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Preparation of ordered mesoporous carbons containing well-dispersed and highly alloying Pt–Co bimetallic nanoparticles toward methanol-resistant oxygen reduction reaction

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ABSTRACT

A simple route is described for the synthesis of well-dispersed and highly alloying PtCo bifunctional nanoparticles supported on ordered mesoporous carbons ($Pt_{100-x}Co_x$/OMC) by the simultaneous pyrolysis of carbon and metal precursors in a mesoporous silica as the hard template. A variety of different spectroscopic and analytical techniques was used to thoroughly characterize the $Pt_{100-x}Co_x$/OMC samples. By X-ray diffraction, N_2 adsorption/desorption isotherms and transmission electron microscopy, it was found that $Pt_{100-x}Co_x$/OMC possessed well-dispersed Pt/PtCo nanoparticles (2–3 nm) supported on high surface area ($\sim$1000 $m^2\,g^{-1}$) and regular pore channels ($\sim$2.8 nm). Among $Pt_{100-x}Co_x$/OMC catalysts, the $Pt_{50}Co_{50}$/OMC was found to have superior electrocatalytic activity and the tolerance to methanol crossover during oxygen reduction reaction as compared to typical commercial electrocatalysts. This may be attributed to the dispersion and unique nanostructure of highly alloyed PtCo nanoparticles supported on $Pt_{50}Co_{50}$/OMC evidenced by X-ray absorption spectroscopy.

1. Introduction

Direct methanol fuel cells (DMFCs) and polymer electrolyte membrane fuel cells (PEMFCs) have been considered as two of next-generation electrical power sources for light-duty vehicles and stationary or portable applications [1–3] as an alternative to conventional power sources, for example, internal combustion engines and secondary batteries [4–6]. For the past few years, much effort from government, industry, and academy has been devoted to developing DMFCs/PEMFCs and great advances have been achieved; however, the remaining barriers to widespread use are including (i) the high costs of Pt-based electrocatalysts [7–9], (ii) the poor kinetics of both anode and cathode reactions [10,11], (iii) durability of carbon supported catalysts [12–14] and (iv) the crossover of methanol from the anode to the cathode through the proton exchange membranes [15–17]. In terms of the first two problems, progressive increase on price of Pt that is the active species in the most of the presently used electrocatalysts requires a decrease in the usage of Pt and/or an increase in the mass specific activity of the active species. Thus, supporting materials with high surface area conducive to Pt dispersion, proper textural properties favor to kinetics of both anode and cathode reactions, and high electronic conductivity are highly desirable [18]. With respect to the last two ones [19–22], structural stability and surface properties of the catalyst supports as well as the methodologies invoked in incorporating Pt catalyst onto the support are crucial for the dispersion and stability of the metal nanoparticles during DMFCs/PEMFCs operations in terms of eliminating CO-poisoning and methanol crossover [23,24] at anode and cathode, respectively.

Recently, alloying of Pt with transition metals such as Fe [25,26], Co [27–29], Ni [30,31] and Cr [32] catalysts has been intensively studied and shown enhanced activity toward oxygen reduction reaction (ORR) and high tolerance toward methanol crossover. In general, alloyed catalysts should be performed at high temperatures to assist the formation of alloy metal components. PtCo alloy supported electrocatalysts for ORR have been also prepared via the addition of Co species onto carbon-supported Pt metal catalysts and then alloying at high temperatures more than 973 K in inert gas or hydrogen [33,34]. However, the alloyed particles so fabricated easily aggregate to form larger particles during treatment at high temperatures. To circumvent this problem, Pt-based alloy catalysts for the ORR in DMFCs/PEMFCs are then prepared by the reduction of metal precursors with chemical reductants such as $NaBH_4$ at low temperatures in place of catalyst treatment at high temperatures under hydrogen flow [35–37]. Nevertheless, the alloying degree of the metal catalysts prepared in this way is generally relatively low. It is well-known that the catalytic performance of the alloyed catalysts strongly depends on their metal particle size and alloying

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degree. Thus, there are still high demands to explore new preparation methods to attain the alloyed particles with a uniformly small size and a high alloying degree.

