INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–8

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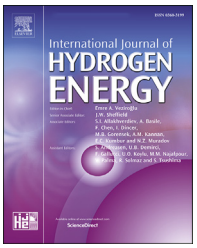

Fe, N codoped porous carbon nanosheets for efficient oxygen reduction reaction in alkaline and acidic media

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ARTICLE INFO

Article history:
Received 20 March 2018
Received in revised form
15 May 2018
Accepted 23 May 2018
Available online xxx

Keywords:
Electrospinning
Doped
Porous carbon nanosheets
Oxygen reduction reaction

ABSTRACT

Electrospinning typically employed to fabricate nanofibers was first used to prepare Fe and N doped porous carbon nanosheets (Fe–N/CNs) as oxygen reduction reaction (ORR) electrocatalysts. Polyacrylonitrile nanofibers containing a small amount of ferrocenes (Fer-PAN) were produced by electrospinning. When Fer-PAN was preoxidized at 300 °C in the air (Fer-PAN-300), nanosheets were formed and occupied the interspace between nanofibers. Fe–N/CNs was finally obtained using carbonized Fer-PAN-300 at 900 °C in N_2. The Fe–N/CNs incorporated the advantages of carbon nanofiber webs and porous nanocarbon materials, inclusive of comparatively high conductivity and large specific surface area. In both alkaline and acidic electrolyte, the Fe–N/CNs took on similar even better ORR catalytic activity than other catalysts reported elsewhere, and better stability than those of commercial Pt/C.

Introduction

The global energy crisis and environmental issues pose major threat to the human community [1–5]. Developing new energy technologies is the primary path to solve the above noted issues. Fuel cells and metal-air batteries are reliable, efficient and low-polluting new energy technology [6–10]. The cathode reaction of fuel cells and metal-air batteries is ORR (short for oxygen reduction reaction), and an effective electrocatalyst is critical for the sluggish kinetics of ORR [11–15]. Carbon supported platinum nanoparticles (Pt/C) is now the commercial electrocatalysts for ORR, whereas the large-scale applications of the fuel cells and metal-air batteries are limited by electrocatalysts, which is attributed to the high cost and poor long term stability of Pt/C. Accordingly, the non-platinum electrocatalysts had become a study focus in recent years, involving heteroatom-doped carbon materials, transition metal compounds, macrocyclic transition metal complexes, etc. [16–18].

Particularly, heteroatom-doped carbon materials were highly expected by virtue of their low cost, high

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https://doi.org/10.1016/j.ijhydene.2018.05.140
0360-3199/

electrocatalytic activity and stability. Among them, transition metal and nitrogen co-doped carbon materials (M-N/C) were a type of promising non-platinum catalysts with high performance. Especially, in virtue of abundant raw materials and superior catalyst activity for ORR, the Fe/N dual-doped carbon materials have been favored by the researchers. But the role of Fe was not yet very clear. At present, considerable evidences supported that Fe-N_x moieties were the catalytic active sites for ORR. For instance, Kramm et al. [19] demonstrated that Fe–N_4 and Fe–N_2 moieties were active sites by Mössbauer spectroscopy. Electrocatalysts containing Fe-N_x and Fe–Fe_3C@C were prepared by Joo et al. [20]. The study showed that Fe-N_x was the major active site catalyzing the ORR via 4e-process. Besides, heterometalloporphyrinic porous carbons were obtained by heat treating metal-organic frameworks (MOFs) from alternating monomeric iron and cobalt metalloporphyrins, as Bu et al. [21] reported. Because the M-N moieties have been retained during carbonization, the new carbon materials exhibited Pt-like electrocatalytic activity for ORR under alkaline and acidic conditions.

