



High-Performance Non-Noble Electrocatalysts for Oxygen Reduction Using Fluidic Acrylonitrile Telomer as Precursor



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ABSTRACT

Non-noble-metal catalysts have shown promising oxygen reduction reaction (ORR) activity in proton exchange membrane fuel cells (PEMFCs). Herein, by using sulfur-terminated fluidic acrylonitrile telomere (ANT) as precursor, an N and S dual-doped Co/ANT/C catalyst was prepared via a facile heat treatment of the mixture of Co salt, ANT and carbon black, in which cobalt salt was uniformly-dispersed and interacted with ANT. As such, the increasing contact area between ANT and cobalt salt leads to a highly catalytic activity toward oxygen reduction reaction. Most importantly, by using ANT as precursor, the catalyst showed a remarkable improvement in the onset potential and current density as compared with those prepared from pure carbon black, cobalt salt/C or catalyst using high molecular weight polyacrylonitrile as precursor. Besides, the as-made Co/ANT/C catalyst demonstrated a comparable catalytic activity with commercial expensive Pt/C at high loading. In addition, the catalyst participated promotes a direct four-electron reduction of O₂ to H₂O and long term operation stability in an alkaline medium. Owing to its superb ORR performance, low cost and facile synthesis approach, such prepared Co/ANT/C catalyst has great potential applications in PEMFCs.

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1. Introduction

As one of the most promising power sources, proton exchange membrane fuel cells (PEMFCs) are believed to be attractive alternatives to fossil fuels. Notably, the reactions at the anode and cathode in PEMFCs are both catalyzed by Pt or Pt-based materials [1]. Especially in the cathode, the oxygen reduction reaction (ORR) with extremely sluggish kinetics requires a much more amount of Pt (usually 0.4 mg cm⁻²) [2,3]. The ORR mechanism of the commercial Pt/C catalyst had been widely investigated and commercial Pt/C had also been proved to be a reliable catalyst for PEMFCs [4,5]. However, the Pt based catalyst has several drawbacks such as carbon monoxide poisoning, methanol crossover effects and low operational stability, and most importantly, the limited annual output and extremely-high price of Pt source greatly hindered its practical application in PEMFCs [6,7].

To overcome the drawbacks of Pt catalyst, the development of non-noble metal catalysts has become one of the most emerging investigations in PEMFCs and enormous efforts have been committed during the past few decades. Since Jasinski's pioneering work, which showed that cobalt phthalocyanines were ORR active [8], non-noble ORR catalysts based on transition metal and carbon materials doped with heteroatoms, including boron [9], halogen [10], nitrogen [11], phosphorus [12], sulfur [13] and the co-doping has been widely reported [14,15] considering their low cost, high activity, long-term stability and simple preparation approaches [16–19]. Although the exact catalyst mechanism remains unclear, the ORR activity was mostly attributed to the formation of nitrogen macrocycles (e.g. Co-N₄ chelate) during the high temperature pyrolysis of transition metal and N-containing precursors [20].

On the other hand, N-containing polymers provided as nitrogen and carbon precursors in the preparation of non-noble-metal ORR catalysts have shown reliable catalytic activity and durability. In contrast to the approach which using nitrogen-containing atmosphere or chemical vapor deposition (CVD) process, polymer with the higher molecular weight can avoid evaporation or sublimation of the CN_x source during heat treatment. After optimization of the

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preparation methods of the catalyst, various nitrogen polymers have been explored. By using polyaniline as the precursor, Zelenay et al. [21] prepared Co/Fe/polyaniline/C composite and the catalysts exhibited an activity approaching to commercial Pt/C ORR catalyst in acid media with good stability. Other N-containing polymers, including polyvinylpyrrolidone [22], polypyrrole [23], or others [24,25], have also been used as precursors successfully. Comparing with the above-mentioned N-containing polymers, Polyacrylonitrile(PAN) has a higher nitrogen content and better ability to undergo a graphitization, but the catalyst using PAN as the precursor did not perform well as expected [26]. The low ORR catalyst activity may be attributed to the poor compatibility of PAN with metal salt. Note that while using polymer as a precursor, the polymer were either synthesized in the porous carbon materials or immersed into the pores from polymer solutions. Because active sites are only created at the interphase boundary of reacting components, it is impossible to obtain much active site in such inhomogeneous mixture of carbon materials with PAN and metal salts.

Recently, we developed a novel fluidic nitrogen-containing carbon precursor, acrylonitrile telomer (ANT) for the preparation of Fe/N/C oxygen reduction catalyst [27]. The unique properties of ANT promoted better contact between several components and the obtained catalyst showed excellent activity and durability. Herein, we prepared a novel N and S dual-doped ORR catalyst by using fluidic acrylonitrile telomer (ANT) as a dual-doped precursor and CoCl_2 as transition metal salt. The present method has two unique features to improve the performances of the catalyst. First of all, the unique fluidic nature of ANT significantly improves the compatibility with the CoCl_2 to form a uniform mixture, so-called “hybrid”. When the “hybrid” was treated with stabilization and carbonization, cobalt atoms can be coordinated with N on the carbon framework to form active Co-N_x-C sites [28,29], which are essential for high activities of the catalysts. Second, the high N content of ANT generates the pyridinic, pyrrolic, or graphitic N structure in the process of carbonization. And S atoms can be also doped into carbon framework to improve the catalyst activity [30]. For demonstration, we successfully prepared low-cost Co/ANT/C catalysts with an excellent electrocatalytic activity and long-term operation durability for oxygen reduction, which was comparable to the commercial Pt/C catalyst.

