Cobalt and Nitrogen Co-Doped Electrospun Carbon Nanofibers as a Bifunctional Oxygen Electrocatalyst

T J Li and H G Wang*

School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China

*E-mail: wanghengguo@cust.edu.cn (H. g. Wang)

Abstract. Nowadays, it is urgent to prepare a bifunctional electrocatalyst with effectively improve catalytic properties towards ORR and OER, replacing precious metals and commercial catalysts. Cobalt nitrogen co-doped carbon nanofibers (Co-N/CNFs) are successfully synthesized via solvothermal, pyrolysis of electrospun nanofibers containing cobalt phthalocyanine and melamine. The electrochemical characterization of Co-N/CNFs-800 is carried out using cyclic voltammetry, and Tafel studies compared with Pt/C and RuO₂. The Co-N/CNFs-800 exhibits the higher ORR catalytic activity with half-wave potential (0.77 V) and the lower OER overpotential (370 mV). Furthermore, the activity parameter of Co-N/CNFs-800 (0.83 V) is much lower than that of Pt/C (0.95 V), and closer to RuO₂ (0.82 V). This research opens an effective method to synthesize an excellent bifunctional electrocatalyst for ORR/OER.

1. Introduction

Rechargeable metal-air batteries have obtained great progress owing to its high efficient, cleanness and environment-friendly [1-3]. In this energy system, oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) play prominently important roles. Till now, Pt/C and IrO₂/RuO₂ have been used as the standard catalysts to overcome high activation overpotential and sluggish kinetics during ORR and OER process. While their large-scale application is impeded owing to high cost, poor durability and scarcity [4-6]. Therefore, it is urgent to explore nonprecious bifunctional ORR/OER catalysts [7-8].

As we all known, phthalocyanines are consisted of a central transition metal atom bound to a π-conjugated ligand, characterized by high conjugate structure and chemical stability. However, no matter from the stability of the catalyst qualitative or active, the electrocatalytic performance of these transition metal macrocyclic compounds still be poor than precious metal [9]. Recently, catalysts of transition metal phthalocyanine mixed with different types of nanomaterials are considered to be the most potential catalysts for electrocatalytic reactions.

Electrospinning is a facile efficient technique to obtain polymer nanofibers. Most importantly, these nanofibers could provide more active sites by introducing various metals on the surface of the nanofibers [10]. Furthermore, high temperature carbonizes combing with chemical modifications, such as doping of heteratoms (such as N, P, S, and so on) under nitrogen atmosphere could offer more exposed active sites and effectively improve catalytic performance [11].

In this report, we report a method of synthesized carbon nanofibers (CNFs), modified with cobalt and nitrogen (Co-N/CNFs-800) via electrospinning, solvothermal and annealing process. Introduction of cobalt and nitrogen into CNFs, enlarge the effective surface area and provide more active sites.
Benefiting from unique design, the obtained Co-N/CNFs-800 exhibit excellent catalytic performance for both OER and ORR.

2. Experiment

2.1. Electrocatalyst Synthesis:
PAN (1 g) was dissolved in DMF (10 mL). The above mixture solution with stirring for 12 h obtained the spinning precursor. This precursor solution was added into a syringe with a 16-gauge needle for electrospinning, the operating voltage of 15 KV maintained during the whole electrospinning process. The obtained electrospun films were stripped off from the collector covered by aluminum foil after 12 h. After that, the films were immersed into the uniformly mixed solution, which consisted of absolute ethanol (25 mL), 4-Nitroptalonitrile (0.2 g), Co(Ac)2•6H2O (0.1 g) and ammonium molybdate (15 mg). The above solution was transferred into 50 mL autoclave and treated at 190 °C for 3 h. Then, the dried nanofiber films loaded with cobalt phthalocyanine were carbonized with melamine (0.5 g) under N2 atmosphere at 800 °C for 2 h with a heating rate of 2 ºC/min, which was denoted as Co-N/CNFs-800.

2.2. Electrochemical characterizations:
The electrochemical performance tests were using three-electrode cell system in the KOH solution. The cell system consists of a counter electrode (carbon rod) and a reference electrode (Hg/HgO), respectively, a rotating disk electrode (RDE, Pine Research Instrument, USA) with 5.0 mm in diameter was used as the working electrode. The well-dispersed catalysts solution (10 μL) was dripped onto the surface of the RDE, which included the catalysts (5 mg), ethanol (1 mL) and Nafion solution (50 μL). Subsequently, the mixture was dried at room temperature for 30 min. The ORR tests were measured in O2-saturated 0.1 M KOH solution at room temperature, the LSV curves were obtained under different rotating speeds between 400 and 1600 rpm from 1.0 to 0.2 V at the scan rate of 10 mV /s. The LSV curves of OER were tested in alkaline solution 1 M KOH ranging from 1.0 to 0.2 V. For OER measurements, the LSV curves were obtained at scan rate of 10 mV /s in O2-saturated 1 M KOH solution.

3. Results and discussion

We can obtain the morphologies and size of the Co-N/CNFs-800 (Figure 1a) according to the scanning electron microscopy (SEM). The Co-N/CNFs-800 shows the clear cracked nanofibers with the diameter of ca.500 nm. A magnified SEM image (Figure 1b) displays that the surface of the nanofibers is not smooth, and some particles are shown to cover on the surface of the nanofibers.

Figure 1. SEM images of Co-N/CNFs-800. (a) Low and (b) high-resolution SEM images.

The phase compositions of the Co-N/CNFs-800 are confirmed by XRD pattern (Figure 2). The three specific diffraction peaks at 44.3 °, 51.5 ° and 76.1 ° could be attributed to the (111), (200)and
(220) crystal planes of Co (JCPDS 15-0806). Thus, this indicates that cobalt is successfully deposited into the Co-N/CNFs-800.

