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Bimetallic Fe-Co promoting one-step growth of hierarchical nitrogen-doped carbon nanotubes/nanofibers for highly efficient oxygen reduction reaction

Qin Liu [a], Shubo Cao [a], Yejun Qiu [a,*], Lei Zhao [b,*]

[a] Shenzhen Engineering Lab of Flexible Transparent Conductive Films, Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, University Town, Shenzhen 518055, China
[b] Tianjin Academy of Environmental Sciences, 17 Fukang Road, Nankai District, Tianjin 300191, China

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ABSTRACT

Polyacrylonitrile (PAN)-based nitrogen-doped carbon nanotubes/nanofibers (NCNTs/NFs) are successfully synthesized by one step using electrospinning technique in combination with impregnation of FeCo-containing solutions and subsequent heat treatment process. Interestingly, individual Fe or Co nanoparticles promotes to create many big pores on the fiber surface, while bimetallic Fe-Co ones promote the growth of carbon nanotubes from the PAN-converted carbon sources to form NCNTs/NFs, during high temperature treatment in NH_3 atmosphere. Especially, the nanotubes have relatively higher density when adopting the Fe/Co ratio was 1:1. The formed FeCo-containing NCNT/NF (FeCo-NCNT/NF) materials using Fe/Co ratio of 1:1 reveals a comparable catalytic activity but a much higher stability in comparison to commercial 20% Pt/C catalyst, and after 12 h, its activity still remains about 94%. The excellent ORR properties maybe due to the high crystallinity of carbon to resist electrochemical oxidation. This kind of bimetallic FeCo-NCNT/NF materials is of great potential in fuel cells.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is considered as a promising alternative energy device due to its low operational temperature and high theoretical efficiency [1–4]. In a PEMFC system, the electrocatalysts that promote oxygen reduction reaction (ORR) on the cathode are a key factor to affect the whole performance of a cell. Currently, the most efficient and commercially used ORR catalysts are Pt and Pt-based materials because no other materials could possess extremely excellent ORR activity in the practical application of PEMFCs [5]. However, apart from high price and limited resources, Pt-based materials also have a serious drawback of CO or methanol poison which leads to the significant decrease of the whole cell performance [6]. Therefore, it is important to develop alternative cheap catalysts with attractive performance. Among them, nonprecious metal (NPM) or even metal-free catalysts have aroused great interest due to the excellent activity and stability during ORR. Particularly, nitrogen-doped carbon nanomaterials (NCNMs), such as nanotubes [7,8], graphene [9], and mesoporous carbon [6,10–12], have become hot catalyst materials due to excellent electrocatalytic activity, long-term operation stability, and tolerance to crossover effect for ORR since the report of Dai's group in 2009 [13]. However, most of them exhibited much lower electrocatalytic activities than commercial Pt-based catalysts in acid solutions, which greatly restrict their widespread application in PEMFCs.

Recently, transition metal-nitrogen-carbon complexes (M-N/C, M=Fe, Co, Ni, etc.) have been widely researched as a kind of promising NPM catalyst with prominent activity and stability during ORR in acid electrolytes [14–20]. In fact, since the discovery of cobalt phthalocyanine in 1964 [21], these metal macrocyclic molecules catalysts (such as porphyrins and phthalocyanines) were investigated as ORR electrocatalysts, while they still possessed stability problems in acid media leading to the rapid loss of catalytic activity. Then, the researchers found that heat treatment at high temperature (above 600 °C) had great effect on improving catalyst stability because the catalyst structure was modified by the pyrolysis process [22], and this discovery confirmed that the structure of metal macrocyclic molecules was unnecessary [23]. Moreover, these metal macrocycles were also expensive. Thereafter, numerous M-N/C catalysts were synthesized by adopting a variety of precursors containing carbon, nitrogen and transition metals [24,25]. Herein, several different methods have been explored to improve the activity and stability of M-N/C catalysts, such as synthesis con-

* Corresponding authors.
E-mail addresses: yejunqiu@hitsz.edu.cn, qiuyejun2016@aliyun.com (Y. Qiu), zhaoeca@126.com (L. Zhao).

