



Influence of pyrolyzing atmosphere on the catalytic activity and structure of Co-based catalysts for oxygen reduction reaction



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ARTICLE INFO

Article history:

Received 29 May 2013

Received in revised form

30 September 2013

Accepted 11 October 2013

Available online 29 October 2013

Keywords:

Oxygen reduction reaction

Non-precious metal catalyst

Nitrogen-doping

Co-based catalyst

Pyrolyzing atmosphere

ABSTRACT

In this study, impact of pyrolyzing atmosphere on the catalytic activity and structure of non-precious metal Co-based catalysts for oxygen reduction reaction in acid and alkaline medium are investigated. These non-precious metal Co-based catalysts are prepared from pyrolyzing carbon-supported cobalt diethylenetriamine chelate (CoDETA/C) in Ar, N₂ and CO₂ atmosphere, respectively. X-ray diffraction indicates that metallic Co nanoparticles with different size are present on each catalyst. X-ray photoelectron spectroscopy shows that the Nat.% is CoDETA/C-Ar (1.54) > CoDETA/C-N₂ (1.39) > CoDETA/C-CO₂ (0.42), pyridinic-N and amino-N in CoDETA/C-N₂ is the highest among these three catalysts, while pyrrolic-N, graphitic-N and oxidized-N in CoDETA/C-Ar is higher than that in the other two catalysts. Electrochemical activity demonstrated by cyclic voltammograms and rotating ring disk electrode in O₂-saturated acid and alkaline electrolyte shows that pyrolyzing atmosphere has an important effect on the catalytic activity and a maximum catalytic activity is obtained in N₂ atmosphere, followed by in Ar then CO₂ atmosphere, in terms of onset and half-wave potentials, ORR peak potential and current, limiting current, number of electrons transferred and H₂O selectivity. The increase in catalytic activity may mainly attribute to the enhanced contents of pyridinic-N and amino-N.

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1. Introduction

Renewable energy sources attract growing attention to fulfill energy requirements in the future, while simultaneously reduce environmental pollution. Proton exchange membrane fuel cells (PEMFCs) have been recognized as the most promising energy converting devices in terms of zero emissions and high efficiency by converting stored hydrogen into electricity. In practice, they need Pt and Pt-alloy catalysts to promote hydrogen oxidation at the anode and oxygen reduction reaction (ORR) at the cathode. Considering Pt is expensive and limited availability and need of higher Pt loadings at the cathode than at the anode, it will be more advisable to replace Pt by non-precious metal catalysts [1]. Transition metal macrocycle complexes (metal-N₄), such as metalloporphyrins and metallophthalocyanines, adsorbed on carbon support and heat treated in an inert atmosphere, have been widely studied as the most promising catalysts to replace Pt/C catalyst [2–5], since Jahnke discovered the beneficial effects of heat-treatment in inert atmosphere to improve their catalytic activity and chemical stability in 1976 [6].

However, non-precious metal ORR catalysts could be obtained from the heat-treated mixture of transition metal salts and

nitrogen-containing precursors, such as polyacrylonitrile, polypyrrole and triethylenetetramine [7–10]. Moreover, non-precious metal ORR catalysts could also be prepared through heat-treatment of iron tripyridyltriazine complexes and cobalt di-quinolyldiamine derivatives, respectively [11,12]. Regarding the synthesis route of these non-precious metal ORR catalysts, heat-treatment has been recognized as a very important and sometimes necessary step for improving the catalytic activity [2–15]. Many heat-treatment techniques, such as traditional furnace-heating [2–12], microwave heating [13], plasma treatment [14] and ultrasonic spray pyrolysis [15] have been applied to prepare non-precious metal ORR catalysts.

Heat-treatment can affect the fundamental property of the catalyst and its carbon support, including the loading level of the catalyst on the support, the number of catalytic sites, the acid–base property of the support, and the distribution of the catalyst particles on the support [16]. Although heat-treatment effect on these non-precious metal ORR catalysts properties has been well documented, a full understanding of the mechanism of catalytic activity improvement has not yet been achieved. Employing NH₃ and CH₃CN as nitrogen precursors, based on the time-of-flight secondary ion mass spectrometry results, Dodelet and co-workers claimed that the origins of the high catalytic activity, especially the catalytic active sites responsible for this performance after heat treatment were that CoN₄/C active sites existed in Co-based catalysts [17]. Popov's group

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proposed that active sites with pyridinic nitrogen were responsible for the catalytic ORR activity [18], whereas they also reported that quinone groups introduced by nitric acid treatment, in addition to increasing the dispersion of the Co-based chelate complexes, played a role in forming the active site for oxygen reduction [19]. Atanassov and his coworkers proposed a dual-functionality active site where O_2 was initially reduced at a Co^{2+} containing N–C type site in a 2e process to form HO_2^- , which can react further in the series type ORR mechanism at the decorating Co_xO_y/Co surface nanoparticle phase [8]. Oh and his co-worker examined the role of transition metals (Co or Fe) on nitrogen-modified carbon-based ORR catalysts synthesized by the pyrolysis process in the presence of polypyrrole (PPy) and ethylenediamine (EDA) with different amounts of transition metals [20]. The results indicated that transition metal itself did not behave as an active site for ORR, while the total nitrogen content and the active nitrogen functional groups, such as pyridinic-N and graphitic-N, were strongly dependent on the type of transition metal and the amount of transition metal used [20]. They also believed that transition metals served to catalyze the formation of active nitrogen functional groups for the ORR by doping nitrogen into carbon [20]. Although the nature of the active sites for ORR is not yet clear, the catalytic activity of these catalysts depends on (1) the nature of the metal and its precursor as well as the nature of the nitrogen precursor, and (2) the heat-treatment strategy. As far as the second point is concerned, many studies have been done to optimize the heat treatment temperature, few research has been carried out to investigate the effect of pyrolyzing atmosphere on the catalytic activity of these non-precious metal ORR catalysts [16].

