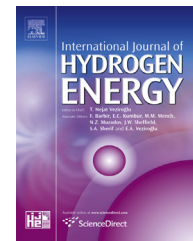


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# Nitrogen-doped porous carbon nanofiber based oxygen reduction reaction electrocatalysts with high activity and durability

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## ABSTRACT

Sluggish oxygen reduction reaction (ORR) is one of the critical challenges in polymer electrolyte membrane fuel cell (PEMFC) technologies. Carbon materials doped with various heteroatoms have been exactly proved as promising alternative catalysts and even the catalyst supports for the ORR in fuel cells. In this work, we have developed nitrogen-doped porous carbon nanofibers (N-PCNF) as novel ORR catalysts. The obtained N-PCNF shows excellent electrocatalytic performance and durability for ORR both in basic and acid solutions. Furthermore, the N-PCNF acted as support to deposited platinum (Pt) nanoparticles, the Pt nanoparticles with uniform size were well dispersed not only on the surface but also the cross-section of N-PCNF. The electrocatalytic activity and stability of the resultant Pt/N-PCNF along with the commercial one (JM20) were investigated. As a result, the Pt/N-PCNF exhibited enhanced ORR activity when compared with Pt supported on PCNF (Pt/PCNF) as well as the state-of-the-art JM20. In addition, enhanced stability of Pt/N-PCNF, coupled with ORR activity and electrochemical surface area (ECSA) retention after accelerated durability test (ADT) in acid media was observed. These results indicated that the N-PCNF can not only work as the non-precious electrocatalysts toward ORR, but also a promising candidate as catalyst supports.

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## Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are regarded as the reliable sustainable energy conversion devices due to their outstanding advantages including excellent energy densities, high energy conversion efficiencies and zero by-product emissions [1–4]. One of the most critical challenges for widespread commercialization of PEMFC especially in the automotive infrastructure is the development of high active, excellent durability, and low price electrocatalyst for the

sluggish oxygen reduction reaction (ORR) [5–8]. Until now, Pt-based electrocatalysts along with Pt-based alloys have been generally considered as the most suitable ORR electrocatalysts [9–11]. However, they still suffer from various disadvantages such as low earth-abundance, high cost, and poor durability during long time operation of fuel cells [1]. Thus, designing alternative ORR electrocatalysts with high catalytic performance to supersede Pt or reduce the Pt dosage is of great interests [9]. Unflagging efforts have been focused on several aspects, including Pt nano-structure controlling [12–15],

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supports fabrication [4,16–18], and even non-precious metal electrocatalysts design [19–25].

Hitherto, carbonaceous materials doped with various heteroatoms have been confirmed as an efficient way to prepare non-precious electrocatalysts for ORR [10,26–29]. Numerous researchers reported that the non-precious electrocatalysts can be obtained by doping carbon-based materials with heteroatoms (including N, S, B, Fe or Co) [20,24]. Among them, nitrogen-doped carbon materials including N-doped carbon nanotubes (NCNT) [25,30], N-doped carbon nanographene (NG) [23,24,31–33], and N-doped carbon nanospheres [34] have been widely prepared, investigated and always exhibited excellent catalytic performance for ORR.

Most of the studies are focused on the nitrogen-doped carbon nanotubes and graphenes to date, however, few investigations are conducted on the carbon nanofibers [35–39]. Carbon nanofibers are regarded as a promising conducting material because they act as efficient pathways for the electrons transporting through freely [40]. Liu et al. [35] found that urea-treated carbon nanofibers can be used as efficient catalytic materials for ORR. The N-doped carbon nanofibers exhibited much better catalytic activity and durability than the traditional carbon nanofibers. Qiu and coworkers [41] investigated three different surface modification methods such as acidification with a  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture, heat treatment in  $\text{NH}_3$ , and the combined treatment of the above two process to prepare the N-doped carbon nanofibers. As a result, the combined technique achieved much better catalytic performance both in acid solutions and alkaline solutions. These studies do confirmed the carbon nanofibers as efficient catalysts toward catalyzing ORR.

