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Heteroatom-doped carbon nanorods with improved electrocatalytic activity toward oxygen reduction in an acidic medium

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ABSTRACT

High-performance heteroatom-doped carbon catalysts with large surface areas were prepared by pyrolyzing nanorod precursors that had been synthesized by polymerizing a mixture of aniline (An) and β-naphthalene sulfonic acid (NSA). The catalysts were characterized by scanning and transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, N_2 adsorption/desorption isotherms, and elemental analysis. We intensively investigated how the catalysts' structure and catalytic performance were affected by (i) the ratio of NSA to An and (ii) the addition of Fe. The catalysts retained their nanorod morphology after pyrolysis. The optimal NSA/An ratio was 3/2 and the optimal Fe content was 3 wt%. The catalysts showed excellent activity toward oxygen reduction in an acidic medium, with the onset potential, half-wave potential, and limiting current density values reaching 0.86, 0.73 V (vs. reversible hydrogen electrode), and 5.28 mA cm^{-2}, respectively. We suggest that the catalysts' high performance may be due to the co-doping effects of nitrogen, sulfur, and iron, as well as the large surface area created by the nanorod structures.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are widely recognized as efficient and clean energy conversion devices. As one of the key components of a PEMFC, the electrocatalyst plays a critical role in determining the fuel cell's performance, durability, and cost. Due to the difficulty of breaking the strong O—O bond, the oxygen reduction reaction (ORR) on the cathode is six or more orders of magnitude slower than the hydrogen oxidation reaction on the anode. Facilitating the sluggish ORR still requires a high loading of platinum – a scarce precious metal. Hence, developing high-performance non-precious metal catalysts is a significant goal to achieve the large-scale commercialization of PEMFCs [1–4]. Among non-precious metal ORR catalysts, carbon-based materials are the most promising Pt alternatives. However, their ORR activities are still far inferior to the activity of conventional Pt/C catalysts in acidic electrolyte, an important component in a PEMFC [4–12].

Generally, catalytic activity depends on (i) the intrinsic activity of a single active site and (ii) the density of active sites. On the one hand, the intrinsic activity can be improved by introducing heteroatoms (e.g., N, S, B, and P) into carbon materials. Among these heteroatoms, N has been widely used

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and investigated. Theoretical calculations suggest that N itself is not the active site. The ORR activity originates from the high electron affinity of the N atom. N induces a positive charge density on the adjacent C atoms, which boosts oxygen adsorption and subsequently weakens the O—O bonds [4,13]. For S-doped carbon materials, the mechanism is still unclear, but it cannot be the same as that for N because of the similar electro-negativity of S (2.58) and C (2.55) [14–17]. It is speculated that spin density, which determines the catalytic active site [18,19], may be the dominant factor in regulating the catalytic properties of S-doped carbons [17]. In addition to nonmetals, transition metal species such as Fe and Co, have also been used as important dopants in carbon materials to improve ORR activity, in spite of the ambiguity over their exact catalytic mechanisms [6,10,12,20]. On the other hand, active site density can be improved by altering the heteroatom content in the carbon material and by creating novel structures with larger specific surface areas [12,21]. Both active site control at the atomic scale and structural control of the materials are important in the design, synthesis, and optimization of ORR catalysts.

Recently, polyaniline (PANI) has been discovered to be an excellent low-cost, N-containing precursor for the fabrication of carbon-based catalysts [6,20,22]. In this study, we chose PANI as the nitrogen source, β-naphthalene sulfonic acid (NSA) as both the sulfur source and the structure-directing agent, and $FeCl_3$ as the iron source. Nitrogen, sulfur, and iron co-doped carbon nanorods with high catalytic performance towards the ORR in an acidic medium were prepared. The structure and ORR catalytic activity of these catalysts are discussed in detail.

