Chinese Journal of Catalysis 39 (2018) 1427–1435

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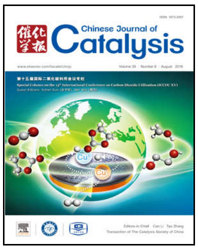
journal homepage: www.elsevier.com/locate/chnjc



Article

Induced growth of Fe-N_x active sites using carbon templates

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ARTICLE INFO

Article history:
Received 4 January 2018
Accepted 27 May 2018
Published 5 August 2018

Keywords:
Oxygen reduction reaction
Non-precious-metal electrocatalyst
Fe-N_x
Induced growth
Carbon template

ABSTRACT

Highly active Fe-N_x sites that effectively improve the performance of non-precious metal electrocatalysts for oxygen reduction reactions (ORRs) are desirable. Herein, we propose a strategy for introducing a carbon template into a melamine/Fe-salt mixture to inductively generate highly active Fe-N_x sites for ORR. Using ^{57}Fe Mössbauer spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction, we studied the structural composition of the Fe and N co-doped carbon catalysts. Interestingly, the results showed that this system not only converted inactive Fe and Fe-carbides into active Fe-N_4 and other Fe-nitrides, but also improved their intrinsic activities.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are one of the most promising candidates for clean electricity generation technologies; they have attracted increasing attention because of the limited supply of fossil fuel resources and environmental pollution caused by traditional energy production methods [1]. The catalytic species at the PEFC cathode typically includes Pt, which has a low natural abundance resulting in a significant restriction of the ability to meet global market demand; thus, non-precious metal catalyst alternatives are highly desired. To date, Fe-N_x doped carbons (Fe-N/C) are considered to be the most promising potential alternatives to Pt and its alloys as ORR catalysts at the cathodes of PEFCs [1–7].

Therefore, Fe-N/C catalysts with superior catalytic activities are being actively pursued through a variety of strategies; these include: (1) adjusting the type and amount of Fe compound [8–11] and N source [11–13]; (2) altering the synthetic conditions, *e.g.*, tuning the temperature [9,10,14] and pressure [15] of pyrolysis methods as well as investigating non-pyrolyzing routes such as axial ligand tethering [16], covalent grafting [17], and ball-milling [18]; (3) forming nanostructures, such as core-shell nanoparticles [18], ordered mesoporous carbons [19], arrays [20], thin graphene sheets [14,21,22], and amorphous carbon spheres [23]; (4) building composites including binary materials, such as graphene/carbon nanotubes [9], graphene/carbon black [24,25], graphene nanoribbons/carbon nanotubes [26], and carbon nanoparticles/carbon nanofibers

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This work was supported by the National Natural Science Foundation of China (21606149, 2163308), the China Postdoctoral Science Foundation (2016M591678), the Shanghai Rising-Star Program (18QB1404400), and the Shanghai Scientific Research Project (18511110803).

DOI: 10.1016/S1872-2067(18)63107-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 8, August 2018

[27], and ternary hybrids, such as carbon nanospheres/carbon nanotubes/graphene sheets [10]; (5) introducing post-processing, such as acid-washing [14,19–21], pore-forming [28], and reheating [28,29]; and (6) designing different typical Fe phases [29–31] to regulate the generation of Fe-nitrides, Fe-carbides, and Fe-nanoparticles. All these efforts are aimed at enhancing the ORR catalytic activities of the compounds.

Concurrently, significant progress has been made in identifying the detailed compositions of the Fe-based species through spectroscopic studies. A growing body of work suggests that the mode of Fe-N_x coordination plays a key role in promoting the electrocatalytic performance for ORR [7–36]. Moreover, it should be noted that Fe and Fe carbides have recently been identified as possible active species [37–42]. For example, adjacent Fe-carbides particles can boost the ORR activity of Fe-N_x sites [41,42], and Fe nanoparticles encapsulated in CNTs can modify the electronic structure of the carbon atoms [31], thereby indirectly participating in electrocatalysis. However, the extent of the role of Fe remains controversial, although it is clear that their ORR activity is inferior to that of the Fe-N_x sites [29–31]. Further, in-depth studies focused on the Fe-N_x species have revealed that Fe-N_4, and/or other Fe-nitrides, may be the primary contributors to the electrocatalytic performance of Fe-N/C catalysts. This information provides direction for the development of highly active ORR electrocatalysts. However, there is yet to be a rational strategy for the preferential induction of dense growth of highly active Fe-N_x sites.

