



Nitrogen doped sublimed carbon as non-noble metal catalyst for oxygen reduction reaction



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ABSTRACT

A sublimed carbon has been synthesized by a simple solid-state pyrolysis method and the carbon works as non-noble metal oxygen reduction catalyst after doping with nitrogen. The content of nitrogen introduced by doping is found to be a factor influencing the electrocatalytic activity. The nitrogen doped carbon can find potential applications in fuel cells and other devices where oxygen reduction reaction works as cathode reaction.

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1. Introduction

Fuel cell is among the most promising alternative energy sources for the near future due to a lot of advantages such as high energy conversion efficiency, clean, simple structure, and quick start up at low temperature [1,2]. However the efficiency of fuel cell is limited by the slow kinetics of cathodic oxygen reduction reaction (ORR) [2,3]. To deal with this problem Pt and its alloys are usually used as catalyst for the ORR to reduce the over potential. The use of Pt will inevitably increase the cost of fuel cell. Besides the price Pt-based catalysts also have drawbacks such as easily be poisoned by CO during the reaction and not enough stability [4]. Thus cheaper cathode catalyst alternative to Pt has become a hot topic in fuel cell research. Enormous efforts have been made to develop non-noble metal catalysts in the last several decades [5–7]. In 1964 Jasinski group reported the cobalt phthalocyanines (CoPc) as ORR catalyst for the first time, which started a new research field of non-noble metal catalyst for ORR [8]. This group of catalyst is classified as metal macro cyclic compounds; the metal can be Fe, Co, Ni or other transition metal. The active sites of this kind of catalyst are explained to be the metal–nitrogen bonds on the carbon matrix [9].

By using a ball milling method the activity of Fe–N–C catalyst reaches similar level with Pt/C catalyst in fuel cell test [1,10]. However in half cell test the activity of the best Fe–N–C catalyst is

inferior to Pt/C in acidic environment and close to Pt/C in alkaline solution [11]. Parallel to the metal macro cyclic compounds other materials are also studied as non-noble metal catalyst for ORR. Tungsten carbide has been studied as a possible candidate alone or as support material [11–13]. Metal nitrides and oxides have also been studied as non-noble metal catalyst for ORR [14,15].

A breakthrough is realized by the discovery of ORR activity of a nitrogen doped carbon nanotube [16]. Following this lots of nitrogen doped carbon materials are studied and it is realized that nitrogen doped carbon can facilitate the initial adsorption of oxygen and benefit the break of oxygen–oxygen band [16–18]. However the accurate active sites of the nitrogen doped carbon are not clear. Different explanations are proposed such as pyridinic nitrogen, pyrrolic nitrogen or graphitic nitrogen [19]. The nitrogen doping of carbon can be realized by two procedures. The first one is known as in situ doping where nitrogen is doped into the carbon matrix during the synthesis of the carbon material which is represented by chemical vapor deposition (CVD) or modified CVD methods [20–22]. The second is post-synthesis process where the doping is realized by the pyrolysis of the mixture of carbon material and N-containing precursors [23–25]. The high temperature of the pyrolysis introduces morphological and structural defects during nitrogen doping. Generally, after the in situ process pyridinic nitrogen and/or pyrrolic nitrogen are formed [26] while after the post-synthesis doping process graphitic nitrogen is formed [27].

In this work, we report the synthesis of a sublimed carbon (SC) by the pyrolysis of cation exchange resin at high temperature, and nitrogen doped sublimed carbon (NDSC) is prepared using glycine

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or NH_3 as nitrogen sources. NDSC shows good ORR activity in alkaline solution and the effect of different nitrogen doping method are discussed.

2. Experimental

All chemicals are of analytical grade and used as received from Aladdin Industrial Inc. All water is ultrapure water from HITECH laboratory water purification system with the impedance of 18.3 M Ω .

2.1. Preparation of sublimed carbon (SC)

SC is prepared by the pyrolysis of cation exchange resin at high temperature. In a typical synthesis procedure, 20 g D113 cation exchange resin was added to 250 ml HCl solution (1 mol/L), and then the mixture was stirred for 24 h at room temperature. The resin was washed until the pH value of the filtrate reached 7, then it was dried at 60 °C for a night. Then the dried resin was mixed with 0.3 mol/L FeCl_2 solutions at N_2 atmosphere under magnetic stirring for 10 h, and then the resin was filtered and dried. This procedure was repeated 5 times. The resultant resin was placed in a quartz boat and pyrolyzed at 1150 °C for 1 h with the heating rate of 20 °C/min under N_2 atmosphere. SC was formed on the top wall of the quartz tube. The clusters of SC are collected, grinded and washed with HCl to remove residual Fe.

2.2. Preparation the nitrogen doped sublimed carbon (NDSC)

Two different methods are used to dope nitrogen to SC. The first one is the pyrolysis of SC with NH_3 at 900 °C for 1 h and the sample is labeled as NDSC-1. The second is the pyrolysis of the mixture of as-prepared SC and glycine under N_2 condition. Briefly, SC and glycine with the mass ratio of 1:6 was mixed by 40 ml water under vigorous stirring. Then the suspension was heated and magnetically stirred until solution was evaporated. The sample was transferred to the quartz tube and heated at 900 °C for 1 h under N_2 atmosphere. The sample is labeled as NDSC-2.

