Synthesis of ZIF-69-derived Electrocatalyst with Low loading Platinum for Oxygen Reduction Reaction

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Abstract. Here, we report a facile preparation of a low-platinum catalyst derived from ZIF-69 denoted as Pt@ZC-69. Nitrogen-abundant ZIF-69 could act as a support to efficiently encapsulate trimethyl (methylcyclopentadienyl) platinum (IV) (MeCpPtMe3@ZIF-69) precursor. After high-temperature reduction, Pt@ZC-69 with uniform Pt-loading was obtained. In the acidic medium, the Pt@ZC-69 presented a desirable performance, the half-wave potential could reach 0.845 V vs. RHE, while the Pt content is less than 10% of the commercial 20 wt.% Pt/C. Moreover, Pt@ZC-69 also possessed robust stability (40 mV decays after 20000 cycles).

1. Introduction

The gradual depletion of fossil resources and rising environmental pollution are giving rising to the urgency for developing green and sustainable energy conversion systems with high efficiency. Hydrogen is expected to be an alternative fuel of fossil resources owing to its zero-carbon emission. Proton exchange membrane fuel cells (PEMFCs), in which hydrogen is fed as fuel, could directly convert chemical energy into electric energy. Moreover, without the Carnot cycle limitation, the PEMFCs exhibit an ultrahigh-energy conversion efficiency of up to 83% and no emission of harmful byproducts. PEMFCs are constituted by anode at which hydrogen is oxidized to produce electrons and protons (HOR), and cathode, which occurred an oxygen reduction reaction (ORR) to produce water. The half-cell reaction equation can be written as follows:

\[
\text{HOR: } 2H_2 \rightarrow 4H^+ + 4e^- \\
E^0 = 0 \text{ V (vs. RHE)}
\]

\[
\text{ORR: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \\
E^0 = 1.23 \text{ V (vs. RHE)}
\]

The kinetics rates of above two half-cell reaction can both limit the PEMFCs’ performance. Thus, the electrocatalysts are of great significance to accelerated HOR and ORR process which suffer from the high reaction barrier in PEMFCs. So far, Pt and Pt-based catalysts loaded on porous carbon are still regard as the best HOR/ORR catalysts. Nevertheless, there are still barriers that limit the commercial mass market of PEMFCs. Compared with HOR, the reaction kinetics of ORR is about 5 orders of magnitude slower than HOR, which leads to the tenfold dosage for platinum catalysts on cathode than anode. In a PEMFC, about 80–90% catalysts are used to drive the ORR process while the traditional commercial platinum catalyst (20% Pt/C) suffers a high cost due to its scarcity. Thus, it is of great importance to develop low Pt-loading catalysts with high ORR activity.
As the sub-family of metal organic frameworks (MOFs), zeolite imidazolate framework materials (ZIFs) are constructed of tetrahedral metal ions nodes and imidazolate linkers. Recently, ZIFs have exerted a tremendous fascination with the synthesis of various electrocatalysts. For instance, utilized the ZIFs-derived substrate for compositing the functional species. The high nitrogen content in ZIFs-derived carbon can sufficiently anchor and disperse the metal sites. Besides, the porous structure of ZIFs can boost the sufficient exposing of active sites. The above advantages inspired the way to decreased the metal loading. Given that, intensive studies have focused on exploring ZIFs and derivatives for the preparation of the low Pt-loading PEMFCs cathode catalysts.

Herein, we develop a facile strategy to synthesis low Pt-loading catalyst. The Pt precursor was successfully loaded on the ZIF-69 substrate via a solid-phase grinding method. After thermal reduction treatment, ZIF-69-derived catalyst with low Pt-content was prepared. Furthermore, the obtained catalyst presents the desirable ORR performances in acid condition.