In this work, we suggest the following effective solution for inducing the formation of Fe-N_x active sites: Introducing a carbon template into the precursor mixture containing melamine and Fe salts results in preferential generation of active Fe-N_x sites rather than inactive Fe and Fe-carbide compounds. This was confirmed through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy characterization. This method enhances the intrinsic ORR activities of the active species.

2. Experimental

2.1. Preparation and characterization of the catalysts

In brief, the carbon catalysts are synthesized via heat-treatment of the precursor mixtures. To generate the binary FeN carbon nanotube/carbon nanosphere (CNT/CS) catalyst, we first dispersed 4 g of melamine and 20 mg of $FeSO_4 \cdot 7H_2O$ into 50 mL of deionized water with vigorous ultrasonication. After addition of the CS template (typically 50 mg), the Fe salts and melamine molecules preferentially absorb onto the surface of the CS agglomerations. After thoroughly blending the precursor mixture, it was dried in a rotary evaporator at 60 °C and then heated at 900 °C for 1 h in a tube furnace under ultrapure argon. Using suitable analogous procedures, FeN-CNT and N-CS were also obtained.

The ^{57}Fe Mössbauer spectra were recorded at room temperature using an MS 500 instrument (Oxford Instruments, U.K.), and the data were fitted using Reciol software. XPS measurements were performed on a Kratos Ltd. XSAM-800 spectrometer with Mg K_α radiation, and the data were fitted via Gaussian/Lorentzian fitting using XPSPEAK41 software. XRD patterns of the catalysts were obtained using an XRD-6000 X-ray diffractometer (Shimadzu) with a Cu K_α radiation source operating at 40 kV and 30 mA. Scanning electron microscopy (SEM) images were obtained using a field-emission S-4800 microscope (HITACHI). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F microscope. N_2 adsorption isotherms of the catalysts were recorded using an ASAP2020 surface area and porosity analyzer (Micromeritics, USA).

2.2. Electrochemical measurements

Electrochemical experiments were performed using a CHI 440 electrochemical workstation and rotator in a standard three-electrode cell using a Pt foil counter electrode. The ORR tests were performed in O_2-saturated electrolytes at a potential scan rate of 5 mV/s, and CV curves were scanned in Ar-saturated electrolytes at a potential scan rate of 100 mV/s. The catalyst loadings were 0.6 and 0.1 mg/cm^2 for the prepared catalysts and 20 wt% Pt/C, respectively. To calibrate the reference electrodes to the reversible hydrogen electrode (RHE) scale, the RHE zero potential was estimated from the value at which the current crosses zero by measuring the polarization curves of the hydrogen electrode reactions on the Pt/C-loaded electrode in electrolytes saturated with H_2. The calibration values were $E(\text{RHE}) = E(\text{reference}) + x\text{V}$, where x equals 0.915 and 0.32 in alkaline and acid solutions, respectively.

A rotating ring-disk electrode (RRDE) was used as the working electrode. The electron transfer numbers (n) and peroxide yields were calculated based on the following equations:

$$n = 4I_D/(I_D + I_R/\text{N}) \quad (1)$$

$$\text{HO}_2^- (\%) = 200I_R/(\text{N} \times I_D + I_R), \quad (2)$$

where I_D and I_R represent the disk and ring currents, respectively, and N is the current collection efficiency of the Pt ring (0.25 in our system).

2.3. Calculation of the specific activity, mass activity, and turnover frequency

The specific activities (SAs), mass activities (MAs), and turnover frequencies (TOFs) of the catalysts were calculated using the following equations:

$$\text{SA (A/C)} = j_k/ECSA \quad (3)$$

$$\text{MA (A/g)} = j_k/m_{\text{catalyst}} \quad (4)$$

$$\text{TOF (A/site)} = \text{MA}/[(C_{\text{Fe,XPS}} \times A_{\text{Fe-N}x\text{,Mössbauer}}) \times \text{NA}/M_{\text{carbon}}] \quad (5)$$

respectively, where j_k, $ECSA$, m_{catalyst}, $C_{\text{Fe,XPS}}$, $A_{\text{Fe-Nx,Mössbauer}}$, and NA represent the kinetic current density, electrochemical surface area, catalyst loading, Fe atomic percent in the catalyst (determined by XPS), area percent of Fe-N_x species (determined from the Mössbauer spectra), Avogadro's constant (6.02 × 10^{23}), and atomic weight of carbon (12.01 amu).

3. Results and discussion