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# Biomass-derived porous heteroatom-doped carbon spheres as a high-performance catalyst for the oxygen reduction reaction

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## ABSTRACT

A high-performance, spherical, heteroatom-doped carbon catalyst for the oxygen reduction reaction (ORR), with a porous structure and a high surface area, has been prepared through a hydrothermal treatment process and subsequent carbonization procedures using brewer's yeast powder, ferric chloride, and ammonium hydroxide as precursors. We found that the addition of iron had a significant effect on the catalyst's spherical morphology and ORR activity. Electrochemical measurements demonstrated that the catalyst has excellent ORR performance, with a half-wave potential 28 mV more positive (0.861 V vs. RHE) than that of commercial 20 wt.% Pt/C (0.833 V vs. RHE) in an alkaline medium. The catalyst also displays remarkable methanol tolerance and durability. The abundance of active N and P species and the porous structure may be responsible for this catalyst's high ORR performance. The present work provides a facile way of using economical, environmentally friendly, and renewable biomass to develop a high-activity cathode electrocatalyst for fuel cell applications.

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered one of the most promising clean, sustainable energy technologies to date because of their high energy conversion efficiency and negligible harmful emissions [1–4]. In PEMFCs, the most effective electrocatalysts for both the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode are platinum and platinum alloys. However, platinum's scarcity (and consequent high cost) is therefore the main barrier to fuel cell

commercialization [5]. Most platinum is used up at the cathode because the ORR is much slower than the HOR. Thus, extensive research efforts in the field of PEMFCs have been focused on developing high-performance, nonprecious metal catalysts (NPMCs) to replace Pt-based catalysts for the ORR [6].

Among NPMCs, heteroatom-doped, carbon-based catalysts [7–16] possess great potential due to their high ORR activity, long-term stability, and low cost. Furthermore, the ORR performance of carbon-based catalysts can be significantly enhanced through doping with heteroatoms [17–20]. Heteroatom dopants include nonmetal elements, such as B [21,22], N [23,24], F [25,26],

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S [9,10], and P [27,28], as well as transition metal elements, such as Fe [1,7], Co [29,30], Ni [31,32], and Mn [33,34].

Unfortunately, most heteroatom-doped carbon materials are obtained by using a variety of toxic, environmentally hazardous, and expensive chemicals as precursors [35,36]. Hence, it is essential to find green, renewable, and inexpensive precursors. Biomass of various kinds is preferable for transforming into carbon materials because it is cheap, naturally abundant, cyclically sustainable, and readily available. In addition, biomass contains numerous heteroatoms (e.g., N, B, S, and P) considered ideal precursors for the green synthesis of heteroatom-doped carbon materials, and carbon materials with high specific surface areas can be obtained by using dehydrated, carbonized biomass [37–41]. The high surface areas and high porosities of carbon materials are thought to improve their ORR performance in facilitating mass transfer [37,38,42,43].

Brewer's yeast powder (BYP) is a byproduct of brewing beer. Hence, it is abundant and inexpensive. BYP consists mainly of carbohydrates and yeast. It is rich in nitrogen and phosphorus [44], which can be doped into a carbon matrix. We therefore proposed that BYP could be an ideal precursor in the preparation of heteroatom-doped carbon ORR catalysts.

Herein, we report a facile and cheap approach for preparing a high-performance, spherical, heteroatom-doped, carbon-based ORR catalyst using BYP as the precursor. The carbon spheres had a high surface area and a porous structure, and they exhibited outstanding ORR catalytic activity. Compared with commercial 20 wt.% Pt/C catalyst, the half-wave potential of our catalyst in an alkaline medium exhibited a 28 mV positive shift. The catalyst also displayed outstanding methanol tolerance and stability, and it followed a 4-electron transfer process. Moreover, we found that adding ferric chloride and ammonium hydroxide to the biomass precursor significantly enhanced the catalyst's performance. The large amounts of heteroatom dopants, active N species and P species, and highly porous structure likely played pivotal roles in promoting this catalyst's ORR performance.

