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Three-dimensional iron, nitrogen-doped carbon foams as efficient electrocatalysts for oxygen reduction reaction in alkaline solution

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ABSTRACT

Three-dimensional (3D) Fe, N-doped carbon foams (3D-CF) as efficient cathode catalysts for the oxygen reduction reaction (ORR) in alkaline solution are reported. The 3D-CF exhibit interconnected hierarchical pore structure. In addition, Fe, N-doped carbon without porous strucuture (Fe-N-C) and 3D N-doped carbon without Fe (3D-CF') are prepared to verify the electrocatalytic activity of 3D-CF. The electrocatalytic performance of as-prepared 3D-CF for ORR shows that the onset potential on 3D-CF electrode positively shifts about 41 mV than those of 3D-CF' and Fe-N-C respectively. In addition, the onset potential on 3D-CF electrode for ORR is about 27 mV more negative than that on commercial Pt/C electrode. 3D-CF also show better methanol tolerance and durability than commercial Pt/C catalyst. These results show that to synthesize 3D hierarchical pores with high specific surface area is an efficient way to improve the ORR performance.

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1. Introduction

Slow kinetic characteristic of the cathodic oxygen reduction is one of the primary factors limiting the commercialization of fuel cells [1], so, to develop high efficient oxygen reduction reaction (ORR) electrocatalysts is of great importance. Currently, Pt and Pt-based catalysts are still the promising cathodic materials for ORR and dominate the application in fuel cells [2,3]. However, the prohibitive cost, scarcity, and declining activity of Pt-based catalysts have impeded widespread applications and commercialization of fuel cells [4]. Consequently, alternative electrocatalysts based on non-precious metals have been actively pursuing in the last decade.

Many efforts to obtain replacements of Pt-based catalysts and other precious metals such as carbon materials for ORR resulted in some new contenders. For example, in the work of Mentus et al. [5–8], N-doped carbon derived from polyaniline and ordered mesoporous carbon showed enhanced ORR catalytic activity in alkaline medium. And, the catalyt loading on the electrodes influences the kinetics of ORR, e.g. More positive onset potential and higher current densities with enlarged loadings can be achieved for N-doped

carbon catalysts [5]. Especially Fe, N-doped carbonaceous nano-materials as the ORR catalysts have several notable advantages, for instance, inertness for CO poisoning, long-term operational stability, and cost-effective [9–17]. Their catalytic activity origanated from the active sites of $FeN_2C_4^+$ ion [12]. It was found that further improvement in the catalytic activity of these carbons could be achieved via developing specific morphology and structure of Fe, N-doped carbon-based materials, such as iron encapsulated within pod-like carbon nanotubes [18], mesoporous carbons supported Fe-N_x electrocatalysts [19,20], and N-enriched core-shell structured Fe/Fe$_3$C-C nanorods [21]. Besides, it was also found that carbonaceous materials with relatively large surface area and pores are more favorable for ORR than these with inaccessible narrow pores [22]. Recently, it was reported that three-dimensional (3D) carbon materials were developed as electrocatalysts for ORR [23–25]. Due to their unique 3D network structure, high specific surface area and excellent electrical properties, 3D carbon materials showed superior catalytic performance for ORR [26,27]. Despite significant progress has been made in carbon materials for ORR, there were a few reports about developing 3D carbon foams doped with N as catalysts for ORR. It is an attractive target to develop Fe, N doped carbon materials with unique 3D structure.

In this study, a template-free approach was developed to prepare 3D Fe, N-doped carbon foams (3D-CF), which possesses hierarchical pores including micro- and mesopores. The

morphologic results showed that Fe, N-doped carbon foam with 3D structure was successfully prepared by this method. Its morphology and electrocatalytic properties were investigated in this study.

2. Experimental

2.1. Material synthesis

3D-CF were synthesized by two-step method including a hydrothermal and a thermal treatment. Sucrose and melamine were employed as carbon and nitrogen-carbon precursors to react with transition-metals (Fe). 1 g of melamine was dissolved in 20 mL of boiling water in a flask, and then 2 g of sucrose was added with stirring. 20 mL of concentrated sulfuric acid was added dropwise into the mixture with vigorous stirring and kept stirring for 1 h. After that, the mixture was transferred into a Teflon-lined autoclave and heated at 180 °C for 10 h. The resulting mixture was washed with ultrapure water until pH of filtrate was neutral, followed by drying in oven at 60 °C. 1 g of ferric chloride ($FeCl_3$) was dissolved in 5 ml of ultrapure water, into which the obtained black product was added with stirring, and then dried at 90 °C. The dried sample was ball-milled for 6 h at 250 rpm. Subsequently, the mixture was carbonized at 800 °C for 2 h under N_2 atmosphere. In order to remove unstable iron species, the obtained powder was immersed in HNO_3 solution (2 mol L^{-1}) for 24 h with stirring, then washed with deionized water until pH of filtrate was neutral and dried at 60 °C for 12 h. The 3D-CF were obtained.

