

Co and N co-doped carbon nanotubes as efficient catalysts for oxygen reduction reaction

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ABSTRACT

In hydrogen fuel cells, the sluggish oxygen reduction reaction (ORR) requires the catalysts used. Unfortunately, the precious platinum based catalysts still exhibit the best ORR activity in the commercial hydrogen fuel cells. Therefore, developing non-precious metal catalysts ORR become an important aspect for the utilization of hydrogen energy by using hydrogen fuel cells to develop non-precious catalysts and understand their active sites of ORR, herein the cobalt and nitrogen co-doped CNTs, nitrogen-doped CNTs and cobalt doped CNTs were prepared, respectively, and their catalytic properties toward ORR were tested and compared. The surface composition, microstructure and ORR performance of the samples were examined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), pore/specific surface analyzer and electrochemical methods. The results demonstrate that as the catalyst, the cobalt and nitrogen co-doped CNTs owns the highest ORR limiting current density, the most positive ORR onset potential and the largest transfer electron number close to four, and thus exhibits the better ORR catalytic performance compared to the other two samples of the nitrogen-doped CNTs and the cobalt doped CNTs. The good ORR performance of cobalt and nitrogen co-doped CNTs can be attributed to its active sites of nitrogen containing functional groups, cobalt or cobalt oxides, Co-N_x

1. Introduction

Hydrogen fuel cells can convert chemical energy into electricity through the electrochemical oxidation of hydrogen and the electrochemical reduction of oxygen in the separated electrodes and are considered as one of the ideal power sources for automotive and stationary applications due to their high energy efficiency, high power density, as well as low/zero emissions [1–3]. However, to become commercially available, hydrogen fuel cells have to overcome the barrier of high cost caused by the exclusive use of platinum and platinum-based precious metal catalysts in both hydrogen oxidation and oxygen reduction at the electrodes. Therefore, the numerous efforts have been focusing on developing non-precious metal catalysts or metal-free catalysts [4,5].

One of the most promising non-precious metal catalysts in hydrogen fuel cells is carbon-supported transition metals or their compounds, which have gained increasing attention due to their promising activity towards ORR, along with the utilization of abundant and inexpensive raw materials [6–8]. Since the ORR activity of cobalt phthalocyanine in the alkaline electrolyte was found in 1964 [9], transition metal macrocycle compounds have been the focus of transition metal-based catalysts, such as (Fe, Co)/(porphyrins, phthalocyanines) [10–12]. However, stability issues arose from catalyst structure decomposition in the presence of acid resulted in the loss of catalytic activity [13]. It was found that high-temperature heat treatment on metal macrocycle compounds can not only enhance the stability of the catalysts but also increase their catalytic activity significantly, despite the atomic configuration of macrocycle compounds was found to partially or entirely decompose [14–16], indicating that the expensive macrocycle compounds of transition metal are not requisite for getting catalytically active sites, but the nitrogen species in transition metals or carbon supports are significant [17–19].

Carbon nanomaterials are attractive materials for catalyst support in fuel cells due to their microstructure and novel properties such as nanometer size, high accessible surface area, good electronic conductivity and corrosion resistance. Since Gong et al., reported the high ORR activity of nitrogen-doped CNTs in 2009 [20], the doped carbon materials as either metal-free catalyst or catalyst supports have been one of the hottest topics in the catalysts of fuel cell. Nitrogen-doped carbons can be prepared either through post-treatment on the as-prepared carbons with nitrogen-containing agents such as urea, hydrazine hydrate, and so on [21–23], or direct carbonization of nitrogen-containing precursors such melamine, polyaniline, polypyrrole and so on [24–26]. The ORR activity of N-doped carbons relates not only the nitrogen amount but also the types of nitrogen containing functional groups [27,28], besides specific surface area, pore structure and conductivity of N-doped carbons [29]. The catalysts of N-doped carbons supported transition metal or compounds can be synthesized either through the heat-treatment of transition metal macrocycle compounds [30–32] or by loading transition metals on the doped carbons [33–36]. Generally, they both require a subsequent heat-treatment process to enhance the stability of catalysts

[37–39]. These heat-treatment processes have been confirmed to result the formation of coordination of metal and nitrogen (M-N_x). Consequently, it has been recognized that the catalytic activity toward ORR mainly originates from the M-N_x sites of catalysts [40–42].

