

# Synthesis of dual-doped non-precious metal electrocatalysts and their electrocatalytic activity for oxygen reduction reaction

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## Abstract

The pyrolyzed carbon supported ferrum polypyrrole (Fe-N/C) catalysts are synthesized with or without selected dopants, *p*-toluenesulfonic acid (TsOH), by a facile thermal annealing approach at desired temperature for optimizing their activity for the oxygen reduction reaction (ORR) in O<sub>2</sub>-saturated 0.1 mol/L KOH solution. The electrochemical techniques such as cyclic voltammetry (CV) and rotating disk electrode (RDE) are employed with the Koutecky-Levich theory to quantitatively obtain the ORR kinetic constants and the reaction mechanisms. It is found that catalysts doped with TsOH show significantly improved ORR activity relative to the TsOH-free one. The average electron transfer numbers for the catalyzed ORR are determined to be 3.899 and 3.098, respectively, for the catalysts with and without TsOH-doping. The heat-treatment is found to be a necessary step for catalyst activity improvement, and the catalyst pyrolyzed at 600 °C gives the best ORR activity. An onset potential and the potential at the current density of  $-1.5 \text{ mA/cm}^2$  for TsOH-doped catalyst after pyrolysis are 30 mV and 170 mV, which are more positive than those without pyrolyzed. Furthermore, the catalyst doped with TsOH shows higher tolerance to methanol compared with commercial Pt/C catalyst in 0.1 mol/L KOH. To understand this TsOH doping and pyrolyzed effect, X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) are used to characterize these catalysts in terms of their structure and composition. XPS results indicate that the pyrrolic-N groups are the most active sites, a finding that is supported by the correspondence between changes in pyridinic-N content and ORR activity that occur with changing temperature. Sulfur species are also structurally bound to carbon in the forms of C–S<sub>n</sub>–C, an additional beneficial factor for the ORR.

## Key words

non-precious metal electrocatalyst; dual-dopant; heat-treatment; oxygen reduction reaction; polymer electrolyte membrane fuel cell

## 1. Introduction

Fuel cells are considered as one of the most promising candidates for energy converting devices in power-intensive applications such as stationary, portable, and automobile power supplies due to their advantages such as high energy density, high power density and high energy conversion efficiency, as well as their low or zero emissions [1,2]. Nevertheless, two big challenges are remained at the current stage including prohibitive cost and inadequate durability, which still hamper the commercialization of fuel cell technology.

Regarding the high cost, Pt-based catalysts which have been regarded as the most electrocatalyst for ORR, contribute over 50% of the total cost of a fuel cell stack [3]. Accordingly, the replacement of high-cost and scarce precious-metal cat-

alysts with commercially available alternatives has attracted much attention from both industrial and academic researchers in catalysis. For this purpose, the carbon-supported transition metal materials (M-N<sub>x</sub>-C, M = Fe, Co, Ni, V, Mn, etc.), which consequently favor the molecular adsorption of oxygen and its reduction, have evoked great interest due to their promising catalytic activity towards the ORR, along with the utilization of abundant, inexpensive precursor materials [4,5]. On the other hand, it has been recognized that the nitrogen sources in the catalyst precursors during the M-N<sub>x</sub>-C synthesis play a crucial role in ameliorating ORR activity as well as stability [6,7]. And this is the reason why several different types of nitrogen-containing macrocycles, inorganic salts and organometallic compounds have been employed as the precursors to form metal-nitrogen complex catalysts [8–14].

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Polypyrrole (PPy), a well known electrically conducting polymer, with many pyrrole-type N atoms, altering surface, and easy preparation and doping, has been widely used for the synthesis of M-N<sub>x</sub>-C catalysts since it was first investigated by Yuasa in 2005 [13]. It was found that the pyrolyzed Co-PPy/C catalyst could deliver enhanced catalytic activity and stability, and the surface modification of a carbon particle with PPy provided a simple system allowing the immobilization of cobalt ions at the surface by coordination processes and displaying electrocatalytic activity for the four-electron reduction of O<sub>2</sub>. Later, Zelenay and his co-worker [4] presented a different way to synthesize Co-PPy/C electrodes catalyst for oxygen reduction reaction. They deposited PPy on carbon black to form a catalyst support (PPy/C) via an oxidative polymerization process using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant. After impregnating cobalt ions, a carbon-supported cobalt catalyst (Co-PPy/C) was generated. Research showed that sodium borohydride (NaBH<sub>4</sub>) as reductive agent can improve the catalyst activity and stability, and Co-N<sub>2</sub> may be the active sites.

