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# A facile synthesis of Pd/C cathode electrocatalyst for proton exchange membrane fuel cells

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## ABSTRACT

A carbon supported palladium (Pd/C–NaBH<sub>4</sub>–NH<sub>3</sub>) catalyst was synthesized via modified sodium borohydride reduction method using ammonia as the complexing reagent. The Pd/C catalysts were characterized by means of powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Rotating disk electrode (RDE), cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and single cell measurements were employed to evaluate the activities of the catalysts. The as-prepared catalysts with face-centered cubic (fcc) structure are uniformly dispersed on the carbon supports. Twinned and polycrystalline structures are observed in the HRTEM image of Pd/C–NaBH<sub>4</sub>–NH<sub>3</sub>. The results indicate that the Pd/C–NaBH<sub>4</sub>–NH<sub>3</sub> catalyst shows high activity for the oxygen reduction reaction. Single cell with Pd/C–NaBH<sub>4</sub>–NH<sub>3</sub> as the cathode displays a maximum power density of 508 mW cm<sup>-2</sup>. The favorable performance of the Pd/C–NaBH<sub>4</sub>–NH<sub>3</sub> catalyst may be attributed to the uniformly dispersed nanoparticles and more crystalline lattice defects.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are attractive energy conversion devices for portable power and electric vehicle applications owing to their high efficiency, high power density and low pollutant emissions. However, there are still many crucial issues, such as cost, durability, reliability and operation flexibility, hindering their widely applications. The high price and the limited resources of Pt-based catalysts are among the main challenges hindering their further commercialization. Therefore, non-platinum catalyst with high activity in acidic electrolyte is urgently required.

As palladium possesses a similar valence electronic configuration and lattice constant to platinum and yet highly methanol-tolerant ability [1,2], researchers have devoted to

develop palladium-based catalysts as promising catalysts for oxygen reduction reaction (ORR) in PEMFCs and DMFCs [3–7]. A great deal of effort has been made to the synthesis of Pd nanoparticles with uniform dispersion [8–11]. In these preparation processes, surfactants are used as protective agents to form stable and uniform palladium colloids. However, it is difficult to remove the surfactants which strongly absorbed on the active site of Pd, leading to the decrease of catalytic activity. Therefore, development of novel synthesis methods without surfactants is pursued to simplify the preparation process and enhance the catalytic activity of the Pd-based catalysts.

In this work, a facile synthesis route of Pd/C electrocatalyst with high activity for ORR is developed by using the modified sodium borohydride reduction method. NH<sub>3</sub> is used as a ligand of Pd<sup>2+</sup> precursor to form strong Pd–NH<sub>3</sub> complex. Normally, different types of oxygen functional groups (e.g. carboxyl

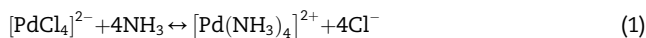
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groups, phenol groups, lactone groups, ether groups) are present on carbon material [12]. These oxygen functional groups are either negatively charged or with  $\pi$ -electron structure, hindering the adsorption of the complex anion  $[\text{PdCl}_4]^{2-}$ . The added ammonia changes complex anion  $[\text{PdCl}_4]^{2-}$  to complex cation  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  (Eq. (1)).



The  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  is apt to adsorb on the surface of carbon materials due to the electrostatic interaction between  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  and oxygen functional groups. The adsorbed  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  can be in-situ reduced by reduction reagent. In-situ reduction of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  prevents the Pd nanoparticles from large scale aggregation and obtains uniformly dispersed Pd particles on the carbon supports.

This preparation route of Pd/C is facile and low-cost which is in favor of commercial application of PEMFCs. The Pd/C catalyst obtained in this method shows high activity for ORR.

## 2. Experimental

### 2.1. Catalyst preparation

The Pd/C catalyst with Pd metal loading of 20 wt.% was obtained by modified sodium borohydride ( $\text{NaBH}_4$ ) reduction method as follows. At first,  $\text{PdCl}_2$  was dissolved in the hydrochloric acid to obtain  $\text{H}_2\text{PdCl}_4$  solution. 8.67 mL 0.022 mol  $\text{L}^{-1}$   $\text{H}_2\text{PdCl}_4$  was mixed with 20 mL ethylene glycol and 20 mL deionized water, which was followed by addition of 1 mL ammonia (25 wt. %) to the  $\text{H}_2\text{PdCl}_4$  solution. The color of the solution changed from yellow to colorless, demonstrating the formation of the Pd– $\text{NH}_3$  complex. Then, 80 mg Vulcan XC-72R carbon black pre-dispersed in 20 mL ethylene glycol was added into the mixture. After vigorous stirring for 20 min with bubbling high purity nitrogen into the mixture, excessive  $\text{NaBH}_4$  solution was added drop by drop and stirred for 5 h. Finally, the slurry was precipitated for 40 h followed by filtering and drying under vacuum at 60 °C for 12 h. The as-prepared catalyst was obtained and denoted as Pd/C– $\text{NaBH}_4$ – $\text{NH}_3$ .

