



Metal-organic framework derived hierarchically porous nitrogen-doped carbon nanostructures as novel electrocatalyst for oxygen reduction reaction



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ABSTRACT

The hierarchically porous nitrogen-doped carbon materials, derived from nitrogen-containing isorecticular metal-organic framework-3 (IRMOF-3) through direct carbonization, exhibited excellent electrocatalytic activity in alkaline solution for oxygen reduction reaction (ORR). This high activity is attributed to the presence of high percentage of quaternary and pyridinic nitrogen, the high surface area as well as good conductivity. When IRMOF-3 was carbonized at 950 °C (CIRMOF-3-950), it showed four-electron reduction pathway for ORR and exhibited better stability (about 78.5% current density was maintained) than platinum/carbon (Pt/C) in the current durability test. In addition, CIRMOF-3-950 presented high selectivity to cathode reactions compared to commercial Pt/C.

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1. Introduction

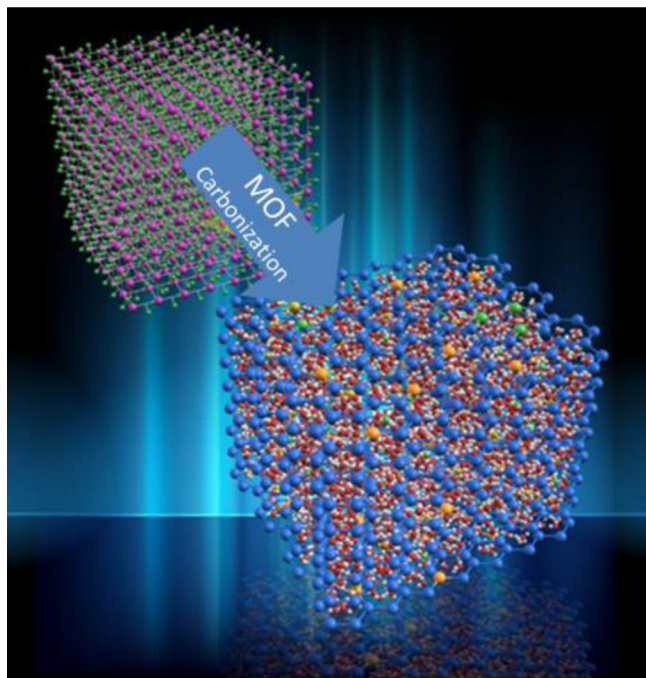
The oxygen reduction reaction (ORR) plays an important role in controlling the performance of fuel cells and metal-air batteries [1–3]. Due to the ever increasing global energy consumption and demand, there has been significant interest in the development of technologies for efficient electrocatalysts for improved electrocatalytic activity toward ORR. Traditionally, platinum (Pt) and Pt-based materials are widely used as active electrocatalysts for ORR. However, the high cost and slow kinetics of oxygen reduction limit their commercialization [3–5]. Due to the complexity of reaction, large Pt loadings are required for ORR (0.4 mg cm^{-2}) as compared to hydrogen oxidation (0.05 mg cm^{-2}) [5,6]. Under fuel cells operation conditions, Pt catalysts tend to agglomerate or detach from the support, which not only has adverse impact on the performance of fuel cells but also diminishes their overall lifetime [7,8]. Additionally, the Pt-based electrodes suffer from their susceptibility to time-dependent drift and carbon monoxide (CO) poisoning. As a result, the total cost of the whole system increases. Therefore, extensive studies have been carried out

recently to develop alternative transition metal and metal-free catalysts to replace Pt-based electrodes for fuel cell applications. Developments for alternative catalysts in ORR, including metal oxides (such as manganese dioxide and lead dioxide) [9,10], metal macrocyclic compounds (such as iron and cobalt based materials) [11,12] and heteroatom-doped carbon related materials (e.g. fluorine, nitrogen, sulfur, selenium and boron), have received a great deal of attention [13–19]. Among them, the heteroatom-doped carbon materials have been proved to be promising metal-free electrocatalysts towards ORR because of their increased chemical reactivity and improved electronic properties which can be tailored by controlling the amount of dopant [20–22]. In particular, nitrogen-doped carbon materials exhibit excellent catalytic activity as a result of unique electronic properties, low cost, CO tolerance and rather good stability [13,23,24].

In addition to the heteroatom-doping, the morphologies of catalyst materials also play a significant role in enhancing ORR activities. Generally, those rationally designed materials involving high porosity and surface area are favorable for the high ORR activity. Metal-organic-frameworks (MOFs) (Scheme 1) [25–30], highly ordered 3D framework structures, are composed of well-organized metal centers and organic linkers. Due to controlled porosity and high surface area, they have attracted much attention for their use in various applications including energy storage, gas capture and catalysts [26,27,31–33]. Recently, we and others

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Scheme 1. MOF-derived hierarchically porous nitrogen-doped carbon nanostructures.

reported that MOF derived hierarchically porous carbon materials exhibited superior electrochemical performances [34–36]. In this study, we demonstrated that previously reported [36] nitrogen doped carbon derived from nitrogen-containing isorecticular metal-organic framework-3 (CIRMOF-3-950) through direct carbonization, with high porosity and surface area, exhibited excellent electrocatalytic activity for ORR through 4-electrons reduction pathway. In the current durability test, about 78.5% initial current density was maintained, which is significantly superior to commonly used commercial Pt/C. Moreover, the possible methanol crossover effects were minimized by the inactivity of CIRMOF-3-950 to methanol oxidation compared to Pt/C.

