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Pyrolyzing cobalt diethylenetriamine chelate on carbon (CoDETA/C) as a family of non-precious metal oxygen reduction catalyst

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ABSTRACT

Using diethylenetriamine ligand, a family of non-precious metal oxygen reduction catalyst is synthesized by pyrolysis of cobalt-diethylenetriamine chelate on carbon at elevated temperature from 600 to 900 °C. Cyclic voltammetry results show that pyrolysis temperature plays an important impact on improving catalytic activity and the maximum activity is obtained at 800 °C with its peak potential of 719 mV (SHE). For the best catalyst HT800, rotating-ring disk electrode measurement indicates that the number of electrons transferred is 3.80–3.85 at potential of 0.5 V with rotating rates from 100 to 1600 rpm and the catalyst loading of 648 μg cm⁻². XRD indicates that the cobalt-nitrogen chelate decomposes above 600 °C and nanometallic α-Co with different sizes is synthesized. Raman indicates that there are more defective sites on the carbon surfaces induced by N doping. Combined XPS data with electrochemical results, it indicates that a higher total N content does not lead to a higher ORR activity.

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1. Introduction

Oxygen reduction reaction (ORR) is an important process in many fields, including energy conversion (fuel cell, metal-air battery), corrosion and biosensing [1]. To date, carbon-supported platinum and its alloys are the most promising catalysts for both the ORR at the cathode and the hydrogen oxidation reaction at the anode in fuel cell. Due to the slower kinetics of the ORR, there must be higher loading of platinum at the cathode to promote the performance of fuel cell. However, the high cost, limited supply and poor durability of platinum remain the major barriers to the development of

fuel cell. Thus, numerous efforts have been made to develop non-precious metal catalysts to replace Pt-based catalysts [2–6]. Among them, heat-treated carbon-supported non-precious metal complexes with macrocyclic ligands, such as porphyrins and phthalocyanines that contain four nitrogen donors (MN₄ chelates) have been expected to be the most promising non-precious metal catalysts [7–9], since Jahnke showed the beneficial effects of heat treatment in an inert atmosphere to improve their catalytic activity and chemical stability in 1976 [10].

It has also been demonstrated that expensive macrocycle ligands were not necessary to obtain these catalysts.

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Following this approach, many non-precious metal catalysts have been synthesized via various cheap nitrogen-containing compounds [11–15]. For example, heat-treated mixtures of nitrogen-containing precursor, such as di-quinolyldiamine [11], phenantroline [12], cyanamide [13] and ethylenediamine [14,15], together with Fe or Co salt were considered as the promising ORR catalysts. However, the active sites of these catalysts are still debated in the literature [16–20]. Some researchers proposed that the transition metal coordinated to nitrogen, namely MN_x structure, served as the active sites for the ORR [16–18]. Others believed that the transition metal itself did not play any role in the ORR, while specific nitrogen-containing functional groups, such as pyridinic-N and graphitic-N, were the catalytic site by enhancing electron donor property of the nitrogen-modified carbon-based catalysts [19,20]. Although the exact nature of the active site for the ORR is controversial, it is believed that there are four elements to influence the activity of these non-precious metal catalysts: (1) a choice of transition metal, usually in the form of metal salts; (2) a nitrogen-containing source, such as porphyrins, polypyrrole, NH_3 and CH_3CN ; (3) a source of carbon support, such as BP 2000; and (4) heat treatment, usually higher than 800 °C. Recently, Byon and co-workers reported a Fe–N–C catalyst prepared from graphitic carbon nitride ($g-C_3N_4$), Fe salt and chemically reduced graphene, and they believed that an average Fe coordination of 3N (Fe– N_3) in bulk was considered as the catalytic active site [21].

Motivated by this research, we develop a class of highly active oxygen reduction catalyst by employing diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, DETA), a simple and cheap N_3 -structure ligand, as the nitrogen precursor to prepare non-precious metal ORR catalyst in this paper. We also study the influence of heat treatment on the catalytic activity and structure. The catalysts are subjected to a wide range of analytical techniques, including thermogravimetry (TG), energy dispersive X-ray spectroscopy (EDS), X-ray diffractometry (XRD), Raman spectra and X-ray photoelectron spectroscopy (XPS). Catalytic activities are demonstrated by cyclic voltammograms (CVs) and rotating-ring disk electrode (RRDE) measurements in O_2 -saturated acidic solution at room temperature.