In this paper, we study the influence of pyrolyzing atmosphere on the catalytic activity and structure of non-precious metal Co-based catalysts. Three types of pyrolyzing atmospheres (argon, nitrogen and carbon dioxide) are chosen. The catalyst structures are characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Catalytic activities for the ORR are demonstrated by cyclic voltammograms (CVs) and rotating ring disk electrode (RRDE) measurements in O_2 -saturated acid and alkaline solution at room temperature.

2. Experimental

2.1. Preparation of non-precious metal Co-based catalysts

Briefly, cobalt chloride ($CoCl_2$) was dissolved in ethanol at room temperature. Next, diethylenetriamine (DETA) was added into the solution to form the CoDETA chelate. Then commercially available carbon black (Black Pearls 2000), which had been refluxed in 30 wt.% H_2O_2 solution at room temperature in order to introduce oxygen functional groups on the carbon surface, was added to the above mixture under stirring condition. The carbon-supported suspension was stirred for 1 h and then dried to remove the ethanol by rotary evaporator. The resulting powders were divided into triplet and heat-treated at $800^\circ C$ for 90 min at the rate of $5^\circ C/min$ in argon (Ar), nitrogen (N_2) and carbon dioxide (CO_2) atmosphere, respectively. The nominal metal Co loading with respect to carbon support was 10 wt.%. For convenience, the CoDETA/C catalyst heat-treated in Ar atmosphere is hereafter labeled as CoDETA/C-Ar, and the others are named in a similar manner, namely CoDETA/C- N_2 and CoDETA/C- CO_2 .

2.2. Electrochemical measurements

Catalytic activities for ORR of these Co-based catalysts were studied by CVs and RRDE measurements. The electrochemical measurements were carried out in a conventional three-electrode cell

filled with 0.5 M H_2SO_4 and 0.1 M KOH solution at room temperature and ambient pressure, respectively. The RRDE electrode (AFE7R9GCPT, purchased from Pine Instruments) consists of a GC disk (5.61 mm diameter) surrounded by a Pt ring (6.25 mm inner diameter and 7.92 mm outer diameter). The catalyst ink was prepared by ultrasonically dispersing 8 mg catalyst powder in 1.0 mL high-purity water and 50 μL 5 wt.% Nafion solution for 15 min. Then 20 μL of this ink was deposited onto the disk electrode and air-dried for use.

A Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. All potentials reported in this study are converted to the reversible hydrogen electrode (RHE) scale. The calibration of SCE reference electrode was performed in a standard three-electrode system with polished Pt wires as the working and counter electrodes, and the SCE as the reference electrode. Electrolytes (0.1 M KOH and 0.5 M H_2SO_4) were pre-purged and saturated with high purity H_2 . Cyclic voltammograms (CVs) was then run at a scan rate of 1 mV/s, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions [21,22]. In 0.5 M H_2SO_4 solution, the potential scan range was set between -0.2 and 0.8 V (vs. SCE), while in 0.1 M KOH solution, the potential scan range was between 0.2 and -0.8 V (vs. SCE). The potential scan rate was fixed at 5 mV/s among all the electrochemical measurements.

Initially, the catalysts loaded on the GC disks were electrochemically cleaned by sweeping the potential until steady CVs were obtained. For each catalyst ORR tested, CVs was first collected in N_2 -saturated electrolyte solution to determine the non-faradic current. Next, the electrolyte solution was purged with O_2 for at least 15 min, and then CVs was recorded in O_2 -saturated electrolyte solution. The faradic current was determined by subtracting the CVs in N_2 -saturated solution from that obtained in O_2 -saturated solution. The current-potential curves were obtained with the electrode rotated at 900 rpm. For all the measurements, the ring potential was held at 1.0 and 0.5 V (vs. SCE) in order to oxidize any H_2O_2 produced in acid solution and any HO_2^- produced in alkaline solution, respectively [19,21–23].

2.3. Characterization of non-precious metal Co-based catalysts

Crystallographic structures of the catalysts pyrolyzed in different atmosphere were determined by XRD. The XRD measurements were performed on a Germany Bluker D8-Advance X-ray diffractometer using a Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The operating current was 40 mA and the voltage was 40 kV. The intensity data were collected at the scanning angle range from 20° to 80° with a scan rate of $10^\circ/min$ and the step size of 0.02° .

We calculate the average size of the Co particles in these three Co-based catalysts using the following Scherrer formula.

$$d = \frac{0.89 \lambda}{B \cos \theta} \quad (1)$$

where d is the diameter of the particle, λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), θ is the Bragg angle and B is the full width at half maximum of the Co(1 1 1) Bragg peak of the sample.

Surface analysis of the catalysts before the electrochemical measurements was performed by XPS measurements. The XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with the Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54° . For the fine scans, the pass energy was fixed at 93.90 eV with the step size of 0.2 eV, and the number of scans was 20 to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The powdered samples were directly pressed to a

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