



A non-noble material cathode catalyst dual-doped with sulfur and nitrogen as efficient electrocatalysts for oxygen reduction reaction



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ABSTRACT

The behavior of Fe-based dual-doped non-noble metal electrocatalyst (Fe-N/C-TsOH) pyrolyzed at different condition and the repercussion for the oxygen reduction reaction (ORR) has been studied. Cyclic voltammetry (CV) and rotating disk electrode (RDE) with Tafel theory as well as Koutecky-Levich were used to quantitatively obtain the oxygen reduction reaction (ORR) kinetic constants and the reaction mechanisms. The pyrolyzed catalysts showed significantly improved ORR activity as well as different ORR mechanism, indicating that heat-treatment is a necessary step for improving catalyst activity. In addition, the optimal heat-treatment temperature was found to be 600 °C, and the overall ORR electron transfer numbers were found to be about 3.899, suggesting that the ORR catalyzed by Fe-N/C-TsOH-600 is a 4-electron transfer process from O₂ to H₂O. Furthermore, the catalysts also have been subjected to chemical treatments in 0.5 mol·L⁻¹ H₂SO₄ to remove impurities and reheating was employed to optimize the electrocatalytic activity of the catalyst towards the ORR in alkaline medium. And the activity of the catalyst for the ORR increases obviously after H₂SO₄ leaching and reheating. This effect account to the removal of impurities and purify the active sites as well as the factor that increase the amount of smaller pores which can provide a large surface area and expose more ORR-relevant active sites. In order to understand the heat-treatment effect on catalyst, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are employed to detect surface structure changes. The results revealed a fact that the temperature of thermal treatment has a direct influence on crystal structure and compositions of the catalysts.

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1. Introduction

In response to increasing awareness of environmental factors and limiting energy sources, modern surface science must solve challenging problems in the area of clean energy conservation. Polymer electrolyte membrane (PEM) fuel cells are considered as one of the most promising technology to replace internal combustion engines for portable, stationary and automobile application [1,2]. This is mainly due to their advantages such as high power density, high energy density and high energy conversion efficiency, as well as their low/zero emission [3]. However, the high cost and vulnerability of the platinum (Pt)-based catalyst as well as the sluggish oxygen reduction reaction (ORR) on the cathode have plunged the development of fuel cells for more than a century [4,5]. Thus, the ongoing search for non-

noble metal electrocatalysts with high ORR activity and good durability has driven much of the applied and fundamental fuel cell research in recent years, several kinds of materials have been explored, such as transition metal macrocyclic compounds [6–9], transition metal chalcogenides [10–12] and carbon supported transition metal-nitrogen complex (M-N/C compounds, normally M = Fe or Co [13,14]) and so on. Among these materials, pyrolyzed M-N/C is considered the best promising electrocatalysts for the factor that they have demonstrated some ORR activity and stability close to that of commercially available Pt/C catalysts, as well as low cost and simple synthetic procedures.

Although much research has been done on the pyrolyzed M-N/C catalysts, their catalytic ORR mechanisms are not yet fully understood due to the structures of precursor metal complexes can be partially destroyed during the pyrolysis process. Regarding both the catalytic activity and stability of pyrolyzed M-N/C catalysts, there is a general agreement in the literature that four factors are necessary in achieving an active and stable non-Pt

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metal ORR catalyst: transition metal, nitrogen coordinators on these catalysts, source carbon support and pyrolysis [15]. As established by Dodelet and co-workers [15–17] and now widely confirmed by experiments, nitrogen is a necessary component of the catalyst site in order to form an active catalyst. This is why several different types of nitrogen-containing compounds have been employed as the precursors to form M-N/C complexes. So far, the most common N sources are carbon carrier modified with N, NH₃, acetonitrile, N-containing polymers, and pyrrole [18].

Over and above, co-doped carbons with two different heteroatoms become one promising option for the ORR by taking advantages of different heteroatoms in conjugated carbon backbone that can create new non-electron-neutral sites [19]. For instance, vertically aligned multiwalled carbon nanotube array co-doped with phosphorus (P) and nitrogen (N) with a relatively high P-doping level [20] has been demonstrated to exhibit a high ORR electrocatalytic activity, superb long-term durability, and good tolerance to methanol and carbon monoxide, significantly outperforming their counterparts doped with P or N only. Nevertheless, there are some parameters such as onset potential and limited diffusion current density still need to be improved. Apart from P-N co-doped carbon materials, S-N co-doped carbon materials have also been synthesized recently and tested in electrocatalytic researches in ORR. It was thought that the sulfur group doped to the M-N/C might be helpful for entrapping M ions in an environment rich in pyrrole-type nitrogen or pyridine-type nitrogen. For instance, N/S co-doped Vulcan XC-72R has been demonstrated to show superior ORR performance with excellent activity [21] and durability [22]. In a previous work [23], a p-Toluenesulfonic acid (TsOH)-doped Fe-N/C catalyst, namely Fe-N/C-TsOH, has been successfully developed in our group. Its electrochemical performance towards the ORR was greatly improved from that of the undoped Fe-N/C catalyst, the catalyzed ORR by Fe-N/C-TsOH is more likely than that by Fe-N/C to follow a 4e-transfer reaction to reduce oxygen directly into water. Besides, we found the TsOH-doped Fe-N/C catalyst pyrolyzed at 600 °C exhibited higher activity than that pyrolyzed at other temperature. However, the reported results were only from preliminary experiments. As part of a continuing effort, we studied the ORR kinetics catalyzed by the obtained catalysts with diversity pyrolyzing condition and the effects of heat treatment temperature of those catalysts have been comparatively investigated by using electrochemical measurements such as CV, as well as RDE with Tafel theory and XRD, XPS analysis.

