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# A high performance non-noble metal electrocatalyst for the oxygen reduction reaction derived from a metal organic framework



Yangzhi Bai <sup>a,b</sup>, Baolian Yi <sup>a</sup>, Jia Li <sup>c</sup>, Shangfeng Jiang <sup>a</sup>, Hongjie Zhang <sup>a</sup>, Zhigang Shao <sup>a,\*</sup>, Yujiang Song <sup>c,#</sup>

<sup>a</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

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## ABSTRACT

The development of a non-precious metal electrocatalyst (NPME) with a performance superior to commercial Pt/C for the oxygen reduction reaction (ORR) is important for the commercialization of fuel cells. We report the synthesis of a NPME by heat-treating Co-based metal organic frameworks (ZIF-67) with a small average size of 44 nm. The electrocatalyst pyrolyzed at 600 °C showed the best performance and the performance was enhanced when it was supported on BP 2000. The resulting electrocatalyst was composed of 10 nm Co nanoparticles coated by 3–12 layers of N doped graphite layers which as a whole was embedded in a carbon matrix. The ORR performance of the electrocatalyst was tested by rotating disk electrode tests in O<sub>2</sub>-saturated 0.1 mol/L KOH under ambient conditions. The electrocatalyst (1.0 mg/cm<sup>2</sup>) showed an onset potential of 1.017 V (vs. RHE) and a half-wave potential of 0.857 V (vs. RHE), which showed it was as good as the commercial Pt/C (20 μg<sub>Pt</sub>/cm<sup>2</sup>). Furthermore, the electrocatalyst possessed much better stability and resistance to methanol crossover than Pt/C.

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## 1. Introduction

For its high energy conversion efficiency, high power density, low operating temperature, long life span, and low or zero emission of pollutants, fuel cell technology has attracted attention [1,2]. The commercial Pt/C catalyst remains the most popular electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells [3–5]. However, the limited reserve, relatively low stability, CO poisoning and deactivation by crossover methanol have prevented Pt-based electrocatalysts from widespread commercialization in fuel cells [6,7]. Therefore, the develop-

ment of a high performance non-precious metal electrocatalyst (NPME) for the replacement of Pt-based electrocatalysts would be an ideal solution [8].

In recent years, metal organic framework (MOF) as a precursor has been employed for the preparation of NPMEs. MOFs are crystalline porous materials with a periodic network formed by the self-assembly of transition metal ions and organic ligands [9]. Due to their tunable pores, ultra-low density, and high specific surface area [7], MOFs have drawn tremendous attention as a new class of porous materials with potential applications in hydrogen storage [10,11], CO<sub>2</sub> capture [12],

\* Corresponding author. Tel: +86-411-84379153; Fax: +86-411-84379153; E-mail: zhgshao@dicp.ac.cn

# Corresponding author. E-mail: yjsong@dlut.edu.cn

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chemical separation [13,14], catalysis [15], biomedical imaging [16,17], chemical sensors [18] and magnetic applications [19]. Compared to the commonly used NPME precursors comprising a carbon support, nitrogen-containing ligands and transition metal salts, MOF possesses a periodic 3D-network structure that can provide not only abundant desired moieties but also a uniform and regular porous structure [20]. Hence, many MOFs have already been selected for the preparation of ORR electrocatalysts. Li et al. [21] synthesized a NPME with high electrochemical performance in both acidic and alkaline condition by heat-treating a mixture of a novel Co-containing MOF material with giant polyhedral cages, dicyandiamide (DCDA) and iron species. Zhang et al. [22] reported an alkaline NPME produced by the pyrolysis of triphenylphosphine and highly porous doped carbon nanofibers derived from ZIF-8 nanofibers.

