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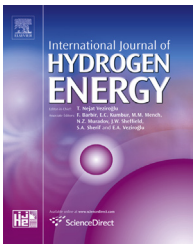

The effect of different nitrogen sources on the electrocatalytic properties of nitrogen-doped electrospun carbon nanofibers for the oxygen reduction reaction

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ABSTRACT

Nitrogen-doped carbon nanofibers (NCNFs) for use as electrocatalysts for the oxygen reduction reaction (ORR) were prepared by carbonizing electrospun polyacrylonitrile (PAN) nanofibers. In order to investigate the effect of nitrogen doping on the electrocatalytic activity different nitrogen-containing chemicals including melamine, aniline, urea, and polyaniline were added into the PAN solutions prior to electrospinning. It was found that the electrocatalytic activity of the NCNFs is strongly dependant on the type and amount of nitrogen-containing chemical added. The NCNFs which showed the best electrocatalytic activity were obtained with a aniline/PAN mass ratio of 20:3. These showed an ORR peak (vs Hg/Hg_2Cl_2) at −0.047 V in KOH electrolyte and 0.426 V in H_2SO_4 electrolyte with improved stability in both media. The present work shows that the electrocatalytic performance of the NCNFs can be improved by appropriate selection of the nitrogen doping source, resulting in a promising ORR catalyst for future application.

Introduction

Fuel cells have been attracting wide attention due to their high efficiency in energy conversion and low emission of pollutants [1,2]. The oxygen reduction reaction (ORR) is one of the most important factors influencing the performance of fuel cells and electrocatalysts are of great significance for ORR with the desired current density, overpotential, and stability [3,4]. Conventionally, plantinum (Pt) is used as the electrocatalysts for ORR, however the large-scale application of fuel cells is hampered by the high cost and scarcity of Pt [5]. In addition, Pt electrocatalysts suffer from deactivation in the presence of CO and methanol [6]. Much effort has been devoted to searching for alternatives to Pt as the ORR catalysts. For example, Pt-free electrocatalysts such as transition metal chalcogenides [7,8], Pd-based alloys [9], gold nanoclusters [10], Fe/Co-doped carbon [11–16], and nitrogen-doped carbon [6,17–20] have been

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found to have electrocatalytic activity suitable for ORR. Nitrogen-doped carbon materials (NCMs) such as carbon nanotubes [21,22], carbon fibers [19], graphene [23,24], carbon nanocapsules [18], and mesoporous carbon [17,25,26] have been demonstrated to possess favorable electrocatalytic activity for ORR due to their unique electronic properties [21,22]. The NCMs possess strong tolerance to CO poisoning and crossover effects and show long-term operational stability [27]. Consequently, the NCMs are of tremendous interest as low-cost cathodic catalysts for fuel cells.

The electrocatalytic activity of the NCMs is mainly dependent on the forms of the doped nitrogen atoms [6,19,28] although the origin of the electrocatalytic activity has not been fully concluded. Different doping forms, including pyridinic-N, pyrrolic-N, or graphitic-N, have been reported to contribute to the electrocatalytic activity for ORR [6,13,19,27–29]. According to published results pyridinic-N or pyrrolic-N are the most widely reported as the origin of the ORR activity in NCMs [13,19,20,27–29]. Apart from the preparation parameters the form of the nitrogen dopant is closely related to the type of compound used as the nitrogen source. Many nitrogen sources have been used to dope carbon materials using different process to obtain different doping forms of nitrogen. For example, the chemical vapor deposition route has used pyridine [6] and ethylenediamine [30] as the nitrogen sources, resulting in the generation of 49% graphitic-N and 35.1% pyridinic-N, respectively, which are considered as important active sites for ORR. In the case of the polymer-conversion route the application of poly(2-methyl-1-vinylimidazole), poly(4-vinylpyridine), poly(3-methylpyrrole), and poly(p-pyridazine-3, 6-diyl) can produce pyridinic-N with the content of 62%, 40%, 50%, and 40% [31], respectively. Alternatively, the post-treatment route has used NH_3 [25] and HNO_3 [32] as the nitrogen sources to prepare NCMs. When using NH_3 as the doping source 46.9% pyridinic-N and 10.0% graphitic-N were obtained while using HNO_3 as the doping source gave 51% pyrrolic-N, which were regarded as the active sites for ORR.

