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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

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.

E. Chemicals and reagents

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

chemical states of samples were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS was recorded with an ESCALAB250 surface analysis system using Al K α radiation. The deconvolutions of the C 1s, N 1s and Co 2p spectra were performed using a non-linear least squares fitting program with a symmetric Gaussian function.

Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode cell filled with 0.1 M KOH solution at room temperature. A glassy carbon electrode (GCE) coated with the catalyst ink was used as the working electrode. A platinum plate with surface area (1 cm²) was used the counter electrode. The Hg/HgO was chosen as the reference electrode. The GCE was polished by using the slurry of alumina (Al₂O₃, 0.3 and 0.05 μ m), then rinsed thoroughly with ethanol and deionized water in an ultrasonic bath to remove any alumina residues. The catalyst ink was prepared by ultrasonic dispersing 10 mg of catalyst powder in 2 mL ethanol, into which 50 μ L of 5 wt% nafion solution (DuPont) was added and the suspension as prepared was ultrasonically dispersed to get the homogenous solution. A quantity of 20 μ L of the catalyst ink was pipetted out and dropped on the top surface of GCE, finally, the GCE coated with the catalyst ink was dried under a vacuum at 80 °C for 12 h.

Cyclic voltammogram (CV) and linear scan voltammetry (LSV) measurements were performed with an electrochemical analysis system of Reference 3000 workstation (Gamry Instruments, USA). The rotating disk electrode (RDE, RDE710 Rotating Electrode, Gamry Instruments, USA) coated with the catalysts was used for LSV tests. All potentials reported in this work were referenced to the reversible hydrogen electrode (RHE), $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \text{ pH} + 0.098$.

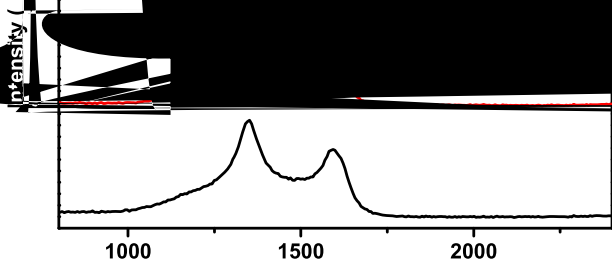
and then the furnace was heating to 800 °C in high pure N₂ atmosphere with a rate of 10 °C min⁻¹ and then the sample was kept at 800 °C for 1 h. The obtained sample is named as the NCNT800. The nitrogen and cobalt co-doped CNTs was prepared as following procedure, the PPy@CNTs of 200 mg and Co(NO₃)₂·6H₂O of 130 mg were ultrasonically dispersed in 50 mL deionized water and then the solution was heated to 80 °C and stirred magnetically for 0.5 h. And then the pH value of the solution containing PPy@CNTs was adjusted to 11 by using 0.1 M NaOH solution. After that 25 mL of 0.17 M NaBH₄ were dropped in the solution. The obtained solid product were filtered and washed several times by deionized water and then dried at 80 °C for 12 h in vacuum condition. Finally, the obtained black powders were heat-treated at 800 °C in high pure N₂ gas by using the same procedure as preparing the NCNT800, the sample was named as the Co-NCNT800. The cobalt doped CNTs were prepared as the same procedure of preparation the Co-NCNT800, but the replacing the PPy@CNTs by the same amount of CNTs as raw materials.

Sample characterization

The powder X-ray diffraction device (XRD, X'pert Powder, Rigaku D/MAX-2500X, Cu K α), micro-Raman spectrometer (HORIBA Xplora Plus, excited by 532 nm lase) and the specific surface area (SSA) and pore structure analyzer (Micromeritics, ASAP2020) was used to characterize the composition and structure of samples. The SSA of samples was determined according to the Brunauer Emmett Teller (BET) method. The

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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 Co₃O₄, CoO and Co₂O₃ 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	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Adsorption average pore width (nm)	Micropore volume (cm ³ /g)
NCNT800	197.1	0.288	11.90	0.082
Co-CNT800	142.8	0.301	7.67	0.001
Co-NCNT800	153.7	0.283	10.57	0.024

identified a bonding energy of 781.5 eV for the Co-NCNT800 sample [53]. The metal N_x sites are often considered as the active sites for ORR [54]. Nevertheless, we shouldn't omit the catalytic effect of the cobalt oxides on ORR [55]. As shown later, the Co-CNT800 with the surface composition only containing cobalt oxides still exhibits the observed ORR activity. The cobalt oxides should be formed due to the oxidation of surface of metallic Co since the exposed metallic cobalt interacts with the aerobic atmosphere or a small amount of oxygen in the electrolyte.

The catalytic properties of samples toward ORR were analyzed by the electrochemical methods. Cyclic voltammograms (CV) of samples in 0.1 M KOH solution are shown in Fig. 6. The ORR peaks around the potential range of 0.6–0.9 V can be observed for the samples, indicating the ORR activity for the catalysts we prepared. It can be noted that the Co-NCNT800 owns the ORR peak potential of 0.861 V, which is much more positive than the NCNT800 (0.64 V) and the Co-CNT800 (0.66 V). Moreover, the Co-NCNT800 also exhibits much higher ORR peak current density than the other two samples. The ORR peak current density excluding the capacitive current is 0.73, 0.132 and 2.972 mA cm⁻² for the NCNT800, Co-CNT800 and Co-NCNT800 in turns. Based on the CVs results, it can be concluded that the Co-NCNT800 owns the best ORR activity among samples. The ORR activity of NCNT800 arises mainly from the pyridinic-N and quaternary-N functional groups [55–57]. For the Co-CNT800, the cobalt oxide contributes to the ORR activity. The Co-NCNT800 has not only pyridinic-N and quaternary-N, but also cobalt oxides, and additional Co-N_x coordination site. These active sites and their combination should give the Co-NCNT800 an excellent ORR property.

To further understand the ORR kinetics of the catalysts we prepared, the linear scan voltammetry (LSV) of samples in O₂-saturated 0.1 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 loading at 1600 rpm) are shown in Fig. 7a, the NCNT800 shows much higher limiting current density of oxygen diffusion (0.2 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 cobalt and nitrogen can more significantly bring the sample ORR activity. Moreover, from the ORR onset potential and the limiting current, the Co-NCNT800 exhibits a comparable ORR

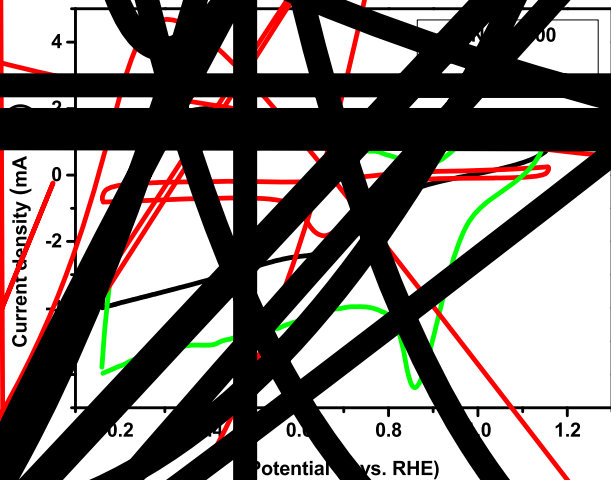


Fig. 7. Cyclic voltammograms of (a) Co-NCNT800, (b) Co-CNT800 and (c) NCNT800 in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹.

The ORR mechanism based on electron transfer number was analyzed by using K-L equations [56, 57]:

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

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

$$J_K = nFkC_0$$

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.

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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.

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