by adjusting the Ca/P molar ratio to 1.50 in the precipitation sequence [25]. In a typical procedure, 5 mL  $\text{PdCl}_2$  ( $2 \text{ mg mL}^{-1}$ ) was added into 30 mL ethylene glycol and the pH was adjusted to 12 using 1 M KOH solution under moderate stirring. Subsequently, 20 mg HAP was added into the system and ultrasonically treated for 30 min. The mixture was placed into a 50 mL Teflon-lined autoclave and heated at  $100^\circ\text{C}$  for 6 h, and then air-cooled to room temperature. As a result, Pd nanoparticles deposited on HAP were obtained. In order to improve the conductivity, 20 mg XC-72 was added to the above system and ultrasonically stirred for 6 h. Finally, the product was collected by filtration and washed with double distilled water and absolute ethanol, dried under vacuum condition. The obtained catalyst was labeled as Pd/HAP.

The control experiment was conducted under the same conditions described as the preparation of Pd/HAP in the absence of HAP and was labeled as Pd/C.

### 2.3. Characterization

The crystallographic phases and purity information of the prepared samples were characterized by XRD, and the corresponding XRD patterns were recorded on a Bruker D & Advance X-ray diffractometer with a Cu K $\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The element compositions and distributions of the catalyst were characterized

by FESEM (JSM 6701F) operating at 5.0 kV. The morphology of the catalysts were measured by JEOL-100CX HRTEM operated at 200 kV.

### 2.4. Electrochemical measurement

All the electrochemical measurements were carried out in a three-electrode cell by using a Solartron 1287 (Solartron Analytical, England) electrochemical workstation. A glassy carbon disk ( $0.0706 \text{ cm}^2$ ) coated with catalyst was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum foil ( $1 \text{ cm}^2$ ) as the counter electrode. Before the catalyst was loaded, the glassy carbon electrode was polished mechanically with  $\gamma$ -aluminate powder under an abrasive paper to obtain a mirror-like surface, washed with DD water and absolute ethanol and allowed to dry at room temperature. The working electrode was prepared as follows: 3 mg of catalyst was added into 0.3 mL of ethanol and 30  $\mu\text{L}$  of 5 wt% perfluorosulfonic acid, which was dispersed by ultrasonication for approximately 10 min to obtain a homogeneous suspension. Next, 15  $\mu\text{L}$  of the dispersion was uniformly dispersed on a freshly polished glassy carbon electrode and dried under ambient conditions. The metal loading of the as-prepared catalysts on glassy carbon electrode was  $386 \mu\text{g cm}^{-2}$ . Current densities were calculated by the ratio of current to the geometric surface area of working electrode. All electrochemical measurements were performed at  $25 \pm 1^\circ\text{C}$ .

Electrochemical CO-stripping voltammograms were obtained by oxidizing pre-adsorbed CO ( $\text{CO}_{\text{ad}}$ ) in 1 M KOH at a scan rate of  $50 \text{ mV s}^{-1}$ . CO was purged through 1 M KOH for 30 min to allow the complete adsorption of CO onto the catalyst. The working electrode was kept at  $-0.2 \text{ V}$  vs. SCE, and excess CO in the electrolyte was removed by purging with high-purity  $\text{N}_2$  for 30 min. The amount of  $\text{CO}_{\text{ad}}$  was evaluated by integrating the CO-stripping peak and correcting for the capacitance of the electric double-layer. The activity of the catalysts in the electrooxidation of ethanol was evaluated in a solution containing 1 M ethanol and 1 M KOH, and cyclic voltammetry measurements were performed by applying a linear potential scan at a sweep rate of  $50 \text{ mV s}^{-1}$ .

### 2.5. Fabrication and measurement of a DEFC

The DEFC performance test was performed using a single cell with an active area of  $4.0 \text{ cm}^2$ . The Pd loading and Pt loading for Pd/HAP catalyst and 40% commercial Pt/C are  $0.5 \text{ mg cm}^{-2}$ , respectively. The alkaline DEFC was composed of a membrane electrode assembly (MEA), which consisted of an anion-exchange membrane (A201, Tokuyama Corporation) and two electrodes. To prepare the anode diffusion layer, the obtained Pd/HAP catalyst was mixed into isopropanol along with 5 wt.% Nafion solution. The resulting mixture was ultrasonically agitated with vigorous mechanical stirring to form a homogeneous ink. The ink was sprayed on a carbon paper, which served as the backing layer of the anode electrode held on a heating table at  $60^\circ\text{C}$  to form the catalyst layer. To prepare the cathode layer, the ink consisting of 40% commercial Pt/C catalyst and Nafion ionomer was prepared using the same method as described above. Finally, anode and cathode were placed onto the two sides of the membrane and pressed at room temperature for 5 min to form the MEA. The MEA was sandwiched between two graphite bipolar plates. The fuel cell tests were conducted on a Scribner Associates Model 850e test station. The solution containing 1 M ethanol and 1 M KOH was pumped to the anode at a rate of  $1.0 \text{ mL min}^{-1}$ , while dry pure oxygen at a flow rate of 100 standard cubic centimeters per minute (sccm) was fed to the cathode. During the measurements, the fuel cell working conditions, including the

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