We have prepared nitrogen-doped carbon nanofibers (NCNFs) by carbonizing the electrospun polyacrylonitrile (PAN) nanofibers in NH_3, where NH_3 acts as the nitrogen doping source [19] and when carbonized at 1000 °C the majority of the doped nitrogen is pyrrolic-N which gave excellent electrocatalytic performance for ORR. The electrospinning technique allows different nitrogen-containing chemicals to be added and allows the effects of different nitrogen sources on the doping form and the electrocatalytic performance of the NCNFs to be investigated. As stated above, the nitrogen doping form is strongly dependent on the type of the applied sources. Therefore, further work is required to search suitable nitrogen doping source and thus to improve the ORR electrocatalytic performance further.

Electrospinning is a simple and versatile method capable of producing continuous polymer and polymer-based composite nanofibers with diameters down to a few nanometers [12–16,32–34]. Inorganic nanofibers such as carbon [32–34], metals [35], carbides [36,37], and many oxides [38–40] can be easily synthesized by calcining the electrospun precursor fibers. Besides the NCNFs [19] metal/N-co-doped carbon (M-N-C) nonofibers have been prepared by electrospinning [12–16], which show excellent electrocatalytic performance for ORR. For example, Zamani et al. prepared Fe–N–C nanofibers by electrospinning, obtaining the most active non-precious ORR catalysts prepared by electrospinning [16]. One outstanding advantage of the electrospinning technology is its simplicity in producing composite nanofibers and doping of the inorganic nanofibers, which can be easily realized by adding the desired chemicals into the electrospinning solution. Because of this merit electrospinning provide a convenient tool for investigating the N doping of carbon nanofibers (CNFs).

In this work, the NCNFs were prepared by carbonizing electrospun PAN nanofibers using different nitrogen-containing chemicals including melamine, aniline, urea, and polyaniline as the nitrogen sources. The effects of the different nitrogen sources, the amount added, and carbonizing temperature on the form of nitrogen doping and the resulting electrocatalytic activity for ORR have been investigated systematically. The results obtained indicate that the electrocatalytic activity of the NCNFs is strongly dependant on the type and the amount of the nitrogen source added. The NCNFs formed using aniline as the nitrogen source exhibit the best electrocatalytic performance with the ORR peak at −0.047 V in a KOH electrolyte and 0.426 V in a H_2SO_4 electrolyte.

Experimental method

The electrospinning solutions were prepared by dissolving PAN (Aldrich, product number: 181,315, Mw = 150,000) in dimethylformamide (DMF) with a concentration (wt./v%) of 3% first. Then the nitrogen sources including melamine, aniline, urea, and polyaniline were added into the PAN solutions in different amounts, respectively. The precursor nanofibers containing different nitrogen sources and PAN were electrospun by a conventional electrospinning setup [34], which mainly consists of a high voltage power supply (0–50 kV) (DWP503-2ACCD, Dongwen High Voltage Power Supply Company, China) and an ordinary hypodermic syringe with a stainless steel needle. Graphitic papers were used as the substrates to collect the electrospun nanofibers. The distance between the needle nozzle and collecting substrate was set at about 15 cm and the electrospinning voltage is 10–15 kV. The stabilization was carried out in air at 250 °C for 2 h with a heating rate of 5 °C min^{-1}. The carbonization was carried out in NH_3 atmosphere with a flow rate of 80 mL min^{-1} for 2 h at different temperatures with a heating rate of 7 °C min^{-1}. As a contrast, the carbon nanofibers (CNFs) were also prepared from the pure PAN nanofibers by carbonization at 1000 °C in NH_3.

Scanning electron microscopy (SEM, HITACHI S-4700), Raman spectroscopy (Renishaw RM-1000), and transmission electron microscope (TEM, JEM-2100HR) were used to characterize the structure of the samples. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to determine the composition and bonding states of the samples.

The electrochemical tests were performed on an electrochemical workstation (CHI760C, Shanghai Chenhua Instrument Co., Ltd., China). Cyclic voltammogram (CV) and rotating-disk electrode (RDE) polarization curves were