## Materials and methods

### Materials

The BYP was purchased from Guangzhou Ebele Health and Wellness Products Technology, Ltd. Ferric chloride (anhydrous  $\text{FeCl}_3$ , chemically pure) and ammonium hydroxide ( $\text{NH}_3 \cdot \text{H}_2\text{O}$  25%, analytical grade) were purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion solution (5 wt.%) was purchased from DuPont Corporation. Commercial 20 wt.% Pt/C catalyst was purchased from Johnson Matthey. Distilled water was used in all experiments. All chemicals were used without any further purification.

### Catalyst preparation

The typical catalyst preparation was as follows. First, 4.00 g BYP and 1.60 g  $\text{FeCl}_3$  were dispersed in 60 mL deionized water. The mass ratio of  $\text{FeCl}_3$  to BYP was 2:5. After this mixture was stirred constantly for 12 h, 2 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added drop-

wise, and the stirring continued for another 12 h. The mixture was then transferred into a 100 mL Teflon-lined steel autoclave and sealed. After that, the autoclave was kept at 190 °C for 8 h. The resulting products were separated by centrifugation, washed with distilled water and ethyl alcohol, and dried at 80 °C. The dried powders were pyrolyzed at 900 °C for 60 min in Ar flow, followed by leaching in 1 M  $\text{H}_2\text{SO}_4$  at 80 °C for 8 h. The acid-leached powders were then pyrolyzed again at 900 °C for 165 min in Ar flow and finally treated at 900 °C for another 15 min in  $\text{NH}_3$  flow. We call the resulting sample BY-Fe-A. To investigate the effect of the  $\text{FeCl}_3$ /BYP ratio on the ORR activity, other biocarbon materials were prepared with mass ratios of 3:10, 1:2, or 3:5. For comparison, another two catalysts were prepared using the same procedures: one was derived directly from BYP without the addition of metal salts or  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , and the other was derived from a mixture of BYP and  $\text{FeCl}_3$  without any  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . We designate these two catalysts BY and BY-Fe, respectively.

### Physical characterization

Scanning electron microscopy (SEM) images were obtained on a Merlin field-emission SEM (Carl Zeiss). Transmission electron microscopy (TEM) images were recorded with a JEM-2100 instrument operating at 200 kV. X-ray diffraction (XRD) was conducted on a TD-3500 powder diffractometer with  $\text{Cu-K}\alpha$  radiation, operated at 40 kV and 30 mA. Raman spectra were acquired on a LabRAM Aramis Raman spectrometer (HJY, France) using a laser wavelength of 632 nm. X-ray photoelectron spectroscopy (XPS) was performed on a PHI-5000 VersaProbe II system. The specific surface areas and pore-size distributions of the samples were investigated using the Brunauer–Emmett–Teller (BET) method on a Tristar II 3020 gas adsorption analyzer. The iron contents of the catalysts were measured through inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Prodigy ICP-AES system (Leeman Labs Inc., USA).

### Electrochemical testing

Electrochemical measurements were carried out in a standard three-electrode system using an Ivium electrochemical workstation (Netherlands) in 0.1 M KOH electrolyte at room temperature. A glassy carbon electrode (GCE, 5 mm diameter) was used as the working electrode substrate, an Ag/AgCl electrode in 3.0 M NaCl was the reference electrode, and a Pt wire was the counter electrode. The potential of the Ag/AgCl reference electrode was calibrated versus a reversible hydrogen electrode (RHE) in 0.1 M KOH ( $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.982 \text{ V}$ ) [6]. Before every measurement, the GCE was polished to a mirror finish with  $\alpha\text{-Al}_2\text{O}_3$  slurry (50 nm) on a microcloth, followed by cleaning via ultrasonication in deionized water and drying under an infrared lamp. Next, 20  $\mu\text{L}$  catalyst ink, prepared by dispersing 5.0 mg catalyst in 1 mL Nafion/ethanol solution (0.25 wt.% Nafion), was dropped onto the GCE surface and dried under an infrared lamp. The loading for all catalysts was approximately 0.5  $\text{mg cm}^{-2}$ .

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed in 0.1 M KOH solution at a scan rate of 10  $\text{mV s}^{-1}$  with a rotating disk electrode (RDE)

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