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Article

Preparation of MOF(Fe) and its catalytic activity for oxygen reduction reaction in an alkaline electrolyte

Guoqiang Song^a, Zhiqing Wang^a, Liang Wang^c, Guoru Li^c, Minjian Huang^c, Fengxiang Yin^{b,c,*}^a College of Pharmacy & Life Science, Changzhou University, Changzhou 213164, Jiangsu, China^b State Key Laboratory of Organic-inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China^c Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou 213164, Jiangsu, China

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ABSTRACT

Effective bifunctional catalysts play a vital role in large-scale commercial applications of rechargeable lithium-air batteries. In this article, a metal-organic framework, MOF(Fe), was prepared by a hydrothermal process using ferric nitrate as the metal ion precursor and trimesic acid as an organic ligand. The structure of the MOF(Fe) was characterized by X-ray diffraction, N₂ adsorption-desorption, Transmission electron microscopy, Fourier transform infrared spectroscopy and Thermo-gravimetric analysis. The activity for the oxygen reduction reaction (ORR) and the kinetic behavior of the ORR using the MOF(Fe) were investigated by cyclic voltammetry and rotating disk electrode voltammetry, respectively, using an alkaline electrolyte. The characterization results showed that the MOF(Fe) was highly crystalline with abundant micropores, large specific surface area and high thermal stability. The MOF(Fe) exhibited excellent catalytic activity for the ORR. The ORR mechanism varies with the applied potentials. The ORR occurs through a two-electron pathway at potentials in the range of −0.30 to −0.50 V, but shifts to four-electron pathway with the potentials in the range −0.50 to −0.95 V. In addition, the MOF(Fe) shows excellent catalytic activity for the oxygen evolution reaction (OER) in an alkaline electrolyte. This work opens a new route for the development of effective non-precious metal catalysts based on MOFs for the ORR and OER.

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1. Introduction

The theoretical energy density of the lithium-air battery is about 11.1 kWh/kg, which is equivalent to that of the gasoline-oxygen system [1–3] and is 10 times higher than that of the state-of-the-art lithium ion battery [2–4]. In addition, the lithium-air battery is light, non-toxic, pollution-free, and low cost. Therefore, lithium-air batteries have been regarded as very promising secondary batteries. However, the oxygen evolution reaction (OER) during the charging process and the oxygen

reduction reaction (ORR) during discharge are sluggish, resulting in large overpotentials, which significantly lower the round-trip efficiency and cycle life of the battery. This limits the practical application of the unit as a secondary battery. In recent years, bifunctional catalysts [5] for the OER and the ORR have been proposed for applications in lithium-air batteries. The bifunctional catalysts accelerate the OER and also the ORR, reducing the charge/discharge overpotentials and thereby significantly enhancing the performance of the lithium-air battery. These findings pave the way for the commercialization of

* Corresponding author. Tel: +86-10-64412054; Fax: +86-10-64419619; E-mail: yinfx@mail.buct.edu.cn

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the rechargeable lithium-air battery.

At present, IrO_2 is considered to be the best catalyst for the OER. However, Ir is very rare and expensive, and even more expensive than Pt [6,7], and cannot meet the requirements of commercialization. Recently, some non-precious metal catalysts, such as perovskites [8] and nickel-based catalysts [9–11] have shown good OER activity in alkaline media and these materials are considered to be promising OER catalysts. Carbon-supported Pt and Pt-alloy catalysts have also shown excellent ORR activity. Recently, the nano Au particles have shown good ORR catalytic performance in alkaline medium [12], but Pt and Au are similarly very expensive. Among non-precious metal catalysts for the ORR, Fe- and Co-based catalysts [13–16] exhibit good activity in an acidic medium, while Mn oxides [17,18], perovskites [19,20], and spinels [21,22] have good ORR activity in an alkaline medium. However, it also has been demonstrated that Fe-based catalyst is also active toward ORR in alkaline medium [23]. In addition, carbon-based materials also show potential to be applied for ORR applications [24]. Nevertheless, the performance of these catalysts is such that they need improvement to meet the requirements of the commercial lithium-air battery. Recently, great efforts have been made to develop effective bifunctional catalysts for the OER and the ORR, to significantly reduce the charge/discharge overpotentials of the lithium-air battery. Pt-Au/C catalyst is considered to be the current state-of-the-art bifunctional catalyst. However, Pt, Au, and other precious metals are for such catalysts to be considered as being suitable for large-scale commercial applications of the lithium-air battery [22,23]. Among the non-precious metal bifunctional catalysts, Fe-, Co-, and Mn-based oxides exhibit good bifunctional catalytic activity. Moreover, Fe, Co, and Mn are abundant and cheap. Although these catalysts have the potential for use in the lithium-air battery their current performance is relatively low and requires improvement to meet commercial requirements [24–27].

