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FeS-decorated hierarchical porous N, S-dual-doped carbon derived from silica-ionogel as an efficient catalyst for oxygen reduction reaction in alkaline media

Sa Liu [a, *], Zheng Yang [a], Mengli Li [a], Liwen Liu [a], Yan Wang [a], Wenjie Lv [a], Zhenglong Qin [a], Xinsheng Zhao [b, **], Ping Zhu [a], Guoxiang Wang [c]

[a] School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, PR China
[b] School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, PR China
[c] School of Light Industry & Chemical Engineering, Dalian Polytechnic University, Dalian 116034, PR China

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ABSTRACT

To improve the catalytic activity towards oxygen reduction reaction (ORR) on the non-precious metal catalyst, developing transition metal and heteroatom doped carbon materials with abundant active sites and nanoporous structure is crucial but challenging. Herein, a novel FeS-decorated three-dimensional hierarchical porous N, S co-doped carbon catalyst is derived from silica based ionogel, of which 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][TfO]) acts as source of N and S, and porous silica framework, *in suit* originated from silicane by sol-gel process, acts as a template to get a large specific surface area (987.5 $m^2 g^{-1}$). The obtained catalyst shows excellent ORR activity in 0.1 M KOH (positively shifted half-wave potential of 0.87 V), high selectivity (electron-transfer number of 3.99), remarkable stability (only 3 mV negative shift of half-wave potential after 5000 potential cycles) and perfect methanol-tolerance effect. The remarkable electrochemical performance of the obtained catalyst is mainly attributed to the well-controlled hierarchical porous structure and homogeneous distribution of highly active sites (N, S-dual-doped carbon, Fe-N_x and/or FeS).

1. Introduction

Oxygen reduction reaction (ORR) is a core reaction in fuel cells, which are one kind of the most hopeful energy conversion technologies today [1–3]. However, the high cost and limited reserves of precious metal Pt-based catalysts towards ORR restrict the commercialization of fuel cells. Thus, developing non-precious metal catalysts (NPMCs) with sufficient catalytic activity for ORR is crucial but challenging.

Among various candidates, heteroatom (such as N, S, P and B *etc.*) doped carbon-based catalysts with or without transition metals complexes have received considerable attention [4–9], because of their low price, high electrocatalytic activity, superior stability and excellent methanol-tolerance. Doping heteroatom (especially N and S) into carbon materials can tune and control the electronic nature of carbon to improve their ORR activity [4,10,11]. What is more, introducing a transition metal (such as Fe and Co) to form M-C–N catalyst is another effective strategy [12]. Since Jasinski et al. [13] discovered that the Co-phthalocyanine showed electrocatalytic activity towards ORR in 1964, many important achievements have been made for the M-C–N catalyst [1]. However, to further improve the catalytic activity, it still requires to solve the following two critical factors [2,14]: (1) the inherent nature of active sites in M-C–N catalysts, which is determined by the elemental composition and the interactions between different components; (2) the density and utilization of active sites, which depend on the microstructure of M-C–N, including its surface area and nanoporous structure.

The catalytic activity is to be found strongly dependent on the synthetic chemistry of catalysts [15]. Particularly important factors are the structure of the nitrogen-carbon precursor, transition metals, heating conditions, supporting templates, and post treatments. In addition, the integration method of nitrogen, carbon, and

* Corresponding author.
** Corresponding author.
E-mail addresses: liusa@jsnu.edu.cn (S. Liu), xinshengzhao@jsnu.edu.cn (X. Zhao).

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metal species is crucial for achieving high activity. However, the intrinsic nature of active sites in M-C–N catalysts still remains elusive to date [1,2,16], although a number of efforts have been made by different physical and chemical technologies. It is commonly accepted that there probably include two different types of active sites in terms of the nitrogen functionalities on the surface of carbon (C-N_x, such as pyridinic and graphitic N) [5] and M-N_x species (such as FeN_{2+2}, FeN_2 and FeN_4) [17–19]. In addition, despite the controversy, the iron-based nanoparticles/nanocrystals (for example, metallic Fe [20], Fe_3C [21,22], iron sulfides [10,23]) presumably play an indispensable role in boosting the catalyst activity by the following two ways: (1) directly as the activity center [10,21,23,24] and/or (2) the synergetic role in activating the neighboring activity sites (such as Fe-N_x and/or C-N_x) [25,26].

The most traditional synthetic method for M-C–N catalyst is based on pyrolyzing the mixture of nitrogen-containing compounds, carbon materials, and transition metal precursors. However, the ORR activity of these catalysts is usually low compared with that of Pt-based catalyst, due to limited exposure of active sites and poor mass-transport properties caused by their low surface area. One widely used strategy to increase the surface area is introduction of a three-dimensional (3D) nanoporous structure by using hard or soft template-assisted method [1,27]. A silica template is usually served as pore forming substance [28–31]. For example, Feng and Müllen et al. [29] prepared a family of mesoporous Co–N–C and Fe–N–C catalysts with remarkable ORR activity in acid media by employing silica colloid, ordered mesoporous silica SBA-15 and montmorillonite as templates, respectively. Yin and Qiao et al. [29] also prepared hierarchical porous N-doped graphene foams functioned by iron using silica nanoparticles as a template, which had a large specific surface area (918.7 $m^2 g^{-1}$) and abundant active sites. However, it should be noted that most of reported methods using silica as template to prepare porous M-C–N catalysts involve direct mixing the silica hard-template, carbon, nitrogen and metal precursors, followed by pyrolysis and then removal of the template [29,30]. This method frequently fails in forming the uniform porous structure, due to the silica nanoparticles difficultly dissolved in the solvent and incompatible with the other precursors. As we know, the sol-gel process is a typical wet-chemical technique used for the fabrication of both silica and gels materials (such as carbon aerogel [32] and silica ionogel [33]) with designed porous structure. What is more, the microstructure and pore-size of the resulting materials can be controlled through synthesis conditions, such as the composition and drying method of gel, temperature and duration of the pyrolysis *etc*. [33].