2. Materials and synthesis

2.1. Preparation of stock solution
N,N-Dimethylformamide (DMF) and N-Methylpyrrolidone (NMP) were mixed at a volume ratio of 1:1 and ultrasonicated for 5 min to form a homogeneous solution. Then, 2.20 g Zn(Ac)$_2$$\cdot$2H$_2$O, 1.13 g 2-nitroimidazole (nIm), and 1.53 g 5-chlorobenzimidazole (cbIm) were added into 50 mL DMF/NMP mixed solution and uniformly dispersed by ultrasonication for 5 minutes to generate Zn(Ac)$_2$$\cdot$2H$_2$O, nIm, and cbIm stock solution, respectively. The concentrations of all three stock solutions are 0.2 M.

2.2. Synthesis of ZIF-69
5 mL Zn(Ac)$_2$$\cdot$2H$_2$O stock solution, 5 mL nIm stock solution and 5 mL cbIm stock solution were added into a 20 mL hydrothermal reactor. The reactor was placed in an 85 ºC oven and reacted for 24 hours. The resultant liquid was centrifuged, and the collected solid product was washed by DMF/NMP three times. Afterward, the products were processed solvent replacement with absolute ethanol one time per day for three times. Finally, the product was centrifuged and dried at 100 ºC in a vacuum for 8 h.

2.3. Synthesis of MeCpPtMe$_3$@ZIF-69
300 mg of ZIF-69 and 10 mg MeCpPtMe$_3$ precursor were mixed and ball milled at 50 Hz for 5 min to obtain MeCpPtMe$_3$@ZIF-69.

2.4. Synthesis of Pt@ZC-69
The MeCpPtMe$_3$@ZIF-69 was annealed at 800 ºC (5 ºC/min) for 1 h in a tube furnace under Ar flow. After the temperature cooled to room temperature naturally, the catalyst was obtained.

2.5. Preparation of ink
2 mg Pt@ZC-69 and 10 µL 5 wt% Nafion were dispersed in the mixed solution of 55 µL isopropanol, 45 µL ethanol, and 95 µL ultrapure water uniformly. After sonication for 60 min in an ice bath, the catalyst ink was prepared.

2.6. Preparation of working electrode
10 µL dispersion was pipetted onto the polished glassy carbon electrode and dried under vacuum at 25 ºC for 10 min.

2.7. Electrochemical test
N$_2$ or O$_2$ was purged into the electrolyte continuously for 30 minutes, respectively. The electrode was rotated at 1600 rpm during the measurements, the linear sweep voltammetry (LSV) was conducted at a scan rate of 10 mV/s within the voltage range of 0−1.2 V vs. RHE.
3. Results and discussions

ZIF-69 was first prepared by hydrothermal method, the powder X-ray diffraction (PXRD) pattern shows good accordance with the simulated result. Afterward, the MeCpPtMe3 precursors were encapsulated into the channels of ZIF-69 by a solvent-free solid-phase grinding approach. The ZIF-69 substrate of as-synthesized MeCpPtMe3@ZIF-69 maintained original crystallinity after the above operations, which was demonstrated by the PXRD pattern that remains unchanged (Figure 1).

![Figure 1. PXRD patterns of simulated ZIF-69, synthesized ZIF-69 and MeCpPtMe3@ZIF-69.](image)

The morphologies of ZIF-69 and MeCpPtMe3@ZIF-69 were studied by scanning electron microscopy (SEM). The as-prepared ZIF-69 possesses a regular morphology with a uniform particle size of ~400 nm-length and ~100 nm-width. Furthermore, the SEM image displayed that after the encapsulation of Pt-precursor, ZIF-69 substrate retains its morphology and size (Figure 2).

![Figure 2. SEM images of ZIF-69 and MeCpPtMe3@ZIF-69.](image)

The N2 ad/desorption was carried out to investigate the effect of the MeCpPtMe3 encapsulation on the porosity of ZIF-69. A significant decrement of Brunauer-Emmett-Teller (BET) surface area was observed, which indicated the entry of the Pt-precursors into the pores of ZIF-69 (Figure 3).
After calcinated the MeCpPtMe₃@ZIF-69 under high temperature in Ar atmosphere, Pt-loaded ZIF-69-derived carbon (Pt@ZC-69) was obtained. The diffraction peaks presented in Pt@ZC-69 illustrated that Pt precursor could be reduced and form the Pt nanoparticles during the calcinated treatment (Figure 4).