2.3. Physical characterizations

The crystal structure were determined on an X-ray diffractometer (XRD, D/Max-III A, Rigaku Co., Japan, $\text{CuK}\alpha$, $\lambda = 1.54056 \text{ \AA}$ radiation). The morphologies of all samples were performed by transmission electron microscopy (TEM, JEM-2100HR, JEOL Ltd., Japan) operating at 200 kV. The Raman spectra were carried out using a Laser Micro-Raman Spectrometer (Renishaw inVia, Renishaw plc, UK). The elements analysis was measured by X-ray photoelectron spectroscopy (XPS), ESCA Lab 250 (Thermo VG) with 200 W Al K α radiation in twin anode and the distance between X-ray gun and sample is about 1 cm. The analysis chamber pressure is about 2×10^{-7} Pa and the pass energy is 20 eV for high resolution scans. Thermogravimetry–Fourier transform infrared spectrometry is performed on TG-209 (NETZSCH)/Vector TM-22 (BRUKE).

2.4. Electrochemical characterizations

The ORR measurements were carried out on a potentiostat (PINE instruments) with a three-electrode system at 25 °C. The rotating disk electrode (RDE) with the diameter of 5 mm was used as working electrode; a platinum foil (1.0 cm \times 1.0 cm) and Ag/AgCl (saturated KCl) were used as counter electrode and reference electrode, respectively. ORR was evaluated in the oxygen-saturated 0.1 M KOH electrolyte. The catalysts ink was prepared by same formula: 2.5 mg finely grounded catalyst powders mixed with 5 μl

5 wt% Nafion solution (DuPont Co. Ltd.) and 0.25 ml absolute alcohol in an ultrasonic bath with stirring. Then 10 μl of catalyst ink was deposited onto the electrode and dried naturally under ambient atmosphere. Linear sweep voltammetry (LSV) was performed with a scan rate of 10 mV/s, and the rotating speed was from 400 to 2500 rpm, voltage range from 0.2 V to -0.8 V (vs. Ag/AgCl) for 0.1 M KOH. Koutecky–Levich (K–L) plots were analyzed at selected potentials. The electron-transfer number (n) was calculated by the slopes and intercepts of their linear fit lines on the basis of the K–L equation as follows [28]:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

in which J is the measured current density; J_K and J_L are the diffusion limiting kinetic-limiting current densities, ω is the rotation speed in rpm, n is the electron transfer number, Faraday constant (F) is 96,485 C/mol. The bulk concentration of oxygen (C_0) is 1.2×10^{-6} mol/cm 3 in 0.1 M KOH. The diffusion coefficient of oxygen (D_0) is 1.9×10^{-5} cm 2 /s in 0.1 M KOH. The kinetic viscosity (ν) is 0.01 cm 2 /s.

3. Results and discussion

3.1. Physical characterization of the materials

The pyrolysis of ion exchange resin is a novel method to prepare graphene proposed by Fu group. This method can produce graphene with high output, good quality and good crystalline structure [29,30]. Different from reported results, in this work a novel carbon material is found on the top of the inner wall of the quartz tube after pyrolysis. Fig. 1a is the photo of the quartz tube, clusters of carbon with metallic luster accumulated on the top surface. The resin is supposed to be carbonized and then graphitized into graphene after high temperature pyrolysis. The carbonization and graphitization of resin happen in the quartz boat and the product is left in the boat. However in our synthesis the product sublimed from the boat and accumulated on the top of the quartz tube. This is the reason why this kind of carbon material is named sublimed carbon. The sublimed carbon is gathered as shown in Fig. 1b. The cluster is inevitably broken during the collecting process, but obviously the size of the cluster is at the centimeter level.

It is necessary to explain why and how the sublimed carbon is formed. Fig. 2 shows the proposed formation mechanism. Fig. 2a is the structure of D113 resin, which is composed by acrylic copolymer and $-\text{COOH}$ group. The H^+ of $-\text{COOH}$ group can be exchanged by other cations. In Fig. 2b the H^+ is substituted by Fe^{2+} , which works as catalyst for the graphitization during the pyrolysis. Fe^{2+} can be exchanged into the chain of the resin, or it can be physically absorbed on the surface of the resin. In both situations Fe^{2+} can work as graphitization catalyst. It is proposed that when Fe^{2+} substitutes the position of H^+ , it will facilitate the break of carbon–carbon bond between $-\text{COOH}$ and the acrylic chain of the resin at high temperature as shown in Fig. 2c. The realization of the sublime process has two vital factors: one is the availability of Fe^{2+} in the acrylic chain of the resin, which is controlled by the concentration of FeCl_2 and times of the repeat in exchanging. The other is the heating rate of pyrolysis process. It is found that only at fast heating rate can sublimed carbon be found.

To reveal the formation mechanism of the sublimed carbon TG–FTIR is used to study the pyrolysis process. As shown in Fig. 3a the first 8% weight loss from 30 °C to 260 °C is the loss of water since no peak is observed in corresponding FTIR of Fig. 3b. From 260 °C to 513 °C the fast weight loss is caused by the formation of

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