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Graphical abstract

MOF-derived hierarchically porous nitrogen-doped carbon nanostructures were synthesized, which exhibited the enhanced electrochemical performance for oxygen reduction reaction.

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.

Keywords

metal-organic framework; porous carbon; nitrogen doping; electrocatalysis; oxygen reduction reaction.

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 reported that MOF derived hierarchically porous carbon materials exhibited superior electrochemical performances [34, 35, 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 , $\geq 99.8\%$), 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 ($\text{AlK}\alpha$). The spectrometer was calibrated against both the $\text{Au } 4f_{7/2}$ peak at 84.0 eV and the $\text{Ag } 3d_{5/2}$ peak at 368.3 eV. Static charging when present was corrected with a neutralizer (flood gun) by placing the carbon peak ($\text{C } 1s$) 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 μL 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 $^\circ\text{F}$. CIRMOF-3-600 and Pt/C on GC electrodes were prepared in the same way. And the calculated loading was $101.9\text{ }\mu\text{g cm}^{-2}$. 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 voltammetry (CV) measurements with scan rate of 50 mV/s for both ORR and methanol crossover tests were performed after purging nitrogen or oxygen into KOH solution for 30 min. Linear sweep voltammetry (LSV) measurements were performed in O_2 -saturated electrolyte for ORR test. The scan rate was 10 mV/s. Additionally, current durability tests were also performed at a constant voltage of -0.3 V in a 0.1 M KOH solution saturated with O_2 at a rotating rate of 200 rpm.

3. Results and discussion

3.1 Synthesis and Characterization of CIRMOF-3

IRMOF-3 materials were synthesized based on a simple solvothermal method reported elsewhere [36]. In brief, zinc nitrate tetrahydrate and 2-aminobenzene-1,4,-dicarboxylate were added to dimethylformamide (DMF) and sonicated several minutes before holding at 100 $^\circ\text{C}$ for 24 h. After synthesis, the solvent DMF in MOF was washed and exchanged with chloroform (for three times) and stored in chloroform. After that, the as-synthesized MOFs were transferred to a tube furnace for further carbonization at two different temperatures 600 $^\circ\text{C}$ or 950 $^\circ\text{C}$ for 6 h in the presence of argon. Carbon materials obtained at 950 $^\circ\text{C}$ offered metal free CIRMOF-3-950, otherwise carbonization of MOFs at low temperatures (600 $^\circ\text{C}$) resulted in the formation of

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4 carbon materials containing ZnO [36]. Pure CIRMOF-3-600 was obtained after hydrogen
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6 chloride etching to remove ZnO. Figure 1 shows the scanning electron microscope (SEM)
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8 images of CIRMOF-3-950. The images demonstrate that the cubic shape was mainly maintained
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10 during the carbonization process. With higher magnification, CIRMOF-3-950 presents a porous
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12 structure.
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16 To further investigate the porous structure, the Brunauer-Emmett-Teller (BET) surface area
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18 was examined by nitrogen adsorption-desorption measurements. The results are shown in Figure
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20 2a, which reveals a typical type II adsorption isotherm. CIRMOF-3 started to adsorption nitrogen
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22 at low relative pressure, indicating the presence of micro-pores. At high relative pressure, a sharp
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24 increase of nitrogen appeared, which was probably caused by meso- and macro-pores between
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26 particles. An intermediate flat region appeared between these two regions. The pore size
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28 distribution was obtained from nitrogen isotherms using density functional theory (DFT). It
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30 indicates the presence of meso- and micro-pores. It is also observed that CIRMOF-3-950 had
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32 higher surface area ($553 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.342 \text{ cm}^3 \text{ g}^{-1}$) than CIRMOF-3-600 (393
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34 $\text{m}^2 \text{ g}^{-1}$ and $0.234 \text{ cm}^3 \text{ g}^{-1}$). This was probably caused by the sublimation of Zn from the
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36 previously formed ZnO and ligands decomposition during carbonization at 950°C . While the
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38 lower surface area and porosity at lower carbonization temperature might result from the not
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40 fully developed carbon network. The high surface area and large pore volume in CIRMOF-3-950
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42 might provide more active sites for ORR, which will further facilitate its catalytic activity.
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51 The information of chemical composition and the content of nitrogen in CIRMOF-3 materials
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53 were obtained by X-ray photoelectron spectroscopy (XPS) analysis. As expected, the result
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55 (Figure S1a and S1b) reveals the presence of nitrogen, which demonstrates the successful doping
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57 of nitrogen. Additionally, the nitrogen content decreased from 7 at% to 3.3 at% as carbonization
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temperature increased from 600 °C to 950 °C. That is because C-N bonds are preferably cleaved at high temperature as compared to C-C bond. Figure 3a and 3b show the deconvoluted N 1s peaks of both CIRMOF-3-600 and CIRMOF-3-950. The three different peaks at 398.5, 400.3 and 400.9 eV were attributed to pyridinic nitrogen, pyrrolic nitrogen or pyrridone and quaternary nitrogen, respectively. Figure 3c reveals that the composition of nitrogen functional groups of CIRMOF-3-950 is different from that of CIRMOF-3-600. CIRMOF-3-950 presents a large percentage of quaternary nitrogen (76.13%) because quaternary nitrogen is more stable at high temperature than other nitrogen functional groups [37, 38]. In the case of CIRMOF-3-600, the content of pyridinic nitrogen is a little bit more than quaternary nitrogen and pyrrolic nitrogen. Furthermore, CIRMOF-3-950 exhibits more highly ordered graphitic structure than CIRMOF-3-600 as shown in Figure 3d. This might result in overall higher electrical conductivity of CIRMOF-3-950, and therefore influences the catalytic activity and durability of electrocatalysts.

