



Tuning the performance of nitrogen, phosphorus co-doped nanoporous carbon for oxygen reduction reaction



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ARTICLE INFO

Article history:

Received 21 July 2017

Revised 10 September 2017

Accepted 11 September 2017

Available online 9 October 2017

Keywords:

Nitrogen

Phosphorus

Nanoporous

Non-precious electrocatalyst

Oxygen reduction reaction

ABSTRACT

Heteroatom-doped porous carbon materials have been widely investigated as cost-effective oxygen reduction reaction (ORR) catalysts. In this study, a series of nitrogen, phosphorus co-doped porous carbon (NP-PC) catalysts are prepared and characterized. Optimized precursors' mass ratio, suitable pyrolysis temperature and appropriate heating rate are intensively studied. Notably, among as-prepared catalysts, NP-PC-950-10 executes an approximate $4e^-$ oxygen reduction pathway and delivers a nearly equal ORR performance to that of commercial 20 wt.% Pt/C (C-Pt/C) catalyst. The stability and methanol crossover resistance of NP-PC-950-10 are also superior to C-Pt/C. These superior electrocatalytic performance may be ascribed to its well-developed porous structure, large Brunauer–Emmett–Teller (BET) surface area ($1050.45 \text{ m}^2 \text{ g}^{-1}$), and good synergistic effect between nitrogen and phosphorus. This study will provide a new insight for exploring cost-efficient non-precious metal electrocatalyst of clean energy conversion systems.

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1. Introduction

Fuel cells have been considered as one of the most promising clean and sustainable energy technologies [1,2]. However, its sluggish oxygen reduction reaction (ORR) kinetics on Pt-based catalysts greatly hinder the chemical–electrical energy conversion efficiency [3,4]. Furthermore, the scarcity, insufficient durability and high cost of Pt significantly limit the large-scale commercialization of fuel cell technologies [5]. These imperfections have spawned considerable research for achieving comparable performance of the commercial 20 wt.% Pt/C (C-Pt/C) catalyst [6–8]. It is highly desirable but admittedly challenging to explore low-cost, highly active and durable catalysts for ORR.

At present, it has been widely demonstrated that heteroatom-doped porous carbon materials can be employed as efficient ORR electrocatalysts, and accordingly make the commercialization available [9–11]. This promising potential may be due to the appearance of the porous structure and the synergistic effect of doped heteroatoms. However, little attention has been paid to investigating

the condition of preparation. For the binary doped porous carbon materials, recent studies have found that control of pyrolysis temperature can maximize the surface area of carbon materials, subsequently enhancing its electrocatalytic performance [12,13]. It is believed that the large surface area is favorable to the catalytic active density by exposing more active sites [14]. In principle, heating rate in the pyrolysis process and mass ratio of precursors also play key roles in carbon materials. So the influence of preparation process on the carbon material is great, which is worthy of study.

Based on the above, to realize the large-scale production and superior ORR performance of catalyst, detailed optimized conditions of a novel nitrogen, phosphorus co-doped porous carbon (NP-PC) are investigated and discussed in this work. Herein, a series of NP-PC catalysts were prepared via independent control of precursors' mass ratio, pyrolysis temperature and corresponding heating rate. Interestingly, owing to the optimized pyrolysis process, as well as the good synergistic effect between nitrogen and phosphorus. Among as-prepared samples, NP-PC-950-10 exhibits a comparable ORR activity to C-Pt/C. More importantly, NP-PC-950-10 delivers superior stability and stronger tolerance to methanol than C-Pt/C. In addition, its morphology, porous structure, and chemical states of doping elements were investigated in detail to illustrate the contribution to promoted ORR performance, respectively. It is highly expected that cost-efficient NP-PC-950-10 can be a promising electrocatalyst for ORR.

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2. Experimental

To obtain optimal preparation conditions of NP-PC catalyst, in this study, precursors' mass ratio, pyrolysis temperature and heating rate were studied in detail, respectively.

2.1. Effect of precursors' mass ratio

In brief, different precursor powder mixtures (pentaerythritol, melamine, ammonium polyphosphate and FeCl_3 (0.5% of the total mass)) were constructed using a ball milling method (12 h). For these mixtures, FeCl_3 was used as an activation reagent. Then, the mixtures were heated in a nitrogen atmosphere by a tube furnace (800 °C, heating rate: 5 °C min^{-1}). The resulting solids were dipped with 0.5 M H_2SO_4 for 12 h to remove residual FeCl_3 . Subsequently, the solids were washed with ultrapure water, and dried at 60 °C in a vacuum for 12 h. After cooling to room temperature, a series of NP-PC-800-5 catalysts were obtained. According to the different mass ratios of pentaerythritol/melamine/ammonium polyphosphate, the as-prepared catalysts were denoted as 1:1:1, 1:1:2, 1:1:3, 1:2:1, 1:2:2, 1:2:3, 1:3:1, 1:3:2, 1:3:3.

2.2. Effect of pyrolysis temperature

For comparison purpose, aforementioned experiment procedure was performed to prepare NP-PC-T-5 catalysts at different pyrolysis temperatures ($T = 700, 750, 800, 850, 900, 950, 1000, 1050, 1100$ °C, respectively). The mass ratio of pentaerythritol/melamine/ammonium polyphosphate was 1:1:1.

2.3. Effect of heating rate

To study the effect of heating rate, the pyrolysis temperature was kept at 950 °C, and mass ratio of pentaerythritol/melamine/ammonium polyphosphate was 1:1:1. According to the above process, the as-prepared catalysts were denoted as NP-PC-950-k ($k = 2, 5, 10$ °C min^{-1} , respectively). In this study, the C-Pt/C catalyst was employed as a reference for comparison.

