



Experimental identification of the active sites in pyrolyzed carbon-supported cobalt–polypyrrole–4-toluenesulfinic acid as electrocatalysts for oxygen reduction reaction



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HIGHLIGHTS

- Co–PPy–TsOH/C as electrocatalysts towards oxygen reduction reaction (ORR).
- Effects of acid leaching and second heat treatment on catalyst performance.
- Effects of cobalt loading on catalyst performance.
- The identified ORR active site in the Co–PPy–TsOH/C catalysts.

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ABSTRACT

A series of carbon supported cobalt–polypyrrole–4-toluenesulfinic acid have been pyrolyzed in an argon atmosphere at 800 °C, then structurally characterized and electrochemically evaluated as oxygen reduction reaction (ORR) catalysts in aqueous 0.5 M sulfuric acid. The structures are cobalt bonded to nitrogen species (Co–N_x) along with metallic cobalt and cobalt oxide. When the cobalt loading in the compound is less than 1.0 wt%, the predominate form is Co–N_x, when the loading is higher than 1.0 wt%, metallic Co and Co oxide particles co-exist with the Co–N_x compound. At a Co loading of ~1.0 wt%, the catalyst gives the best ORR activity. Both metallic Co and Co oxide are not active for catalyzing ORR, and block the catalytically active Co–N_x species from the surface and reduce the catalytic activity since the diffusion limiting current density on a rotating disk electrode (RDE) increases when the electrode blocking agents are washed away with acid.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs), as a kind of clean and high efficiency energy conversion devices, have been recognized as the potential future power sources for many applications such as the zero/low-emission vehicles, stationary and portable power stations [1,2]. However, there are still some obstacles such as high cost and insufficient durability hindering their commercialization. In overcoming these two major challenges, PEMFC electrocatalysts for cathode oxygen reduction reaction (ORR) have been identified as one of the major target materials for further development and performance improvement. At current state of technology, the platinum

(Pt)-based ORR electrocatalysts seem to be the most practical in terms of both catalytic activity and stability. However, the limited supply and high cost of Pt are the barriers for the sustainable applications. Thus, reducing Pt usage or replacing Pt with non-noble metal catalysts is critical to PEMFC commercialization [3,4].

Regarding non-Pt ORR catalysts, several types of transition metal-based materials have been explored, including (1) transition metal macrocyclic compounds, [5–7] (2) carbon supported transition metal-nitrogen complexes (M–N/C compounds, normally M = Fe or Co) synthesized by pyrolysis using metal salt, carbon, and nitrogen sources as the precursors, [8–11] and (3) transition metal chalcogen compounds [12–14]. Among them, the pyrolyzed M–N/C compounds have been confirmed as the most efficient ORR catalyst in recent years due to their relatively high electrocatalytic activity, low cost and simple synthetic procedures.

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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. This pyrolysis process cannot only produce M–N_x group such as M–N₂ and M–N₄ but also produce metallic and metal oxide species on the carbon particle surface. Although M–N_x groups were proposed as the ORR active sites, the contribution of metallic and metal oxide species to the ORR activity seemed not to be distinguished from that contributed by M–N_x sites [8,15,16]. Lee et al. [17] proposed that M–N_x–C (X = 2 or 4) could be the active sites, which might be responsible for two- and four-electron transfer ORR pathways. Some literature reported that metal–nitrogen bond would not survive during the high temperature pyrolysis but the metal and/or its oxide particles might work as the real ORR active sites in pyrolyzed M–N/C catalysts [6,9]. Normally, the central metal atom in the catalysts is believed to play a very important role [18]. Through acid washing the pyrolyzed catalysts with intention to remove metallic and metal oxide species, no significant change in the ORR performance before and after acid washing could be observed, suggesting that the metals and metal oxides themselves probably not contribute too much to ORR activity, but the actual active sites might rely on other insoluble surface species [19–21]. Some literature reported that the ORR active sites should be composed of carbon and nitrogen such as the pyridinic nitrogen (–C=N–C–) sitting on the edge planes of the carbon layer [22,23] and the graphitic-N which is bonded to three carbon atoms inside the carbon layer [24–26]. Li et al. [27] reported that the cooperative interaction (synergy) among the metal, nitrogen and carbon should be the key factor in improving the ORR kinetics. Even though the active sites for ORR in pyrolyzed M–N/C catalysts is still under discussion, some consensus have been drawn: [4,28,29] (i) the nitrogen and carbon atoms are necessary for catalytic ORR activity, and (ii) the presence of the metal atoms during the high-temperature pyrolysis of carbon supported transition metal–nitrogen complexes can contribute to the ORR enhancement catalyzed by the resulting catalysts.

