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Mesoporous non-noble metal electrocatalyst derived from ZIF-67 and cobalt porphyrin for the oxygen reduction in alkaline solution

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ABSTRACT

Mesoporous carbon materials were prepared using zeolitic imidazolate framework (ZIF-67) as a support to prevent the aggregation of Co (II) Meso-Tetra (4-methoxyphenyl) porphine (CoTMPP) during the carbonization process. The obtained carbon materials possessed a surface area of 216 $m^2 g^{-1}$ with a porous structure, displaying a comparable oxygen reduction reaction (ORR) performance to commercial Pt/C with 5 $\mu g_{Pt} cm^{-2}$ and better electrochemical properties than that of 20 wt% Pt/C in terms of durability and tolerance against methanol crossover in 0.1 M KOH. The remarkable electrochemical property was attributed to abundant exposure of active sites, including Co-N_x, N-doped carbon as well as Co-containing species.

1. Introduction

Pt based electrocatalysts have been regarded to be the most practical choice due to their highly efficient catalytic performance in the proton exchange membrane fuel cells (PEMFCs). However, the high price and limited resource of Pt hampered the large-scale production of Pt-based electrocatalysts. Besides, Pt based electrocatalysts are unfavorable for endurance tests due to their sensitivity to CO and CH_3OH. For the aspect of commercial viability, it is imperative to develop low cost of alternative electrocatalysts with highly efficient electrocatalytic properties. In the past decades, versatile types of non-noble metal electrocatalysts (NNMEs), containing metal oxides [1,2], macrocyclic compounds [3–5], metal free heteroatom-doped carbon [6–8], metal-nitrogen/carbon [9,10], metal carbide [11,12] or sulfide [13–15] have been investigated as alternatives for Pt-based electrocatalysts. In particular, porphyrin like Me-N_x (Me = Fe or Co) based NNMEs has been an appealing research topic since Co-phthalocyanine used toward the ORR in alkaline medium reported by Jasinski in 1964 [16]. Subsequently, the increasing work began to focus on the synthesis of NNMEs that included the active sites of MeN_x. Traditionally, NNMEs were obtained by the direct pyrolysis of metal based macrocyclic complex under high temperature. While the activity and durability of the electrocatalysts were not good enough for the practical use. Thus, various electrocatalysts with high surface area, hierarchical porous structure and high density of active sites were under investigated to enhance the activity for ORR. On one hand, NNMEs were prepared by supporting the precursor of metal macrocycles on carbon materials to increase the performance toward ORR [17–19]. On the other hand, highly efficient NNMEs were fabricated through different synthesis strategies [20]. Especially in the last decades, for example, the break through work was achieved by Feng and co-workers in 2013. Well-controlled mesoporous structures of electrocatalyst with a narrow mesopore size distribution, high Brunauer-Emmett-Teller (BET) surface area and abundant metal-N_x like active sites, was derived from vitamin B12 (VB12) using a hard template (silica colloid, ordered mesoporous silica SBA-15 and montmorillonite) synthesis approach [21]. While, considering the hazard of HF as a template removing agent, our group has prepared porous carbon electrocatalysts using iron phthalocyanine (FePc) as the precursor and magnesium oxide (MgO) as a hard template, in which MgO could be easily removed by HCl solution [22]. Besides, Xie and co-workers self-assembled hemin into nanoporous structure, followed by the heat-treatment at 950 °C and acid-leaching with H_2SO_4 at 80 °C. The obtained NNMEs displayed comparable ORR performance to commercial Pt/C in alkaline solution [23]. Very recently, Li and co-workers self-assembled iron porphyrin (5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine iron (III) chloride, FeTMPPCl) on carbon black to fabricate core/shell structured electrocatalyst, which displayed highly efficient ORR performance in both alkaline and acid media [24]. Inspired by other's work and the basis of our previous research [22,25], we began to investigate NNMEs with zeolitic imidazolate frameworks

