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N-doped and N/Fe-codoped porous carbon spheres derived from tetrazine-based polypyrrole as efficient electrocatalysts for the oxygen reduction reaction

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ABSTRACT

N-doped and N/Fe-codoped carbon materials are currently recognized as the most efficient electrocatalysts for the oxygen reduction reaction (ORR) because of their high catalytic activity, excellent stability, and superior tolerance to fuel. In this work, a novel kind of tetrazine-based polypyrrole spheres (PTPys) is prepared by protonic acid catalyzed Friedel-Crafts polymerization of bis(*N*-pyrrolyl)-1,2,4,5-tetrazine (TPy) with dimethoxymethane in dichloroethane. The resultant PTPys with a diameter of 100–300 nm are directly pyrolyzed at 900 °C to give N-doped porous carbon spheres (N/Cs-900 electrocatalyst). The N/Fe-codoped porous carbon spheres (Fe/N-Cs-900 electrocatalyst) are then constructed by mixing PTPys with $Fe(OAc)_2$ followed by pyrolysis at 900 °C. The as-synthesized N/Cs-900 and Fe/N-Cs-900 electrocatalysts both have a well-defined spherical architecture together with a relatively high N content, high surface area and porosity. Owing to the synergistic influences, Fe/N-Cs-900 electrocatalyst exhibits excellent ORR activities in both alkaline and acidic electrolytes together with superior poisons tolerance in acidic media, whereas N/Cs-900 electrocatalyst displays ORR activity primarily in alkaline electrolyte. This approach can synthesize heteroatom-doped porous carbon spheres dispensing with the need for any templates, which is of great explored potentiality and utilized value.

1. Introduction

Fuel cells (FCs) are a kind of very important energy conversion devices with promising development potential since they can transform chemical energy from fuels into electric energy directly [1,2]. Although FCs can guarantee clean and effective energy conversion with almost zero emissions, they seem to be not as powerful as batteries in terms of energy efficiency [3], due primarily to the slow kinetics of the cathodic oxygen reduction reaction (ORR) that is known to be caused by the state-of-the-art platinum (Pt) and its alloy electrocatalysts [4,5]. In addition, the Pt-based electrocatalysts are highly expensive and concurrently suffer from poor stability, low poison tolerance, and high overpotential, which seriously hamper the development and commercial application of FCs [1,4–9]. Recently, significant effort has been devoted toward designing and synthesizing high-performance ORR electrocatalysts. General speaking, the most ideal electrocatalyst for ORR in FCs should have such features as high surface area for maximum exposure of catalytic active sites [9], high electrical conductivity for facile electron transfer [10–12], hierarchical pore structure for efficient mass transport [13], high stability for a long lifetime [14], and much more affordable price for high-volume production [15].

From an electrocatalyst point of view, N-doped carbon materials (N/C) as well as transition-metal (M) incorporated N/C (M/N-C, M = Fe, Co, Ni, Cu, etc.) [4,16–24] are at least partially with the above characteristics. Traditionally, both N/C and M/N-C electrocatalysts can be prepared by post-synthesis and direct pyrolysis approaches. The former method involves direct pyrolysis of a carbon matrix (carbon nanotube [6,9,25], graphene [11,26,27], porous carbon [10,13,28]) with a N-rich precursor for the purpose of synthesizing N/C electrocatalyst, while pyrolysis of a carbon matrix with either a mixture of M salt and N-rich compound or a single N-enriched, M-containing complex can afford M/N-C electrocatalyst [29]. Compared to commercial Pt/C electrocatalyst, both N/C and M/N-C electrocatalysts prepared by this method usually exhibit lower ORR activities due to that the carbon matrix cannot be uniformly mixed with those N-rich and/or M-containing precursors, which restricts the formation of a high-density of ORR active sites and leads to a decrease in ORR activity [30]. However, both of the two electrocatalysts have several advantages including low-

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cost, high stability, and excellent fuel tolerance [31,32]. In order to facilitate the formation of ORR active sites, N/C and M/N-C electrocatalysts can also be prepared by directly pyrolyzing a single precursor that concurrently contains C and N sources (i.e., polyaniline [22,33], polypyrrole [34], polyacrylonitrile [35], etc.) in the former case and simultaneously contains C, N, and M sources in the latter case (i.e., polyaniline-Fe complex [22], prussian blue [36], etc.). This method guarantees that the ORR active sites can be fully formed because the N or N/Fe atoms are homogeneously distributed and fixed in the precursors. However, their ORR activities still have room to improve because of the undeveloped pore structures that result in a low degree exposure of ORR active sites [37]. That is to say, the available ORR active sites are still lower compared to the in situ formed active sites.

In order to expose the ORR active sites to a large extent, it is beneficial to construct N/C and M/N-C electrocatalysts with high surface area together with high porosity, in which ORR active sites can be distributed all over the electrocatalyst bulk including both outer and inner surfaces. At present, both hard-template strategy [9] and porous organic polymers (POPs)-based precursor [38–44] were adopted to realize this goal. Indeed, the hard-template strategy can guarantee finely tuned porosity for the final N/C and M/N-C electrocatalysts. However, the preparation and removal of hard template are generally laborious and tedious, which hinder the practical usage of such electrocatalysts. In order to surmount the obstacle, POPs have been widely adopted to construct these N/C and M/N-C electrocatalysts. The POPs-based precursors possess several merits including that they can be used to synthesize self-supported N/C and M/N-C electrocatalysts with high surface areas and high porosities, along with that they can promise the uniform N-doping and N/M-codoping. More importantly, recent progress in the field of ORR electrocatalysts has verified that ORR activity can be dramatically enhanced by converting the bulk electrocatalyst into nano/microsized ones. Up to now, various N/C and M/N-C electrocatalysts with architectures of tube [45,46], fiber [14,47], sheet [11,48], box [38], and sphere [19,49–52] etc. have been successfully fabricated. In particular, porous sphere-like structure has gained enormous attention because of the much higher surface area and porosity compared to its bulk counterpart. This porous sphere-like structure can lead to a full exposure of ORR active sites and meantime promise effective mass transport for the ORR [49]. Undoubtedly, the structure control of ORR electrocatalysts is also of great significance to promoting their catalytic activities.