3.2 Electrocatalytic activity of CIRMOF-3-600 and CIRMOF-950 towards ORR

In order to evaluate the specific electrocatalytic performance of CIRMOF-3-600 and CIRMOF-3-950 towards ORR, cyclic voltammetry (CV) tests were carried out in N₂ and O₂-saturated 0.1 M KOH solution from 0.2 V to -1.0 V vs. Ag/AgCl at a scan rate of 50 mV s⁻¹, respectively. The current densities were all normalized with respect to the geometrical area (0.196 cm²). As shown in Figure 4a, featureless voltammetric currents within the potential range were observed for all electrodes in N₂-saturated solution. In contrast, when the solution was saturated with O₂, all the CV curves presented well-defined characteristic ORR peaks. This demonstrates the electrocatalytic activities of CIRMOF-3 towards ORR. In detail, the peak potential of CIRMOF-3-950 positively shifted (around 115 mV) with higher current compared to CIRMOF-3-600. The peak current density also increased from 0.78 mA cm⁻² to 1.05 mA cm⁻²

when annealing temperature was increased from 600 °C to 950 °C. These values were comparable to commercial Pt catalysts. Recent studies have proved that pyridinic and quaternary nitrogen act as active sites for the ORR activity [39]. These sites cause the net positive charges on their adjacent carbon atoms, which not only facilitates oxygen adsorption, but help attracting electrons from anode. Therefore, the better electrocatalytic activity of CIRMOf-3-950 could be attributed to the high surface area, large percentage of pyridinic nitrogen and quaternary nitrogen and the high degree of graphitic carbon.

Additionally, the electrocatalytic properties of CIRMOf-3-600 and CIRMOf-3-950 were compared with commercial Pt/C catalyst. The rotating disk electrode (RDE) linear sweep voltammetry (LSV) was performed in O₂-saturated 0.1 M KOH solution at a rotating rate of 1600 rpm. As shown in Figure 4b, the onset potential of CIRMOf-3-950 increased positively from -0.23 V to -0.08 V as the annealing temperature was increased from 600 °C to 950 °C, which is close to that of commercial Pt/C (-0.05 V). CIRMOf-3-950 also showed a much higher current density than that of CIRMOf-3-600, which are well agreed with CV analysis mentioned above. All these parameters indicate the good electrocatalytic activity of CIRMOf-3-950 toward ORR. This may rise from the high content of pyridinic nitrogen and quaternary nitrogen of CIRMOf-3-950 as well as its high surface area and pore volume. Further insight of the electron transfer kinetics of ORR process on these catalysts was studied by LSV on an RDE. The rotating speeds were from 225 rpm to 2500 rpm with a scan rate of 10 mV s⁻¹ in O₂-saturated 0.1 M KOH electrolyte. As shown in Figure 4c and Figure S2, the current densities increased with rotating rate significantly for both CIRMOf-3-950 and CIRMOf-3-600 electrodes due to the faster oxygen flux to electrode surface under high rotating rate and consequently larger current. The number of electrons transferred in ORR can be obtained according to the corresponding

Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) at various electrode potentials which were analyzed using Koutecky-Levich equation:

$$J^{-1} = J_L^{-1} + J_K^{-1} = B^{-1}\omega^{-1/2} + J_K^{-1} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

Here J is the measured current density, J_L is the diffusion-limiting current density, J_K is the kinetic current density, ω is the electrode rotating speed in rad s^{-1} , n is the overall electron-transfer number in oxygen reduction, F is the Faraday constant ($F=96485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 , D_0 is the diffusion coefficient, ν is the kinetic viscosity of the electrolyte, and k is the electron-transfer constant. Figure S3 and Figure 4d show K-L plots of IRMOF-3-600 and IRMOF-3-950 at different potentials. Each plot shows a good linear relationship between J^{-1} and $\omega^{-1/2}$, revealing the consistent electron-transfer at different potential and the first-order reaction kinetics with respect to the concentration of dissolved O_2 [38]. By using the values $C_0=1.2\times 10^{-3} \text{ mol L}^{-1}$, $D_0=1.9\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu=0.01 \text{ cm}^2 \text{ s}^{-1}$, the number of transferred electrons can be calculated based on equation (1) through (3). ORR in alkaline solution proceeds either via a two-electron reduction pathway in which hydrogen peroxide is formed as an intermediate or via a four-electron reduction pathway where O_2 is directly reduced to OH^- [38]. The four-electron pathway is generally preferred in fuel cell since it gives a faster reduction rate. Figure 4e shows that the number of electrons transferred for ORR on CIRMOf-3-950 and Pt/C electrodes were around four, while ORR on CIRMOf-3-600 showed a 2-electron reduction pathway. This is consistent with the results in Figure S2, where CIRMOf-3-600 exhibited a typical two-step

shape in LSV curves. Moreover, CIRMOF-3-950 also presented a higher kinetic current compared with CIRMOF-3-600 in Figure 4e, which is consistent with the LSV curves in Figure 4b. The four-electron transfer pathway and high kinetic current density further confirmed the better ORR electrocatalytic activity of CIRMOF-3-950 in alkaline solution. This different catalytic activity might be attributed to the different content of nitrogen, pore volume, surface area and degree of graphitic carbon between these two materials.

Current durability is an important parameter of fuel cells. To demonstrate the stability of CIRMOF-3-950 catalyst, a comparison test with commercial Pt/C was performed by current-time chronoamperometry at a constant voltage of -0.3 V vs. Ag/AgCl in O₂-saturated 0.1 M KOH electrolyte at a rotating rate of 200 rpm. As shown in Figure 5a, about 78.5% relative current was persisted after reaction for 20000 s. In contrast, only about 66% of the initial current density was maintained for commercial Pt/C. This confirmed that CIRMOF-3-950 exhibited a much better stability than commercial Pt/C catalyst for ORR in alkaline medium.

Another important parameter of electrocatalysis is the selectivity for cathode reactions since the small-molecule fuels, such as methanol, could penetrate through the polymer electrolyte membrane from anode to cathode easily and consequently compromises the whole cell performance [20]. Therefore, CIRMOF-3-950 and commercial Pt/C were subjected to methanol crossover tests. Figure 5b and 5c present the CV curves of CIRMOF-3-950 and Pt/C electrodes in O₂-saturated 0.1 M KOH solution before and after the addition of methanol, respectively. The CIRMOF-3-950 presented a stable ORR without any electroactivity specific to methanol when methanol was added into 0.1 M KOH solution, suggesting the remarkable tolerance to possible crossover effects. However, for Pt/C electrode, the characteristic methanol reduction/oxidation

peaks showed up in the KOH solution containing 1 M methanol. This test further confirmed the priority for ORR of CIRMOf-3-950.

4. Conclusions

In summary, hierarchically porous nitrogen-doped carbon nanostructures were synthesized through the carbonization of nitrogen containing MOF. The resultant 3D nitrogen-doped nanoporous carbon is able to provide a high specific surface area, large pore volume and high degree of graphitic carbon, and thus maximize the availability of active sites. The optimized CIRMOf-3-950 showed high activity and four-electron reduction pathway for ORR and exhibited better stability than Pt/C in the current durability test. In addition, CIRMOf-3-950 was inactive to methanol oxidation compared to commercial Pt/C, which minimized the possible methanol crossover effects. This novel nitrogen-doped carbon material with hierarchical structures holds great promise in fuel cell.