For comparison, 3D N-doped carbon without Fe (3D-CF') was prepared by the same synthesis method as 3D-CF but without Fe, and Fe, N-doped carbon without 3D structure (Fe-N-C) was also synthesized. The detail procedure is as follows: 1 g of melamine was dissolved in 20 mL of boiling water in a flask, into which 2 g of sucrose and 1 g of ferric chloride were added with stirring, following by drying at 60 °C. The dried sample was ball-milled for 6 h at 250 rpm, and then carbonized at 800 °C for 2 h under N_2 atmosphere. The obtained powder was immersed in HNO_3 solution (2 mol L^{-1}) for 24 h with stirring to remove the iron, then washed with deionized water until pH of filtrate was neutral and dried at 60 °C for 12 h.

2.2. Physical characterization

X-ray diffraction (XRD) patterns on a Shimadzu XD-3A (Japan), using filtered Cu-Kα radiation (40 kV, 30 mA). Raman spectrum was obtained on a Ft-Raman spectroscopy (RFS 100, BRU-KER) employing Nd: YAG laser wavelength of 1064 nm. The sorption isotherm was performed on Quantachrome Autosorb-1 volumetric analyzer. The specific surface area was determined by Brunauer-Emmett-Teller (BET) method and the density functional theory DFT method was employed for analyzing the full range of pore size distribution. Scanning electron microscopy (SEM) images were conducted on Carl Zeiss Ultra Plus. Transmission electron microscopy (TEM) and high angle annular dark field scanning transmission electron

microscopy (STEM) measurements were carried out on a JEOL 2010 FEG microscope with the acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) was acquired with a VG Escalab210 spectrometer fitted with Mg 300 W X-ray source. Accurate binding energies are determined by referencing to the C 1s peak at 285.0 eV.

2.3. Electrochemical characterization

The electrochemical measurements were performed using an Autolab electrochemical workstation (CHI650). A common three-electrode electrochemical cell was used for the measurements. The counter and reference electrode were a Pt wire and an Ag/AgCl (saturated KCl solution) electrode, respectively. The working electrode was a glassy carbon disk (5 mm in diameter). The thin-film electrode was prepared as follows: 5 mg of catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25% Nafion) for 15 min. 8 μl of the dispersion was transferred onto the glassy carbon disk using a pipette, and then dried in the air. The loading of the catalysts on the electrode was 20.4 μg cm^{-2}. All the experiments were conducted at 25 °C which controlled by a electro-thermostatic water cabinet, and the commercial Pt/C (20 wt%, J.M. Corp.) was compared with the as-prepared samples under the same condition.

3. Results and Discussion

The fabrication process of 3D-CF is illustrated in Scheme 1. Initially, sucrose and melamine solution mixed with concentrated sulfuric acid were hydrothermally treated at 180 °C for 12 h to form a 3D skeleton (Scheme 1a). Subsequently, the sample was ball-milled with $FeCl_3$, and then the as-prepared powder was heated at 800 °C for 2 h under N_2 atmosphere. The final product was black powder composed of Fe, N-doped carbon foams as shown in Scheme 1b.

Fig. 1 show the typical SEM images of 3D-FC and Fe-N-C samples. SEM image of 3D-CF in Fig. 1a indicates loose structure, which likes that of foam, containing an interconnected, porous 3D framework with continuous macropores in the micrometer range. But SEM image of Fe-N-C in Fig. 1b displays a rock fragment-like morphology. There is no doubt that the different morphologies of 3D-CF and Fe-N-C were derived from the different synthesis methods. In addition, to further observe the structure of 3D-CF, TEM and STEM measurements were also carried out. As shown in Fig. 2a, the contrast varies in the different parts of the carbon lump. Dark round uniform particles are dispersed in the matrix. The distributions of C, N and Fe in 3D-CF are verified by the STEM (Fig. 2b) and corresponding elemental mapping images (Fig. 2 c-e). As shown in Fig. 2c and d, the uniform distribution of C and N elements on the whole was achieved in 3D-CF. Fig. 2e shows that the Fe element was distributed throughout the part. While, a few brigh spots can be observed, which were corresponding to the round spots Fig. 2b. Therefore, it can be assumed that Fe species are present in Fe–N_x moieties and crystalline Fe particles which would further confirmed by the following XRD patterns.
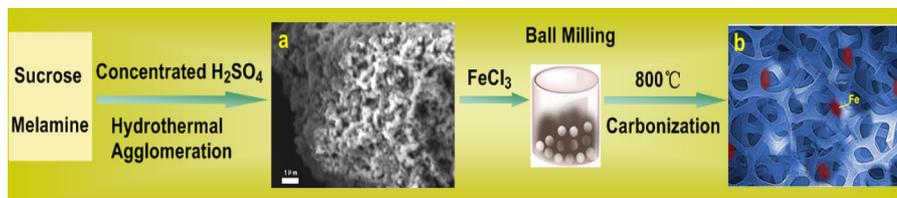
Scheme 1. Fabrication process for the 3D-CF sample; (a) SEM image of foams prepared by hydrothermal self-assembly; and (b) Ideal structure model of 3D-CF with Fe,N-doping.