The metal-organic framework (MOF) is a new type of porous material in which the organic ligands coordinate to the metal ion centers in a bridging mode [31,32]. Compared with traditional porous materials, MOFs have high specific surface area [33,34] and a readily adjustable structure and function [35]. MOFs can be used as supports or as catalysts, and the functional groups and metal ions of MOFs can be designed directly as the active sites for catalytic reactions. Although MOFs have been regarded as excellent catalytic materials [36], there have been very few reports on the use of MOFs as electrocatalysts [37–39]. Mao et al. [37] studied the ORR activity of MOF Cu^{II} -bipy-BTC in a medium of pH 6, and found that this MOF exhibited stable activity for the ORR. In addition, a MOF-based composite $(\text{G-dye-FeP})_n$ comprising pyridine-functionalized graphene (G-dye) and an iron porphyrin (FeP) exhibited good catalytic activity for the ORR in an alkaline medium [40]. These preliminary results show that MOFs have a very significant potential as electrocatalysts, especially in ORR catalysis. However, the electrochemical performance of MOF materials and especially the relationship between structure and the ORR catalytic performance have not been studied in detail. In addition, there are few reports on MOFs applied to the OER. Hence, this

work has introduced iron into MOFs and taken the advantage of the unique structures of MOFs, which both are beneficial for ORR catalysis applications. In the present work, $\text{MOF}(\text{Fe})$ was synthesized by a hydrothermal method using ferric nitrate as the metal ion precursor and trimesic acid as the organic ligand. The structure of the $\text{MOF}(\text{Fe})$ was characterized and the electrochemical performances of $\text{MOF}(\text{Fe})$ were investigated in an alkaline electrolyte. The results show that the $\text{MOF}(\text{Fe})$ has good bifunctional catalytic activity for the OER and the ORR. This work opens a new route for the development of effective non-precious metal catalysts based on MOFs for rechargeable lithium-air batteries.

2. Experimental

2.1. Preparation of $\text{MOF}(\text{Fe})$

$\text{MOF}(\text{Fe})$ was prepared by a hydrothermal process. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, Shanghai Sinpeuo Fine Chemical Co., Ltd), 1,3,5-BTC (98%, Aladdin Chemistry Co., Ltd.), 5 mol/L HF (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd) and H_2O were mixed under stirring. The molar ratio of these materials was $1.0(\text{Fe}^{3+}) : 0.66(1,3,5\text{-BTC}) : 2.0(\text{HF}) : 280(\text{H}_2\text{O})$. The resulting mixture was loaded in a Teflon-lined stainless steel autoclave, which was then sealed and placed in an oven at $150\text{ }^\circ\text{C}$ for 84 h, followed by cooling to room temperature. After filtration, the residue was further purified by a two-step process. The powder sample was first purified using hot water at $80\text{ }^\circ\text{C}$ for 3 h, followed by filtration and washing and was then treated with hot ethanol at $60\text{ }^\circ\text{C}$ for 1 h. Further filtration was carried out and the solid was washed until no colored impurities could be detected in the filtrate. The resulting solid (the $\text{MOF}(\text{Fe})$) was dried at $100\text{ }^\circ\text{C}$ overnight under vacuum.

2.2. Characterization of the sample

The powder X-ray diffraction (XRD) pattern was recorded on a D/max 2500 PC type X-ray powder diffraction with $\text{Cu K}\alpha$ radiation operated at 40 kV and 100 mA. Fourier transform infrared (FT-IR) spectra of the $\text{MOF}(\text{Fe})$ sample were recorded on a Nicolet 5700 FTIR spectrometer using a KBr powder pressed tablet with scans from 4000 to 400 cm^{-1} . N_2 adsorption-desorption isotherms and pore size distributions were obtained on an ASAP 2010C Micromeritics automatic analyzer. The specific surface area of the sample was calculated by the BET method and the pore size distribution of was determined from the desorption branch using the BJH model. Thermogravimetric analysis (TGA) was carried out on a TG 209 F3 thermoanalyzer with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from room temperature to $850\text{ }^\circ\text{C}$ under air. The morphology of the sample was revealed using transmission electron microscopy (TEM, JEOL JEM-2100).

2.3. Preparation of the working electrode and the rotating disk electrode

Preparation of the working electrode involved using 4 mg

MOF(Fe) and 1 mg carbon black Super P (SP, Timcal), 50 μL Nafion (5%, DuPont) which were ultrasonically dispersed in 1 mL of ethanol for 30 min, and the obtained catalyst ink (50 μL) was dropped onto a $1 \times 1 \text{ cm}^2$ carbon paper (TGP-H-060, Toray). After drying at 80 $^{\circ}\text{C}$, the working electrode was obtained.

For the preparation of the rotating disk electrode a glassy carbon (GC) electrode with geometric area of 0.196 cm^2 was polished using a succession of metallographic abrasive papers and a $0.3 \mu\text{m}$ -alumina slurry. The solid was then rinsed with deionized water until it was clean. After drying, 10 μL of the above catalyst ink was coated onto the GC electrode. After drying at 80 $^{\circ}\text{C}$, the rotating disk electrode was obtained.

2.4. Electrochemical measurements

The OER and ORR catalytic activity tests were carried out in an electrochemical workstation (CHI 760E, CH Instruments, Inc.) at room temperature using a standard three-electrode system in KOH aqueous solution (0.1 mol/L). The KCl-saturated Ag/AgCl electrode and carbon rod were used as counter electrode and reference electrode, respectively. Cyclic voltammetry was carried out between -1.0 and 0.2 V at a scanning speed of 50 mV/s in a N_2 -saturated electrolyte, until the curve was stable. Then ORR catalytic activity was tested using linear sweep voltammetry with a scanning speed of 5 mV/s in a N_2 - or O_2 -saturated electrolyte. The ORR current using the catalyst was determined by subtracting the current in the N_2 -saturated electrolyte from that obtained in an O_2 -saturated electrolyte. The rotating disk electrode tests were performed in an O_2 -saturated electrolyte at rotation rates in the range of 100 – 2500 r/min with a scan rate of 5 mV/s . The durability of catalysts for the ORR was tested using chronoamperometry at -0.4 V (vs. Ag/AgCl) in an O_2 -saturated electrolyte at a rotation rate of 1600 r/min . The OER was tested by linear sweep voltammetry in a N_2 -saturated electrolyte with scanning speed of 5 mV/s in range of 0.2 – 1.0 V (vs. Ag/AgCl).

