Iron and nitrogen co-doped carbon derived from soybeans as efficient electro-catalysts for the oxygen reduction reaction

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A B S T R A C T

Iron and nitrogen co-doped carbon (Fe-N/C) materials were fabricated by one-step pyrolysis of the mixture of $FeCl_3$ and the low-cost biomass soybeans in N_2 atmosphere at different temperatures. The physical properties of the prepared Fe-N/C catalysts were evaluated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) et al., the catalytic activity and stability of the Fe-N/C catalysts toward the oxygen reduction reaction (ORR) in alkaline solution were investigated by the electrochemical techniques. The results show that Fe is mainly in the form of Fe_3O_4 with the particle size of about 10 nm and encapsulated by thin graphite layers, and the content of Fe decreases from 1.19 to 0.24 wt.% with the increase of pyrolysis temperature from 600 to 900 °C. The ORR activity on the sample prepared at 700 °C (Fe-N/C-700) is preferable among the series of Fe-N/C catalysts, with the half-wave potential of the ORR shifting negatively only about 0.020 V as compared to that on the commercial Pt/C (40 wt.%, JM). The superior electro-catalytic performance of the Fe-N/C-700 catalyst would be due to the higher degree of the graphitization, the higher total contents of the pyridinic-N, quaternary-N/graphitic-N, as well as the relatively higher Fe_3O_4 content and surface area. The electron transfer number of the ORR on the Fe-N/C-700 catalyst approaches four indicating the 4-electron transfer pathway. Besides, the methanol tolerance and durability are superior to those on the Pt/C.

1. Introduction

With the gradual recognition of the energy crisis and environmental protection [1], it is urgent to find renewable and highly efficient clean energy sources, such as fuel cells, super-capacitors, solar cells, and so on [2]. Among these candidates, fuel cells attract numerous attentions because of their higher power efficiency, diversiform raw fuel materials and environmental amity et al. [2,3]. The cathode oxygen reduction reaction (ORR) is one of the key steps for fuel cells due to its sluggish kinetics and the main voltage-drop of the cells [4,5]. As the ORR catalysts, Pt and its alloys are widely used because of their relatively high activity and stability. However, many issues about the high cost, limited reserves, instability over long-term operations, and the susceptibility to fuel crossover effect et al. [6–9] hinder the large-scale application. Thus, great efforts have been devoted to develop the non-Pt materials as the promising substitutions, for example

precious metals Pd [10], Ag [11], transition metal oxides [7], organics macrocycles compounds [12], non-metal atoms doped carbons [13], and so on.

Among these various candidates for the non-Pt ORR catalysts, nitrogen-doped carbon catalysts are considered to be the most potential candidate to replace the Pt-based catalysts [14] due to their comparable or even superior ORR activity, long-term stability, especially, immunity to methanol/CO [15,16]. However, the traditional raw materials for the nitrogen sources are often harmful organic compounds (e.g., ethylenediamine [17], 1,2-phenylenediamine [18], aniline [19], acetonitrile [20]), and the carbon skeleton are mostly based on some expensive nano-carbon materials, such as carbon nanotubes [21], nanofibers [22,23], graphene complexes [24], and so on. Furthermore, in order to enhance the catalysts unit volume activity, the costly, complicated and even harsh synthetic methods, such as electrospining [23], chemical vapour deposition [25], aerosol pyrolysis [26], self-assembly of 3D aerosols [27,28], silica-based template synthesis [14] et al. are often used. All of these nitrogen/carbon sources and the preparation methods mentioned above are not suitable for large-scale cost-efficient application.

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Thus, it is urgent and significant to synthesize N-doped carbon catalysts with the nature of high efficiency, green, convenience, as well as the excellent performance toward the ORR. Then, some biomasses are extensively used to synthesis the porous and activated electrocatalysts, like human hair [29], egg white [30], catkin [31], ginkgo leaves [32], and so on. Soybean, as a common cheap, easily available and environment-friendly crop, contains high protein and carbonhydrates contents, being about 36.49 wt.% and 30.16 wt.%, respectively [33]. The high protein content guarantees that soybean is a good nitrogen source, and the high N-containing content is of great benefit to enhance the amount of doped nitrogen and the numbers of the active sites. On the other hand, the high carbonhydrates content means soybean is also a good carbon source. Therefore, using soybeans as the raw material for the N-doped carbon is practicable. Meanwhile, it is known the existence of Fe species would contribute to the decomposition and the graphitization of the soybeans [34], and the co-existence of Fe with N and C may enhance the ORR activity.

In this work, we demonstrate a facile and green route to synthesize Fe-N/C catalysts by one-step pyrolysis of the mixture of soybean powder and $FeCl_3$ at different temperatures (from 600 to 900 °C). The physical properties of the prepared catalysts have been characterized, and the ORR activity and stability, as well as the methanol tolerance of the Fe-N/C catalysts in alkaline solution have been determined and compared with those of the commercial Pt/C.

2. Experimental

2.1. Chemicals and materials

The raw soybeans purchased from a local market were washed for several times and dried to constant weight for use. The Pt/C (40 wt.%) was obtained from J.M. Corp., and the other chemicals $FeCl_3 \cdot 6H_2O$, NaOH, H_2SO_4 bought from Guangdong Xilong Chemical Co. Ltd. were analytical reagents and used as received without any further treatment unless otherwise specification.

