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A Pt-free catalyst for oxygen reduction reaction based on Fe–N multiwalled carbon nanotube composites

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ABSTRACT

An iron-based non-precious metal (NPM) catalyst was synthesized by chemically coating a polymer containing nitrogen, such as polyaniline (PANI), on multiwalled carbon nanotubes (MWCNTs), followed by iron complexation and heat treatment in a decomposable source of nitrogen (ammonia) at high temperature. Its excellent activities for oxygen reduction reaction (ORR) in both acidic and alkaline media were confirmed by thin film rotating disk electrode technique. Also, durability test was performed in both media. After 20,000 (0.65–1.0 V) potential cycles, the half-wave potential decayed by only 40 mV in 0.1 M $HClO_4$, while in 0.1 M KOH it gained 25 mV. In addition, no activity decay was observed by adding methanol in the acidic solution indicating its excellent tolerance to methanol oxidation.

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1. Introduction

Cost and durability are considered as the main challenges facing the commercialization in mass scale of polymer electrolyte fuel cells (PEFCs) [1]. A large portion of PEFC systems cost is still associated with cathode catalyst for oxygen reduction reaction (ORR) [2–4]. Nevertheless, great efforts have been so far made to develop advanced ORR catalysts with lower cost and higher activity and durability aiming to replace a substantial amount of the costly Pt-based materials, which are commonly used in today's fuel cells technologies [3,5,6]. Among them, non-precious metal (NPM) catalysts consisting of transition metals (in particular, Fe and Co)–nitrogen complexes on carbon support prepared by high temperature pyrolysis are the most promising approaches [7–11]. Despite the fact that the nature of the catalytic sites in NPM catalysts are still as a topic of debate, it is generally accepted that ORR activity and durability are largely influenced by the type of the transition metals (M) in the catalyst, the type of C and N precursors used, the ratios of M/N and N/C on the surface, and the synthesis conditions [12]. For example, an excellent ORR activity has been reported by the Dodelet group by mixing a carbon support with iron precursor, and then heating the materials in ammonia as the source of nitrogen [8]. On the other hand, a similar activity has been achieved by the Zelenay group by polymerizing the aniline (nitrogen precursor) on high surface area carbon support in the presence of iron precursor, and then heating the mixtures in an inert gas [10]. The same group and others explored NPM catalysts supported on multiwalled carbon nanotubes (MWCNTs) [13–16]. To the best of our knowledge, the approach of chemically coating polymer containing nitrogen, such as polyaniline (PANI) on CNTs and heat treatment in a decomposable source of nitrogen, such as ammonia in order to increase the total nitrogen content (aiming to increase the graphitic nitrogen) merits to be studied. Moreover, none of the previous reported works has performed comparative studies of the activity and durability under long cycling in both alkaline and acidic media. Herein, we report an iron-based NPM catalyst through polymerization of aniline on CNTs and subjecting to heat treatment in ammonia at 900 °C. The resulted material shows excellent ORR activity and durability under potential cycling in both acidic and alkaline media. It is important to note that cycling in acidic medium caused a drop in iron content due to dissolution. Yet, the activity of the catalyst did not decay dramatically as one can expect.

2. Experimental

2.1. Synthesis of Fe-N-C/CNTs

Multiwall carbon nanotubes (CNTs) were purchased from Cheap Tubes Incorporation, USA (http://www.cheaptubesinc.com/) and

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were acid washed in-house before use. The BET area of the acid washed CNTs was in the range of 170 $m^2\ g^{-1}$. Aniline (Aldrich) was distilled before use. Ammonium persulfate $\{(NH_4)_2S_2O_8\}$ (Aldrich) was used without further purification. MilliQ UV-plus water (Millipore) was used throughout all experiments.

In a typical experiment, 5.0 g of aniline was mixed with 50 ml water. Thereafter, 37% HCl was added dropwise with continuous stirring until aniline became completely miscible with water. Then, 1.0 g of CNTs was added into the mixture and sonicated for 0.5 hr in a sonication bath to obtain well dispersed slurry and kept overnight under stirring to impregnate aniline into CNTs surface. As an oxidant agent, 10.0 g of $\{(NH_4)_2S_2O_8\}$ was dissolved in water and added in dropwise to the mixture and kept overnight under stirring to ensure proper and complete polymerization. The obtained product, named as PANI/CNTs was then filtrated and washed with Di-water for several times until pH became less acidic (pH = 6), then dried under vacuum at 80 °C overnight.

In the next step, 1.0 g of the dried PANI/CNTs was dispersed in water in form of slurry using ultrasonication. On the other hand, 0.48 g of $FeCl_3{\cdot}6H_2O$ (to give 10 wt.% Fe) was dissolved in water and added to the slurry. The mixture was then kept on a magnetic stirrer overnight to ensure complexation of $FeCl_3$ onto PANI/CNTs.

Before heat treatment, two methods were tried to dry the mixture: oven drying and freeze drying. Based on the ORR measurements, freeze drying method was found to lead to a higher activity. Freeze drying might help keep better dispersion or complexation of $FeCl_3$ on PANI/CNTs. Freeze drying was performed with a Freeze Dryer (Labconco) for 3 days. The final product was then heat treated in 10% NH_3/N_2 at 900 °C for 1 hr (3 hr for ramping temperature from 25 °C to 900 °C). The resulted catalyst was denoted as Fe-N-C/CNTs.