2. Experimental Section

2.1. Synthesis of ANT

Firstly, ANT was synthesized by a simple radical telomerization of acrylonitrile (AN) with 3-mercaptopropionic acid (3-MPA) as chain transfer agent (CTA). The details of the ANT synthesis can be found in our previous work [27]: a mixture of acrylonitrile (AN, distilled prior to use, Aldrich), 3-MPA (98%, Aldrich) and azobisisobutyronitrile (AIBN, recrystallized in ethanol twice, Aladdin Reagents) (AN/3-MPA/AIBN = 100/80/0.1 molar ratio) was placed in a 3-bottle flask with reflux condenser. Polymerization was carried out at 65 °C under constant nitrogen flow for 24 h. The mixture was distilled at 90 °C to remove unreacted monomer and

then at 125 °C to remove 3-MPA under reduced pressure. The average degree of polymerization of the synthesized telomer ranges from 2 to 10, and the product is syrup-like yellow liquid under room temperature. The reaction of the radical telomerization of ANT is shown in Fig. 1.

2.2. Synthesis of Co/ANT/C

Commercial carbon black Ketjenblack EC-300J (Akzo Nobel) was mixed with acetone solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (ACS grade, Aladdin Reagents) and ANT. After acetone was volatilized, EC-300J particles and CoCl_2 aggregates were coated with ANT polymer. The mixture was stabilized under air at 120 °C, 180 °C, 240 °C for 24 h, 12 h and 9 h, respectively. Then, the mixture was further carbonized in a tubular oven at the temperature varied from 700 to 1100 °C under constant argon flow for 1 h with 5 °C min⁻¹ of heating rate. Finally, the as-made product was passed through a 200 mesh sieve to reduce the particle size. Heat-treated EC-300J, heat-treated EC-300J adding CoCl_2 (Co/C) and catalyst using commercial high molecular weight polyacrylonitrile (HMWPAN, $M_w = 150000$ g/mol, dissolved in hot DMF) as precursor (Co/HMWPAN/C) were also synthesized as reference samples.

2.3. Preparation of catalyst ink

Johnson Matthey Hi-Spec 3000 Pt/C (20 wt. % Pt) was used as reference. Catalysts were weighted with 0.001 mg accuracy and then were added with a mixture of ultra-pure water, iso-propanol and Nafion solution (5 wt. %, Aldrich). First, the ink was prepared by dispersing 4.9 mg of catalyst and 10.9 μL of 5 wt % Nafion solution (20 wt % of Nafion to catalyst ratio) in 1 mL of 4:1 v/v iso-propanol/water mixed solvent by 30 min sonication to form a homogeneous dispersion. Then the catalyst ink was applied to the polished glassy carbon (GC) electrode by pipette.

2.4. Electrochemical measurements

The surface of the GC disc working electrode was polished by using an electrode polishing kit, first with 0.5 micron alumina, second with 0.05 micron alumina. To remove the alumina particles, the GC was ultrasonicated in distilled water and ethanol for two times, respectively.

The ink was dried slowly to obtain a uniform catalyst distribution on the electrode surface in air. Cyclic Voltammetry (CV) and Rotating Disk Electrode (RDE) measurements were carried out in an O₂-saturated 0.1 M KOH solution using GC, Pt foil and Ag/AgCl as working, counter and reference electrodes to constitute a three-electrode electrochemical cell. Ag/AgCl was filled with 3.5 M KCl and combined with a KNO₃ salt bridge to avoid chloride ion contamination. Ag/AgCl scale was used to refer to all potentials. Prior to the RDE test, the catalyst was cycled between -0.9 and 0.3 V at 50 mV s⁻¹ for 20 cycles to remove surface contaminants. Then RDE linear voltammetry was performed from -0.8 to 0.2 V in positive direction at 5 mV s⁻¹. Each sample was repeated from electrode preparation to RDE measurement for at least 5 times to ensure reproducibility.

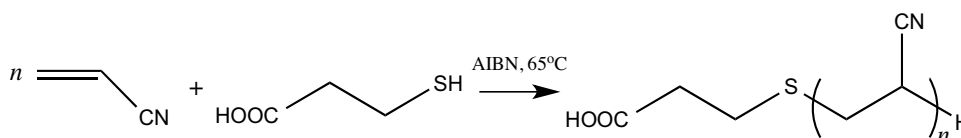


Fig. 1. Telomerization of ANT with 3-MPA using AIBN as initiator.

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