As we know, electrospinning provided a simple and cost-effective approach to fabricate carbon nanomaterial as ORR electrocatalysts [22]. Among these electrocatalysts, metal and nitrogen-doped carbon nanofibers (M-N/CNFs) was most commonly reported and has excellent ORR catalytic activity [23,24]. In this work, electrospinning was first used to prepare Fe and N doped porous carbon nanosheets (Fe–N/CNs) as ORR electrocatalysts, the process as presented in Fig. 1. Polyacrylonitrile (PAN) nanofibers containing a small number of ferrocenes (Fer-PAN) were produced by electrospinning. Then Fer-PAN were preoxidized at 300 °C in the air, denoted as Fer-PAN-300. During this process, the viscosity and liquidity of PAN rose up with the increment of temperature [25]. 3D network structure of nanofibers began to disappear, and nanosheets were formed and occupied the interspace between nanofibers under the effect of those factors and the sublimation of ferrocene. Meanwhile, a large amount of pores appeared on nanofibers and nanosheets. Fe–N/CNs was finally obtained by carbonized Fer-PAN-300 at 900 °C in N_2. Fe–N/CNs had larger surface area than common M-N/CNFs, which was an advantage of the Fe–N/CNs as electrocatalysts [26–28]. Satisfactorily, Fe–N/CNs took on Pt-like catalytic activity under alkaline and acidic conditions, which was attributed to Fe, N doped and the porous structure of Fe–N/CNs that provided transport channels for reactants and products.

Experimental

Material

Polyacrylonitrile (PAN, MW = 85,000 g/mol), Ferrocenes, *N*,*N*-dimethyl formamide (DMF), Perchloric acid ($HClO_4$), Potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co.,Ltd, China. The above reagents were used without further purification.

Catalyst synthesis

The Fe–N/CNs was synthesized by electrospinning method and subsequent pyrolysis. PAN was used as polymer, carbon and nitrogen sources, and ferrocene ($Fe(C_5H_5)_2$) was used as iron precursor. To prepare the precursor solution, 1 g PAN was dissolved in 10 ml DMF and stirred at room temperature for 4 h. After PAN was completely dissolved, 0.1 wt% ferrocene was added into the prepared solution. The mixed solution was stirred sequentially to form no bubbles and homogeneous solution and then electrospun by a conventional electrospinning setup at room temperature. During electrospinning, graphitic papers were used as collection substrates for nanofibers. The solution was supplied at a flow rate of 1 $ml \cdot h^{-1}$. The distance between the needle and collection substrate was maintained at 18 cm, and the voltage was 18 kV.

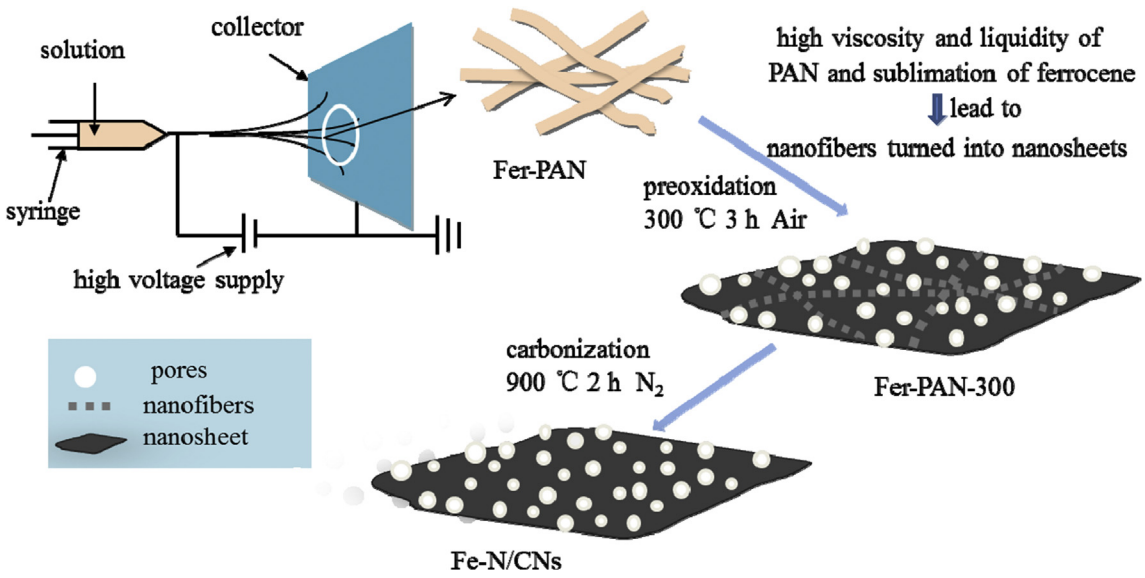

Fig. 1 – Illustration of the preparation of the Fe–N/CNs.

Please cite this article in press as: Dong L, et al., Fe, N codoped porous carbon nanosheets for efficient oxygen reduction reaction in alkaline and acidic media, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.140