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# Effects of composition on electrochemical properties of a non-precious metal catalyst towards oxygen reduction reaction

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## ABSTRACT

A family of non-precious metal catalysts, Co-PPy-TsOH/C, has been synthesized with different amount of pyrrole and *p*-toluenesulfonic acid (TsOH). Elemental contents of Co, N, C, S, H and O in the obtained catalysts have been measured with physicochemical techniques and the performance of these catalysts towards oxygen reduction reaction (ORR) have been evaluated with electrochemical techniques. Then, the results obtained have been discussed with principal component analysis and linear correlation analysis to find the correlation/anticorrelation between the composition and electrochemical properties. It is revealed that the used amount of pyrrole has much more apparent effect than TsOH on elemental contents in the Co-PPy-TsOH/C catalysts, while both of them influence the ORR activity and mechanism of the catalysts. Besides, the effects of the contents of each element on the electrochemical performance have also been analyzed to guide the future development of similar catalysts.

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## 1. Introduction

Environmentally friendly energy conversion systems attract growing attention to fulfill the energy requirements in the future. Proton exchange membrane fuel cells (PEMFCs) are promising sources of clean energy by converting chemical energy directly into electricity. In practice, catalysts are needed to promote the electrochemical reactions of hydrogen oxidation at the anode and oxygen reduction at the cathode in

PEMFCs, especially the sluggish oxygen reduction reaction (ORR) [1–3]. At present, carbon supported Pt and its alloys have been proved and accepted to be the most efficient catalyst for ORR. However, high cost and limited resources of the noble metal platinum and its low utilization have constrained the commercialization of PEMFCs [1]. Therefore, development of low cost and efficient non-precious metal electrocatalyst for ORR has become an urgent task for worldwide fuel cell people, and numerous efforts have been made in recent decades [4–8].

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Among various non-precious metal electrocatalysts for ORR, carbon supported transition metal-based nitrogen-containing catalysts (M-N/C) have been considered as the most promising replacement for the existing platinum-based catalysts for ORR in PEMFCs, and extensive researches have been conducted on M-N/C catalysts of carbon-containing metalloporphyrin, carbon-containing metallophthalocyanine, carbon-containing metal-conducting polymer and others prepared by high temperature pyrolysis of simple metal salts, nitrogen sources and carbon [9–12]. The results showed that the catalytic performance of M-N/C catalysts towards ORR is closely related to the used metal type and its precursor and content, nitrogen source and its content, heat treatment temperature and time as well as the structure of the catalysts [13–23]. However, a widely accepted consensus has not been achieved to date. The actual catalytic active sites and mechanism of the M-N/C catalysts towards ORR are still unclear, conflicting results have been reported in literature. For example, M-N<sub>4</sub> has been proposed to be the ORR active site in heat-treated carbon-supported metalloporphyrins and phthalocyanines [24], while Lee et al. presented that pyrrolic (or pyridinic) nitrogen and graphitic nitrogen may be responsible for the ORR activity of the pyrolyzed M-N/C catalyst and M-N<sub>2</sub> is responsible for the activity of the unpyrolyzed M-N/C catalyst [25]. Another viewpoint is that metal-nitrogen bond does not exist anymore in the catalyst after pyrolysis at high temperature but the metal and/or its oxide particle works as the real ORR active site in M-N/C catalysts [20]. On the contrary, however, it has also been suggested that the metallic atoms and the oxide themselves hardly contribute to ORR activity of the M-N/C catalysts, but the actual active sites may rely on the light elements such as C, N and O [26,27]. Moreover, Li et al. demonstrated that the individual interactions between the carbon and nitrogen, carbon and metal, and metal and nitrogen are not critical to the enhancement of ORR performance, while the cooperative interaction (synergy) among the metal, nitrogen and carbon is the key towards improving the ORR kinetics [28].