Taking into account that the catalytic activity is largely depends on the catalytic sites density on the supports surface. Introducing porosity and defects on the surface of fibers for increasing the special surface area, thus improve the catalytic sites density seems to be effective [37]. Electrospinning is an easy, reliably, and cost-effectively technique to prepare fibers with thin diameter into nanometer size [37]. The porous carbon nanofibers can be fabricated by electrospinning suitable polymer blends solution containing carbon precursor polymer (CPP) and thermally decomposable polymer (TDP) followed by carbonization at relatively high temperatures. Dae-Soo Yang et al. [40] used the solution mixed poly(acrylonitrile) (PAN) with poly(ethylene oxide) (PEO) for electrospinning nanofibers and followed by carbonization and thus the N-doped porous carbon nanofibers have been successfully obtained. In their process the porosity can be easily tuned via varying the ratio of the two materials. They found the favorable sample for improved ORR performance can be prepared when the solution ratio is 1:1 and carbonization at 1000 °C. Their study indicated that the trade-offs between electrical conductivity and nitrogen content can be important for the active sites density which do benefit the ORR activity. Our group has already successfully prepared the porous carbon nanofibers (PCNF) derived from electrospinning poly(acrylonitrile) (PAN)/poly(methyl methacrylate) (PMMA) followed by carbonization with suitable diameter and controlled porosity, and even used as the electromagnetic wave absorption materials [42], co-support for commercial electrocatalyst [43], and the electrocatalyst support for PEMFC [44].

In the present work, we developed nitrogen-doped porous carbon nanofibers (N-PCNF) by thermal treatment PCNF with dicyandiamide (DCDA) as the nitrogen resource and investigated the electrocatalytic activity and durability of N-PCNF for ORR both in basic and acid media; meanwhile N-PCNF was used as the support to deposited Pt nanoparticles. The nature of Pt/N-PCNF, along with Pt/PCNF and JM20 was characterized. Their electrocatalytic activity and durability toward ORR were also measured and discussed.

## Experimental

### Preparation of the nitrogen-doped carbon nanofibers (N-PCNF)

The PCNFs and pristine CNFs were prepared as we reported before [43]. Briefly, the spinning solution was consist of 70wt polyacrylonitrile (PAN) and 30wt polymethylmethacrylate (PMMA). The diameter of capillary tip was about 0.40 mm. Electrospinning process was carried out under a conduct difference of 18 kV provided by a variable high voltage power supply and an extrusion rate of 15  $\mu\text{l}/\text{min}$  controlled by a syringe pump. The nanofibers were collected on the grounded aluminum foil placed on the surface of an adjustable lab jack as the target. The distance between the target and the tip of the syringe needle was 18 cm, ambient temperature and relative humidity were kept at 25 °C and 30% respectively. The obtained mat was dried under vacuum overnight to remove the residual solvents. The pre-oxidation process was carried out at 280 °C for 1 h and followed by carbonization.

The N-PCNFs were prepared by the by thermal treatment PCNFs with dicyandiamide (DCDA) [24]. Typically, 50 mg PCNFs, 200 mg DCDA and 100 mg  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were added into 80 mL ethanol and followed by ultrasonic for 1 h. The mixture was continuously stirred for another 24 h at 60 °C and dried. The dried sample was then calcined at 900 °C for 1 h under  $\text{N}_2$  atmosphere. After cooling down, the sample was poured into 10% HCl solution and stirred for 24 h to remove the inactive metal species and subsequently the product was heat treated again as above.

### Synthesis of N-PCNF supported platinum nanoparticles (Pt/N-PCNF)

Pt was deposited onto N-PCNF and PCNF using a traditional ethylene glycol (EG) technique [44]. Briefly, 80 mg of carbon materials were first added into a flask with 50 mL of EG under ultrasonic treatment for 1 h to form a homogeneous slurry, a certain amount of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  aqueous solution (7.53 mg  $\text{mL}^{-1}$  of Pt) was then slowly added to the slurry to ensure 20wt% Pt content, followed by ultrasonic and stirred for 1 h. And then the slurry was heated to 130 °C and maintained for 3 h in  $\text{N}_2$  atmosphere under reflux conditions. After cooling down, the slurry were separated in the centrifuge and washed several times. Finally, the sample was dried at 80 °C in vacuum oven for 12 h.

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