2.2. Electrochemical measurements

For ORR activity measurement, approximately 5 mg of the dried catalyst Fe-N-C/CNTs was dispersed in a mixture of water and isopropanol alcohol (30%, v/v) and 60 μl of 1.66 wt.% Nafion® (prepared from 5 wt.%, Aldrich). The mixture was ultrasonicated for 10–20 min to obtain a uniform ink. Then, 20 μl of the ink suspension was deposited on the pre-cleaned glassy carbon substrate (5 mm diameter, Pine Instruments) and allowed to dry. For high loading of catalyst, we repeated the operation for several times to achieve the desired loadings. A Ag–AgCl electrode (calibrated and converted to RHE) and Pt mesh were used as a reference and counter electrode, respectively. All the potential reported in this paper were converted to RHE. Before testing ORR activity, each electrode was cycled in nitrogen saturated 0.1 M $HClO_4$ and 0.1 M KOH solutions until a stable CV was obtained (generally for 10–15 cycles between 0 and 1.2 V at 20 $mV\ s^{-1}$). ORR activity was evaluated in both oxygen saturated acidic (0.1 M $HClO_4$) and alkaline (0.1 M KOH) media using a rotating disk electrode (RDE) technique at rotation speed of 400 rpm with a scan rate of 5 $mV\ s^{-1}$. Catalysts durability was also investigated in oxygen saturated 0.1 M $HClO_4$ and 0.1 M KOH under potential cycling between 0.65 and 1.0 V for 20,000 cycles using square-wave signal of 5 s at each potential. ORR activity was evaluated in fresh electrolytes in a separate cell after every 5000 cycles. After 20,000 cycles, the ORR activity was measured again in 0.1 M $HClO_4$ containing 0.1 M methanol to evaluate its methanol tolerance. All the currents were normalized to the geometric area of electrodes. The ring current densities in the RRDE measurements were corrected according to the collection efficiency (30%) of the system.

2.3. Characterization

High-end field-emission scanning electron microscope (FESEM, Tescan-Lyra-3) and energy-dispersive X-ray spectroscopy (EDX, Oxford-Xmax) were used to provide morphology and elemental composition information. TEM analysis was performed with FEI Titan ST operated at 300 kV with a point resolution of 2.0 Å.

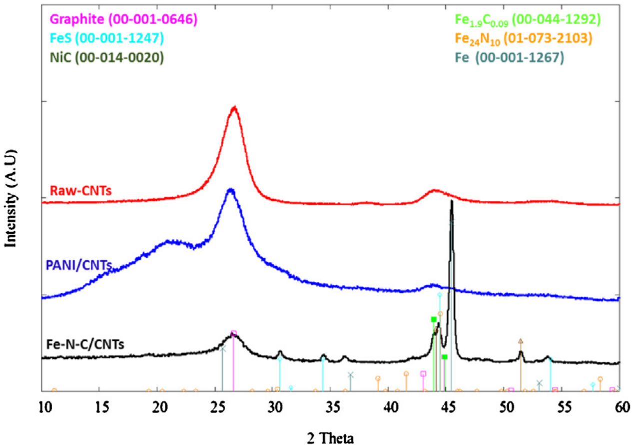

Fig. 1. XRD patterns of raw CNTs, PANI/CNTs and Fe-N-C/CNTs (obtained after HT at 900 °C in 10% NH_3/N_2 of $FeCl_3$/PANI/CNTs). The S in FeS and Ni in NiC of Fe-N-C/CNTs came from persulfate used for polymerization of aniline and impurity in the raw CNTs (The EDX spectrum showed that Raw-CNTs contain 99 wt.% of carbon and trace of oxygen and nickel.).

X-ray diffractions (XRD) patterns were collected using a Rigaku Miniflex II instrument with a monochromator of CuKα1 (1.5406 Å) at 30 kV, 15 mA. The XRD patterns were recorded in the static scanning mode from 5° to 60° (2θ) at a detector angular speed of 2° $\theta\ min^{-1}$ and step size of 0.02°. Peak matching was determined with Philips X'Pert plus (V.2) using patterns diffractions files (PDF-2) from ICDD (2011).

Raman spectra were taken on an iHR320 Horiba Spectrometer with charge-coupled device (CCD) using monochromatic laser (300 mW, 532 nm), grating of 1200 lines mm^{-1} and an aluminum substrate. Raman spectroscopy provided further information on the defects in CNTs that may be created during heat treatment in NH_3.

BET area measurements were conducted using ASAP-2020 Physisorption Analyzer from Micrometrics.

3. Results and discussion

Fig. 1 shows the XRD patterns of as received CNTs, PANI/CNTs, and Fe-N-C/CNTs. The similar intensity of (0 0 2) diffraction peak of graphitic carbon at ~26° before and after polymerization of aniline on CNTs suggests that the polymerization did not cause a noticeable structure change in CNTs. The arising of a broader shoulder at ~20° due to PANI in PANI/CNTs confirms the successful polymerization. However, when the system was subjected to complexation with $FeCl_3$ and followed by heat treatment in ammonia at 900 °C, a composite-like material consisting of Fe–N and Fe–C function groups was formed. The significant decrease in peak intensity at 26° also suggests the formation of nitrogen-doped carbon as a result of sacrifice of graphitic structure. A similar XRD pattern for Fe-N-C catalyst was reported by Tsai et al. [17]. The sharp diffraction peak at 45° in Fig. 1 may be due to free Fe nanoparticles. The structure changes of CNTs are also supported by the Raman spectroscopic data (Fig. 2). The peaks centered at 1334 cm^{-1} and 1596 cm^{-1} are referred to D- and G-band, respectively [18]. The D-band is related to the vibrations of sp^3 bonds associated to the bonded carbon atoms of disordered graphite, while the G-band is related to the vibration of all sp^2 bonds in well-graphitized structures [19]. The intensity ratio of the D- to G-band (D/G) interprets the degree of disorder that could occur in the carbon structure. The D/G ratios of raw-CNTs and Fe-N-C/CNTs catalyst were estimated to be 0.37 and

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