Chinese Journal of Catalysis 37 (2016) 1119–1126

available at www.sciencedirect.com

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

Article (Special Issue on Electrocatalysis Transformation)

Catalytic properties of graphitic and pyridinic nitrogen doped on carbon black for oxygen reduction reaction

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ARTICLE INFO

Article history:
Received 20 March 2016
Accepted 11 May 2016
Published 5 July 2016

Keywords:
Carbon black
Heat-treatment
Oxygen reduction reaction
Nitrogen doping
Carbon-based catalysts

ABSTRACT

Pure graphitic nitrogen (G-N) was doped on carbon black by Hummers method and a following heat treatment was used to transform the G-N to pyridinic (P)-N. An oxygen reduction reaction (ORR) study showed that the G-N site doped on carbon gave a two-electron ORR with H_2O_2 as the main product, while the P-N site gave the four-electron process of ORR and decreased the production of H_2O_2. The results help the understanding and design of doped N-based ORR electrocatalysts.

1. Introduction

Exploring efficient electrocatalysts for the sluggish oxygen reduction reaction (ORR) is desirable for the commercialization of fuel cells [1] and metal-air batteries [2]. In the past decade, intensive studies have been done to develop low cost, high efficient ORR electrocatalysts, such as the doped N-based metal-free and Pt-free electrocatalysts [3,4]. Concerning the active sites on N-doped carbon materials for ORR, there are four types of N-based active sites, namely, pyridinic N (P-N), pyrrolic N (Py-N), graphitic N (G-N) and oxidized N (O-N) [5]. In spite of extensive studies, the structure-activity relationship or catalytic mechanism on the different N-containing active sites on carbon is still not clear. Debated questions related to the catalytic activity of different N-containing groups still exist [6,7]. Some experimental data showed that P-N and Py-N were catalytically active [8–13], while others indicated that G-N was active [14–18]. Some reports claimed that both P-N and G-N contributed to the catalytic property but with different roles [6,19]. These observations suggested that to get clear understanding of these N-containing active sites for ORR, it is desirable to get the structure-activity relationship of different doped N-based active sites on carbon. For this goal, some clean models with only one type of N doped site have been reported. In 2013, Wei's group [20] reported a selective synthesis of P-N and Py-N-doped graphene and showed that the pyridinic and pyrrolic sites with a planar structure were catalytically active for the ORR. Qiao's group [7] further showed that the carbon atoms close to P-N were the main active sites among the different nitrogen doping configurations.

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This work was supported by the National Basic Research Program of China (973 Program, 2012CB932800, 2014CB932700), the National Natural Science Foundation of China (21422307, 21303180, 21433003, 21503212, 21503211), and the "Recruitment Program of Global Youth Experts" of China.

DOI: 10.1016/S1872-2067(16)62456-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 7, July 2016

In this work, we used a common carbon black, Vulcan XC-72 (VXC-72) and an acid oxidation (Hummers method) treatment [21] and showed that the Hummers acid oxidation treatment led to pure G-N doping on carbon, and a following heat treatment led to Py-N doping with adsorbed NO_3^- or NO_2^- as the N precursor. Furthermore, for the ORR process, a 2e⁻-pathway with H_2O_2 as the main product was found on the G-N-based active sites while a 4e⁻-pathway existed on Py-N sites with water as the main product, which was consistent with a recent report [22].