To evaluate the effect of the ammonia, another Pd/C sample (20 wt.%) was prepared by conventional sodium borohydride reduction method as comparison. The preparing process and reagents were the same as described above for Pd/C– $\text{NaBH}_4$ – $\text{NH}_3$  catalyst except adjusting pH to approximately 2 by adding 4 mL 2.0 mol  $\text{L}^{-1}$  NaOH in ethylene glycol instead of ammonia. The catalyst was denoted as Pd/C– $\text{NaBH}_4$ .

### 2.2. Physicochemical characterizations

The powder X-ray diffraction (XRD) patterns of the two samples were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer over a  $2\theta$  range of 10–90°, using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The (2 2 0) peaks of the Pd face-centered cubic (fcc) reflection patterns were fitted to Gaussian line shape on a linear background. The average grain sizes of the as-prepared catalysts were calculated by Scherrer's equation [13] from the Pd (2 2 0) peak fitted to Gaussian.

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2000EX microscope operated at 120 kV. The sample was placed in a vial containing ethanol and ultrasonically agitated to form homogeneous slurry. A drop of the slurry was dispersed on a holey amorphous carbon film on a Cu grid for analysis. Particle size distributions were obtained by manually measuring 200 particles from bright-field micrographs randomly. The mean particle size  $d_m$  was calculated with the following formula [14]:

$$d_m = \frac{\sum_i n_i d_i}{\sum_i n_i} \quad (2)$$

where  $n_i$  is the number of particles and  $d_i$  is the diameter of the particle with the number of  $n_i$ .

High resolution transmission electron microscope (HRTEM) images were performed on a TECNI F30 field emission electron microscope with acceleration voltage of 300 kV.

### 2.3. Electrochemical characterizations

Electrochemical measurements were performed on CHI 600 electrochemical station (CH Corporation, USA) with a rotating disk electrode (RDE) system (EG&G model 636). A standard three-electrode electrochemical cell was used. A large-area Pt foil (3  $\text{cm}^2$ ) and a saturated calomel electrode (SCE) served as the counter and the reference electrode, respectively. All the electrode potentials in this paper were quoted to reversible hydrogen electrode (RHE). The test was carried out by means of thin-film RDE technique [15,16]. The working electrode was prepared as follows: 5 mg catalyst was mixed with 1 mL isopropyl alcohol and 50  $\mu\text{L}$  Nafion solution (5 wt.%, DuPont Corp.). The mixture was homogenized in an ultrasonic bath for 30 min to obtain slurry ink. 10  $\mu\text{L}$  of the slurry was spread on the surface of the glassy carbon electrode (area: 0.1256  $\text{cm}^2$ ) and dried in the air to obtain a thin active catalyst layer. The Pd and Pt loadings of RDE were both 0.076 mg  $\text{cm}^{-2}$ . Cyclic voltammetry (CV) measurements were conducted in high purity  $\text{N}_2$  saturated 0.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution between  $-0.01 \text{ V}$  and 1.14 V versus RHE with scan rate of 50  $\text{mV s}^{-1}$ . The ORR polarization curves were obtained in the potential range of 0.24–1.09 V versus RHE with the applied scan rate of 5  $\text{mV s}^{-1}$ . Before the RDE test, the 0.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution was saturated with  $\text{O}_2$  by bubbling  $\text{O}_2$  for 30 min.

### 2.4. Fabrications of membrane electrode assemblies (MEAs) and single-cell tests

The as-prepared Pd/C– $\text{NaBH}_4$ – $\text{NH}_3$  was tested as PEMFCs cathode catalyst. The fabrication of the electrodes and the MEAs was similar to the method reported in our previous work [17]. The process was as follows: Pd/C– $\text{NaBH}_4$ – $\text{NH}_3$  catalyst, 5 wt.% Nafion solution and isopropyl alcohol were mixed to form homogeneous slurry. The slurry was brushed on the surface of wet-proofed carbon paper (SGL, 6 wt.% PTFE). The cathode using the commercial Pt/C (20 wt.%, Johnson Matthey) as electrocatalyst was prepared by the same procedure for comparison. The anode adopted the commercial 28.4 wt.% Pt/C catalyst (TKK Corp.) with Pt loading of 0.3 mg  $\text{cm}^{-2}$ . The MEA was fabricated by hot-pressing the anode and cathode to the

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