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ditions, heat-treatment strategies, alternative carbon supports and transition metal complexes [26,27].

In our previous study, nitrogen-doped carbon nanofibers (NCNFs) [28] deriving from electrospinning were investigated as the electrocatalysts for ORR, and they exhibited excellent activity and stability in KOH solution, but their performance in acid was poor. Carbon nanofibers had been widely considered as a very good candidate for novel catalyst support because of the one-dimensional nanostructure with high specific surface area [29]. So we tried to adopt CNFs to produce novel M-N/C electrocatalysts, and Fe-N/C nanofibers (Fe-N/CNFs) were synthesized [14], which possessed much better stability especially in 0.5 M H_2SO_4 solution than that without Fe, but the activity needed further improvement. If the composition of M in the M-N/C catalysts changed from single transition metal to bimetals or even trimetals, their performance may be greatly improved due to the possible synergistic effect between metals. To the best of our knowledge, no attempt has been made to produce bimetal-N/C catalysts based on carbon nanofibers by electrospinning.

In this paper, we introduced Fe and Co bimetals into the NCNF electrocatalysts and found the growth of plenty of CNTs on the fiber surface to form hierarchical nitrogen-doped carbon nanotubes/nanofibers (NCNTs/NFs), which are often fabricated on the basis of secondary growth mechanism using chemical vapor deposition (CVD) method [30], while we realized this hierarchical carbon structure from only PAN by one step without CVD process and gas carbon sources. And the electrocatalytic performance of the NCNTs/NFs containing Fe and Co bimetals (FeCo-NCNTs/NFs) during ORR was well investigated in acid electrolyte.

2. Experimental details

2.1. Preparation of FeCo-NCNT/NF electrocatalysts

The electrospinning solution with concentrations of 6% (*wt./v*) was prepared by dissolving PAN (Aldrich, M_w = 150000) powder in N,N-dimethylformamide (DMF) and stirring for 24 h at ambient temperature to form a homogeneous solution. Then the precursor PAN solution was electrospun into nanofibers through a conventional electrospinning setup with a high voltage power supply (0–50 kV, DW-P503-2ACCD, Dongwen High Voltage Power Supply Company, China) and a hypodermic syringe with a needle. The PAN nanofibers were produced at a voltage of 20 kV and the distance was 18 cm between the needle and the graphitic papers which were used to collect the nanofibers. After electrospinning, the obtained PAN NFs were stabilized at 230 °C in air for 2 h. Subsequently, the stabilized NFs were impregnated with the mixed solution with $Fe(NO_3)_3$ and $Co(NO_3)_2$, and then dried at 70 °C for 2 h. The metal loading (W_g) of the mixed $Fe(NO_3)_3$ and $Co(NO_3)_2$ was calculated by $wt._{Fe/Co}/(wt._{Fe/Co} + wt._{NFs})$, and different Fe/Co ratios (wt_{Fe}:wt_{Co} = 1:1, 1:3, and 3:1) were utilized. At last, the impregnated nanofibers were carbonized at 1000 °C for 1 h in NH_3 atmosphere and the bimetal FeCo-NCNT/NF catalysts were acquired. Briefly, the preparation steps can be summarized as electrospinning, stabilization, impregnation, and carbonization. For comparison, the stabilized PAN nanofibers without any impregnation and with impregnation of $Fe(NO_3)_3$ solution or $Co(NO_3)_2$ solution, were carbonized under same conditions to prepare the samples of NCNFs, Fe-NCNFs and Co-NCNFs, respectively.