In recent years, application of conducting polymer in M-N/C catalysts for ORR in PEMFCs has attracted a growing body of research. As a carrier, the conducting polymer not only acts as a support that makes catalyst to be fixed on the surface, but also promotes catalyst particles to be well-distributed avoiding occasional agglomeration. More importantly, the chemical state of the catalyst surface could be modified by the conducting polymer, leading to enhanced catalytic activity and durability [29,30]. Among diverse nitrogen-containing conducting polymer, polypyrrole (PPy) has received much more attention because of its excellent environmental stability, facile synthesis and high conductivity [31–34]. Many papers have demonstrated inspirational catalytic performance and stability of Co-PPy/C and Fe-PPy/C as catalysts towards ORR with both electrochemical techniques and PEMFC performance measurements [34–45]. However, as a new member of M-N/C catalysts, the Co- and/or Fe-PPy/C has not been systematically investigated, the effects of preparation, composition as well as structure have not been comparatively reported. This greatly impedes the development and real application of this kind of catalysts in PEMFCs.

In a previous work [35], we have successfully developed a *p*-toluenesulfonic acid (TsOH) doped Co-PPy/C catalyst,

namely Co-PPy-TsOH/C, where TsOH was employed as additive to enhance the conductivity of PPy and modify the surface characteristics. The obtained Co-PPy-TsOH/C catalyst demonstrated much better performance than the undoped catalyst of Co-PPy/C, a peak power density of 203 mW cm<sup>-2</sup> was delivered by the H<sub>2</sub>-O<sub>2</sub> PEMFC with it as cathode catalyst. In another work focusing on the effects of oxidants for pyrrole polymerization [45], the co-relation of structure–morphology–performance has been comparatively investigated by using X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), Raman spectroscopy, transmission electron microscopy (TEM) and X-ray photoemission spectroscopy (XPS). It was found that the pyrrole-ring has been destroyed by high temperature pyrolysis and the nitrogen has inserted into the carbon layers as pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen as well as oxidized nitrogen in the obtained Co-PPy-TsOH/C catalysts. In the meanwhile, metallic cobalt along with small amount of cobalt oxide has been observed in the catalysts [45]. However, we are still not sure about the real active site in this kind of catalysts. Besides, we have found with this research that slight difference in the usage of pyrrole and/or TsOH during catalyst preparation has little influence on the XRD patterns, TEM images and XPS spectra of the resulting catalysts, but affects the elemental composition and the ORR performance apparently. Therefore, we conducted the present work to study the effects of elemental composition on the electrocatalytic activity of the Co-PPy-TsOH/C catalysts towards ORR. We synthesized a class of Co-PPy-TsOH/C catalysts by adjusting the used amount of PPy and TsOH, measured the contents of each element with inductively coupled plasma (ICP) and elemental analysis, and comparatively studied the effects of composition on the catalytic performance towards ORR employing electrochemical techniques along with principal component analysis and linear correlation analysis.

## 2. Experimental

### 2.1. Catalyst preparation

Pretreated BP2000 (Cabot, USA) was used as carbon support of the catalysts in this study. The pretreatment was conducted by ultrasonically blending 8 g BP2000 with 250 mL 6 M HNO<sub>3</sub> solution along with fluxing at 80 °C for 10 h. The resulted solution was then filtered, thoroughly washed with double distilled water, dried in a vacuum oven at 70 °C and finally ground to powders.

The catalyst preparation was performed by a three-step procedure as previously described [45]. The first is the surface modification of BP2000 with PPy, followed by the second step of cobalt impregnation and the last step of high temperature heat-treatment. Specifically, the PPy modified BP2000 was synthesized by in-situ polymerization of pyrrole: after homogeneous dispersion of 0.6 g BP2000 in 100 mL isopropanol, appropriate amount of freshly distilled pyrrole and 100 mL double distilled water were added and stirred for 30 min. Whereafter, designed amount of TsOH and 6 mmol ammonium persulfate were slowly added and the obtained suspension was vigorously stirred for 4 h. The product was

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