In fact, for performance optimization, heat-treatment or thermal activation for catalyst synthesis has been recognized as an important and sometimes necessary step to further improve the activity and stability. Although the heat-treatment effect on catalysts has been well documented, the mechanisms of the catalyst reaction during the heat-treatment process and the resulting improvement in activity are complicated and not fully understood [10,15]. According to the literature [16], thermal treatment has a significant impact on metal particle size and size distribution, particle surface morphology as well as metal dispersion on the support. Another benefit of heat-treatment is to remove any undesirable impurities and allow a uniform and stable distribution of the transition metals on the support, which improves the electrocatalytic activity [15]. In addition, when the catalysts are pyrolyzed at a desired high temperature in a flowing inert atmosphere (nitrogen or argon), M-N precursor is partially or completely decomposed, resulting in a catalyst with much better catalytic activity and stability than an untreated one [17].

Very recently, to further improve the activity, doped or dual-doped carbons with two different heteroatoms (e.g. N, B, P, S or Se) [18,19] become one promising option for ORR by taking advantage of different heteroatoms in conjugated carbon backbone that can create new non-electron-neutral sites. In particular, the sulfur (or sulfo group), which has a close electronegativity to carbon, has been employed as a dual-dopant in the preparation of M-N<sub>x</sub> catalysts [17,20]. It was thought that the sulfur group doped to the M-N<sub>x</sub>-C might be helpful for entrapping M ions in an environment rich in pyrrole-type or pyridine-type nitrogen, thus significantly enhancing ORR activity [10] and durability [17].

Based on above conceptions, we here report a novel dual-doped non-precious metal catalyst, namely Fe-N/C-TsOH, based on carbon-supported ferrum, polypyrrole (PPy) and p-toluenesulfonic acid (TsOH) complex, where PPy and TsOH were used as N- and S-dopant. In particular, TsOH, an organic compound, is known as tosyl group and not only was

used as the S precursor, but also used as an “organic-soluble” acid catalyst to promote the oxidation of pyrrole. A detailed comparative study was carried out through the systematic analysis of Fe-N catalysts with and without TsOH-doping by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM), and the catalytic activities were screened using cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques in oxygen-saturated alkaline solutions. We here demonstrate that TsOH, as a co-dopant, can significantly enhance the electrocatalytic activity of ORR due to the strong synergistic effect of combined S- and N-doping in the catalyst. The Fe-N/C-TsOH, as the cathode catalyst, thus provides a much better ORR performance than that without TsOH-doping.

## 2. Experimental

### 2.1. Catalysts preparation

For the preparation of nitrogen and sulfur dual-doped non-precious metal electrocatalyst, Fe-N-S catalyst (Fe-N/C-TsOH), 120 mg carbon black (Vulcan XC 72R), 50 mg pyrrole and 10 mL methanol were first mixed, followed by 10 min of ultra-sonication. Then this ultrasonication suspension was mixed with 0.25 mL 30% H<sub>2</sub>O<sub>2</sub> and 50 mg TsOH, while milling in a mortar for some time to obtain a slurry. 10 mL methanol with 149 mg FeSO<sub>4</sub>·7H<sub>2</sub>O was added into the mortar, followed by constant grinding for another 45 min, which was then dried in a vacuum at 60 °C for 1 h to obtain a powder. This powder was then pyrolyzed under N<sub>2</sub> atmosphere at 200, 400, 600 and 700 °C, respectively, for 2 h to optimize the thermal temperature with respect to ORR electrolytic activity, forming the final carbon-supported Fe-N-S catalyst. To elucidate the effect of TsOH alone, a baseline sample of carbon loaded Fe-N without TsOH was also prepared under the same conditions depicted above, and is denoted as Fe-N/C in this paper. For a convenience comparison, in figure legends, “RT” means the unpyrolyzed catalyst sample, and the number, for example “600” indicates the pyrolyzed temperature used for catalyst synthesis.

### 2.2. Electrode preparation and electrochemical experiments

Electrochemical measurements were performed in a conventional three-electrode cell using a rotating glassy carbon disk electrode (RDE) (glassy carbon electrode with a disk diameter of 5.0 mm, purchased from Gamry Instruments) which was coated with catalyst to form the catalyst layer as working electrode. According to the electrode preparation method described by Qiao et al. [17], 10 μL of catalyst ink, which consists of 2.0 mg<sub>cat.</sub>/mL, was pipetted onto the glassy carbon (GC) disk electrode. The loading of catalysts was 101 μg/cm<sup>2</sup>. And a calomel electrode with saturated KCl (SCE) and Pt wire were used as the reference and counter electrodes, respectively.

For cyclic voltammograms (CVs), the electrode was

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