Notes

Electronic Supplementary Information (ESI) available: XPS spectra, LSV curves and K-L plot of CIRMOf-3-600.

Acknowledgements

This work was supported by a start-up grant from WSU and a Laboratory Directed Research and Development program at Pacific Northwest National Laboratory (PNNL). SEM characterization was performed at EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research, located at PNNL. PNNL is a multiprogram national laboratory operated for DOE by Battelle under Contract DE-AC05-76RL01830.

References

- [1] K.P. Gong, F. Du, Z.H. Xia, M. Durstock, L.M. Dai, *Science*. 323 (2009) 760-764.
- [2] S. Maldonado, K.J. Stevenson, *J. Phys. Chem. B*. 109 (2005) 4707-4716.
- [3] C.Z. Zhu, S.J. Dong, *Nanoscale*. 5 (2013) 1753-1767.
- [4] P. Kanninen, M. Borghei, O. Sorsa, E. Pohjalainen, E.I. Kauppinen, V. Ruiz, T. Kallio, *Appl. Catal. B Environ.* 156 (2014) 341-349.
- [5] S. Ratso, I. Kruusenberg, M. Vikkisk, U. Joost, E. Shulga, I. Kink, T. Kallio, K. Tammeveski, *Carbon*. 73 (2014) 361-370.
- [6] S. Zhang, Y.Y. Shao, G.P. Yin, Y.H. Lin, *J. Power Sources*. 195 (2010) 1103-1106.
- [7] R. Kou, Y.Y. Shao, D.H. Mei, Z.M. Nie, D.H. Wang, C.M. Wang, V.V. Viswanathan, S. Park, I.A. Aksay, Y.H. Lin, Y. Wang, J. Liu, *J. Am. Chem. Soc.* 133 (2011) 2541-2547.
- [8] S. Zhang, Y.Y. Shao, G.P. Yin, Y.H. Lin, *J. Mater. Chem. A*. 1 (2013) 4631-4641.
- [9] J.M. Morris, S. Jin, J.Q. Wang, C.Z. Zhu, M.A. Urynowicz, *Electrochem. Commun.* 9 (2007) 1730-1734.
- [10] Q. Wen, S.Y. Wang, J. Yan, L.J. Cong, Z.C. Pan, Y.M. Ren, Z.J. Fan, *J. Power Sources*. 216 (2012) 187-191.
- [11] E.H. Yu, S. Cheng, B.E. Logan, K. Scott, *J. Appl. Electrochem.* 39 (2009) 705-711.
- [12] S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J.M. Leger, *J. Electroanal. Chem.* 577 (2005) 223-234.
- [13] Z.Y. Lin, G. Waller, Y. Liu, M.L. Liu, C.P. Wong, *Adv. Energy Mater.* 2 (2012) 884-888.
- [14] K. Ben Liew, W.R.W. Daud, M. Ghasemi, J.X. Leong, W.S. Lim, M. Ismail, *Int. J. Hydrogen Energ.*, 39 (2014) 4870-4883.
- [15] J. Liang, Y. Jiao, M. Jaroniec, S.Z. Qiao, *Angew. Chem. Int. Edit.* 51 (2012) 11496-11500.

- [16] Z. Yang, H.G. Nie, X. Chen, X.H. Chen, S.M. Huang, *J. Power Sources*. 236 (2013) 238-249.
- [17] X.J. Sun, Y.W. Zhang, P. Song, J. Pan, L. Zhuang, W.L. Xu, W. Xing, *ACS Catal.* 3 (2013) 1726-1729.
- [18] N.K. Chaudhari, M.Y. Song, J.S. Yu, *Sci. Rep.* 4 (2014) 5221.
- [19] Z.T. Cui, S.G. Wang, Y.H. Zhang, M.H. Cao, *J. Power Sources*. 259 (2014) 138-144.
- [20] Z.H. Sheng, L. Shao, J.J. Chen, W.J. Bao, F.B. Wang, X.H. Xia, *ACS Nano*. 5 (2011) 4350-4358.
- [21] L.T. Qu, Y. Liu, J.B. Baek, L.M. Dai, *ACS Nano*. 4 (2010) 1321-1326.
- [22] R.L. Liu, D.Q. Wu, X.L. Feng, K. Mullen, *Angew. Chem. Int. Edit.* 49 (2010) 2565-2569.
- [23] M.-Q.Z. Gui-Li Tian, Dingshan Yu, Xiang-Yi Kong, Jia-Qi Huang, Qiang Zhang, and Fei Wei, *Small*. 10 (2014) 2251-2259.
- [24] Y. Li, Y. Zhao, H.H. Cheng, Y. Hu, G.Q. Shi, L.M. Dai, L.T. Qu, *J. Am. Chem. Soc.* 134 (2012) 15-18.
- [25] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.* 38 (2009) 1450-1459.
- [26] J.L.C. Rowsell, O.M. Yaghi, *Micropor. Mesopor. Mat.* 73 (2004) 3-14.
- [27] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Edit.* 48 (2009) 7502-7513.
- [28] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebie, T. Baati, J.F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.S. Chang, Y.K. Hwang, V. Marsaud, P.N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur, R. Gref, *Nat. Mater.* 9 (2010) 172-178.
- [29] J.L.C. Rowsell, O.M. Yaghi, *Angew. Chem. Int. Edit.* 44 (2005) 4670-4679.
- [30] H. Furukawa, N. Ko, Y.B. Go, N. Aratani, S.B. Choi, E. Choi, A.O. Yazaydin, R.Q. Snurr, M. O'Keeffe, J. Kim, O.M. Yaghi, *Science*. 329 (2010) 424-428.