However, the real catalytically active sites of these transition metal based catalysts are still on the controversy. Using the carbide-derived carbons as a template to prepare the ORR catalysts with and without transition metal elements, Jaouen et al., gave their evidence that the true ORR activity is from the nitrogen-carbon structure in the outer surface of the nitrified carbon layer [43]. Although N-doped carbon materials are exhibiting their advantages in ORR catalysis [44,45], they are not be fully identified as metal-free catalyst since even trace metal elements contained in carbon materials can probably catalyze the ORR. However, the residual metals in carbon materials are difficult to be removed completely [46].

In the studies on ORR catalysts, much more attentions have been paid on the active sites of ORR, which are either oriented to metal and metal compounds sites or nitrogen-containing sites [47]. However, it should also be noted that there are possible synergistic effects of the different active sites on ORR.

In this work, three kinds of catalysts of the cobalt and nitrogen co-doped CNTs, the cobalt doped CNTs and the nitrogen-doped CNTs were prepared, respectively. These catalysts have a common characteristic experiencing the heating treatment in high pure nitrogen gas at 800 °C. The ORR properties of catalysts were examined and compared. The results demonstrate that the catalyst of nitrogen and cobalt co-doped CNTs combines the active sites of the nitrogen containing functional groups, cobalt and cobalt oxides and Co-N_x structure, therefore, exhibits the excellent performance of electrolytic ORR close to commercial Pt/C catalyst used in hydrogen fuel cells.

2. Experimental

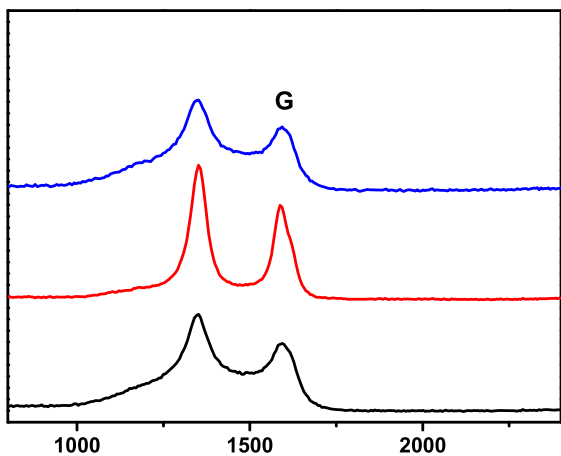
2.1. Chemicals and reagents

Pyrrole (C₄H₅N, C. P. grade, ≥ 99.8%), Ammonium Persulfate ((NH₄)₂S₂O₈, A. R. grade, ≥ 99.7%), Hydrochloric acid (HCl, 1 M), Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, A. R. grade, ≥ 99.7%), Sodium borohydride (NaBH₄, G. R. grade, ≥ 99.7%), Potassium hydroxide (KOH, A. R. grade, ≥ 99.7%), and Sodium hydroxide (NaOH, A. R. grade, ≥ 99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ultrapure N₂ and O₂ (supplied by the Anshan Angang gas Limited Liability Company) were used for de-aeration and the oxygen reduction reaction tests, respectively. All the aqueous solutions were prepared with ultrapure water supplied by an ultrapure water system.

The catalysts were synthesized through the routes as shown in Fig. 1. The catalyst of nitrogen-doped carbon nanotubes (NCNTs) was prepared by using the technology of thermal conversion of polymer coating [48]. The polypyrroles coated CNTs (PPy@CNTs) were firstly prepared by in-situ chemical polymerization of pyrrole onto the CNTs. The PPy@CNTs as prepared were placed into a horizontal furnace