In this work, innovative porous Fe–C–N catalyst is derived from the Fe-doped silica ionogel, which was prepared by the sol-gel process by non-hydrolysis reacting tetramethoxysilane (TMOS) with formic acid (HCOOH) within an ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][TfO]) as the solvent. Meanwhile, [EMIm][TfO] also acted the resource of N and S, iron (III) acetylacetonate ($Fe(acac)_3$) acted as iron source and 3D porous silica framework acted as template. The procedure is shown in Scheme 1. Our protocol allows for the simultaneous optimization of both hierarchical porous structure and surface functionalities of N, S-dual-doped carbon with Fe-N_x active sites. Meanwhile, FeS nanocrystals are anchored on the functionalized carbon to form additional active sites. Therefore, the obtained FeS-decorated hierarchical porous N, S co-doped carbon catalysts demonstrate outstanding ORR activity, excellent stability and good tolerance to methanol in alkaline media. The enhanced electrochemical performance enables the proposed catalyst to be the promising NPMCs candidate to commercial Pt/C in energy conversion and storage devices, such as alkaline fuel cells and metal-air batteries.

2. Experimental

2.1. Materials

Iron (III) acetylacetonate ($Fe(acac)_3$), tetramethoxysilane (TMOS), formic acid (HCOOH, 98%) and commercial Pt/C (20 wt% Pt) were purchased from Alfa Aesar. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]TfO) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Science.

2.2. Synthesis of ionogel-Fe–C–N catalyst

The typical Fe–C–N catalyst with a nominal $Fe(acac)_3$ content of 15 wt% was prepared as follows: $Fe(acac)_3$ (0.459 g) was dispersed uniformly in the mixed solution of [EMIM]TfO (10 mmol) and ethyl alcohol (40 mmol) under constant ultrasonic treatment for 1 h, then TMOS (10 mmol) was added and the solution was under sonication for 30 min. HCOOH (78 mmol) was added to the solution under sonication for 5 min. After that the solution was allowed to gel for 36 h at 40 °C. Then the gel was crushed into power. The resulting power was pyrolyzed under nitrogen atmosphere at 1000 °C for 2 h. Then, the power obtained was immersed into 40 ml of 10 wt% HF with stirring at room temperature overnight to remove the SiO_2 substrate. To further remove the other inactive species, the catalyst was etched by refluxing in 20 ml of 2 M H_2SO_4 at 110 °C for 8 h. Finally, the catalyst was heat-treated again in a nitrogen atmosphere at 1000 °C for another 2 h and was denoted as Ionogel-Fe–C–N catalyst.

2.3. Synthesis of control catalysts

To validate the role of silica template, the control catalyst IL-Fe–C–N was prepared in parallel by the same method as that for Ionogel-Fe–C–N except for no sol-gel process: $Fe(acac)_3$ (0.459 g) was dispersed uniformly in the mixed solution of [EMIM]TfO (10 mmol) and ethyl alcohol (40 mmol) under constant ultrasonic treatment for 1 h, then the mixture was pyrolyzed under nitrogen atmosphere at 1000 °C for 2 h. The power obtained were then etched by refluxing in 20 ml of 2 M H_2SO_4 at 110 °C for 8 h. Finally, the catalyst was heat-treated again in a nitrogen atmosphere at 1000 °C for another 2 h.

Another control catalyst Ionogel-C–N was also prepared in parallel by the same method as that for Ionogel-Fe–C–N except for no addition of $Fe(acac)_3$.

2.4. Characterization

Power X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 ADVANCE power X-ray diffractometer with a Cu Kα (λ = 1.5418 Å) radiation source. Raman spectra was obtained from a LabRAM HR800 Laser Confocal Micro-Raman Spectroscopy with 532 nm excitation laser. The morphologies of the catalysts were characterized by Tecnai 12 transmission electron microscope (TEM) and FEI Tecnai G2 F20 high resolution TEM (HRTEM). Scanning electron microscope (SEM) with a field emission scanning electron micro-analyzer (HITACHI S-8010) was carried out with energy dispersed X-ray spectroscopy (EDS). The specific surface areas (SSA) and the pore-size distributions (calculated by DFT method) were analyzed by N_2 adsorption/desorption isotherm with a Quantachrome Autosorb IQ_2-VP instrument. The surface properties were determined by X-ray photoelectron spectroscopy (XPS) from an ESCALAB 250Xi (Thermo Fisher) attached with an Al Kα X-ray radiation.