![XRD pattern of Co-N/CNFs-800](image)

**Figure 2.** XRD pattern of Co-N/CNFs-800.

**Figure 3a** shows that CV curve of Co-N/CNFs-800 in O_2-saturated 0.1 M KOH solution. It can be found that the numerical value of the cathodic peak potential is 0.73 V, suggesting its effective ORR activity. Furthermore, the measurements of the LSV curves are obtained at the rotating speeds 400 to 1600 rpm (**Figure 3b**). Obviously, due to the shortened diffusion distance at higher rotation speeds, the limited current density increases with the increasing rotating speed.

![CV curve and LSV curves](image)

**Figure 3.** (a) CV curve of Co-N/CNFs-800. (b) LSV curves of Co-N/CNFs-800 for ORR at different rotating speeds.

The ORR performances of Co-N/CNFs-800 and Pt/C are assessed in O_2-saturated 0.1 M KOH solution. By comparison, at the same rotating speed of 1600 rpm, the Co-N/CNFs-800 LSV curve
exhibits the onset potential of 0.86 V, half-wave potential of 0.78 V, and the limited current density of -3.42 mA cm$^{-2}$; and for the Pt/C, the LSV curve shows the onset potential of 1.01 V, half-wave potential of 0.83 V, and the limited current density of -5.28 mA cm$^{-2}$ (Figure 4a). Furthermore, the Tafel plots of Co-N/CNFs-800 exhibits good ORR performance as for the smaller Tafel slope of 65.1 mV dec$^{-1}$, less than the Pt/C of 67.8 mV dec$^{-1}$ (Figure 4b), demonstrating the faster kinetic process of Co-N/CNFs-800 catalyst for ORR [12].

Figure 4. ORR performances of Co-N/CNFs-800 and Pt/C. (a) LSV curves and (b) Tafel plots of the samples.

Figure 5a exhibits the Co-N/CNFs-800 and RuO$_2$ performances for OER. The LSV curve of Co-N/CNFs-800 displays a potential of 1.6 V at a current density of 10 mA cm$^{-2}$ and the overpotential of 370 mV, which is close to that of the RuO$_2$ (1.54 V, 310 mV). In addion, as for the OER Tafel plots, the slope of Co-N/CNFs-800 (91.1 mV dec$^{-1}$) is a little bit higher than that of RuO$_2$ (77.5 mV dec$^{-1}$) (Figure 5b), manifesting the fast-kinetic process of Co-N/CNFs-800 catalyst for OER.

Figure 5. OER performances of Co-N/CNFs-800 and RuO$_2$. (a) LSV curves and (b) Tafel plots of the samples.

Furthermore, the potential difference of Co-N/CNFs-800 ($\Delta E$= 0.83 V) is calculated by the half-wave potential ($E_{1/2}$) for ORR, and potential at 10 mA cm$^{-2}$ ($E_{10}$) for OER ($\Delta E = E_{10} - E_{1/2}$) (Figure 6).
Obviously, the potential difference of Co-N/CNFs-800 is smaller than Pt/C (0.95 V), and a little higher than RuO₂ (0.82 V), demonstrating the Co-N/CNFs-800 possess good bifunctional activity towards ORR/OER, which can be used in practical application for rechargeable Zn-air batteries.

Figure 6. Combined ORR/OER LSV curves of Co-N/CNFs-800, RuO₂ and Pt/C

4. Conclusions

Co-N co-doped carbon nanofibers are successfully synthesized via a simple electrospinning method, solvothermal and pyrolysis procedure. Owing to these effective modification methods and the unique structure, the obtained novel electrocatalyst (Co-N/CNFs-800) shows the faster kinetic process and better electrocatalytic performances for ORR and OER in alkaline condition compared to the commercial catalysts. Therefore, our work could provide an effective method for synthesizing bifunctional catalysts, which can be utilized for rechargeable Zn-air batteries and even wider practical applications prospect.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China(Grant No. 21965025), and the Education Department of Jilin Province (JJKH20190584KJ).

References

[1] Ahn S and Manthirama A 2019 J. Mater. Chem. A 7 8641-52
[2] Shao Q, Liu J, Wu Q, Li Q, Wang H, Li Y and Duan Q 2019 Nano-Micro Lett. 11 4-17
[3] Meng F, Zhong H, Bao D, Yan J, Zhang X 2016 J Am Chem Soc. 138 10226-31
[4] Li Q, Shao Q, Wu Q, Duan Q, Li Y H, Wang H G 2018 Catal Sci Technol. 8 3572
[5] Cheng Y, Wang Y, Wang Q, Liao Z, Zhang N, Guo Y and Xiang Z 2019 J. Mater. Chem. A 7 9831-6
[6] Shao Q, Liu J, Wu Q, Li Q, Wang H, Li Y and Duan Q 2019 Nano-Micro Lett. 11 1-14
[7] Shao Q, Li Y, Cui X, Li T, Wang H, Li Y, Duan Q and Si Z 2020 ACS Sustainable Chem. Eng. 8 6422-32
[8] Liu X, Park M, Kim M G, Gupta S, Wu G 2015 Cho J Angew Chem Int Ed. 54 9654-8
[9] Guo K, Xi B, Wei R, Li H, Feng J and Xiong S 2020 Adv. Energy Mater. 10 1902913-21
[10] Qiu Y, Yin J, Hou H, Yu J, Zuo X 2013 Electrochim Acta. 96 225-9
[11] Hou Y, Cui S M, Wen Z H, Guo X R, Feng X L 2015 Chen J H. Small. 11 5940-8
[12] Gonzalez-Huerta R, Ramos-Sanchez G and Balbuena P 2014 J. Power Sources. 268 69-76