2. Experimental

2.1. Catalyst preparation

The preparation of catalysts was done in two steps: (i) modification of carbon support by hydrogen peroxide (H_2O_2) and (ii) synthesis of non-precious metal Co-based catalysts.

- (i) Modification of carbon support by H_2O_2 . 10.0 g commercially available carbon, namely Black Pearl 2000 (BP 2000) from Cabot Company, was ground in a planet-wheel agate mill with 100 g agate balls at 400 rpm for 2 h. The H_2O_2 -oxidated treatment was achieved by mixing 10.0 g BP 2000 powder with 500 mL 30 wt.% H_2O_2 solution under stirring condition for 24 h. The suspension was then filtered, washed with deionized water, dried in an oven at 80 °C, and finally grounded to powder for use.

- (ii) Synthesis of non-precious metal Co-based catalysts. In a typical synthesized method, 0.404 g inorganic cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was dissolved in 50 mL ethanol at room temperature. Next, 1.0 mL diethylenetriamine (DETA) was added into the above solution under stirring condition to form the CoN_3 chelate (CoDETA). Then 1.000 g the pre-treated BP 2000 was added to the above solution under stirring conditions. The carbon-supported CoDETA chelate suspension was stirred for 1 h and then dried to remove ethanol by a rotary evaporator at 50 °C under reduced pressure for 15 min. The resulting powder was put into quartz tube and placed in the middle of the quartz tube and then pyrolyzed in high-pure Ar atmosphere at a set temperature (600, 700, 800 and 900 °C) for 90 min with a heating ramp of 5 °C min^{-1} . After that, the CoDETA/C catalysts were grinded to obtain fine powder products. The nominal metal Co loading with respect to carbon was kept at 10 wt.%. In this way, four catalysts were thus synthesized at different heat-treated temperatures and for convenience, the CoDETA/C catalyst pyrolyzed at 600 °C is hereafter labeled as HT600, and the others are named in a similar manner, namely HT700, HT800 and HT900.

2.2. Electrochemical measurements

Electrochemical measurements were carried out in a single-compartment conventional three-electrode cell filled with 0.5 M H_2SO_4 solution at room temperature. A rotating ring disk electrode (RRDE, AFE7R9GCPT, purchased from Pine Instruments) with a glassy carbon disk ($d = 5.61$ mm) and Pt ring was used as the working electrode. Platinum mesh was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. All potentials presented in this study are referred with respect to standard hydrogen electrode (SHE). The catalyst ink was prepared by blending 8 mg finely ground catalyst with 1.0 mL distilled water and 50 μL 5 wt.% Nafion solution in an ultrasonic bath for 15 min. Then 20 μL of this ink was deposited onto the surface of disk electrode for air-drying to gain the catalyst loading of 648 $\mu g cm^{-2}$.

To obtain the background capacitive currents, cyclic voltammograms (CVs) were recorded in N_2 -saturated 0.5 M H_2SO_4 solution by scanning the disk potential from 1.04 to 0.04 V at a scan rate of 5 $mV s^{-1}$ after steady cycle (at least 10 cycles). While for the oxygen reduction activity measurements, CVs were recorded in O_2 -saturated 0.5 M H_2SO_4 solution by scanning the disk potential from 1.04 to 0.04 V at a scan rate of 5 $mV s^{-1}$ after steady cycle (at least 10 cycles). For more quantitative measurements of the ORR activity, linear sweep voltammograms of the RRDE was obtained when the disk electrode recorded by the potential from 1.04 to 0.04 V at a scan rate of 5 $mV s^{-1}$ for different rotation rates (100, 400, 900 and 1600 rpm). In order to oxidize any hydrogen peroxide produced, the ring electrode was recorded by maintaining the potential at 1.2 V. The net faradic currents were obtained by subtracting the background capacitive currents. All measurements were obtained with a bipotentiostat CHI 750D.

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