3. Results and discussion

3.1. Characterization of the sample

3.1.1. XRD, N_2 adsorption-desorption, and TEM results

XRD pattern of the as-prepared MOF(Fe) sample is shown in Fig. 1. The main diffraction peaks of the MOF(Fe) sample are

Fig. 1. XRD pattern of the MOF(Fe) sample.

Fig. 2. N_2 adsorption and desorption isotherms and pore size distribution (insert) of the MOF(Fe) sample.

observed at 2θ values of approximately 3.4° , 4.0° , 4.2° , 4.8° , 5.3° , 5.9° , 6.2° , 6.8° , 10.2° , 10.4° , 10.8° , 11.0° , 12.6° , 13.7° , 14.2° , 17.9° , 18.6° , 18.9° , and 19.1° . The XRD pattern of the MOF(Fe) sample is consistent with that of the MIL-100(Fe) prepared by Hasan et al. [38]. These results show that the MOF(Fe) exhibits well developed crystallinity.

N_2 adsorption-desorption isotherms and the pore size distribution of the MOF(Fe) sample are shown in Fig. 2. N_2 adsorption-desorption isotherms of the MOF(Fe) sample are of type I [42–45], indicating that the MOF(Fe) sample is a microporous material. When the relative pressure p/p_0 is in the approximate range of 0 – 0.15 , the amount of adsorbed N_2 increases dramatically because of microporous nature of the MOF(Fe). When the relative pressure $p/p_0 \geq 0.15$, the amount of N_2 adsorbed increases slowly with an increase in p/p_0 . The pore size distribution of the MOF(Fe) sample is shown in Fig. 2, where it can be seen that there is a uniform pore size distribution and that the average pore diameter is 1.2 nm . The specific surface area calculated using the N_2 desorption branch of the MOF(Fe) sample is $1600 \pm 300 \text{ m}^2/\text{g}$, and the pore volume is $0.72 \text{ cm}^3/\text{g}$. These results indicate that the MOF(Fe) sample not only has a well-developed crystallinity but also has a high specific surface area and abundant micropores.

The TEM images of the MOF(Fe) sample are shown in Fig. 3. The samples comprise irregular particles with diameters in the range 50 – 300 nm . In addition, the lattice line width is about 2 – 3 nm , suggesting that the MOF(Fe) sample has a high crystallinity, in consistent with the XRD results.

3.1.2. FT-IR results

Figure 4 shows the FT-IR spectrum of the MOF(Fe) sample. The strong and broad peak located at 3410 cm^{-1} is assigned to

Fig. 3. TEM images of the MOF(Fe) sample.

Fig. 4. FT-IR spectrum of the MOF(Fe) sample.

the O–H vibration, indicating the presence of bound water and free water [46]. The strong peaks at 812 and 711 cm^{-1} are characteristic of a 1,3,5-tri substitution of the benzene ring [46]. The strong absorption peak near 1709 cm^{-1} can be assigned to the C=O stretching vibration in the 1,3,5-BTC. The peaks observed at 1620, 1575, 1450, and 1384 cm^{-1} have been identified as the asymmetric and symmetric vibrations of carboxyl groups, respectively. The $\Delta\nu(\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO}))$ is at 170 and 191 cm^{-1} , suggesting that the carboxyl groups of 1,3,5-BTC coordinate to the metal ion centers in a bidentate bridging mode. These results suggest that the structure of MOF(Fe) contains the basic 1,3,5-BTC skeleton and the carboxyl groups of 1,3,5-BTC are deprotonated [47]. In addition, the peak at 484 cm^{-1} is related to the Fe–O stretching vibration [48,49]. The results show that MOF structure is formed by the Fe ions and 1,3,5- H_3BTC organic ligands.

3.1.3. TG results

TG curve of the MOF(Fe) sample is shown in Fig. 5. There are three stages of mass loss occurring between room temperature and 850 °C. Based on FT-IR analysis, the first mass loss (about 7.5%) in the range of room temperature to 302 °C is attributed to the release of both bound and free water molecules from within the MOF(Fe) sample [50]. When the temperature increases from 302 to 382 °C, the 1,3,5-BTC framework of MOF(Fe) begins to collapse, and the mass loss increases rapidly. When the temperature increases to 382 °C, the framework of MOF(Fe) undergoes a total collapse. With an increase in temperature from 382 to 850 °C, MOF(Fe) completely decomposes

Fig. 5. TG curve of the MOF(Fe) sample.

into iron oxide [50,51]. The total mass loss of the whole process is about 58.7%. These results reveal that the MOF(Fe) sample has a good thermal stability below 300 °C.

3.2. The catalytic activity of MOF(Fe)

To enhance the conductivity of the MOF(Fe) sample, carbon black (Super P, SP) was mixed with MOF(Fe) during the preparation of the working electrode. The OER and ORR catalytic activities of MOF(Fe) + SP, Pt/C (20% Pt, Johnson Matthey) and SP are shown in Figs. 6 and 7, respectively. All potentials discussed here are relative to the reference electrode of Ag/AgCl. As shown in Fig. 6, SP shows a low OER catalytic activity, and its current density is only 0.025 mA/cm^2 at 0.9 V. The OER activity of MOF(Fe) + SP is significantly higher and the current density is 2.30 mA/cm^2 at 0.9 V which represents a 92-fold increase relative to that found for SP at the same potential. In addition, the catalytic activity of MOF(Fe) + SP for the OER is also much higher than that of Pt/C, because the OER current density of Pt/C is 0.955 mA/cm^2 at 0.9 V. As shown in Fig. 7, SP has a low ORR catalytic activity. Its ORR onset potential (the onset potential is defined as the potential when the current density reached $-2 \mu\text{A}/\text{cm}^2$) is -0.21 V , and its current density is only $-0.08 \text{ mA}/\text{cm}^2$ at -0.3 V . The ORR catalytic activity of MOF(Fe) + SP is significantly higher, the ORR onset potential is -0.12 V , and the

Fig. 6. The OER activities of the samples. (1) MOF(Fe) + SP; (2) Pt/C; (3) SP.