for all the samples. The peaks around 2θ of 44.2° , 51.6° and 75.6° for the Co-CNT800 and Co-NCNT800 originate from the metallic cobalt of Co (111), Co (200) and Co (220), respectively. The cobalt is produced mainly through the reduction of Co^{3+} adsorbed on the carbon surface by the reducing agent of NaBH_4 , and partially formed due to the carbothermal reduction reaction of the absorbed cobalt ions and cobalt oxides with carbons. It is easily noted that compared to the Co-CNT800, C (002) peak intensity of Co-NCNT800 become weak, which can be attributed to the nitrogen doped amorphous carbon layer on the CNTs, decreasing the graphitization degree of sample. This can be further confirmed by the Raman spectra of samples. Raman spectroscopy technique has been well demonstrated to characterize the degree of structural order of materials. As shown in Fig. 3D,G bands at 1350 cm^{-1} and 1590 cm^{-1} for the Co-CNT800 and Co-NCNT800 can be clearly seen, the latter shows more weak and broad peaks, probably due to the outer nitrogen doped amorphous carbon layer of sample decreasing scattering intensity, lightly. Since the D and G band reflects the defect and graphitization degree of carbon materials, respectively, the intensity ratio (I_D/I_G) can give us the structural order information of samples. The I_D/I_G is 1.36 and 1.43 for Co-CNT800 and Co-NCNT800, respectively, indicating that there are more defects in carbon matrix of Co-NCNT800. The more defects such as the edges of graphene along with nitrogen containing species in carbon matrix should enhance the activity for oxygen adsorption and thus probably improve the ORR performance of catalysts.

The N_2 adsorption-desorption isotherms of samples are shown in Fig. 4. All the isotherm belongs to type IV isotherm, at super low pressure ($P/P_0 < 0.1$), the adsorption volume of samples rise rapidly, indicating more micropores in the samples. The increase of adsorption volume at high relative pressure suggests a large mesoporous volume in the samples. The SSA and pore parameter of samples is listed in Table 1. The NCNT800 has the biggest SSA owing to the nitrogen doped porous carbon layer converted from the PPy coating containing more micropores. The Co-NCNT800 also exhibits relative higher SSA and microporous volume than the Co-CNT800,



since its support has the similar pore structure with the NCNT800.

X-ray photoelectron spectroscopy (XPS) is a useful tool to study the surface composition of materials. Fig. 5a is the XPS survey spectra of samples, the peaks around binding energy of 282.5, 398.5, 532.2 and 780.7 eV are assigned to C 1s, N 1s, O 1s and Co 2p. Table 2 gives the relative atomic percentage of C, O, N and Co of samples according to the XPS analysis results. The elemental cobalt content of Co-NCNT800 (1.37 at %) is much higher than the Co-CNT800 (0.42 at %), which can be attributed to the improved hydrophilicity and surface activity of NCNT support of Co-NCNT800 enhancing the deposition of cobalt or its compounds. It can be also noted that the higher oxygen content of the Co-NCNT800, which should arise from the higher cobalt oxides and oxygen containing species onto the surface of sample. The Co-NCNT800 has almost the same nitrogen content with the NCNT800, suggesting that cobalt doping does not influence the nitrogen amount of sample. The N 1s spectra of NCNT800 and Co-NCNT800 are shown in Fig. 5b, c. The peaks around the binding energy of 397.5, 400.1 and 401.5 eV are assigned to pyridinic-N, pyrrolic-N and quaternary-N of both samples [49,50]. Significant difference between the two samples is that there is another peak around 399.5 eV arising from Co- N_x coordination structure [51] only for the Co-NCNT800, which is most probably produced by the co-doping of cobalt and nitrogen in the sample. Moreover, it worthy to note that the relative content of quaternary-N of Co-NCNT800 is much higher than the NCNT800 as shown in Table 3, indicating that the doping cobalt in the sample enhances the conversion of pyrrolic-N into quaternary-N. It had been demonstrated that the quaternary-N functional groups in the nitrogen doped carbon can supply the better activity toward ORR in our previous study [52].

