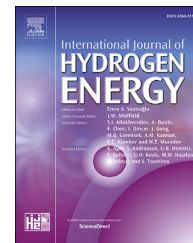




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# Phenolic resin/chitosan composite derived nitrogen-doped carbon as highly durable and anti-poisoning electrocatalyst for oxygen reduction reaction

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## ABSTRACT

Developing non-precious catalysts with high activity and superior durability is eager demand for the wide spread fuel cells. In this study, a novel kind of nitrogen-doping carbon based material (PR-C) has been fabricated with phenolic resin and chitosan, in which the low-cost and renewable biomass material chitosan is used as the nitrogen source. Notably, compared with Pt/C, among the resultant catalysts, the PR-C (1:3.5) catalyst has long-term stability, superior tolerance to methanol poisoning, and favorable electrocatalytic activity for oxygen reduction reaction (ORR). Consequently, as-prepared catalyst (PR-C) utilized phenolic resin/chitosan is promising as a low-cost and renewable catalyst for ORR.

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## Introduction

Heteroatom-doping carbon material as electrocatalyst is one of the hot-spots for oxygen reduction reaction (ORR), which can markedly change its catalytic activity, conductivity and other properties [1–10]. Hence, it is noteworthy to find available, facile and inexpensive raw materials to prepare

commercially viable nitrogen-doped carbon based materials [11,12]. As reported, a wide variety of dopants, such as B [13,14], N [15–20], P [21–23] and S [24,25], etc., have been successfully doped into carbon. Among them, due to superior activity, high selectivity and strong anti-methanol poisoning ability, the nitrogen-doped carbon material has become one of the research priorities in recent years. Consequently, choosing an appropriate nitrogen-containing raw material as

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nitrogen source is all-important to prepare of nitrogen-doped non-precious catalysts.

Among the various carbon materials, biomass is focused by many researchers for their renewable property, rich source, low prices and environmentally-friendly [26,27]. In the pioneer's study, many biomass raw materials, e.g., cattails [28], ginkgo biloba [29], cassava flour [30] and glucosamine hydrochloride [31] have been commendably used as precursors to prepare nitrogen-doped carbon based catalysts. To select an appropriate nitrogen-containing natural biomass material, we considered, chitosan with high nitrogen-content would be an ideal source [32]. Interestingly, it can uniformly coat the substrate in liquid phase, which allows the nitrogen atoms homogeneous embedded in the carbon lattice of prepared nitrogen-doped carbon material. Thus, it can widely use in the bioprocessing technology [33,34]. Therefore, using chitosan to prepare nitrogen-doped carbon catalysts for ORR is profound.

In this work, a series of PR-C (m:n) catalysts (m:n is the mass ratio of phenolic resin and chitosan) were designed and fabricated, in which the biomass chitosan was used as nitrogen source and phenolic resin as carbon source. Subsequently, the physicochemical properties, electrochemical behaviors and morphology structures of those were investigated. Particularly, among as-prepared catalysts, the PR-C (1:3.5) catalyst exhibits excellent catalytic activity, high stability and strong resistance to methanol poisoning for ORR.

## Experimental

### Preparation of PR-C (m:n) catalysts

The PR-C (m:n) catalysts were prepared via mixing of phenolic resin with chitosan in liquid phase. The preparation process of PR-C (m:n) catalysts is as follows: Firstly, phenolic resin was dissolved in ethanol (50 mL) and then magnetic stirred for about 12 h. Meanwhile, chitosan was added into another solution (ultra-pure water (350 mL) and acetic acid (3.5 mL)), and magnetic stirred until it completely dissolved. Then,  $\text{FeCl}_3$  (n<sub>Chitosan</sub>: n<sub>FeCl<sub>3</sub></sub> = 5: 2) was added and stirred for 12 h. Secondly, after mixed the two solutions (phenolic resin solution and chitosan solution), it was kept stirring for 12 h and then evaporated by rotary evaporator. The resulting solid was dried in an oven at 50 °C for 2 h, and then the sample was grinded with an agate mortar. After that, the sample was treated in a tube furnace under N<sub>2</sub> for two times (500 °C for 2 h and 800 °C for 2 h), and then treated with H<sub>2</sub>SO<sub>4</sub> (100 mL, 0.5 M, 24 h) for two times. Following that, the solid was filtered. The PR-C (m:n) catalysts (m:n is the mass ratio of phenolic resin and chitosan) were obtained after dried in an oven at 50 °C for 12 h.