Herein, we present a facile method to synthesize spherical N/C and M/N-C electrocatalysts by direct pyrolysis of tetrazine-based polypyrrole spheres (PTPys) and the mixture of PTPys and $Fe(OAc)_2$, respectively. We chose bis(*N*-pyrrolyl)-1,2,4,5-tetrazine (TPy) (Scheme S1, Fig. S1–3, see Supporting Information, SI) as the monomer for the preparation of spherical polypyrrole networks was due to that TPy had a relatively high N content (39.6 wt%). The TPy was polymerized through the Friedel-Crafts reaction in dichloroethane using dimethoxymethane (DMM) and methanesulfonic acid as the cross-linker and catalyst, respectively. The merit of this polymerization system lies in that the influence of metal residues on N/C electrocatalyst can be completely eliminated because no metal-containing precursor is used in the entire electrocatalyst synthesis process. In addition, Fe/N-C electrocatalyst can also be easily synthesized by mixing PTPys with $Fe(OAc)_2$ followed by pyrolysis. The as-synthesized N-doped and N/Fe-codoped porous carbon spheres (denoted as N/Cs-900 and Fe/N-Cs-900, respectively) were fully characterized and their ORR performances in both alkaline and acidic electrolytes were systematically investigated. It was demonstrated that the metal-free N/Cs-900 electrocatalyst showed ORR activity primarily in alkaline electrolyte, whereas the Fe/N-Cs-900 electrocatalyst displayed promising ORR activities in both alkaline and acidic electrolytes together with superior poisons tolerance in acidic media.

2. Experiment section

2.1. Synthesis of N/Cs and Fe/N-Cs electrocatalysts

For the preparation of N/Cs electrocatalysts, PTPys (400 mg) were directly pyrolyzed at different temperatures (800, 900 and 1000 °C) in a tube furnace in N_2 atmosphere for 2 h with a constant heating rate of $5\,^{\circ}C\,min^{-1}$. The pyrolysis products are referred to as N/Cs-*x*, where *x* represents the pyrolysis temperature. The carbon yields were found to be 33.6%, 28.6%, and 12.0%, respectively, for the N/Cs-800, N/Cs-900, and N/Cs-1000 electrocatalysts.

For the preparation of Fe/N-Cs electrocatalysts, PTPys (400 mg) and $Fe(OAc)_2$ (14.8 mg) were firstly dispersed in ethanol (30 mL) and sonicated at room temperature for 3 h. After evaporating to dryness, the solid was dried in vacuum. Subsequently, the dried mixture was pyrolyzed at $800-1000\,^{\circ}C$ in a tube furnace in N_2 atmosphere for 1 h. After cooling, the pyrolysis products were leached by H_2SO_4 aqueous solution (0.5 M) at 80 °C for 24 h to remove redundant Fe and its compounds. After further washing with water, the products were then subjected to a second pyrolysis at $800-1000\,^{\circ}C$ for 1 h under N_2 atmosphere. The resultant electrocatalysts were denoted as Fe/N-Cs-*x* (x = 800, 900, or 1000).

2.2. Electrochemical measurements

The electrochemical measurements were carried out on a CHI760D electrochemical workstation (Shanghai Chenhua Co., China) with a three-electrode cell at ambient temperature using 0.1 M KOH or 0.5 M H_2SO_4 solution as the electrolyte. The glassy carbon (5 mm in diameter) and Ag/AgCl (3 M KCl) electrodes were used as the working electrode and reference electrode, respectively. Platinum wire was used as the counter electrode in alkaline electrolyte, whereas graphite rod was used as the counter electrode in acidic electrolyte. All measured potentials in this study were converted to reversible hydrogen electrode (RHE) according to the following equation:

$$E_{(RHE)} = E_{Ag/AgCl} + 0.198 + 0.059 \times pH$$

Rotating ring-disk electrode (RRDE, Pine Research Instrumentation) measurements were carried out in O_2-saturated 0.1 M KOH or 0.5 M H_2SO_4 solution to estimate the peroxide yield and the electron transfer number (n) during ORR.

3. Results and discussion

3.1. Preparation and characterization of N/Cs-900 and Fe/N-Cs-900 electrocatalysts

In the present study, the tetrazine-based polypyrrole with well-defined spherical architecture (PTPys) was initially synthesized by Friedel-Crafts polymerization of TPy monomer with dimethoxymethane (DMM) cross-linker using methanesulfonic acid as the catalyst (Scheme S2, see SI). The dropwise addition of methanesulfonic acid to the TPy/DMM solution is the key process in the synthesis of polymer spheres. When the first drops of methanesulfonic acid were added, a very small fraction of TPy was protonated and became insoluble in dichloroethane, which aggregated to form tiny particles as confirmed by dynamic light scattering (DLS) analysis (Fig. S4, see SI). The Friedel-Crafts polymerization therefore occurred within the particles and adsorbed newly protonated TPy molecules on their surface to grow. At the same time, the polymerized particles might congregate together to form small particle nuclei. With the gradual addition of protonic acid catalyst, the continuous growth of polymer particles finally resulted in the formation of polymer spheres. In this synthesis procedure, aggregation issue of polymer spheres can be able to overcome efficiently due to the electrostatic repulsion between these charged particles. Another merit of