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Comparative investigation on the properties of carbon-supported cobalt-polypyrrole pyrolyzed at various conditions as electrocatalyst towards oxygen reduction reaction

Xianxia Yuan^{a,*}, Hao-Dong Sha^a, Xin-Long Ding^{a,d}, Hai-Chuan Kong^a, He Lin^b, Wen Wen^b, Taizhong Huang^e, Zhi Guo^b, Zi-Feng Ma^a, Yong Yang^c

^a Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

^b Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academic of Science, Shanghai 201204, China

^c State Key Laboratory of Physical Chemistry of Solid Surface & Department of Chemistry, Xiamen University, Xiamen 361005, China

^d Shanghai Keyuan Chemical & Gas Engineering Design Co., Ltd., Shanghai 200235, China

^e Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, School of Chemistry and Chemical Engineering, University of Jinan, Shandong 250022, China

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ABSTRACT

A series of non-precious metal catalysts named as Co-PPy-TsOH/C towards oxygen reduction reaction (ORR) were synthesized by pyrolyzing carbon supported cobalt-polypyrrole at various temperatures for diverse durations. The catalytic activity of these catalysts was evaluated with electrochemical techniques of cyclic voltammetry, rotating disk electrode and rotating ring-disk electrode. Physicochemical techniques, such as XRD, TEM and XPS, were employed to characterize the structure/morphology of the catalysts in order to understand the effects of pyrolysis conditions on the ORR activity. The results showed that both pyrolysis temperature and the duration have essential effects on the structure/morphology as well as ORR activity of the Co-PPy-TsOH/C catalysts, pyrolyzing the precursor at 800 °C for 2 h is the optimal condition to synthesize the catalyst with the best ORR performance.

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Introduction

Energy crisis is more and more serious in recent years, development of an efficient, clean and regenerative energy is a

crucial and urgent task for the whole human in the world. Fuel cells, as devices that convert chemical energy in fuel directly into electricity via electrochemical reactions, have demonstrated wide application prospects in many areas, such as

* Corresponding author.

E-mail addresses: yuanxx519@163.com, yuanxx@sjtu.edu.cn (X. Yuan).

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transportation, stationary power station and portable electric devices. Among various types of fuel cells, proton exchange membrane fuel cells (PEMFCs) have attracted much more attention owing to the merits of high power density, high energy conversion efficiency, fast start-up and low emissions, and have been considered as potential candidates of high power suppliers. However, wide scale commercialization of PEMFCs suffers from high cost and limited resource of Pt-based catalysts used in the cathode for accelerating oxygen reduction reaction (ORR) [1]. Therefore, tremendous efforts have been conducted to develop cost-reduced and efficient non-precious metal catalysts in the last several decades, wherein transition metal-based nitrogen-containing complexes, such as metalloporphyrin, metallophthalocyanine, metal-conducting polymer and so on, have been most actively researched and approved to have promising catalytic performance [2–14]. As one of the nitrogen sources for this kind of catalyst, polypyrrole (PPy) is attracting growing interest, owing to the flexible structure, high surface area, high conductivity, facile synthesis and excellent environmental adaptability [15,16], and the corresponding Co-based catalyst, namely Co-PPy/C, has become a hot topic in the research field of non-precious metal catalysts for ORR in PEMFCs [17–25]. However, there are still many pending challenges for Co-PPy/C as ORR catalyst, even though many great progresses have been achieved in recent years [6]. For example, the ORR mechanism catalyzed by Co-PPy/C is still unclear at present; the true function of PPy in Co-PPy/C as catalyst towards ORR is contentious; little attention has been paid to the relationship between morphology/structure and catalytic performance of Co-PPy/C catalysts, it remains unknown which structure of PPy is preferred for high activity catalysts; the aging mechanism of Co-PPy/C catalysts remains largely unknown.

