



Embedding platinum-based nanoparticles within ordered mesoporous carbon using supercritical carbon dioxide technique as a highly efficient oxygen reduction electrocatalyst



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ABSTRACT

Ordered mesoporous carbon (OMC) has shown great promising as superior support in the creating highly efficient and stable cathodic catalyst for oxygen reduction reaction (ORR) due to its many merits but there are still many challenges. We demonstrate in this work a facile and large-scale strategy to efficiently embed Pt-based crystals within OMC using supercritical carbon dioxide (scCO₂) technique. Typically, PtFe/OMC catalysts with the highly dispersive, ultrafine sizes (1.3–2.3 nm), controllable compositions and loadings have been successfully fabricated. Through control of experimental process and loadings, most of crystals can be deposited into mesochannels of OMC. The integration of highly dispersive and ultrafine PtFe crystals as well as high surface area, mesoporous structure and good electrical conductivity of OMC supports make PtFe/OMC promising as active and stable electrocatalysts toward ORR. By careful comparison, PtFe/OMC catalysts show the overwhelmingly better or comparable electrochemical performance compared with previously reported mesoporous carbon supported Pt-based catalysts. These attractive materials hold great potential in cathodic electrocatalyst for fuel cells and the scCO₂ technique is quite superior for constructing OMC with various embedded nanoparticles (such as PtPd, PtCu etc.).

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are useful as clean power sources that represent a potential alternative to environmentally unfriendly fossil-fuel use owing to their fascinating features including high theoretical efficiency, high power density and green emission [1–3]. It always meets three major criteria: cost, performance and durability because most membrane electrode assembly (MEA) catalysts used currently are mainly based on platinum (Pt) [4]. Given the above challenges, most research efforts are focused on enhancement of the electrocatalytic activity of Pt-based catalysts towards oxygen reduction reaction

(ORR) [5–7]. Specifically, the current performances of the Pt catalysts alloyed with the less noble late transition 3d metal M (M: Fe, Co, Ni, and Cu etc.) and with de-alloying, core-shell, hollow, or crystalline structure [8–10] are impressive, reflecting the higher mass and specific activities of PEMFCs compared to the current United States Department of Energy (US DOE) targets that have brought the technology close to pre-commercial viability [4]. Besides, the supports for Pt-based nanoparticles are also crucial for the design of highly efficient cathodic electrocatalysts for fuel cells. Up to now, porous carbon is one of the most widely adopted supports for design and fabrication of fuel cell catalysts [11,12].

Mesoporous carbon is one of the superior materials for supporting Pt catalysts that has shown the enhancement in electrochemical performances owing to the large specific surface area, mesoporous structure and excellent electrical conductivity [13]. Specifically, the large surface area of OMC is beneficial for highly dispersive of Pt-based nanoparticles, which can enhance the mass activity. The specific activity can be significantly improved by the

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abundant pores and high pore volume of OMC because of the facilitated mass diffusion. In addition, owing to the excellent electrical conductivity of OMC, the sufficient electron pathways can be provided by OMC, which also lead to high specific activity [14,15]. However, there are still many challenges. First, the wet chemical reduction is the most common method to disperse the Pt-based nanoparticles onto the OMC supports [16]. But, owing to the lack of surface functionalities, the ionic metal precursors are not easy to be adsorbed on the OMC, which causes the weak particle-carbon interaction and particle aggregation [17]. Consequently, the detachment of particles happens during potential cycling, which results in the substantial degradation of electrocatalytic performance. In order to get the highly dispersive of particles, surface modification for OMC is necessary [18,19]. However, the electrical conductivity of carbon supports, unfortunately, could be decreased due to the surfactants, and the interactions between particles and carbon supports are weakened. Second, for most of the OMC-supported Pt-based catalysts, particles are mainly dispersed on the surface of OMC [16–19]. Recent work showed that the embedment of Pt nanoparticles within the carbon pore walls is beneficial to improve the electrocatalytic performance owing to the advantages of mesoporous structure and the intimate interface between Pt and carbon [20]. For instance, Wu and co-workers reported the highly active and stable catalyst of embedment of Pt nanoparticles in OMC synthesized by the hard template, and followed by the carbon deposition, Pt precursor reduction and graphitization [21]. Importantly, such catalysts also have excellent methanol-tolerant property due to the novel carbon embedment property, which showed the great potential in cathodic catalyst for direct methanol fuel cells (DMFCs). However, the current methods are very complex and the electrocatalytic activity towards ORR is still needed to improve. Thirdly, catalysts embedded in OMC by current methods are still limited to Pt nanoparticles. Thus, it is highly desirable to develop new strategies to embed the Pt-based nanoparticles (such as PtFe, Pt Co, PtCu, etc.) within OMC that is probably further enhance the electrochemical performance.

