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Nitrogen-doped ordered mesoporous carbons as electrocatalysts for methanol-tolerant oxygen reduction in acid solution

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ABSTRACT

A simple method is described for the production of Pt supported on nitrogen-doped ordered mesoporous carbons (Pt-OMCN_x) by the pyrolysis of carbon and metal precursors in a N-containing organo-functionalized mesoporous silica as the primary N sources and hard templates. The resultant Pt-OMCN_x samples were thoroughly characterized by a variety of different spectroscopic and analytical techniques. Results obtained from X-ray diffraction, N₂ adsorption/desorption isotherms and transmission electron microscopy show that Pt-OMCN_x possessed well-dispersed Pt nanoparticles (2–3 nm) supported on high surface area (450 m² g⁻¹) and regular pore channels (2.5 nm). Elemental analysis and X-ray photoelectron spectroscopy indicate that ca. 1.8 wt% of N species presented on the carbon rods of Pt-OMCN_x were mostly quaternary-N (55%) and pyridinic-N (45%). The Pt-OMCN_x was found to have superior electrocatalytic activity and the tolerance to methanol crossover during the oxygen reduction reaction (ORR), which can be attributed to the dispersion and unique nanostructure of Pt nanoparticles particularly in the presence of pyridinic-N atoms in the mesoporous carbon supports.

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1. Introduction

Direct methanol fuel cells (DMFCs) and polymer electrolyte membrane fuel cells (PEMFCs) have been developed as electrical power sources for vehicles, stationary and portable applications for many years [1]. However, the large-scale implementation of fuel cell technology is still hindered by several factors, including (i) the high costs of Pt-based electrocatalysts [2,3], (ii) the poor kinetics of both anode and cathode reactions [4,5], (iii) durability of carbon supported catalysts [6–8] and (iv) the crossover of methanol from the anode to the cathode through the proton exchange membranes [9–11]. Therefore, R & D invoking a cathode catalyst which is more active for oxygen reduction reaction

(ORR), inert to methanol and stable under long-term operations is a demanding task.

Recently, incorporation of heteroatoms (e.g., N, B, and S) on to the carbon supports so as to modify their surface and physicochemical properties have been investigated. Among them, N-doped carbons have received considerable attentions due to the fact that strong electron donor nature of N should promote enhancement in π bonding, leading to an improved stability, electron transfer rate, and hence durability of the carbon supports during electrocatalytic processes [12–14]. Recent research advances [15–17], for example, on fabrication of N-doped carbon nanotubes (NCNT) revealed their better electrocatalytic activity and long-term stability compared to platinum on carbon support (Pt/C). In general, N-doped carbon

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nanostructure materials can be obtained by using following methods: (i) carbonization of N-containing precursors directly during the synthesis of porous carbon nanostructure materials [18–20] (ii) post-treatment of presynthesized carbon nanostructure materials with N-containing gases [21,22]. (iii) chemical treatments with reactive species such as HNO₃, NH₃ and HCN [23,24]. These treatments, however, generally produce C–N functionalities (*e.g.*, amines) that are unstable under typical catalysis conditions. In addition, these methods aforementioned need to be performed under relatively severe conditions in order to attain a desirable amount of incorporated N, which typically accompanied by degradation of surface properties and/or collapse of ultra-fine nanostructures of the carbons. Thus, it is still a high demand to explore new methods to fabricate N-doped nanostructure carbons.

Here we report a novel procedure for the synthesis of a N-doped ordered mesoporous carbon (OMCN_x) nanocomposite with well-dispersed and stable Pt (denoted as Pt-OMCN_x) based on the pyrolysis of furfuryl alcohol and Pt precursors, such as hexachloroplatinic acid in a N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TPTAC) functionalized mesoporous silica, namely TPTAC-SBA-15. The Pt-OMCN_x catalysts so fabricated possess not only high activity but also durability (tolerance to methanol crossover) favorable for ORR and hence should render future practical applications as supported cathodic electrocatalysts for DMFCs and PEMFCs.