In a previous work [19], a *p*-Toluenesulfonic acid (TsOH)-doped Co-PPy/C catalyst, namely Co-PPy-TsOH/C, has been successfully developed in our group. Its electrochemical performance towards ORR was greatly improved from that of the undoped Co-PPy/C catalyst, the catalyzed ORR by Co-PPy-TsOH/C is more likely than that by Co-PPy/C to follow a four-electron transfer reaction to reduce oxygen directly into H₂O and the H₂-O₂ PEMFC with Co-PPy-TsOH/C as the cathode catalyst delivered a peak power density of 203 mW cm⁻² at 80 °C with no back pressure used on either side of the cell. However, the preparation of the catalyst therein has not been optimized and the reported results were only from preliminary experiments. In order to further enhance the catalytic performance towards ORR, a series of Co-PPy-TsOH/C catalysts have been synthesized, in the present work, with diverse pyrolyzing conditions, and the effects of heat treatment temperature and the duration on performance of the obtained catalysts have been comparatively investigated. Then, various physicochemical techniques were employed to understand the results.

Experimental

Catalysts synthesis

The studied Co-PPy-TsOH/C catalysts were synthesized with a similar procedure to that used in our previous work [19].

Specifically: BP2000 carbon powder from Cabot was treated at 100 °C for 8 h in 6 M HNO₃ solution, the resulted emulsion was then filtered, washed, dried and ground to fine particles. 0.6 g of the pre-treated BP2000 carbon was dispersed with sonication in 100 ml isopropanol for 30 min, followed by addition of 3 mmol freshly distilled pyrrole and 100 ml double distilled water. After stirring for 30 min, 100 ml ammonium peroxydisulfate solution with a concentration of 0.06 M and 0.1902 g TsOH were introduced and the resulted solution was vigorously stirred at room temperature for 4 h. After that, the mixture was filtered, washed at least 3 times with double distilled water and alcohol alternately, and then dried at 45 °C under vacuum for 12 h to obtain the PPy-modified carbon of PPy-TsOH/C. After blending 0.5 g PPy-TsOH/C and 0.25 g Co(CH₃COO)₂·4H₂O with 200 ml double distilled water by ultrasonic for 1 h and then vigorous stirring for 2 h, the solvent was evaporated under reduced pressure and the remaining powders, called as catalyst precursor, were pyrolyzed in argon atmosphere at various temperatures for diverse durations.

Electrochemical characterizations

The electrochemical catalytic performance of the prepared Co-PPy-TsOH/C catalysts towards ORR was evaluated with techniques of cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) at room temperature of about 25 °C in a standard three-electrode cell. A 0.5 M H₂SO₄ solution was employed as the electrolyte, a Pt wire and a saturated calomel electrode as the counter electrode and the reference electrode, respectively, and an ink-type electrode was used as the working electrode. The procedure used in this work to fabricate the ink-type electrode is as follows: 6 mg catalyst, 1 ml double distilled water and 50 μl Nafion[®] solution (5 wt%, DuPont) were blended in an ultrasonic bath for 30 min to make a uniformly dispersed ink, 10 μl of which was then deposited onto the surface of a glassy carbon substrate with a pipette and then air-dried. CV curves were recorded, after activation, in the potential range from -0.2–1 V (vs. SCE) at a scan rate of 5 mV s⁻¹ in oxygen saturated 0.5 M H₂SO₄ solution controlled by a CHI750 potentiostat/galvanostat. Both the RDE and RRDE experiments were carried out in argon and oxygen saturated 0.5 M H₂SO₄ solution, respectively, with the same conditions as CV and additional electrode rotation at 900 rpm. For the RRDE experiments, the ink was only deposited onto the disk in the ring-disk electrode and the ring potential was fixed at 1 V (vs. SCE) controlled by a CHI750 potentiostat/galvanostat along with a Pine 636 rotating disk electrode system.

All the potentials reported in the following contents are against normal hydrogen electrode (NHE) except specially stated.

Physicochemical characterizations

Thermal analysis of the catalyst precursor was performed on a TA Instruments-Waters LLC SDT Q600 analyzer in nitrogen atmosphere with a heating rate of 20 °C min⁻¹.

X-ray diffraction (XRD) patterns of the Co-PPy-TsOH/C catalysts were obtained with a Shimadzu LabX XRD-6000 diffractometer using Cu K α radiation ($\lambda = 1.546 \text{ \AA}$) along with

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