The Co 2p spectrum of Co-CNT800 and Co-NCNT800 are shown in Fig. 5d, e. The cobalt with the different price states are the prominent surface composition of both samples. The peaks around the binding energies of 779.1, 780.2, 782.6, 784.7 and 795.6 eV (Co $2p_{1/2}$) are assigned to the Co_3O_4 , CoO and Co_2O_3 species or their mixtures, the peak of binding energy at 803.0 eV maybe the presumable existence of CoO [42]. Especially, noting that a peak of the Co- N_x structure can be

Catalysts

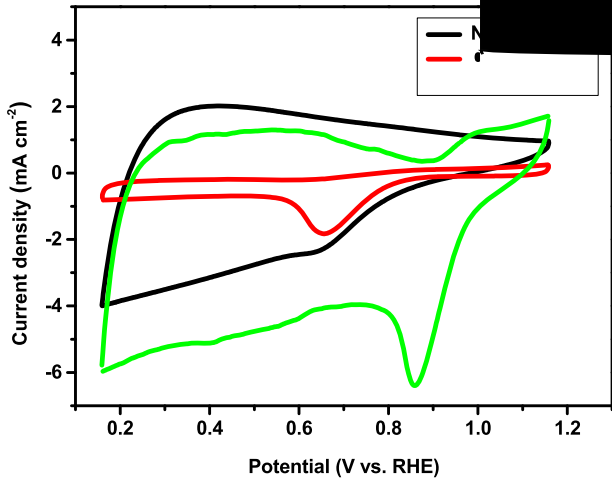
NCNT800
Co-CNT800
Co-NCNT800

Co-NCNT800
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 CNT800 has not
 cobalt oxides, and
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of the catalysts we
 prepared (0.1 mg) of samples in O_2 -
 saturated 0.1 M KOH solution was determined by using the
 rotating disk electrode (RDE) at room temperature. The LSV
 curves of samples as prepared and commercial Pt/C (20 wt%)
 catalyst tested at 1600 rpm are shown in Fig. 7a, the Co-
 NCNT800 owns much higher the limiting current density of
 oxygen diffusion (4.92 mA cm^{-2} at 0.2 V) and more positive the

onset potential of ORR (1.06 V) than the samples of NCNT800
 and Co-CNT800, which further confirms that the co-doping of
 more significantly bring the sample



performance with the commercial Pt/C catalyst whose onset
 potential and limiting current is 1.00 V and 5.16 mA cm^{-2} ,
 respectively.

The ORR mechanism based on electron transfer number
 was analyzed by using K-L equations [58]:

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

$$B = 0.2nFC_0D_0^{2/3}v^{-1/6}$$

$$J_K = nFkC_0$$

In the equations, J , J_K and J_L are the measured current
 density, kinetic current density and limiting diffusion current
 density, respectively. ω is the angular velocity of RDE, n is the
 total electron transfer number of ORR, F (96485 C mol^{-1}) is the

Faraday constant. In the 0.1 M KOH solution, the bulk concentration of oxygen is C_0 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and the diffusion coefficient of O_2 is D_0 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$). The linear K-L plots (J^{-1} vs $\omega^{-1/2}$) of all samples obtained from the LSVs at 0.3 V are shown in Fig. 7b. The transfer electrons number of ORR of NCNT800, Co-CNT800, Co-NCNT800 and 20% Pt/C is 1.72, 3.39, 3.64 and 3.91. Since the value of n suggests the dynamic mechanism of ORR, it can be deduced that, similar with commercial Pt/C catalyst, the Co-NCNT800 catalyzed ORR is mainly based on four-electron process.

C

Among the samples of the NCNTs, the cobalt doped CNTs and the cobalt and nitrogen co-doped CNTs we prepared, the Co-NCNT800 exhibits the best catalytic property toward ORR as the results demonstrated above. It can be concluded that the ORR activity of Co-NCNT800 is not only from the active species of cobalt oxides, nitrogen containing functional groups and Co- N_x coordination but also from the synergistic effects of these active species. These active species of ORR can be produced in the catalyst as the same time through the process of heating the composites of cobalt and PPy@CNTs, in which PPy can be converted into nitrogen containing functional groups, the cobalt oxides and the Co- N_x coordination can also be formed immediately. The simple preparation method and good ORR activity of our non-precious metal catalyst makes it promising in developing the hydrogen based fuel cells with high efficiency and low cost.

A

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