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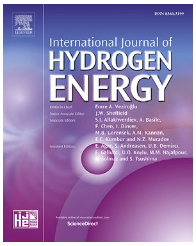

Nitrogen-doped carbon nanoflower with superior ORR performance in both alkaline and acidic electrolyte and enhanced durability

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ABSTRACT

In this work, three new types of nitrogen-doped carbon nanoflower (N–CNF) are synthesized by a template method. The resultant carbon was extensively investigated with the transmission electron microscopy (TEM), X-ray diffraction (XRD), Nitrogen adsorption-desorption isotherms, X-ray photoelectron spectroscopy (XPS), and electrochemical methods. Firstly, the carbon precursor, viz. pyrrole, aniline and phenanthroline, is found to yield a considerable effect on the morphology, which can be attributed to their dynamic motion in the template during the synthesis. All of the N–CNF materials possess well-developed 3D pore structure and high specific surface area, which are beneficial for the mass transfer of the reactant and accessibility of the active sites toward oxygen reduction reaction (ORR). Secondly, the optimal catalyst N–CNF-PHEN-900, which acquires the largest specific surface area (1039 m^2 g^{-1}), exhibits a superior ORR performance in both alkaline and acidic media. N–CNF-PHEN-900 exceeds the commercial Pt/C with 30-mV halfwave potential ($E_{1/2}$) surpassing in alkaline media and is comparable to Pt/C in acidic media ($E_{1/2}$ = 0.76 V). Lastly, N–CNF-PHEN-900 outperforms Pt/C on both durability and methanol tolerance in both alkaline and acidic media. And the rotating ring-disk electrode (RRDE) test indicates N–CNF-PHEN-900 is highly selective to a four-electron transfer pathway in both alkaline (electron transfer number = 3.98) and acidic (electron transfer number = 3.97) media. This work sheds light on the importance of large specific surface area, well-developed pore structure and dopant configuration on electrocatalysis, offering a conjoint viewpoint of developing metal-free catalysts for the ORR.

Introduction

The oxygen reduction reaction (ORR) at the cathode in polymer electrolyte membrane fuel cell (PEMFC) has drawn particular attention, due to the significance to bulldoze the poor-efficiency barrier caused by its sluggish kinetics. ORR occurs either via a highly efficient four-electron pathway or a less efficient two-electron pathway [1–3]. Up to now, the platinum-based catalysts perform the best electrocatalytic activity for ORR [4–6], but their scarcity, high cost and easy to deactivate by poisoning greatly hinder their popularized application for industry scale [7,8]. Extensive studies have

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been focused on finding alternative metal-based catalyst to substitute Pt-based catalysts from the economic standpoint; however, the status quo is far from satisfactory because of the poor electrocatalytic activity and stability in acidic media [9–12]. In recent years, metal-free catalysts for ORR have attracted enormous interest, due to their superior tolerance to both CO and methanol, low cost and operational durability [9,13–15].

Particularly, nitrogen-doped carbon nanomaterials present an excellent performance among the metal-free catalysts [16–18]. For example, Choi et al. [19] modified the reduced graphene oxide with N-doped carbon nanowires (rGO-CN), which showed superior ORR performance to that of the initial rGO. Zhu et al. [20] prepared a N-doped mildly oxidized CNTs (moCNTs) catalyst for ORR via a two-step approach involved polymerization and pyrolyzation. The N-doped moCNTs exhibited remarkable performance toward ORR in acidic media, with an onset potential and half-wave potential achieving 0.87 V and 0.75 V vs. RHE, respectively. Guo and his co-worker prepared a N-doped mesoporous network-like carbon (NMNC) by pyrolyzing the network-like carbonaceous spheres under ammonia atmosphere [8]. The best of the NMNC presented a comparable performance with the commercial Pt/C catalyst (only 32 mV of the half-wave potential negative to the Pt/C). Zhang's group utilized g-C_3N_4 as the template and nitrogen source to synthesize N-doped carbon nanosheet (N–CNS) with microporous and mesoporous structure [21]. The obtained N–CNS exhibited superior electrocatalytic ORR activity to Pt/C.