2.2. Characterization and electrochemical test

The morphology and structure of FeCo-NCNT/NF samples were observed by scanning electron microscopy (SEM, HITACHI S-4700), transmission electron microscopy (TEM, Philips Tecnai G2 F30). The phase, crystallinity, and chemical state of the samples were analyzed by X-ray diffraction (XRD, RigakuD/Max 2500/PC), Raman spectroscopy (Renishaw RM-1000), and X-ray photoelectron spectroscope (XPS, ESCALAB 250, VG Scientific Co. Ltd., UK).

The electrochemical measurements of the FeCo-NCNTs/NFs were performed by using an electrochemical workstation (CHI760C, Shanghai Chenhua Instrument Co., Ltd., China). Cyclic voltammogram (CV) and rotating-disk electrode (RDE) polarization curves were carried out at room temperature in a typical three-electrode electrochemical system, with Ag/AgCl (sat.) (CHI111) reference electrode, a platinum wire (CHI115) as the counter electrode, and a glassy carbon (GC) electrode (3 mm in diameter, 0.0707 cm^2, CHI104) and GC disk (3.5 mm in diameter, 0.0962 cm^2, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd.) were employed as the working electrodes for CV and RDE tests, respectively. Additionally, the GC electrodes were carefully polished to mirror with gamma alumina powders (0.05 μm), thoroughly washed in distilled water and then dried. Before CV and RDE test, the catalyst inks were prepared by dispersing 3 mg catalyst in 1mL ethanol and ultrasonic processing for 1 h to gain homogeneous dispersed sample. The electrochemical measurement mainly included the next steps. 5 μL catalyst ink and 5 μL Nafion solution (DuPont) were successively dropped onto the GC electrode surface and dried in air. The CV curves were recorded in the potential range from −0.2 to 1 V in 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}, and RDE curves were also recorded in the same potential range at the same scan rate and different rotation rates from 400 to 2500 rpm. Before the CV and RDE measurements, O_2 gas was directly bubbled into the solutions for 15 min to obtain O_2-saturated solutions. The current–time (j–t) curves were measured at +0.2 V in 0.5 M H_2SO_4 solution for 12 h under continuous O_2 bubbling with a flow of 40 mLmin^{-1} at the rotation rate of 1600 rpm. In the above test, 20% Pt/C (beijing HongHaiTian Science and Technology Co.,Ltd) catalyst were used in similar conditions for comparison. In this paper, all current densities were normalized in reference to the geometric area of the corresponding GC electrode.

3. Results and discussion

Fig. 1 exhibits the SEM images of the FeCo-NCNT/NF catalyst samples with a metal loading of 2% and different Fe/Co ratios. It can be seen from Fig. 1a the fibers in NCNFs without impregnation process are uniform, smooth and continuous, and their average diameter is about 100 nm. When introducing metals into the NCNFs, the morphology would change greatly. Compared with the pristine NCNFs, the single metal of Fe or Co modified NCNFs present serious fracture structures (Fig. 1b and c) caused by corrosion cracking, meanwhile there exists a certain amount of pores on the fiber surface, especially for Fe-NCNFs. The reason of the above phenomenon lies in the etching roles of NH_3 enhanced by metal Fe and Co particles, which would promote to preferentially etch off the carbon species at the junction of carbon nanofibers and metal nanoparticles [31,32]. For the NCNTs/NFs modified by Fe-Co bimetals, some metal nanoparticles and gown CNTs can be observed on the fiber surface (Fig. 1d–f), thus forming a hierarchical structure simultaneously containing carbon nanotubes and nanofibers. In previous studies [14,33], we demonstrated that NH_3 had etching effect on CNFs at high temperature and metal could enhance this role. So the Fe-Co bimetals probably greatly speed up the etching rate of NH_3. Additionally, they could promote the crystallization of the graphitic structure. Chen et al. have demonstrated that trace Fe^{3+} and Co^{2+} can synergistically catalyze the growth of the carbon nanotubes when melamine serves as the CNT precursor [34]. Here, the etched carbon atoms were used as precursor for growing of