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(ZIFs) as the template supporting for porphyrins. In this work, we chose ZIF-67 as a framework, in which the CoN_x active site was accepted for ORR [26]. The severe aggregation of porphyrin occurred during the carbonation process at higher temperature, which resulted in poor ORR performance. In this study, we coated Co (II) Meso-Tetra (4-methoxyphenyl) porphine (CoTMPP) on the surface of ZIF-67 to fabricate a N-doped carbon material with Co-containing species. Such porous carbon materials exhibited better ORR activity than that of carbonization of CoTMPP alone and comparable ORR performance relative to 20 wt% Pt/C in alkaline solution. Moreover, the obtained sample displayed better electrochemical properties in terms of durability and methanol tolerance in 0.1 M KOH.

2. Experimental

2.1. Reagents

$Co(NO_3)_2{\cdot}6H_2O$ (CAS: 10026-22-9) and 2-methylimidazole (CAS: 693-98-1) for the synthesis of ZIF-67 were purchased from Acros Organic and Alfa Aesar, respectively. The cobalt porphyrin precursor of Co (II) Meso-Tetra (4-methoxyphenyl) porphine (CoTMPP, $C_{48}H_{36}N_4O_4Co$, CAS: 28903-71-1) was provided by Frontie scientific. Methanol (MeOH) and chloroform were obtained from Jin Feng (Tianjin, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Commercial Pt/C (20 wt%) for comparison was purchased from Johnson Matthey (JM) Company (London, UK). All these materials were used directly without further purification. Milli-Q water (resistivity 18.2 MΩ cm at 25 °C) was used for electrochemical test.

2.2. Synthesis of ZIF-67

The synthesis of ZIF-67 was based on a previous procedure with some modifications [27]. Typically, $Co(NO_3)_2{\cdot}6H_2O$ (0.87 g) and 2-methylimidazole (MeIM, 1.0 g) were dissolved in 50 mL of MeOH, respectively, and then mixed together with vigorously stirring for 6 h at room temperature (RT). The resulting purple precipitates were collected by centrifuging, washed with MeOH in sequence for at least three times and finally dried in vacuum at 50 °C overnight.

2.3. Synthesis of carbonized ZIF-67@CoTMPP materials

100 mg ZIF-67 and 150 mg CoTMPP were dispersed in 80 mL chloroform with ultrasound treatment for 30 min and stirred for 1 h at RT before using evaporation technology to remove the solvent. Later, the solid composites were collected for further drying at RM in the vacuum oven. After that, the samples were heat-treated under high temperature from 600 to 900 °C under argon atmosphere for 2 h and acid-leached with 0.5 M H_2SO_4 for 6 h at 80 °C. At last, the obtained product was washed with dionized water until the filtrate became neutral. The final sample was dried overnight and collected for further use. Here, the obtained NNMEs were denoted as ZIF-67@CoTMPP (T), (T = 600 to 900 °C). For further comparability, ZIF-67 was treated under the same temperature, namely ZIF-67 (T).

2.4. Characterization

X-ray powder diffraction (XRD) was recorded on a PANalytical Empyrean-100 diffractometer with Cu Kα radiation at a scanning rate at $6°{\cdot}min^{-1}$. Porous feature was conducted by nitrogen adsorption/desorption at 77 K using an automatic adsorption system (ASAP2020, Micromeritics). Samples were degassed at 250 °C for 5 h prior to the measurement. The specific surface area (S_{BET}) of the samples was calculated using the Brunauer-Emmett-Teller (BET) method, the micropore area (S_{mic}) was calculated using the t-plot method, the total pore volume (V_t) was estimated from single point adsorption at a relative pressure P/P_0 of 0.99 and the pore size distributions (D_{ave}) of all samples were derived from the density functional theory (DFT) model. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250Xi photoelectron spectrometer. Transmission electron microscopy (TEM) was operated on a JEM-2100F at 200 kV.