2. Experimental section

2.1. Chemicals and reagents

Commercial platinum/carbon (Pt/C) 20 wt.% (Pt loading: 20 wt.%, Pt on carbon black) was purchased from Alfa Aesar. Potassium

chloride (KCl, 99.0~100.5%), 2-propanol (C_3H_8O , 99.5%), nafion perfluorinated resin solution (5 wt.% in mixture of lower aliphatic alcohols and water, contains 45% water) were obtained from Sigma–Aldrich, Co. Methanol (CH_3OH , >=99.8%), potassium hydroxide (KOH, 85.0~100.5%) were purchased from J.T. Baker Chemical Co.

2.2. Characterization

SEM images were obtained using an FEI Helios 600 NanoLab focused ion beam–scanning electron microscope (FIB–SEM). Nitrogen adsorption–desorption isotherms were collected using a Quantachrome autosorb-6 automated gas sorption. Brunauer–Emmett–Teller (BET) surface area was calculated from the nitrogen isotherm curves ranging from 0.1 to 0.3 of relative pressure. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS-165 multi-technique electron spectrometer system with a base pressure of 1×10^{-9} torr. The spectra of the surfaces were obtained with an AXIS-165 manufactured by Kratos Analytical Inc. (Spring Valley, NY, USA) using a monochromatic X-ray radiation of 1487 eV (Al $K\alpha$). The spectrometer was calibrated against both the Au $4f_{7/2}$ peak at 84.0 eV and the Ag $3d_{5/2}$ peak at 368.3 eV. Static charging when present was corrected with a neutralizer (flood gun) by placing the carbon peak (C 1s) at about 285 eV.

2.3. Electrode preparation and electrochemical measurements

The catalysts (2 mg mL^{-1}) were prepared by dissolving CIRMOF-3-600, CIRMOF-3-950 or Pt/C into nafion solution which contains nafion, 2-propanol, and water ($v/v/v = 0.025/1/4$). The mixture was ultrasonicated to obtain homogeneous catalyst ink.

The electrochemical measurements were conducted on an electrochemical workstation (CHI 630E) coupled with a three-electrode system. A Pt wire and a Ag/AgCl electrode filled with 3 M KCl aqueous solution were used as the counter electrode and reference electrode, respectively. To prepare the working electrode for ORR and methanol crossover test, $10 \mu\text{L}$ CIRMOF-3-950 catalyst ink was loaded on a glassy carbon (GC) disk electrode (5 mm in diameter, 0.19625 cm^2 in geometric area) and dried at 140 °F. CIRMOF-3-600 and Pt/C on GC electrodes were prepared in the same way. And the calculated loading was $101.9 \mu\text{g cm}^{-2}$. The electrolyte was 150 mL 0.1 M KOH solution for ORR test. And 1 M methanol dissolved in 150 mL 0.1 M KOH for methanol crossover test.

Measurements on rotating disk electrode (RDE) were carried out on an electrode rotator (Princeton Applied Research). Cyclic

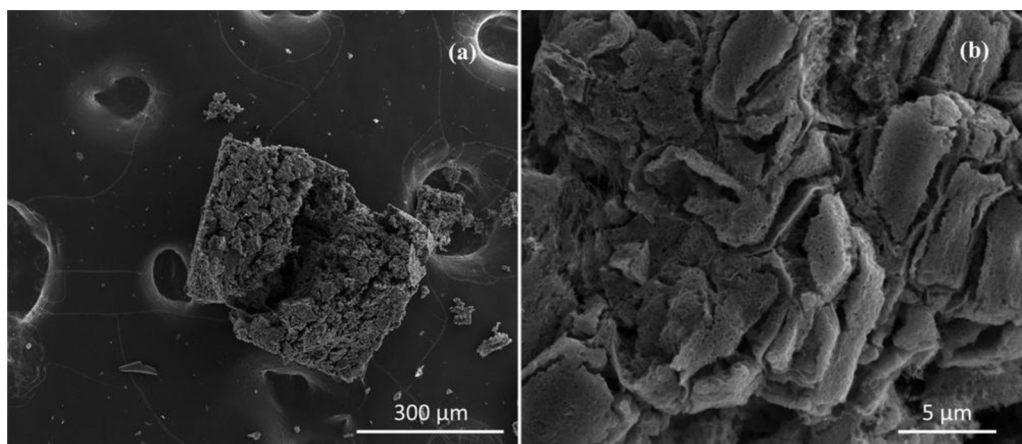


Fig. 1. SEM images of CIRMOF-3-950.

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