The excellent electrocatalytic performance results from some critical properties of the N-doped carbon materials. First, the dopant nitrogen could optimize the electronic property, which plays an important role in ORR performance. Owing to the larger electronegativity of nitrogen (3.04) compared with carbon (2.55), the electronic structure of carbon could be modified by the dopant nitrogen [22]. This modification lead the nitrogen doping-induced charge to transfer from adjacent carbon atoms, which could change the chemisorption mode of O_2 from an end-on adsorption to a side-on adsorption [17,23]. It has been reported that the O–O bond of the side-on adsorption can be more effectively weakened than that of the end-on adsorption during the ORR [24]. Besides, the chemical configuration of the dopant nitrogen also greatly affects the ORR performance of the N-doped carbon materials. As revealed by previous experimental results [25,26], both pyridinic and pyrrolic N which have planar structure, can dramatically improve the electrocatalytic activity toward the ORR. Second, a large specific surface area, which favors the exposure of the active sites, is essential for promoting the ORR as well [8]. As revealed by the literature [27,28], the high surface area is beneficial to expose more active sides to boost the density of the active sides and thus enable more O_2-chemisorption sides. Third, the 3D pore network with well-developed porosity could afford the guaranteed pathway for the mass transfer of the reactants [29]. There are many works about the N-doped carbon materials with favorable chemical configuration of dopant N [30–32]. The classical N-doped carbon materials are the N-doped graphene and the materials derived from graphene. However, these 2D materials would inevitably stack together when deposited on the electrodes due to the π-π interaction [33–35]. As a result, the unique properties (e.g. optimal N configuration) and the active sites of the materials cannot be utilized and exposed, respectively. In this case, a porous material with 3D pore network could easily avoid the lapse of the active sites [36–39]. To achieve an optimal effect, the researchers should fully exert the positive properties of the materials to promote the electrocatalysis. In this way, it is necessary to prepare the N-doped carbon materials associated with the above features of predominant active N species, high surface area and well-developed pore structure, to develop metal-free catalysts with favorable ORR performance.

Herein, we present three new types of N-doped carbon nanoflower (N–CNF) catalyst fabricated by the hard-template method, in which mesoporous silica nanoflower (MSNF) acts as the template and is infiltrated with nitric carbonous precursor. The precursor is found to yield considerable effect on the morphology, and three flower-like morphologies are obtained by respectively injecting pyrrole, aniline and phenanthroline. We have also investigated the effect of pyrolysis temperature on N–CNF fabricated with phenanthroline (N–CNF-PHEN) toward ORR. The halfwave potential of the best-performed catalyst ($E_{1/2} = 0.87$ V) surpasses the commercial Pt/C ($E_{1/2} = 0.84$ V) catalyst over 30 mV in alkaline media, and is comparable in acidic media. In this work, the well-developed 3D pore structure, large specific surface area and predominant active N species conjointly result in an excellent ORR performance and enhanced durability for the obtained N–CNF, which indicates a conjoint rout of developing metal-free catalysts with optimal ORR electrocatalytic activity.

Experimental

Reagents and materials

Cetyl pyridinium bromide monohydrate (CPB) was purchased from Sinopharm Chemical Reagent Co., Ltd. Urea, aniline, cyclohexane and sodium hydroxide were purchased from Guangzhou Chemical Reagent Factory. Tetraethoxysilane (TEOS) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Phenanthroline, n-amyl alcohol and ferrous chloride ($FeCl_2 \cdot 4H_2O$) were purchased from Tianjin Damao Chemical Reagent Factory. Ferric chloride ($FeCl_3 \cdot 6H_2O$) was purchased from Taishan Yueqiao Reagent Plastic Co., Ltd. Pyrrole was purchased from Saen Chemical Technology Co., Ltd. Commercial Pt/C (20 wt%, 40 wt%) of Johnson Matthey Company was used for comparison. Nitrogen gas and oxygen gas were purchased from Guangzhou Zhuozheng gas Co., Ltd. All the reagents were analytical purity. Except aniline and pyrrole would undergo a distillation treatment, all the reagents were used as received.

Preparation of MSNF template

The MSNF template were prepared according to the modified approach reported by Liao et al. [40]. In brief, 2.0 g CPB and 1.2 g urea were dissolved in 60 mL deionized water and the mixture was denoted as solution A. While solution B was prepared by stirring the mixture of 3 mL n-amyl alcohol, 5.4 mL TEOS and

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