Fig. 7. The ORR activities of the samples. (1) MOF(Fe) + SP; (2) Pt/C; (3) SP.

Fig. 8. Linear sweep voltammetry curves on a rotating glassy carbon electrode coated with MOF(Fe) + SP at various rotation rates.

current density is -0.93 mA/cm^2 at -0.3 V . In addition, the ORR onset potential of Pt/C is -0.01 V , and the current density is -2.09 mA/cm^2 at -0.30 V . From the structural characterization results, the high specific surface area and microporous nature of MOF(Fe) cannot only facilitate the diffusion of oxygen, but also provide a substantial reaction interface for the oxygen evolution and oxygen reduction reactions. In addition, the abundance of unsaturated coordination metal ions in the MOF(Fe) framework can provide numerous adsorption sites and catalytic sites, which are advantageous for the OER and ORR.

The activity of the MOF(Fe) + SP catalyst in the ORR was further studied using a rotating disk electrode under various rotation rates. Linear sweep voltammetry curves on a glassy carbon electrode coated with MOF(Fe) + SP at various rotation rates are shown in Fig. 8. The current density increased with an increase in rotation rates because of increases in the rate of oxygen diffusion and its transport in the electrolyte.

The number of the electrons transferred per O_2 molecule in ORR catalyzed by MOF(Fe) + SP can be calculated from the Koutecky-Levich (K-L) equation [52, 53] as follows:

$$1/j = 1/j_k + 1/j_d + 1/j_f \quad (1)$$

The thickness of Nafion film used to bind catalysts on the electrode is sufficiently small so that the resistance of the film is negligible [54], so that Eq. (1) can be approximated as Eq. (2).

$$1/j = 1/j_k + 1/j_d \quad (2)$$

$$j_d = 0.620nFD^{2/3}C_0\nu^{-1/6}\omega^{1/2} \quad (3)$$

$$j_k = nFkC_0 \quad (4)$$

j is the current density of experimental measurement (mA/cm^2), j_k is the kinetic current density (mA/cm^2), j_d is the diffusion-limiting current density (mA/cm^2), j_f is the diffusion-limiting current density through the Nafion film, n is the number of electrons transferred per O_2 molecule, k is the rate constant of the ORR, F is the Faraday constant (96485 C/mol), ω is the angular frequency of rotation, C_0 is the concentration of oxygen in 0.1 mol/L KOH electrolyte ($1.21 \times 10^{-6} \text{ mol/cm}^3$) [55], D is the diffusion coefficient of oxygen in 0.1 mol/L KOH electrolyte ($1.73 \times 10^{-5} \text{ cm}^2/\text{s}$) [55], and ν is the kinematic vis-

Fig. 9. Koutecky-Levich plots for the MOF(Fe) + SP.

cosity of the electrolyte ($0.01 \text{ cm}^2/\text{s}$).

The K-L plots for ORR on MOF(Fe) + SP at different potentials are shown in Fig. 9. There is a near-linear relationship between $-1/j_d$ and $\omega^{-1/2}$, which is consistent with the K-L equation. The K-L curves do not pass through the origin in the range of -0.30 to -0.95 V , indicating that the ORR is a hybrid process, controlled by both diffusion and chemical kinetics in this potential range.

Usually, there are two electron transferred pathways for ORR in an alkaline electrolyte [56]:

(i) Direct four-electron pathway

(ii) Indirect two-electron pathway

or the decomposition reaction

The number of electrons transferred per O_2 molecule in the ORR was calculated by the K-L equation, and was shown in Fig. 10. The mechanism of the ORR involves a two-electron pathway in the range of -0.50 to -0.30 V , but it shifts to a four-electron pathway when the potential increases from -0.50 to -0.95 V , indicating that the ORR reaction comprises a mix-

Fig. 10. The number of electrons transferred per O_2 molecule at different potentials for MOF(Fe) + SP.

Fig. 11. The chronoamperometric responses for the ORR on samples at -0.4 V. (1) MOF(Fe) + SP; (2) Pt/C.

ture of two- and four-electron pathways in this potential range.

The ORR polarization curve under 1600 r/min was treated by the Tafel equation $\eta = a + b \lg i$ ($a = (2.3 RT / i_0) / \alpha F$; $b = -2.3 RT / \alpha F$). It is found that the curve is consistent with the Tafel equation in the range of -0.30 to -0.40 V. The kinetic parameters, obtained by the Tafel equation, were $a = 1.355$ V, $b = 137$ mV/dec and $i_0 = 1.2867 \times 10^{-10}$ A/cm².