2.5. Electrocatalytic activity measurements

The electrochemical measurements were conducted in a conventional three-electrode cell by electrochemical devices of CHI-760E (CH Instruments, Shanghai, China) and VSP-300 (BioLogic, Paris, France) at RT. A Pt-net, Hg/HgO, and as-prepared catalyst-coated glassy carbon (GC) disk were used as a counter electrode, a reference electrode and a working electrode, respectively. Firstly, the 2 mg mL^{-1} electrocatalyst ink was prepared by using ethanol, ultrapure water and 5 wt% Nafion ($V_{ethanol}$:V_{water}:V_{Nafion} = 9:1:0.06). Secondly, the catalyst ink was sonicated for 30 min, and then 60 μL of catalyst ink was dropped onto the surface of GC by six times. Based on the geometric surface area of GC (0.19625 cm^2), the ultimate loading on GC was calculated to be ~0.6 mg cm^{-2}. For comparison, 20 wt% Pt/C from JM was prepared to be 1 mg mL^{-1} and 5 μL or 10 μL was dropped on the surface of GC to obtain the final catalyst loading of 5 μg_{Pt} cm^{-2} and 10 μg_{Pt} cm^{-2}.

Initially, cyclic voltammetry (CV) curves were carried out to clean the surface of prepared electrocatalysts on GC after purging N_2 into three-electrode cell for 10 mins in 0.1 M KOH. Then, CV curves were evaluated to activate the electrocatalyst on GC after purging O_2 into three-electrode cell for 10 mins in 0.1 M KOH. The potential was from 0 to 1.1 V (vs. RHE) and the scanning rate was 100 mV s^{-1}. Secondly, ORR polarization of electrocatalysts was evaluated by using the rotation disk electrode (RDE) test in O_2-saturated alkaline solution at different rotation rates from 625 to 2025 rpm with 5 mV s^{-1} ranging from 0 to 1.1 V (vs. RHE). Thirdly, HO_2^-% and electron transfer number of electrocatalyst was calculated by tested with rotating ring disk electrode (RRDE) technique based on the ORR polarization curves in O_2-saturated 0.1 M KOH from 0 to 1.1 V (vs. RHE) with a constant potential of 1.087 V (vs. RHE).

Durability test was conducted on as-prepared NNMEs and commercial Pt/C at 1600 rpm with a scanning rate of 5 mV s^{-1} before and after 5000 cycles in O_2-saturated 0.1 M KOH solution.

The current–time (i–t) curves of as-prepared NNMEs and 20 wt% Pt/C were measured at the constant potential of 0.5 V (vs. RHE) for 1000 s at a rotation rate of 1600 rpm in O_2-saturated 0.1 M KOH solution. And the 10% (v/v) methanol was injected at approximately 400 s to detect the selectivity of the electrocatalysts between ORR and methanol oxidation in 0.1 M KOH solution.

3. Results and discussion

3.1. Physical characterization of catalysts

In this work, ZIF-67 was used as a template for CoTMPP not only to increase the density of active sites but also to avoid the aggregation during the carbonization step. As shown in Fig. 1, the framework of ZIF-67 was firstly obtained by a typical synthesis approach using $Co(NO_3)_2{\cdot}6H_2O$ and MeIM. Afterwards, CoTMPP (the molecular structure in Fig. 1) was self-assembled on the surface of framework ZIF-67 by rotary evaporation method to have the structure of ZIF-67@CoTMPP. Based on the data of thermal gravimetric analysis (TGA) in Fig. 2a, the framework began to collapse and the structure of ZIF-67@CoTMPP started to carbonize between 400 and 500 °C. Consequently, ZIF-67@CoTMPP was carbonized at high temperature in the range of 600 to 900 °C under Ar atmosphere and then pre-leached in 0.5 M H_2SO_4 to remove acid nonresistant cobalt species as well as any unstable or ORR-nonreactive impurities. Finally, the composite materials were converted to N-doped carbon materials with large specific surface area and nanoporous architecture. For further comparison and simplification, the final product was denoted as ZIF-67@CoTMPP (T), T = 600 to 900 °C as