2. Experimental method

2.1. Catalyst preparation

The TPTAC-SBA-15 was prepared by a co-condensation procedure similar to the method reported previously [25]. Typically, ca. 4 g of Pluronic 123 triblock copolymer (EO₂₀PO₇₀EO₂₀; Aldrich) was dissolved in 125 g of 2.0 M HCl solution at room temperature. After adding tetraethyl orthosilicate (TEOS; 98%, Acros), the resultant solution was equilibrated at 313 K for 1 h to pre-hydrolyze TEOS, and then a given amount of TPTAC was slowly added into the solution. The resulting mixture was stirred at 313 K for 20 h and then transferred into a polypropylene bottle, which was later kept at 363 K under static condition for 24 h. The solid product was recovered by filtration then dried at room temperature. The as-synthesized material was then refluxed in ethanol to remove the organic templates. The solid product (TPTAC-SBA-15) was obtained by filtration and dried at room temperature overnight. Subsequent direct replication of TPTAC-SBA-15 material into Pt-OMCN_x was carried out by using the following procedures. Typically, ca. 0.5 g of TPTAC-SBA-15 was dehydrated at 333 K for 12 h under vacuum. A certain amount of hexachloroplatinic acid (H₂PtCl₆; 39%, Acros) was dispersed in the furfuryl alcohol (FA; 98%, Acros) and trimethylbenzene (TMB; 98%, Acros) under ultrasonication. Oxalic acid (98%, Acros) was used as the acid catalyst for polymerization of FA solution. The mixture solution was infiltrated in TPTAC-SBA-15 by incipient wetness impregnation at room temperature, followed by polymerization at 333 K then at 353 K each for 12 h in air. The resultant composite was treated at 423 K for 3 h,

ramped to 573 K with a heating rate of 1 K/min, then to 1073 K with a heating rate of 5 K/min and maintained at that temperature for 3 h. The carbonization procedure was performed under vacuum. Finally, the resultant black powders were leached with HF (1 wt %) aqueous solution for at least 24 h to remove the silica template, washed with distilled water and alcohol, then dried at 373 K to obtain the Pt-OMCN_x. Similar procedures were adopted for the syntheses of OMCN_x, except that none of Pt precursor was added. The ordered mesoporous carbon (OMC) and Pt supported ordered mesoporous carbon (Pt-OMC) samples were synthesized according to the procedures we reported earlier [26,27].

2.2. Characterization methods

X-ray diffraction (XRD) patterns of all samples were recorded on a PANalytical (X'Pert PRO) instrument using Cu-K α radiation ($\lambda = 0.1541$ nm). The compositions of catalysts were measured by energy dispersive X-ray analysis (EDX, JEOL JEM-2100F). Elemental analyses (EA) were carried out using a CHN elemental analyzer (Heraeus varioIII). X-ray photoelectron spectra (XPS) of samples were measured at the wide-range beamline of National Synchrotron Radiation Research Center in Taiwan. Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 analyzer. The high-resolution transmission electron microscopy (TEM) images were obtained at room temperature using an electron microscope (JEOL JEM-2100F) that has a field-emission gun at an acceleration voltage of 200 kV.

2.3. Electrochemical measurements

The electrocatalytic measurements were performed in a single compartment glass cell with a standard three-electrode configuration. A glassy carbon electrode with a diameter of 5 mm was used as a working electrode and a saturated Ag/AgCl electrode and a platinum wire were used as reference and counter electrodes, respectively. The glossy carbon thin-film electrode was prepared by the following steps: firstly, ca. 5 mg of Pt-loaded carbon sample was added into 2.5 mL deionized water, followed by ultrasonic treatment for 0.5 h. Then, ca. 20 μ L of the resultant suspension mixture was withdrawn and injected onto the glassy carbon electrode, followed by drying in air at 333 K for 1 h. Finally, 20 μ L of 1% Nafion[®] (DuPont) solution was added as a binder under N₂ environment. Electrocatalytic activity measurements of various samples and a commercial Johnson-Matthey Pt/C sample (20 wt% Pt on Vulcan XC-72, denoted as JM-Pt/C) were performed on a galvanostat/potentiostat (CHI Instruments, 727D). Cyclic voltammetry (CV) experiments were done to clean and activate the electrode surface. Prior to each CV measurement, the electrolytic solution was purged with high-purity N₂ (99.9%) for at least 0.5 h to remove the dissolved oxygen, subsequently the experiment was conducted between -0.2 and 1.2 V vs. Ag/AgCl under purging N₂ condition. ORR was evaluated by a linear sweep voltammetry (LSV) technique. The 0.1 M H₂SO₄ electrolyte was saturated with ultrahigh purity oxygen for at least 0.5 h. The polarization curves were obtained between -0.1 and 0.8 V vs. Ag/AgCl at

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