The durability of MOF(Fe) + SP for the ORR was evaluated using a chronoamperometric method at -0.40 V in O₂-saturated KOH aqueous solution (0.1 mol/L) at a rotation rate of 1600 r/min and, for comparison, the durability of a Pt/C catalyst was also evaluated using the identical measurement system. As shown in Fig. 11, after 30000 s, the ORR current retention rate of Pt/C catalyst is 90%, while that of MOF(Fe) + SP is 81%. Although the current ORR catalytic performance of the as-prepared MOF(Fe) is lower than that of Pt/C catalyst, it is expected that more effective electrocatalysts based on MOFs can be achieved through further research.

4. Conclusions

MOF(Fe) prepared by a hydrothermal method has good crystallinity, large specific surface area and high thermal stability. It exhibits good bifunctional catalytic activity for OER and ORR in an alkaline electrolyte. The high specific surface area, abundant micropores, and numerous unsaturated metal ions in MOF(Fe) are advantageous in the OER and ORR. The reaction mechanism of the ORR changes with the applied potential: the ORR takes place by a two-electron pathway in the range of -0.30 to -0.50 V, while a four-electron pathway is exhibited when the potential increases from -0.50 to -0.95 V. The results obtained strongly suggest that such catalysts can open a new route for the development of effective, low price, and environmentally friendly bifunctional catalysts for the rechargeable lithium-air battery.

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Graphical Abstract

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Preparation of MOF(Fe) and its catalytic activity for oxygen reduction reaction in an alkaline electrolyte

Guoqiang Song, Zhiqing Wang, Liang Wang, Guoru Li, Minjian Huang, Fengxiang Yin*

Changzhou University;

Beijing University of Chemical Technology

MOF(Fe) was synthesized by a hydrothermal method and shows excellent bi-functional catalytic activity for the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in an alkaline electrolyte.

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MOF(Fe)的制备及其氧气还原催化性能宋国强^a, 王志清^a, 王 亮^c, 李国儒^c, 黄敏建^c, 银凤翔^{b,c,*}^a常州大学制药与生命科学学院, 江苏常州213164^b北京化工大学有机无机复合材料国家重点实验室, 北京100029^c北京化工大学常州先进材料研究院, 江苏常州213164

摘要: 以硝酸铁为金属离子前驱体、均苯三甲酸为有机配体, 采用水热法合成了金属有机骨架MOF(Fe)催化剂, 应用X射线衍射、N₂吸附-脱附、透射电镜、红外光谱和热重等方法对催化剂的结构进行了表征, 并采用循环伏安法测试了催化剂在碱性电解质中的氧气还原(ORR)催化性能, 同时也采用旋转圆盘电极进一步研究了催化剂的ORR的动力学行为。结果表明, 所制MOF(Fe)具有很好的晶型结构、大比表面积、丰富的微孔以及较高的热稳定性。且表现出很好的ORR催化活性。ORR的反应历程随电位的改变而改变: 电位在-0.3到0.50 V范围内, ORR为2电子途径; 随着电位从-0.50 V升至-0.95 V, ORR从2电子向4电子途径转变。另外, 该催化剂在碱性电解质中也表现出较好的氧气析出(OER)催化性能, 这为制备用于ORR和OER的高效非贵金属催化剂提供了新的途径。

关键词: 金属有机骨架; 水热法; 氧气还原反应; 氧气析出反应; 锂-空气电池

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*通讯联系人. 电话: (010)64412054; 传真: (010)64419619; 电子信箱: yinfx@mail.buct.edu.cn

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1. 前言

锂-空气电池的理论能量密度高达11140 Wh/kg, 与汽油-氧体系相当^[1-3], 是目前高性能锂离子电池的10倍多^[2-4]。另外, 它还具有体系轻、无毒无污染、价格低廉等优点, 是一种极具应用前景的二次电池。然而, 锂-空气电池充电过程发生的氧气析出反应(OER)和放电过程发生的氧气还原反应(ORR)都是慢反应, 导致较大的充放电过电压, 降低了电池的充放电效率和循环性能, 使得锂-空气电池目前难以作为二次电池应用。双功能催化剂^[5]可以加快OER和ORR的反应速率, 既能减小充电过电位、降低充电电压, 又能减小放电过电位、提高放电平台, 从而大大提高锂-空气电池的充放电效率和循环性能, 为实现可充电锂-空气电池商业化提供一条有效途径。

目前, IrO_2 被认为是最好的OER催化剂, 但Ir是非常稀有和昂贵的金属, 甚至比Pt还贵^[6,7], 难以满足商业化的要求。最近, 一些非贵金属催化剂, 如钙钛矿^[8]、镍基催化剂^[9-11]等在碱性介质中表现出较好的OER活性, 被认为是有望替代贵金属的析氧催化剂。碳负载的Pt及其合金催化剂具有最好的ORR活性, 近来人们还论证了纳米尺寸的金颗粒在碱性电解质中具有非常好的ORR活性^[12], 但是Pt和Au的价格昂贵。在非贵金属的ORR催化剂中, Fe和Co基催化剂^[13-16]在酸性介质中具有较好的ORR活性, 而Mn氧化物^[17,18]、钙钛矿^[19,20]以及尖晶石^[21,22]在碱性介质中具有较好的ORR活性, 此外, 部分Fe基催化剂在碱性电解质中也具有很好的ORR活性^[23]。不仅如此, 碳材料在ORR的催化中同样显示出了巨大的潜力^[24]。但是这些催化剂的活性都还有待于进一步提高, 以满足商业化的要求。近年来围绕研发高效双功能催化剂、降低充放电过电压做了大量的研究工作。Pt-Au/C催化剂目前被认为是所研发的双功能催化剂中性能最好的, 但是Pt, Au等贵金属价格昂贵, 不适合可充电锂-空气电池的大规模商业化应用^[25,26]。在研发的非贵金属双功能催化剂中, Fe, Co和Mn等过渡金属氧化物表现出很好的双功能催化活性, 且储量丰富、价格低廉, 但仍难以满足可充电锂-空气电池的商业化要求, 还有待于进一步提高其性能^[27-30]。