In our previous work, we have demonstrated making the supercritical carbon dioxide (scCO₂) technique for the synthesis of three-dimensional graphene-supported Pt-based nanoparticles [22,23]. The organometallic precursors can dissolve into the scCO₂ and be delivered into the small area owing to scCO₂'s low viscosity, zero surface tension and high diffusivity properties [15,24]. But, it is a challenge to controllably embed Pt-based nanoparticles within OMC by scCO₂ technique has not been reported. Herein, we continue the scCO₂ technique to address this challenge through controlling the synthesis process. The embedded PtM nanoparticles with ultrafine sizes, high dispersion, controllable loadings and composition can be achieved. The electrocatalytic performance of as-prepared PtFe/OMC catalysts were studied and compared with commercial Pt/C catalyst and previously reported OMC-supported Pt-based catalysts, which showed the overwhelmingly better performance of PtFe/OMC catalyst.

2. Experimental

2.1. Chemicals and materials

OMC: cmk-3 (specific surface area: 1000 m² g⁻¹, pore diameter: 5.57 nm) was purchased from ACS Materials, LLC. Nafion perfluorinated resin solution (5%), perchloric acid (HClO₄), borane tetrahydrofuran complex solution (borane-THF), isopropanol (99.5%), methanol, tetrahydrofuran (THF), Pt(hfa)₂, Pd(hfa)₂·xH₂O, (hfa = hexafluoroacetylacetonate, Fe(acac)₂, Cu(acac)₂ (acac = acetylacetonate), were purchased from Sigma-Aldrich. High-purity CO₂, oxygen (O₂) and nitrogen (N₂) gas

were purchased from chemical store (Washington State University). Commercial Pt/C catalyst (20 wt%_{Pt}, mainly 2.5–3.5 nm in diameter) was purchased from Alfa Aesar.

2.2. Embedment Pt-based nanoparticles within OMC using scCO₂ technique

The scCO₂ reaction system can be seen in Fig. S1. The typical PtFe/OMC catalyst with Pt content of ~12.0 wt% and Pt:Fe atomic ratio of 1:1 was used to describe this synthesis process. The OMC (5 mg), the metal precursor Pt(hfa)₂ (10 mg) and Fe(acac)₂ (5.8 mg) with a small amount of THF as a modifier were put into a glass cell. This glass cell was then put into a high-pressure reaction cell located on a heater. The reaction cell was heated to 353 K. And then, CO₂ gas was pressurized to 150 atm by pump, and introduced into the reaction cell. The metal precursor with CO₂ and THF formed the supercritical fluid. The temperature was kept at 353 K for 2 h. After then, the temperature was cooled to 333 K, and vented out the CO₂ quickly to remove the precursors without embedment within OMC. And then, the reaction cell was opened, and the borane-THF reducer was injected into cell (outside of glass cell). The system temperature increased to 353 K. After 0.5 h, the temperature was cooled, and then was depressurized by releasing CO₂. The product was obtained by methanol washing under sonication for 5 times.

In addition, Pt/OMC, Pt₃Fe/OMC with Pt content of 13.0 wt%, PtFe/OMC with different Pt contents of 5.4 wt% and 25.6 wt%, PtPd/OMC and PtCu/OMC composites were also synthesized by as-described scCO₂ technique.

2.3. Characterization

The scanning transmission electron microscope (STEM), the high-resolution TEM (HRTEM) analysis and electron diffraction pattern (EDP) were obtained using Titan 80-300 S/TEM operated at 300 kV (FEI Company). The transmission electron microscopy (TEM) was used to characterize the morphologies of products (Philips CM200 UT). The energy dispersive X-ray (EDX) was performed on a Hitachi-4700 field SEM operated at 20 kV. The elemental analysis of products was characterized by X-ray photoelectron spectroscopy (XPS) performed on a Kratos AXIS-165. The particle loading and composition were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES) performed on Thermo-Fisher iCAP 6300. The X-ray diffraction (XRD) obtained by powder X-ray diffractometer was used to analyse the crystal structure of catalysts (Siemens D5000). The mesoporous structures of products were characterized using nitrogen (N₂) adsorption/desorption measurements (Quantachrome autosorb-6 automated gas sorption system).

2.4. Electrochemical measurements

The three electrode system was used to study the electrocatalytic performance on a CHI 630E station (Shanghai CHI Instruments Co.). The counter electrode, reference electrode and working electrode are Pt wire, Ag/AgCl (3 M KCl) and a glassy carbon rotating disk electrode (GCRDE) modified by catalyst film (5 mm in diameter), respectively. For working electrode preparation, the catalyst ink (2 mg mL⁻¹) was prepared firstly by dispersing catalyst in a mixture of isopropanol, 5 wt% Nafion and water with volume ratio of 4/1/160. And then, the surface of GCRDE was modified by dropping 10 μL catalyst ink, followed by drying at 60 °C for 30 min. The target catalyst loadings on the GC RDEs are 1.08 μg_{Pt} for PtFe/HSG (~5.4 wt%_{Pt}), 2.4 μg_{Pt} for PtFe/HSG (~12.0 wt%_{Pt}), 5.12 μg_{Pt} for PtFe/HSG (~25.6 wt%_{Pt}), 2.6 μg_{Pt} for Pt₃Fe/HSG (~13.0 wt%_{Pt}), and 4 μg_{Pt} for commercial Pt/C, respectively. Cyclic

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