The transmission electron microscopy (TEM) image shows that the Pt nanoparticles with uniform particle size (~2 nm) are homogeneously distributed on ZIF-69-derived carbon. The clear lattice fringes of 0.198 nm, which corresponds to the Pt (200) surface, are found in high-resolution TEM (HR-TEM).
The content of Pt@ZC-69 was garnered by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The result reveals that the Pt@ZC-69 is of 16.08% Zn-content and 1.23 wt% Pt-content. The Pt-loading of Pt@ZC-69 was much lower than it of commercial 20% Pt/C catalyst.

The chemical structures of the Pt and N species in Pt@ZC-69 were analyzed by X-ray photoelectron spectroscopy (XPS), as shown in Figure 6. Three valences Pt (Pt⁰, Pt²⁺, and Pt⁴⁺) could be deconvoluted in Pt 4f XPS spectra of Pt@ZC-69, of which Pt⁰ species are considered as the most active sites that can promote the reaction. Additionally, the N 1s indicated that the Pt@ZC-69 was composed of pyridinic N (398.3 eV), pyrrolic N (399.8 eV), and quaternary N (401.1 eV). All three types of nitrogen have been proven as promising active sites for ORR.

![Figure 6. Pt 4f and N 1s XPS spectra of Pt@ZC-69.](image)

The electrocatalytic activity of the Pt@ZC-69 catalyst was investigated in 0.1 M HClO₄ electrolyte. Owing to the synergetic intrinsic advantages of Pt@ZC-69, the catalyst displays a positive half-wave potential at 0.845 V vs. RHE (Figure 7a). It is noteworthy that, although the half-wave potential is merely 20 mV less than it of commercial 20% Pt/C catalyst, the Pt-loading is only 10% of commercial Pt/C. Furthermore, Pt@ZC-69 presents excellent long-term durability, evidenced by only 40 mV decay after the 20000 cycles test (Figure 7b).

![Figure 7. (a) Linear sweep voltammetry (LSV) curves of 20% Pt/C and Pt@ZC-69. (b) LSV curves of Pt@ZC-69 before and after long-term cycling test.](image)
4. Conclusion
In this work, we have raised a rational strategy for the preparation of a low Pt-loading ZIF-69-derived catalyst and evaluated the ORR performance of the resultant catalyst systematically. The as-synthesized Pt@ZC-69 catalyst exhibited promising ORR activity with a positive half-wave potential (0.845 V vs. RHE). Moreover, Pt@ZC-69 exhibits excellent durability with only 40 mV decay after the 20000 cyclic voltammetry (CV) test. Our work brings a facile and effective way for the synthesis of low Pt-loading ORR electrocatalyst.

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Reference
[1] Zheng, Y. (2018) The Hydrogen Evolution Reaction in Alkaline Solution: From Theory, Single Crystal Models, to Practical Electrocatalysts. Angewandte Chemie. International Edition, 57: 7568-7579.
[2] Debe, M K. (2012) Electrocatalyst approaches and challenges for automotive fuel cells. Nature, 486: 43-51.
[3] Gasteiger, H A. (2004) Dependence of PEM fuel cell performance on catalyst loading. Journal of Power Sources, 127: 162-171.
[4] Phan, A. (2010) Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks. Accounts of Chemical Research, 43: 58-67.
[5] Wang, X. X. (2018) Ordered Pt3Co Intermetallic Nanoparticles Derived from Metal–Organic Frameworks for Oxygen Reduction. Nano Letters, 18: 4163-4171.
[6] Du, N. (2017) N-doped carbon-stabilized PtCo nanoparticles derived from Pt@ZIF-67: Highly active and durable catalysts for oxygen reduction reaction. Nano Research, 10: 3228-3237.
[7] Wang, X. X. (2020) Pt alloy oxygen-reduction electrocatalysts: Synthesis, structure, and property. Chinese Journal of Catalysis, 41: 739-755.