### Characterization

Raman spectroscopy was tested by FT-Raman spectrometer (RFS 100/S, Rigaku, Bruker, Germany). Energy dispersive X-ray spectroscopy (EDS, D/Max-2400 Thi-5702, America) and elemental mapping were surveyed by scanning electron microscopy (SEM, Carl Zeiss Ultra Plus, Germany), which was carried out on aluminized paper with an Ultra Plus field

emission scanning electron microscope. The X-ray diffraction (XRD) spectra were acquired on a Cu K<sub>α</sub> radiation source operating at 40 kV and 150 mA (D/Max-2400 diffractometer, Rigaku, Japan). The Brunauer-Emmett-Teller (BET) test was realized on a Physical adsorption instrument (Trister3020/ASAP2020M, Micromeritics, America). The existence state and the surface components of elements were determined by X-ray photoelectron spectroscopy (XPS), which on an X-ray photoelectron spectrometer (Thi-5702, America), with a monochromatic Al K<sub>α</sub> X-ray source ( $h\nu = 29.35$  eV).

The electrochemical tests were using an Autolab workstation (PGSTAT128N, Netherlands). With a typical three-electrode cell, a modified glassy carbon ( $d = 5$  mm) was used as working electrode, an Ag/AgCl electrode as reference electrode, and a platinum wire as counter electrode, respectively. The preparation process was carried out in the following: 5.0 mg catalysts were dispersed in 1 mL Nafion/ethanol (0.25 % Nafion). Then, 8 μL suspensions were quantitatively transferred to the surface of the polished glassy carbon electrode, and drying in the air. Before each measurement, the solution was purged with N<sub>2</sub> or O<sub>2</sub> to ensure gas saturated. In our work, all potentials were measured against Ag/AgCl, and all electrochemical tests were performed in a thermostatic water bath (25 °C).

## Results and discussion

Biomass-derived carbon materials draw more attentions, of which, chitosan is of concern for its high nitrogen-content. Additionally, as a natural renewable biomass raw material, it can reduce resource consumption and production cost. Thus, in this work, a series of PR-C (m:n) catalysts were fabricated, with chitosan as nitrogen source and phenolic resin as carbon source.

Evidently, the polarization curve is accustomed to illustrate the performance of ORR. Clearly, the polarization curve can be divided into three parts: i) Minor higher than  $-0.05$  V is the ORR kinetic control region; ii) Between 0.4 and  $-0.05$  V is the ORR mixing control zone; iii) Below the  $-0.4$  V potential is the ORR diffusion control region. Polarization curves for ORR on different catalysts in O<sub>2</sub> saturated 0.1 M KOH solution is shown in Fig. 1. The ORR onset potential from PR-C (1:0) to PR-C (1:4) is  $-0.087$ ,  $-0.087$ ,  $-0.076$ ,  $-0.078$ ,  $-0.050$ ,  $-0.054$ ,  $-0.055$ ,  $-0.048$  and  $-0.064$  V, respectively. And the half-wave potential from PR-C (1:0) to PR-C (1:4) is  $-0.23$ ,  $-0.25$ ,  $-0.24$ ,  $-0.19$ ,  $-0.13$ ,  $-0.13$ ,  $-0.15$ ,  $-0.087$  and  $-0.11$  V, respectively. Obviously, when achieved a certain percentage (PR-C (1:3.5)), through the polarization curve test, the PR-C (1:3.5) catalyst exhibits the best activity among the as-prepared PR-C (m:n) catalysts. If the mass ratio of phenolic resin and chitosan further increasing, the catalytic activity declines rapidly. Thus, we infer that PR-C (1:3.5) is the best of the as-prepared samples, and speculate that PR-C (1:3.5) is good for ORR.

Frequently, Raman spectroscopy is the most direct and the least destructive technique used to characterize the structures and properties of carbon material, in particularly, the characterization of carbon material defects, disorder and doping information [1,13,35]. Raman spectra of PR-C (m:n) catalysts are shown in Fig. 2. Apparently, two noteworthy peaks expose

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