



## Short Communication

# Synthesis highly active and durable non-precious-metal catalyst with 2,2-pyridylbenzimidazole as novel nitrogen coordination compound for oxygen reduction reaction

Sisi Liu <sup>a,b</sup>, Chengwei Deng <sup>a,b</sup>, Lan Yao <sup>a,b</sup>, Hexiang Zhong <sup>a,\*</sup>, Huamin Zhang <sup>a,\*\*</sup><sup>a</sup> Division of Energy Storage, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, China

## ARTICLE INFO

## Article history:

Received 26 May 2014

Received in revised form 4 August 2014

Accepted 25 August 2014

Available online 2 September 2014

## Keywords:

Oxygen reduction reaction

Nitrogen-doped carbon

Thermal treatment

2,2-Pyridylbenzimidazole

Non-precious metal catalyst

## ABSTRACT

2,2-Pyridylbenzimidazole is used for the first time as nitrogen coordination compound for synthesizing nitrogen-doped carbon catalyst for oxygen reduction reaction (ORR). The as-prepared catalyst exhibits better catalytic activity and stability than commercial carbon supported platinum (Pt/C) catalyst for ORR in alkaline media. Excellent methanol tolerance ability is also demonstrated. We propose that the presence of trace metal residues in this catalyst can profoundly promote ORR.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Direct methanol alkaline fuel cells (DMAFCs) are promising energy-converting devices because of their high energy density, fast electrode kinetics, and simple fuel storage [1]. To date, state-of-the art platinum (Pt)-based catalysts have been considered as the most efficient catalysts for ORR in DMAFCs. However, the scarcity and the poisoning issue of Pt impede practical applications. The possibility of applying non-precious metal catalysts (NPMCs) for ORR has been studied extensively to explore these materials as alternatives to Pt-based catalysts [2,3].

Among all of the NPMCs, N-doped carbon materials are considered among the most promising candidates. The doped nitrogen atoms can break the electroneutrality of carbon materials, thereby creating charged sites favorable for O<sub>2</sub> adsorption to enhance the ORR activity [4], which can be further promoted with the addition of transition metal [5]. Numerous materials such as polyaniline [6], polypyrrole [7], 1,10-phenanthroline [8], 2,6-bis(2-pyridyl)-pyridine [9] have been used as nitrogen source to prepare ORR catalysts. The complex N-doped, metal, and carbon atoms are considered to be the possible active site [10,11].

2,2-Pyridylbenzimidazole (PBZ) is a nitrogen-containing bidentate chelating agent. The two coordination sites are located at the imidazole and pyridine rings. Owing to the molecular structure, PBZ is prone to coordination reaction with different metal ions such as cobalt, copper and iron [12] in forming metal nitrogen-containing complex. However, based on reviewed studies, no related report synthesizing PBZ complex for ORR has been published; thus, the ORR catalytic potential is almost completely unknown.

Herein, PBZ is used for the first time as a nitrogen coordination compound though a simple wet-impregnation method followed by pyrolysis process for synthesizing PBZ/iron compound on carbon support as ORR catalyst. By tuning the PBZ content and pyrolysis temperature, the optimal catalyst presented outstanding ORR activity and stability as well as excellent methanol tolerance ability compared to commercial Pt/C catalyst. Furthermore, the effect of pyrolysis temperature on activity is studied.