As a member of M–N/C catalysts, pyrolyzed cobalt–polypyrrole (PPy)–4-toluenesulfonic acid (TsOH) supported on carbon, (Co–PPy–TsOH/C)_p, has demonstrated exciting ORR performance used as cathode catalyst in PEMFCs [10]. In the effort to obtaining the fundamental understanding about the catalytic active sites and their catalyzed ORR mechanisms, in this work, a series of (Co–PPy–TsOH/C)_p catalysts as well as some contrastive samples were synthesized. The morphologies/structures and compositions were characterized using the powder X-ray diffraction (XRD), the transmission electron microscopy (TEM) images, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP) spectrometric measurements. The catalytic ORR activities of the synthesized catalysts were examined using cyclic voltammetry (CV) and rotating disk electrode (RDE) experiments. Furthermore, the morphology/structure–performance relationship has been discussed to distinguish the catalytic active sites and the role of each element in the catalysts.

2. Experimental section

2.1. Catalysts synthesis

In synthesizing the precursor for the pyrolyzed catalyst of (Co–PPy–TsOH/C)_p, a carbon suspension was first prepared by adding 0.6 g of BP2000 carbon powder (Cabot, USA, pretreated with 6 M HNO₃) to 100 ml of isopropyl alcohol under ultrasonication for 1 h at room temperature. Then, 3 mmol of freshly distilled pyrrole and 100 ml of double distilled (DI) water were added into this carbon

suspension under stirring for 30 min to form a mixture. After that, 100 ml of 0.06 mol l⁻¹ ammonium peroxydisulfate (APS) aqueous solution as oxidant and 0.1902 g of TsOH as additive were introduced into this mixture, followed by an additional vigorous stirring for 4 h. The resulted mixture solution was then filtered, washed and dried at 45 °C for 12 h to obtain the PPy–TsOH impregnated carbon powder material (PPy–TsOH/C). Then, 0.5 g of this PPy–TsOH/C and 0.2 g of Co(Ac)₂·4H₂O were mixed together with 200 ml of DI water. The formed mixture was ultrasonically mixed for 1 h and another vigorous stirring for 2 h, followed by an evaporation process under reduced pressure to obtain the catalyst precursor which is expressed as Co–PPy–TsOH/C. This precursor was pyrolyzed in argon atmosphere at 800 °C for 2 h to obtain the pyrolyzed catalyst of (Co–PPy–TsOH/C)_p.

In order to remove the possible metallic cobalt and/or its oxide on the carbon support surface of the (Co–PPy–TsOH/C)_p catalyst produced in the pyrolysis step, the catalyst was treated with 0.5 M H₂SO₄ solution at 90 °C for 4 h and then washed thoroughly with DI water. The resulting catalyst was referred to as (Co–PPy–TsOH/C)_{p-A} (here the subscripted “A” indicates acid treatment). After the acid treatment, the (Co–PPy–TsOH/C)_{p-A} catalyst was further heat-treated in argon atmosphere under 800 °C for 2 h to obtain the catalyst expressed as (Co–PPy–TsOH/C)_{p-A-p}.

For comparison, the sample material without Co (expressed as (PPy–TsOH/C)_p) and that without PPy–TsOH (expressed as (Co/C)_p) were also prepared with the same procedure as described above.

To investigate the effects of cobalt loading on ORR catalytic activity of the (Co–PPy–TsOH/C)_p catalyst, various amounts of Co(Ac)₂·4H₂O (0.00625 g, 0.0125 g, 0.025 g, 0.05 g, 0.125 g and 0.25 g) were used to deposit onto 0.5 g of PPy–TsOH/C to form Co–PPy–TsOH/C precursors, followed by pyrolysis in argon at 800 °C for 2 h to obtain catalysts containing different levels of Co loading. The obtained catalysts were expressed as (x-Co–PPy–TsOH/C)_p where x represents the designed cobalt content in the catalyst and the values were 0.25 wt%, 0.5 wt%, 1 wt%, 2 wt%, 5 wt% and 10 wt%, respectively.

To verify the cobalt loading effect, a method of impregnation was used for catalyst synthesis. Specifically, 0.5 g of PPy–TsOH/C was dispersed in a saturated solution of cobalt acetate in 100 ml of DI water. The obtained suspension was refluxed at 60 °C for 10 h. After cooling down to room temperature, the product was collected by filtration, washed thoroughly with ethanol and water, and dried under a vacuum at 45 °C for 12 h to give the powders of (Co–PPy–TsOH/C)_i, which was then pyrolyzed in argon atmosphere at 800 °C for 2 h to obtain the catalyst of (Co–PPy–TsOH/C)_{i-p} (here the subscripted “I” indicates the impregnation process).

2.2. Physical characterization

To characterize the crystal structures, XRD patterns of the synthesized catalysts were obtained on a Shimadzu 6000 X-ray diffractometer using Cu K_α radiation (λ = 1.5406 Å). TEM images taken by a JEOL JEM-2100 instrument operated at 200 kV and 30 mA were used to observe the catalyst powders' morphologies. To identify the possible catalyst active sites, XPS measurements were performed with Kratos AXIS ULTRA DLD with Al K_α as excitation source (hν = 14 kV). The data were analyzed and sub-peak fitted with the software of XPS Peak 4.1. The cobalt content in the catalysts was detected using a Thermal iCAP 6000 ICP spectrometer by soaking the catalyst in aqua regia.

2.3. Electrochemical evaluation

The electrochemical activity of the catalysts towards ORR was evaluated in a conventional three-electrode cell containing a

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