金属有机骨架(MOFs)是由金属离子与有机配体相互桥联形成的一种新型多孔材料^[31,32]。与现有多孔材料相比, MOFs具有高比表面积^[33,34], 结构和功能可调^[35]等显著优点; 它不仅可用作催化剂载体, 而且由于其结构

和功能具有可调性, 可以设计将金属离子或MOFs上的官能团直接作为催化反应的活性位, 因此, MOFs是一种非常优秀的催化材料^[36]。目前, 将MOFs材料用作电催化剂的研究刚刚起步^[37-39]。Mao等^[37]在pH为6的介质中测试了MOF Cu^{II} -bipy-btc的ORR活性, 结果表明, 该MOFs材料表现出稳定的ORR催化活性。另外, 报道了一种由吡啶功能化的石墨烯(G-dye)和卟啉铁(FeP)组装的石墨烯-金属卟啉金属有机骨架复合材料(G-dye-FeP)_n, 这种基于MOFs的复合材料在碱性介质中具有较好的ORR活性^[40]。这些初步的研究表明, MOFs具有用于电催化剂, 特别是ORR催化剂的巨大潜力。但是对MOFs材料的电化学特性, 特别是MOFs结构与ORR催化性能的关系研究不够深入, 尤其很少有将MOFs用于氧气析出反应的报道。本工作将Fe元素引入到MOF结构中, 并利用MOF特有的结构, 从而达到较好的ORR催化活性。本文以硝酸铁为金属离子前驱体, 均苯三甲酸为有机配体, 通过水热法制备了MOF(Fe), 并对样品进行了表征, 并在碱性电解质中测试了MOF(Fe)的电化学性能, 结果表明, MOF(Fe)具有很好的OER和ORR双功能催化活性, 该工作为制备用于可充电锂-空气电池的高效非贵金属双功能催化剂提供了新的途径。

2. 实验部分

2.1. 催化剂制备

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, 上海新宝精细化工厂)、1,3,5- H_3BTC (98%, 阿拉丁科技有限公司)、5 mol/L的HF(AR, 上海凌峰化学试剂有限公司)、去离子水, 以摩尔比1:0.66:2:280混合并充分搅拌后, 移入反应釜中, 密闭后置于电热鼓风烘箱中, 在150 °C保持84 h, 然后自然冷却至室温, 过滤后进行两步纯化: 首先在80 °C去离子水中煮3 h, 过滤, 洗涤; 然后在60 °C乙醇中煮1 h, 抽滤, 洗涤直至母液为无色。最后在真空干燥箱中经100 °C干燥, 得到MOF(Fe)样品。

2.2. 催化剂表征

X射线衍射(XRD)分析采用D/max 2500 PC型X射线粉末衍射仪, $\text{Cu K}\alpha$ 射线, 管电压40 kV, 管电流100 mA。傅里叶变换红外光谱(FT-IR)分析采用美国Nicolet公司的5700型傅里叶红外光谱仪, KBr压片, 扫描范围为4000–400 cm^{-1} 。 N_2 吸附-脱附等温线和孔径分布在美国Micromeritics公司的ASAP 2010C上测定, 样品比表面积用BET法计算, 孔径分布采用BJH模型根据脱附曲线计算。采用德国NETZSCH公司的TG 209 F3热重分析仪进

行样品的热重(TG)分析,在空气条件下,以10 °C/min升温研究催化剂的热稳定性.样品的透射电镜(TEM)照片在日本JEOL公司JEM-2100透射电子显微镜上获得.

2.3. 工作电极和旋转圆盘电极制备

称取4 mg的MOF(Fe)和1 mg的导电炭黑Super P(SP, Timcal),然后加入1 ml无水乙醇和50 μ l的Nafion溶液(5%, DuPont),超声30 min得到混合液,再移取50 μ l混合液滴在1 $\times$ 1 cm²碳纸(TGP-H-060, Toray)上,在80 °C干燥后,制得工作电极.

玻碳电极(直径5 mm)采用金相砂纸、粒度为0.3 μ m的Al₂O₃打磨抛光,冲洗干净并干燥后,分别移取上述混合液10 μ l滴于玻碳电极上,在80 °C干燥后制得旋转圆盘电极.

2.4. 电化学测试

OER和ORR催化活性测试都是在电化学工作站(CHI 760E, 上海辰华仪器有限公司)上进行.采用传统三电极体系:碳棒为辅助电极,Ag/AgCl电极为参比电极,电解液为0.1 mol/L的KOH水溶液.在电化学性能测试前,工作电极在N₂饱和的KOH电解质(0.1 mol/L)中,以50 mV/s的扫描速度在-1.0至0.2 V (vs. Ag/AgCl)的电压范围内,用循环伏安法扫描直至曲线稳定.然后分别在N₂和O₂饱和的电解质中,以5 mV/s的扫描速度,采用线性扫描伏安法测试样品的ORR性能. O₂饱和电解质中测得的电流与N₂饱和电解质中测得的电流之间的差值被确定为催化剂的ORR电流.旋转圆盘电极测试在上述相同体系中进行,扫描范围为-1.0–0.2 V (vs. Ag/AgCl),扫描速度为5 mV/s,旋转圆盘转速为100, 400, 900, 1600 和 2500 r/min.保持电位为-0.4 V (vs. Ag/AgCl),旋转圆盘转速为1600 r/min,在O₂饱和的KOH水溶液(0.1 mol/L)中,采用计时电流法测试催化剂的ORR活性保持率. OER活性是在N₂饱和电解质中,采用线性扫描伏安法进行测试,电压扫描范围0.2–1.0 V (vs. Ag/AgCl),扫描速度5 mV/s.