- [31] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, *Chem. Rev.* 112 (2012) 1105-1125.
- [32] P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Ferey, *Angew. Chem. Int. Edit.* 45 (2006) 5974-5978.
- [33] K.-J. Kim, X. Chong, P. Kreider, P. Ohodnicki, J. Baltrus, A. Wang, C.-h. Chang, G. Ma, J. *Mater. Chem. C*, 3 (2015) 2763-2767.
- [34] D. Zhao, J.L. Shui, C. Chen, X.Q. Chen, B.M. Reprogle, D.P. Wang, D.J. Liu, *Chem. Sci.* 3 (2012) 3200-3205.
- [35] E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz, J.P. Dodelet, *Nat. Commun.* 2 (2011) 416.
- [36] R.S. Ju-Won Jeon, Praveen Meduri, Bruce W. Arey, Herbert T. Schaef, Jodie L. Lutkenhaus, John P. Lemmon, Praveen K. Thallapally, Manjula I. Nandasiri, Benard Peter McGrail, and Satish K. Nune, *ACS Appl. Mater. Interfaces*, 6 (2014) 7214–7222.
- [37] S.B. Yang, L.J. Zhi, K. Tang, X.L. Feng, J. Maier, K. Mullen, *Adv. Funct. Mater.* 22 (2012) 3634-3640.
- [38] X.X. Liu, H. Zhu, X.R. Yang, *J. Power Sources*. 262 (2014) 414-420.
- [39] Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat. Commun.* 4 (2013) 2390.

Figure captions

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

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

Figure 2. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution calculated by density functional theory (DFT).

Figure 3. (a) XPS spectra of nitrogen for CIRMOF-3-600 and (b) CIRMOF-3-950. (c) Nitrogen-containing functional groups of CIRMOF-3-600 and CIRMOF-3-950. (d) The percentage of ideal graphitic carbon and amorphous carbon of CIRMOF-3-600 and CIRMOF-3-950 obtained from Raman spectra.

Figure 4. (a) CV curves of CIRMOF-3-600, CIRMOF-3-950 and Pt/C on RDE in N₂-saturated and O₂-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (b) LSV curves of CIRMOF-3-600, CIRMOF-3-950 and Pt/C electrodes in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. (c) LSV curves of CIRMOF-3-950 in O₂-saturated 0.1 M KOH solution with various rotation rates at a scan rate of 10 mV s⁻¹. (d) K-L plots of CIRMOF-3-950 electrodes obtained based on the data extracted from (c). (e) Electron-transfer number (n) in the ORR on CIRMOF-3-600, CIRMOF-3-950 and Pt/C electrodes in O₂-saturated 0.1 M KOH solution and the kinetic current densities (J_k) of the ORR on CIRMOF-3-600 and CIRMOF-3-950 electrodes in O₂-saturated 0.1 M KOH solution.

Figure 5. (a) Chronoamperometric responses of CIRMOF-3-950 and commercial Pt/C electrodes at -0.3 V vs. Ag/AgCl in O₂-saturated 0.1 M KOH solution at a rotation rate of 200 rpm. CV curves of CIRMOF-3-950 (b) and Pt/C (c) electrodes in O₂-saturated 0.1 M KOH solution before and after the addition of methanol.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5