2. Experimental

2.1. Materials and catalyst synthesis

Carbon support (Vulcan XC-72R, with a BET surface area of 235 m²·g⁻¹) was purchased from Cabot, pyrrole (chemically pure), TsOH (analytically pure) and FeSO₄·7H₂O (analytically pure) were purchased from Guoyao. Fe-N/C-TsOH catalyst was prepared using milling method combined with a heat-treated procedure. Briefly, 120 mg Vulcan XC-72R and 50 mg pyrrole dispersed in methanol by 10 min of ultra-sonication. 0.25 mL 30% H₂O₂ and 50 mg TsOH were added into this ultrasonication suspension while milling in a mortar for some time to obtain a slurry. 10 mL methanol with 149 mg FeSO₄·7H₂O was added into the mortar while followed by constant grinding for about 45 min, which was then dried in a vacuum at 60 °C for one hour to remove the solvent methanol. The resulting powders were thermal treated (pyrolysed) in a quartz tubular reactor at set temperature for 2 hours at the rate of 20 °C·min⁻¹ in flowing inert atmosphere. In this way, three different catalyst samples were thus synthesized at different heat-treated temperatures, denoted as Fe-N/C-TsOH, Fe-N/C-TsOH-

600 and Fe-N/C-TsOH-700, respectively. Here, the number indicated the temperature used for catalyst synthesis.

Furthermore, in order to further make clear the mechanism of heat treatment, an aliquot of the obtained catalyst Fe-N/C-TsOH-600 was treated in 0.5 mol·L⁻¹ H₂SO₄ at 90 °C for some hours to removing the acid-soluble phases, denoted as Fe-N/C-TsOH-600HL. Then the resulting samples were washed with distilled H₂O by centrifugation at 2500 r·min⁻¹ for 10 min until the pH of the recovered water was of ca. 6.5 and dried at 60 °C for 4 hours, and subjected to a second heat treatment at 600 °C under N₂ for 2 hours, denoted as Fe-N/C-TsOH-600HLH.

2.2. Physical characterizations

The crystal-phase X-ray diffraction (XRD) patterns were collected on X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 0.15406$ nm) and operated at 40 kV and 40 mA.

Surface characterization of the catalyst samples was carried out by X-ray photoelectron spectroscopy on a PHI Quantera Scanning X-ray Microprobe™ 5300 system (ULVAC- PHI. INC) to determine the surface composition with Al K X-ray anode source (h $\nu = 1486.6$ eV) at 300 W and 15.0 kV.

2.3. Electrochemical measurements

The electrocatalytic activities of catalysts after heat-treatment at different temperatures were determined by both CV and linear sweep voltammetry (LSV) using a rotating glassy carbon disk electrode (glassy carbon electrode with a geometric surface area of 0.19625 cm², purchased from Gamry Instruments). The catalyst ink for RDE was prepared by blending 4 mg of catalyst and 2 mL of methanol/Nafion® solution (50:1 in mass), which was ultrasonically dispersed for 10 min to form a suspension. 10 μ L of this suspension was then pipetted onto the surface of glassy carbon electrode and then dried at room temperature. The loading of catalysts was 101 μ g·cm⁻².

Catalyst coated glassy carbon electrode described above was used as working electrode. A 0.1 mol·L⁻¹ KOH aqueous solution was used as the electrolyte. A saturated calomel electrode (SCE) and Pt wire were used as the reference and counter electrodes, respectively. All measured potentials were converted to the standard hydrogen electrode (SHE). For CV, the electrode was scanned at a scan rate of 50 mV·s⁻¹ in the potential range between -0.80 and 0.30 V to measure the surface behavior of the catalyst in N₂-saturated KOH solution, and the ORR activity of the catalyst in O₂-saturated KOH solutions, respectively. For more quantitative measurements of the ORR activity, LSV was conducted on the catalyst-coated RDE in the potential range between -0.76 and 0.15 V in O₂-saturated KOH solution at various rotation rates from 300 to 2400 r·min⁻¹.

3. Results and discussion

3.1. Electrochemical activities

To evaluate the effects of thermal treatment on the ORR activity, Fig. 1 gives the CV curves of the dual-doped catalysts pyrolyzed at different temperature in O₂-saturated 0.1 mol·L⁻¹ KOH solution obtained at a potential scanning rate of 50 mV·s⁻¹. Normally, the ORR peak potential (E_p) and the reduction peak current density (I_p), which are listed in Table 1, can be used as the indication to evaluate the catalytic activity of the catalyst. There are obvious redox peaks for three catalysts with a characteristic reduction peak associated with the ORR suggesting that the dual-doped catalysts have good ORR activity. However, more excellent positive peak potential value and higher peak current density were obtained for

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