3. 结果与讨论

3.1. 催化剂表征

3.1.1. XRD, N₂吸-脱附和TEM结果

图1为MOF(Fe)催化剂的XRD谱,在3.4°, 4.0°, 4.2°, 4.8°, 5.3°, 5.9°, 6.2°, 6.8°, 10.2°, 10.4°, 10.8°, 11.0°, 12.6°, 13.7°, 14.2°, 17.9°, 18.6°, 18.9°和19.1°出现了MOF(Fe)的主要衍射峰,与文献[41]合成的MIL-100(Fe)的衍射峰的位置基本吻合,表明合成的MOF(Fe)具有很好的晶相结

构.图2为催化剂的N₂吸附-脱附等温线以及孔径分布图.由图可见,MOF(Fe)的N₂吸附-脱附等温线属于典型的I型^[42–45],表明MOF(Fe)为微孔材料.当相对压力 p/p_0 在0–0.15范围内,N₂吸附量急剧增加,这主要是由于在此相对压力范围内,N₂主要被吸附在MOF(Fe)的微孔中,MOF(Fe)丰富的微孔结构提供了众多N₂吸附位点;当相对压力 $p/p_0 \geq 0.15$ 时,随着 p/p_0 的增加,N₂吸附量缓慢上升,这是因为MOF(Fe)的微孔内部已几乎全部被N₂填充,此时N₂吸附主要发生在MOF(Fe)的外表面,而外表面较小,可提供的N₂吸附位点较少,因此对N₂吸附的增加量较小.另外,从MOF(Fe)的孔径分布图可以看出,MOF(Fe)的孔径分布基本均一,平均孔径为1.2 nm.可计算得到MOF(Fe)的比表面积为 1655 ± 300 m²/g,孔容为0.72 cm³/g.由此可见,所制MOF(Fe)不仅具有很好的晶相结构,而且具有高的比表面积以及丰富的微孔结构.

图3为MOF(Fe)催化剂的TEM照片.可以看到,MOF(Fe)的颗粒几何外形不规整,大小约为50–300 nm.还可以看到,MOF(Fe)的晶格线宽度大约在2–3 nm,表明其具有很好的晶相结构,与XRD结果一致.

3.1.2. FT-IR结果

图4为催化剂的FT-IR谱.由图可知,在3410 cm⁻¹附近出现强而宽的吸收峰,可以归属为水分子中O–H键的伸缩振动,表明MOF(Fe)结构中含有配位水或吸附水^[46].在812和711 cm⁻¹处出现的吸收峰可以归属为苯环上1,3,5-三取代的特征吸收峰^[46];在1709 cm⁻¹处的强吸收峰可以归属于1,3,5-BTC结构中的C=O的伸缩振动峰;在1620, 1575, 1450和1384 cm⁻¹处的吸收峰分别可以归属为1,3,5-BTC结构中的–CO₂不对称伸缩振动和对称伸缩振动;由 $\Delta\nu$ ($\nu_{as}(\text{COO}) - \nu_s(\text{COO})$)为170和191 cm⁻¹,可知每个1,3,5-BTC的羧酸基团以双齿配位的.可见,MOF(Fe)结构中含有1,3,5-BTC的基本骨架,并且1,3,5-H₃BTC配体中的羧基均已去质子化^[47].另外,在484 cm⁻¹处的吸收峰可以归属为Fe–O键拉伸振动^[48,49].上述结果表明,Fe离子和有机配体1,3,5-H₃BTC形成了金属有机骨架结构.

3.1.3. TG结果

图5为催化剂的TG曲线.由图可见,MOF(Fe)在室温至850 °C范围内出现三次失重:室温至302 °C时,MOF(Fe)失重了7.5%,结合FT-IR结果可知,该阶段的失重可归结为MOF(Fe)中的吸附水和配位水脱附^[50];当温度从302升至382 °C时,MOF(Fe)的骨架1,3,5-BTC开始分解,晶格结构开始坍塌,失重量急剧增加;至382 °C

时, MOF(Fe)骨架彻底坍塌; 从382 °C升到850 °C过程中, MOF(Fe)彻底分解为铁的氧化物^[50,51], 整个过程总重量损失为58.7%。可以看出, 所制MOF(Fe)在300 °C以下具有很好的热稳定性。