Imidazole zeolite frameworks (ZIFs) are an important class of MOFs. Their thermal and chemical stability, high specific surface area, high nitrogen content, and uniform distribution of transition metals and nitrogen-containing ligands make ZIFs unique NPME precursors [1], in particular, ZIF-67 has a sodalite topology in which every cobalt cation is bridged with four nitrogen atoms of 2-methylimidazolate anions. Wang et al. [23] have made electrocatalysts with ZIF-67, ZIF-8 and  $\text{Co}_2(\text{bdc})_2(\text{dabco})$  in both acidic and alkaline solution. Hu et al. [24] and Chen et al. [25] have made S-doped electrocatalysts for ORR and both oxygen reduction and evolution reactions with ZIF-67. Aijaz et al. [26] have made bifunctional electrocatalysts for oxygen electrodes comprising  $\text{Co}@\text{Co}_3\text{O}_4$  nanoparticles embedded in CNT-grafted N-doped carbon-polyhedra obtained by the pyrolysis of ZIF-67 in a reductive  $\text{H}_2$  atmosphere and subsequent controlled oxidative calcinations. Xia et al. [20] have used ZIF-67 with different particle sizes as precursors to synthesize ORR electrocatalysts in acidic solution. From the results, we can see that the electrochemical performance of NPME is closely related to the size of the ZIF-67 precursors. The smallest ZIF-67 particles (300 nm) showed the best electrochemical performance. This may be because the smaller ZIF-67 supplied more active and easily accessible sites and thus promoted faster mass and electron transfer. In this study, we report the synthesis of the smaller ZIF-67 (about 44 nm) and subsequent pyrolysis with and without a BP 2000 carbon support. The resultant NPME demonstrated high ORR performance in terms of the half-wave potential and is more stable in alkaline medium than a commercial Pt/C catalyst.

## 2. Experimental

### 2.1. Preparation of ZIF-67 and ZIF-67/C

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (> 99%) was purchased from Xilong Chemical Reagent Co. (Guangdong, China) and 2-methylimidazole was purchased from Aladdin Chemical Reagent Co. (Shanghai, China). The chemicals were used as received. Milli-Q UV-plus water (18.2  $\text{M}\Omega \cdot \text{cm}$ ) from a Millipore water system (Synergy® UV, France) was used in the experiments.

In a typical synthesis, 921 mg  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was placed into a 250 mL round bottom flask, followed by the addition of

125 mL of anhydrous methanol. After mild sonication in a water bath cleaner for 5 min,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was homogeneous dissolved in methanol. Next, 2.079 g 2-methylimidazole was added to the mixture. Another 5 min of mild sonication was applied to ensure the complete dissolution of 2-methylimidazole. The mixture was incubated at 25 °C with stirring for 22 h. Finally, ZIF-67 was obtained as a purple precipitate. The product was collected by centrifugation at 8000 r/min for 8 min, followed by drying under vacuum at 80 °C for 4 h.

The synthesis of ZIF-67/C was identical to that described above for ZIF-67, except that 75 mg BP 2000 was added after the addition of 2-methylimidazole.

### 2.2. Electrocatalyst synthesis

The ZIF-67 was pyrolyzed under an argon atmosphere for 2 h at different temperatures ranging from 500 to 900 °C with a heating ramp of 5 °C/min and cooled down naturally to ambient temperature. The electrocatalysts were marked as ZIF-67- $T_c$ , where  $T_c$  stands for the thermal treatment temperature. The heat treatment procedure for ZIF-67/C was the same as that of ZIF-67 and the corresponding electrocatalyst was marked as ZIF-67/C-600. Finally, all the electrocatalysts were ground to a fine powder.

### 2.3. Physical characterization

Transmission electron microscopy (TEM) was conducted on JEM-2000EX operated at 120 kV and JEM-2100 operating at 200 kV. Powder X-ray diffraction (XRD) patterns were collected on a D/MAX2500VB2/PC with a  $2\theta$  range of 5°–90° and a scan speed of 5°/min at ambient temperature. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCA Lab250 Xi spectrometer. The metal content of the electrocatalysts was determined by a PerkinELmer 7300DV inductively coupled plasma atomic emission spectrometry (ICP-OES).

Nitrogen sorption measurements at –196 °C were carried out using a Quantachrome Autosorb-IQ gas adsorption analyzer. The samples were degassed at 90 °C for 2 h and 200 °C for 5 h under vacuum first. The resulting BET surface area was calculated from the adsorption branch. The pore size distribution was fitted using the Quenched Solid Density Functional Theory (QSDFT) method.

### 2.4. Electrochemical measurements

A CHI electrochemical station (Model 760D) and a conventional three-electrode electrochemical cell were used for electrochemical measurements at room temperature. A platinum plate and mercuric oxide electrode (Hg/HgO) were used as the counter and reference electrode, respectively. The electrolyte was 0.1 mol/L KOH aqueous solution. For the preparation of the catalyst ink, some Nafion solution (5 wt%), ultra-pure water and ethanol ( $V_{\text{Nafion}}:V_{\text{water}}:V_{\text{ethanol}} = 0.1:1:9$ ) were mixed with an electrocatalyst and sonicated in a water bath for 10 min to

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