## 2. Experimental section

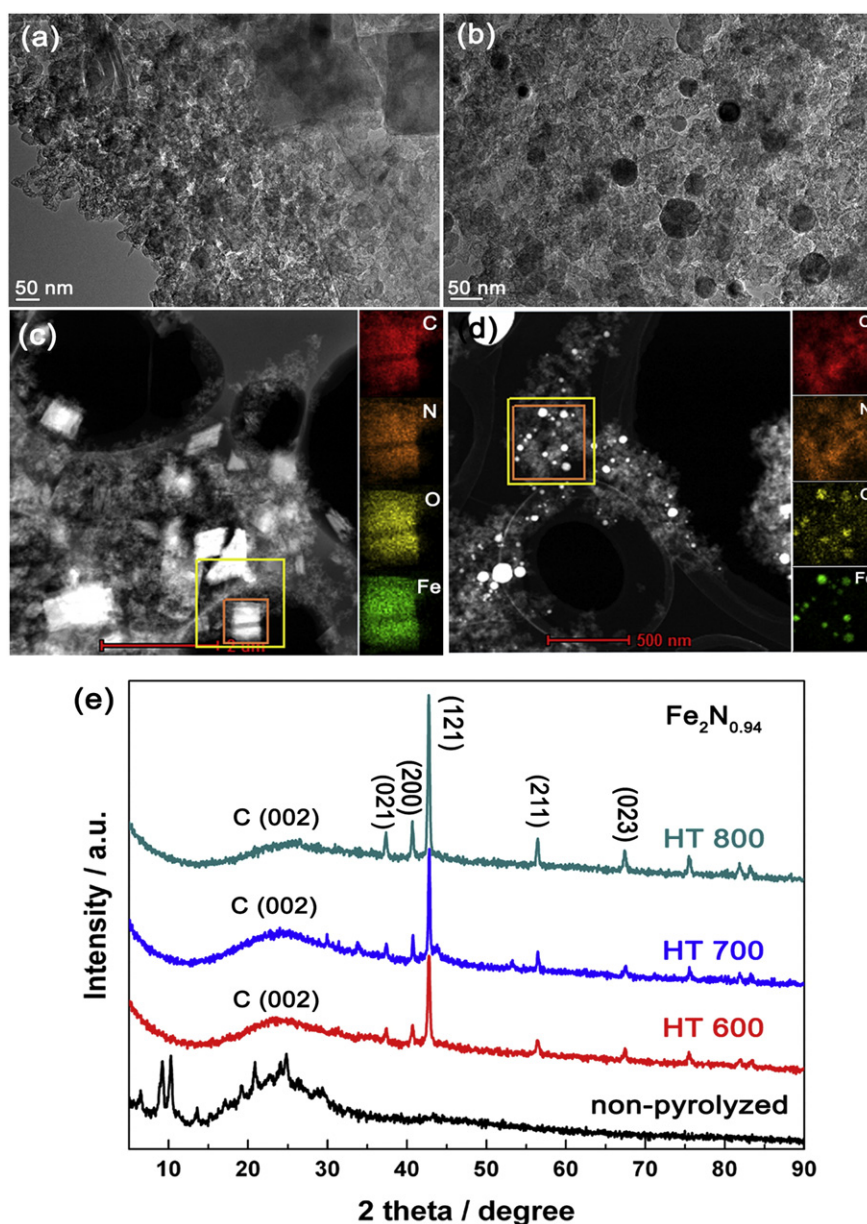
## 2.1. Catalyst preparation

The catalyst was synthesized by the pyrolysis of carbon-supported complex compounds using PBZ (98%, Meryer Chemical Technology Co., Ltd, Shanghai) as chelating ligand. A total of 69.91 mg PBZ was dissolved in 15 mL ethanol, followed by moderate stirring. Designed ferrous sulfate was dissolved in 2 mL deionized water to form a

\* Corresponding author. Tel.: +86 411 84379935.

\*\* Corresponding author. Tel.: +86 411 84379072; fax: +86 411 84665057.

E-mail addresses: [zhonghexiang@dicp.ac.cn](mailto:zhonghexiang@dicp.ac.cn) (H. Zhong), [zhanghm@dicp.ac.cn](mailto:zhanghm@dicp.ac.cn) (H. Zhang).



**Fig. 1.** TEM images of (a) PBZ/Fe and (b) HT-PBZ/Fe-700. HAADF-STEM images with corresponding EDX mapping images of (c) PBZ/Fe and (d) HT-PBZ/Fe-700. (e) XRD pattern for catalyst samples before and after pyrolysis at 600, 700, and 800 °C.

homogeneous light green solution, which was added to the PBZ solution drop by drop; 50 mg carbon black (BP2000) was also added to the final solution to obtain a suspension, which was stirred continuously for 12 h, slowly evaporated at 70 °C, and completely dried overnight in a vacuum oven at 60 °C. The resulting dry powder then underwent pyrolysis at different temperatures in NH<sub>3</sub> to obtain the final catalyst; the resultant catalysts were obtained and denoted as HT-PBZ/Fe-*n* (*n* is the pyrolysis temperature). The same procedure was used to synthesize catalysts without pyrolysis and metal doping, denoted as PBZ/Fe and HT-PBZ-*n*, respectively. A commercial JM 20% Pt/C catalyst was used for comparison.

## 2.2. Physical characterizations

The bulk structure of the catalyst was obtained by X-ray powder diffractometer (XRD, X'Pert PRO diffractometer) under Cu-K $\alpha$  radiation. X-ray photoelectron spectra (XPS) were performed on a Thermo ESCALAB 250XI spectrometer with Al-K $\alpha$  radiation (1486.6 eV)

operated at 150 W. XPS spectra was calibrated by adjusting the binding energy of C 1s to 284.6 eV. TEM images were performed on a JEOL JEM-2100EX (200 kV) microscope. STEM and EDX mapping images were recorded on a Tecnai G2 TF20 microscope.

## 2.3. Electrochemical measurements

Electrochemical measurements were performed in a traditional three-electrode cell at room temperature with a CHI 660B electrochemical station. 1 M NaOH was employed as electrolyte. A catalyst-coated glassy carbon electrode (GCE) (0.1256 cm<sup>2</sup>), graphite plate, and Hg/HgO electrode served as working, counter, and reference electrodes, respectively. To form the catalyst ink, 5 mg catalyst, 50  $\mu$ L 5 wt.% Nafion® solutions, and 1 mL isopropanol mixture were combined ultrasonically for 30 min. The catalyst/GCE was prepared by casting 10  $\mu$ L catalyst ink and air-drying at room temperature. The loading of catalyst (in mg cm<sup>-2</sup>) was 0.379. All potentials were referenced to standard hydrogen electrode (SHE).

Download English Version:

<https://daneshyari.com/en/article/49914>

Download Persian Version:

<https://daneshyari.com/article/49914>

[Daneshyari.com](https://daneshyari.com)