2.2. Synthesis of Fe-N/C catalysts

The detailed processes for the synthesis of Fe-N/C catalysts were as follows: firstly, the soybean milk was prepared by soybean milk machine (Joyoung) with 30 g soybeans and 450 mL distilled water, then 74.7 g $FeCl_3 \cdot 6H_2O$ was added into the soybean milk. To insure the Fe species distributed in the soybean milk uniformly, the soybean milk with $FeCl_3$ was milled for 24 h with the speed of 400 rpm, and then followed by a freeze drying process to guarantee the three-dimensional structures of the Fe-N/C precursors not collapsed. Secondly, the Fe-N/C precursors were annealed at controlled temperatures (600, 700, 800 and 900 °C) for 2 h in purified N_2 with the gas flow rate of 100 mL/min and the heating rate of 5 °C/min, and then cooled to room temperature under N_2 gas protection. Finally, in order to remove the residual soluble Fe species, the heat treated samples were ultrasonically treated in 0.5 M H_2SO_4 for 8 h, then washed by deionized water for several times until the pH of the filtrate approached 7. After dried in vacuum at 70 °C for 10 h, the final products were obtained and denoted as Fe-N/C-T with T being the pyrolysis temperature.

For comparison, the catalyst without Fe doping (N/C-700) was also prepared with the same preparation method as that for the Fe-N/C-700 catalyst except that $FeCl_3 \cdot 6H_2O$ was added.

2.3. Physical characterization

Thermogravimetric (TG) analysis was performed with NETZSCH STA449C instruments under N_2 atmosphere at a heating rate of 5 °C/min. X-ray diffraction (XRD) was performed on Rigaku X-2000 diffractometer using Cu Kα radiation with a Ni filter to analysis the crystalline structures of the catalysts. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were operated on JEOL JEM-2011EM microscope and TitanG2 60-300, respectively, to observe the catalysts morphologies and elements mapping. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Fisher Scientific K-Alph 1063 (UK) using an Al Kα radiation (1486.6 eV) to analysis the element valences. The Fe, C and O/N elemental analysis were carried out on TMAG IRIS Advantage 1000, LECO CS600 and LECO TCH600, respectively. Brunauer–Emmet–Teller (BET) surface area was determined on Micromeritics ASAP 2010 instrument with nitrogen adsorption at 77 K using the Barrett–Joyner–Halenda (BJH) method. Incremental pore size distributions were obtained from the nitrogen adsorption isotherms by the nonlocal density functional theory.

2.4. Electrochemical measurements

Electrochemical measurements were performed with the three-electrode system on CHI 660D electrochemical workstation (Chenhua Company) and bipotentiostat (Pine Instrument). The catalyst film covered glassy carbon (GC) electrode (ϕ 5 mm for rotate disk electrode: RDE and 5.7 mm for rotating ring-disk electrode: RRDE) was served as the working electrode; Pt-wire and Hg/HgO electrode were used as the counter and reference electrodes, respectively. The working electrode was prepared as follows: the homogeneous ink composed of 5.0 mg catalyst, 2 mL anhydrous ethanol and 30 μL Nafion solution (5 wt.%, DuPont) was prepared by sonication for 15 min. Then 40 μL of the ink was evenly cast onto the clean GC disk drop by drop with a syringe, and then dried in air [35]. Before the electrochemical tests, the catalysts were electrochemically cleaned by 20 cycles of cyclic voltammetry (CV) scanning between −0.8 and 0.2 V (vs. Hg/HgO) in N_2-saturated 0.1 M NaOH solution with the scan rate of 100 mV s^{-1}. The electrochemical property and the catalytic activity toward the ORR of the catalysts were characterized through the CV and the linear scanning voltammetry (LSV) curves, which were recorded in N_2- and O_2-saturated 0.1 M NaOH solution, respectively. In order to detect the HO_2^- yields and the electron transfer numbers (n), the RRDE measurements were also performed with the ring potential biased at 0.20 V (vs. Hg/HgO). The HO_2^- yields and the electron transfer numbers (n) of the ORR were calculated by the equations $X_{HO2-} = (2I_{ring}/N)/(I_{disk} + I_{ring}/N)$ and $n = 4 - 2 \times X_{HO2-}$, respectively, where N is the collection efficiency(0.38), I_{disk} and I_{ring} are the currents at the disk and ring electrodes, respectively. The stability of the catalysts was evaluated by the chronoamperometry at −0.40 V (vs. Hg/HgO) in O_2-saturated 0.1 M NaOH solution with the rotation rate of 900 rpm. In this paper, all the initial electrode potentials (vs. the Hg/HgO) tested in 0.1 M NaOH solution were transformed to values (vs. the reversible hydrogen electrode: RHE) by the equation ($E_{vs.RHE}/V = E_{vs.Hg/HgO}/V + 0.924 V$) unless otherwise specification.

3. Results and discussion

3.1. The thermal behavior of the soybean powder

The thermal behavior of the soybean powder in purified N_2 atmosphere was characterized and the TG curve is shown in Fig. 1. It can be seen that three mass loss regions can be observed. In the first region from room temperature to 193 °C, the mass loss is about 8.3 wt.%, which likely results from the loss of the physically absorbed water and lattice H_2O. In the second region from 193 to 510 °C, a sharp mass loss of 64.8 wt.% can be observed which is