3.2. MOF(Fe)催化性能

为了增强MOF(Fe)的导电性, 在制备工作电极的时候, 采用导电炭黑Super P(SP)与MOF(Fe)混合来增加导电性。图6和图7分别是MOF(Fe)+SP, Pt/C(20%Pt, Johnson Matthey)和SP的OER和ORR催化活性结果。本文中, 除有特别说明外, 所讨论的电位是指相对于参比电极Ag/AgCl的电位。由图6可知, SP具有很低的OER催化活性, 当电位为0.9 V时电流密度仅为0.025 mA/cm²; 而MOF(Fe)+SP的OER催化活性显著提高, 当电位为0.9 V时电流密度高达2.30 mA/cm², 是SP在该电位下电流密度的92倍。另外, MOF(Fe)+SP的OER活性明显高于Pt/C, 因为在电位为0.9 V时, Pt/C的OER电流密度为0.955 mA/cm²。由图7可见, SP的ORR催化活性也很低, 它的起始电位(电流密度达到-2 μA/cm²时的电位)为-0.21 V, 在-0.3 V时电流密度仅为-0.08 mA/cm²。而MOF(Fe)+SP的起始电位为-0.12 V, 在-0.3 V时电流密度为-0.93 mA/cm²。Pt/C的起始电位为-0.01 V, 在-0.3 V时电流密度为-2.09 mA/cm²。这些结果表明, 所制MOF(Fe)在碱性电解质中表现出较好的OER和ORR双功能催化活性。由前文可知, MOF(Fe)具有很高的比表面积和丰富的微孔结构, 不仅有利于氧气的扩散和传输, 而且可以为氧析出和氧还原反应提供更大的反应界面; 另外由于MOF(Fe)骨架中的丰富不饱和和配位的金属离子可以提供众多的反应物吸附位点和催化活性位, 进而加速OER和ORR反应。

为了进一步研究MOF(Fe)催化剂的ORR反应的动力学行为, 进行了不同转速下的旋转圆盘电极测试。图8为MOF(Fe)催化剂在旋转圆盘电极不同转速下的线性扫描伏安曲线。由图可知, 随着转速的增大, 电流密度增大。这是由于当旋转圆盘的转速增大时, 有利于氧气在电解液中的扩散和传输。

通过 Koutecky-Levich (K-L) 方程^[52,53]可以对MOF(Fe)催化的ORR反应的电子转移数进行计算, 计算方程式如下:

$$1/j = 1/j_k + 1/j_d + 1/j_r \quad (1)$$

由于电极中粘合催化剂的Nafion膜厚度很小, 以至于它的阻抗可忽略不计^[54], 所以(1)式可以近似为(2)式。

$$1/j = 1/j_k + 1/j_d \quad (2)$$

$$j_d = 0.620nFD^{2/3}C_0\nu^{-1/6}\omega^{1/2} \quad (3)$$

$$j_k = nFkC_0 \quad (4)$$

j 是实验测量的电流密度(mA/cm²), j_k 和 j_d 分别是动力学电流密度(mA/cm²)和扩散极限电流密度(mA/cm²), j_r 是通过Nafion膜的扩散限制电流密度(mA/cm²), n 是每个O₂分子转移的电子数, k 是ORR的速率常数, F 是法拉第常数(96485 C/mol), ω 是旋转圆盘电极的角速率, C_0 是KOH电解液(0.1 mol/L)中的O₂浓度(1.21×10⁻⁶ mol/cm³)^[55], D 是O₂在KOH溶液(0.1 mol/L)中的扩散系数(1.73×10⁻⁵ cm²/s)^[52], ν 是电解液的黏滞阻力系数(0.01 cm²/s)。

图9为MOF(Fe)+SP在不同电位下催化ORR反应的K-L图。可以看出, $-1/j_d$ 对 $\omega^{-1/2}$ 呈良好的线性关系, 且截距不为零, 符合K-L关系式。当电位在-0.30到-0.95 V的范围时, K-L曲线的截距均大于0, 表明电位在此范围内, 反应受扩散和动力学混合控制。

通常, 在碱性电解液中ORR反应有两种电子转移的途径^[56]:

(i)直接四电子途径

(ii)间接二电子途径

$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ 或者伴随进一步的还原反应

或者发生分解反应

从K-L方程计算的ORR反应中每个O₂分子转移的电子数如图10所示, 电位在-0.50到-0.30 V范围内, ORR反应基本为2电子途径; 随着电位从-0.50 V增加到-0.95 V, ORR反应从2电子途径向4电子途径转变, 因此, 该范围内ORR反应是2电子和4电子混合途径。采用Tafel方程 $\eta = a + b \lg i$ ($a = (2.3RT \lg i_0)/\alpha F$; $b = -2.3RT/\alpha F$)对1600 r/min下ORR极化曲线进行了处理, 发现在-0.3到-0.4 V范围内符合Tafel关系, 并对动力学参数进行了计算, 得到 $a = 1.355$ V, $b = 137$ mV/dec, $i_0 = 1.2867 \times 10^{-10}$ A/cm²。

保持旋转圆盘电极转速为1600 r/min, 电位为-0.4 V, 在0.1 mol/L KOH溶液中, 采用计时电流法研究了MOF(Fe)+SP的ORR活性保持率, 为了比较, 也测试了商业Pt/C催化剂的ORR活性保持率, 结果如图11所示。可以看到, 经过30000 s的稳定性测试后, 商业Pt/C催化剂的ORR电流保持率为90%, 而MOF(Fe)+SP的ORR电流保持率为81%。尽管所制MOF(Fe)的ORR催化性能还

低于商业Pt/C, 但是通过深入系统的研究, 有望制备出高效的基于MOFs的电化学催化剂.

4. 结论

采用水热合成法制备了的MOF(Fe)样品具有很好的晶相结构、高的比表面积和很好的热稳定性且在碱性电解质中表现出很好的OER和ORR双功能催化活性, 这

可归因于其高比表面积、丰富的微孔、众多的不饱和金属离子催化活性位. 结果表明ORR的反应历程随电位的改变而改变: 电位为 -0.30 到 -0.50 V范围内, ORR反应为2电子途径; 随着电位从 -0.50 V增加到 -0.95 V, ORR反应从2电子途径向4电子途径转变. 本文为研发用于可充电锂-空气电池的高性能、价廉和环境友好的双功能非贵金属催化剂开辟了新的途径.