2. Experimental

2.1. Sample preparation

The oxidization of VXC-72 was performed by Hummers method [21]. The Vulcan XC-72 was purchased from E-TEK Company. USA. H_2SO_4, $NaNO_3$, $KMnO_4$, H_2O_2 (30%), HCl and KOH were purchased from Beijing Chemical Works. Nafion solution (5 wt%) was obtained from Sigma-Aldrich. All chemicals were used without further treatment. Ultrapure water with a specific resistance of 18.23 MΩ·cm was obtained by reversed osmosis followed by ion exchange and filtration. The once and twice oxidation products were denoted as VXCO-1 and VXCO-2, respectively. VXCO-1 was prepared by stirring 1.0 g VXC-72 powder and 0.5 g $NaNO_3$ into 23.0 mL concentrated sulfuric acid (98%). The ingredients were mixed in a 500.0 mL round-bottomed flask that had been cooled to 0 °C in an ice bath. While maintaining vigorous agitation, 3.0 g $KMnO_4$ was carefully added to the suspension. The ice bath was then removed and the suspension was heated to 35 °C, where it was maintained for 60 min. After that, 46.0 mL water was slowly dropped into the flask, causing violent effervescence and an increase in temperature to 98 °C. The mixture was further stirred for 30 min. Finally, 140.0 mL distilled water and 10.0 mL H_2O_2 were added dropwise and the reaction was terminated. The generated solid VXCO-1 was separated by centrifugation, washed and finally dried under vacuum. The further oxidized product VXCO-2 was based on VXCO-1 formed by the same Hummer method. VXC-72, VXCO-1 and VXCO-2 were then subjected to thermal treatment at 900 °C under N_2, which were denoted as VXC-72(900), VXCO-1(900) and VXCO-2(900), respectively. VXCO-1 was also subjected to a thermal treatment at 800 and 1000 °C under N_2 gas, which were denoted as VXCO-1(800) and VXCO-1(1000), respectively. The resulting black powder was carefully collected because the products had a low mass density and was very easily blown away.

2.2. Characterization

The morphology and dimensions of the samples were obtained using a field emission scanning electron microscope (SEM) (XL30) operated at an accelerating voltage of 10 kV. BET surface areas (A_{BET}) and pore volumes were obtained from N_2 adsorption-desorption isotherms using an ASAP 2020 instrument at –196 °C. The N content in the catalysts were obtained from elemental analysis (EA, Vario EL CUBE, Elementar). X-ray photoelectron spectroscopic (XPS) measurements were performed on an AXIS Ultra DLD (Kratos company) using a monochromic Al X-ray source. The Raman spectrum was obtained on a laser confocal Raman spectroscopy (Labram-010, Horiba-JY) employing the Nd: YAG laser wavelength of 633 nm. X-ray diffraction (XRD) patterns were obtained on a D8 ADVANCE (Bruker company, Germany), using filtered Cu Kα radiation (40 kV, 30 mA).

2.3. Electrochemical measurements

The electrochemical performance was conducted in 0.1 mol/L KOH solution. The counter and reference electrodes were a platinum wire and SCE electrode, respectively. The potential of the electrode was controlled by a CHI 750E system (CH Instrument Co., USA). Cyclic voltammetry (CV) was performed from 0.2 to −1.2 V at 50 mV/s after purging the electrolyte with O_2 or N_2 for 30 min. Linear sweep voltammetry (LSV) measurements were performed using a rotating disk electrode (RDE) at different rotating speeds from 225 to 1600 r/min in an O_2 saturated electrolyte from 0.2 to −1.2 V (vs. SCE) at a sweep rate of 5 mV/s in O_2 saturated KOH solution (0.1 mol/L). For the RRDE measurements, the disk electrode sweep was from 0.2 to −1.2 V vs. SCE while the Pt ring potential was kept at 0.5 V vs. SCE at a scan rate of 5 mV/s after O_2 was purged for about 30 min into the KOH solution (0.1 mol/L). The percentage of HO_2^- generated from the ORR and the electron transfer number (n) were estimated by the following equations [23]:

$$HO_2^-\% = 200 \times \frac{i_R / M}{i_D + i_R / M} \quad (1)$$

$$n = 4 \times \frac{i_D}{i_D + i_R / M} \quad (2)$$

where i_D is the disk current density, i_R is the ring current density and M is the current collection efficiency of the Pt ring disk. M was 0.37 from the reduction of $K_3Fe[CN]_6$.

All the current densities were normalized to the electrode surface area. All electrochemical experiments were carried out at room temperature.

3. Results and discussion

3.1. Catalyst characterization

As shown in Fig. 1(a), after the reaction, the supernatant containing small pieces of graphene oxide (GO) was discarded. The obtained precipitant was either washed directly with a large amount of water by repeated sonication and centrifugation until pH ≈ 7 or re-oxidized one more time. The water-washed samples (VXCO-1 and VXCO-2, representing the samples obtained after one or two acid oxidation, respectively) were then heated at 900 °C for three hours under flowing N_2 to get the final heat treated samples (VXCO-1(900) and VXCO-2(900)). SEM analysis showed that the surface of the carbon nanoparticles became smoother after the acid treatment. The flatness of the surface was in the order: VXCO-2 > VXCO-1 > VXC-72. This result was consistent with the A_{BET}