2. Experimental

2.1. Catalyst preparation

Synthesis of the PANI/NSA precursor was based on a previously reported method [23]. A typical heteroatom-doped carbon catalyst, denoted as C-PANI/NSA, was prepared as follows. Aniline (An) was distilled under reduced pressure before use. Next, 0.74 mL An and 0.416 g NSA were dispersed in 35 mL deionized water with vigorous stirring at room temperature and then cooled to 0 °C. As the initiator, 1.88 g ammonium persulfate (APS) in 5 mL deionized water was slowly added to the above mixture. After polymerization for 24 h in an ice bath, the PANI/NSA precursor was collected on a filter and washed with water and ethanol. It was then dried at 80 °C for 12 h and put into a tubular furnace. After this, it was heated to 850 °C under argon flow at a rate of 10 °C/min, then cooled to room temperature and leached with 0.5 M H_2SO_4 solution at 80 °C for 8 h to remove unstable species. After thorough washing with deionized water, the sample was finally calcined at 850 °C under argon flow for 3 h to achieve further graphitization.

We intensively investigated the effects that the NSA/An ratio and the addition of Fe had on the structure and catalytic activity of the catalysts. Fe was doped by adding a certain amount of $FeCl_3$ into an aqueous dispersion of PANI/NSA precursor, followed by evaporating the solvent completely before carbonization. The sample obtained after carbonization, acid leaching, and further graphitization is denoted as Fe-C-PANI/NSA. The acid leaching was conducted in 0.5 M H_2SO_4 solution at 80 °C for 8 h.

For comparison, a N doped carbon catalyst derived from pure PANI (denoted as C-PANI), and a N and S co-doped carbon catalyst derived from the physical mixture of PANI and NSA (denoted as C-PANI/NSA_{mix}) were prepared. The method of carbonization, acid leaching and further graphitization for C-PANI and C-PANI/NSA_{mix} was the same as that for C-PANI/NSA catalyst. The physical mixture of PANI and NSA (molar ratio of NSA/An = 3/2) was obtained by mixing and milling them thoroughly in a mortar.

2.2. Characterization

Scanning electron microscopy (SEM) was conducted on a Nova NanoSEM 430 scanning electron microscope. Transmission electron microscopy (TEM) was performed on a JEM-2100 transmission electron microscope operated at 120 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded on a Tecnai G2 F20 S-Twin microscope operated at 200 kV. Fourier transform infrared (FTIR) spectra were recorded on a Tensor 27 FTIR spectrometer. X-ray diffraction (XRD) was conducted on a TD-3500 powder diffractometer operated at 40 kV and 30 mA, using Cu–Kα as the radiation source. Specific surface areas were measured using a nitrogen adsorption–desorption method on a Tristar 3020 gas adsorption analyzer. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MK2 X-ray photoelectron spectrometer operated at 12.5 kV and 250 W, using Al–Kα as the radiation source. The bulk contents of C, O, N, and S were measured on a Vario EL cube elemental analyzer.

2.3. Electrocatalytic evaluation

Voltammetry tests were carried out on an electrochemical workstation at room temperature, using a three-electrode configuration. Ag/AgCl (3 M KCl) was used as the reference electrode, and platinum foil was used as the counter electrode. The working electrode was prepared using the following procedure: 20 mg catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25 wt% Nafion) for 30 min, then 5 μL of the dispersion was transferred and spread on a glassy carbon substrate electrode (5 mm inner diameter) using a micropipette, followed by drying under an infrared bulb.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed in 0.1 M $HClO_4$ aqueous solution at respective rotation speeds of 0 and 1600 rpm; the sweep rate was 10 mV s^{-1}. All LSV data were corrected for the N_2 data collected in N_2-saturated 0.1 M $HClO_4$. All potentials in this paper are referenced to a reversible hydrogen electrode (RHE), and the potential difference between the RHE and a Ag/AgCl electrode in the acidic electrolyte is 0.29 V. Cycling stability tests of the catalysts were performed with a rotating disk electrode (RDE) in O_2-saturated 0.1 M $HClO_4$ with the sweep rate of 0.10 V s^{-1}. After each 100 cycles, ORR polarization measurement was conducted with the sweep rate of 10 mV s^{-1} and rotation rate of 1600 rpm.