2.4. Characterization

Transmission electron microscopy (TEM) experiment was performed using a FEI TECNAI G² TF20 (America) microscope. To prepare TEM sample, the obtained catalyst was well dispersed in ethanol and dropped onto lacy carbon support films. Element mapping images were taken with a Zeiss ULTRA Plus (Germany) field emission scanning electron microscope. X-ray diffraction (XRD) analysis was recorded with a Rigaku D/Max-2400 diffractometer (Japan, Cu K_α radiation source, $\lambda = 0.1541$ nm). Raman spectra were obtained on a RFS 100/S (Bruker, Germany) FT-Raman spectrometer. The Brunauer–Emmett–Teller (BET) adsorption isotherms and pore size distribution were measured with an accelerated surface area and porosimetry (ASAP) 2020 system. X-ray photoelectron spectroscopy (XPS) were analyzed on a Thi-5702 (America) spectrometer (a monochromatic Al K_α X-ray source, $h\nu = 29.35$ eV). Inductively coupled plasma mass spectrometry (ICP-MS) analysis was undertaken using Agilent HP4500 (Japan).

All electrochemical measurements were executed at room temperature on a PGSTAT128N Autolab workstation (Netherlands) in a three-electrode system. The reference electrode was an Ag/AgCl electrode (saturated KCl solution). A carbon rod was employed as the counter electrode for measurement. A modified glassy-carbon electrode with a diameter of 5 mm was used as the working electrode. For the ORR, the catalyst ink was obtained as reported in previous work [15]. Briefly, 5.0 mg of catalysts was firstly dispersed in Nafion / ethanol (1 mL, 0.25% Nafion) by sonication for

1 h to achieve a well-dispersed catalyst ink. Then, 8 μL of the uniform suspension was pipetted onto the glassy-carbon electrode and dried in open air, which makes the catalyst loading is 0.2 mg cm^{-2} for all samples. Electrochemical impedance spectrum (EIS) was obtained with a signal amplitude of 10 mV in the frequency range of 10 kHz to 0.01 Hz. In this study, all of the potentials were calibrated to a reversible hydrogen electrode (RHE) by the formula (Eq. (1)) [16]:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.198 \text{ V} \quad (1)$$

The ORR activity of electrocatalysts was assessed via rotating disk electrode (RDE) measurement. The number of transferred electron during ORR was analyzed according to the Koutecky–Levich (K-L) equations, as shown below (Eqs. (2)–(4)) [17,18]:

$$J^{-1} = J_{\text{L}}^{-1} + J_{\text{K}}^{-1} = (B\omega^{1/2})^{-1} + J_{\text{K}}^{-1} \quad (2)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (3)$$

$$J_{\text{K}} = nF\kappa C_0 \quad (4)$$

where J is the measured current density, J_{L} and J_{K} are the diffusion-limiting and kinetic current density, ω is the revolutions of the disk (rpm), n is the transferred electron number during ORR, F is the Faraday constant, κ is the rate constant, and ν (1.13×10^{-2} $\text{cm}^2 \text{ s}^{-1}$) is kinematic viscosity of 0.1 M KOH solution, D_0 (1.9×10^{-5} $\text{cm}^2 \text{ s}^{-1}$) and C_0 (1.2×10^{-3} mol L^{-1}) are diffusion coefficient and bulk concentration of O_2 in 0.1 M KOH, respectively.

3. Results and discussion

3.1. Catalytic performance of catalysts

To examine the effects of precursors' mass ratio, pyrolysis temperature and heating rate in as-prepared catalysts, linear sweep voltammogram (LSV) measurements on a RDE were conducted. As Fig. 1a shows, a series of NP-PC-800-5 catalysts present quite different ORR performance, including onset potentials, half-wave potentials and limiting current densities. Visibly, the limiting current density of catalysts was in the order: 1:1:2 > 1:1:3 > 1:1:1 > 1:2:2 > 1:2:1 > 1:3:1 > 1:2:3 > 1:3:3 > 1:3:2. It is demonstrated that the catalysts with low mass ratio of pentaerythritol/melamine always exhibit high current density, which may be owing to the abundance of graphitic N atoms and defects in NP-PC catalysts and subsequently improve ORR kinetics of catalysts [19]. This is because the mass ratio of pentaerythritol/melamine is associated with the nitrogen content and defect structure of NP-PC catalysts. As Lai et al. proposed that graphitic N and pyridinic N can increase the limiting current density and affect the ORR reaction mechanism [20], respectively. Meanwhile, the defect structure is favorable for the accessibility of a large surface area and more active sites, thus facilitating ORR kinetics [16]. This result is also revealed in their onset potentials and half-wave potentials, which are depicted in Fig. 1b. Actually, the order of onset potential is consistent with half-wave potential, indicating the optimized mass ratio of precursors is 1:1:1 in this study. Moreover, it is suggested that the precursors' mass ratio plays a crucial role for ORR activity. The appropriate mass ratio can be used as a benchmark for further optimization.

Generally, temperature is also important to affect the electrocatalytic performance of carbon materials. From Fig. 1c, this effect of pyrolysis temperature was assessed by LSV. It can be seen that ORR performance of NP-PC-T-5 catalysts increases dramatically with increasing pyrolysis temperature from 700 to 950 °C. While, the electrocatalytic activity of NP-PC-1000-5, NP-PC-1050-5 and NP-PC-1100-5 decreases with increasing temperature. It may

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