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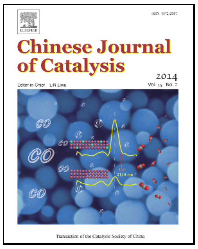

Article

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

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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, N_2 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.

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

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the rechargeable lithium-air battery.

At present, IrO_2 is considered to 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 $(G\text{-dye-FeP})_n$ 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, MOF(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 MOF(Fe) was characterized and the electrochemical performances of MOF(Fe) were investigated in an alkaline electrolyte. The results show that the MOF(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 MOF(Fe)

MOF(Fe) was prepared by a hydrothermal process. $Fe(NO_3)_3\cdot 9H_2O$ (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 $1.0(Fe^{3+}) : 0.66(1,3,5\text{-BTC}) : 2.0(HF) : 280(H_2O)$. The resulting mixture was loaded in a Teflon-lined stainless steel autoclave, which was then sealed and placed in an oven at 150 °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 °C for 3 h, followed by filtration and washing and was then treated with hot ethanol at 60 °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 MOF(Fe)) was dried at 100 °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 Cu K_α radiation operated at 40 kV and 100 mA. Fourier transform infrared (FT-IR) spectra of the MOF(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 °C/min from room temperature to 850 °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