Here we report a novel procedure for the synthesis of an ordered mesoporous carbon with well-dispersed and highly alloying PtCo nanoparticles (denoted as $\mathrm{Pt}_{100-x}\mathrm{Co}_x$/OMC, $x = 0$, 30 and 50) based on the simultaneous pyrolysis of furfuryl alcohol, Pt and Co precursors with different Pt/Co atomic ratios in a mesoporous silica, namely SBA-15. Among $\mathrm{Pt}_{100-x}\mathrm{Co}_x$/OMC samples, the $\mathrm{Pt}_{50}\mathrm{Co}_{50}$/OMC 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. Preparation of catalysts

The template (SBA-15 mesoporous silica) was synthesized according to the procedure reported in the literature [38]. Subsequent direct replication of SBA-15 template into mono (Pt_{100}/OMC) and bifunctional ($\mathrm{Pt}_{100-x}\mathrm{Co}_x$/OMC) samples with various relative metal loading was accomplished by the stepwise method as below. Typically, ca. 0.5 g of calcined SBA-15 was first dehydrated at 673 K for 4 h under vacuum while various amounts of platinum acetylacetonate ($\mathrm{Pt(CH(COCH_3)_2)_2}$), denoted as $\mathrm{Pt(acac)_2}$ (98%, Acros) and cobalt acetylacetonate ($\mathrm{Co(CH(COCH_3)_2)_2}$), denoted as $\mathrm{Co(acac)_2}$ (99%, Acros) were co-dispersed in furfuryl alcohol (FA; 98%, Acros) and trimethylbenzene (TMB; 98%, Acros) under ultrasonication. In addition, the FA and TMB solution were polymerized by the addition of oxalic acid (98%, Acros). The mixture solution was then infiltrated in SBA-15 at room temperature (298 K) by an incipient wetness impregnation method, followed by polymerization first at 333 K then at 353 K each for 12 h in air. The resultant composite was increased the temperature to 1073 K with a heating rate of 1 K/min and eventually maintained at the same temperature for 3 h 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_{100}/OMC and $\mathrm{Pt}_{100-x}\mathrm{Co}_x$/OMC samples.

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). X-ray photoelectron spectra (XPS) were acquired through an energy analyzer with a constant pass energy of 20 eV followed by irradiating a sample pellet (6 mm in diameter) with a monochromatic Al-K_α (1486.6 eV) X-ray under ultra-high vacuum condition (10^{-10} Torr). Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer. For the high-resolution transmission electron microscopy (TEM), samples were first suspended in acetone (99.9 vol.%) by ultrasonication, followed by deposition of the suspension on a lacey carbon grid, then the TEM images were obtained at room temperature using an electron microscope (JEOL JEM-2100F) operating at an electron acceleration voltage of 200 kV. The Pt $\mathrm{L_{III}}$-edge and Co K-edge XANES and EXAFS spectra of the $\mathrm{Pt}_{100-x}\mathrm{Co}_x$/OMC samples were collected at the Wiggler beamlines 17C of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. A Si(1 1 1) double-crystal monochromator was used for selection of energy with a resolution of 2×10^{-4} eV/eV. Two gas-filled ionization chambers were used in series to measure the intensities of the incident beam (I_o) and the beam transmitted through the sample (I_t) on a reference foil (I_r). A third ion chamber was used in conjunction with a reference sample (Pt foil or Co powder for Pt $\mathrm{L_{III}}$-edge or Co K-edge measurements, respectively). Standard procedures were employed to analyze the spectra acquired by X-ray absorption spectroscopy (XAS). Each EXAFS function (χ) was obtained by subtracting the post-edge background from the overall absorption and then normalized with respect to the edge jump step. Subsequently, k^2-weighted $\chi(k)$ spectra in the k-space, ranging respectively from 3.6 to 13.8 Å^{-1} for Pt $\mathrm{L_{III}}$-edge and from 3.6 to 11.5 Å^{-1} for Co K-edge, were Fourier transformed (FT) to the r-space to separate the EXAFS contributions from different coordination shells. A nonlinear least-squares algorithm was applied to fit (without phase correction) the EXAFS spectra in the r-space between 1.5 and 3.2 Å for Pt and between 1.3 and 3.1 Å for Co, respectively. The Pt–Co reference file was determined by theoretical calculation. All computer programs were implemented in an UWXAFS 3.0 package [39] with the backscattering amplitude and the phase shift for the specific atom pairs being theoretically calculated using the FEFF7 code [40].

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 glassy carbon thin-film electrode was prepared by the following steps: firstly, ca. 5 mg of Pt/PtCo-loaded carbon sample was added into 2.5 mL deionized water, followed by ultrasonic treatment for 0.5 h. Then, ca. 20 μL 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 μL of 5% Nafion® (DuPont) solution was added as a binder under $\mathrm{N_2}$ 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 $\mathrm{N_2}$ (99.9%) for at least 0.5 h to remove the dissolved oxygen, subsequently the experiment was conducted between −0.2 and 1.0 V vs. Ag/AgCl under purging $\mathrm{N_2}$ condition. ORR was evaluated by a linear sweep voltammetry (LSV) technique. The 0.5 M $\mathrm{H_2SO_4}$ 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 a scanning rate of 5 mV/s and a rotating speed of 1600 rpm under room temperature condition. Accelerated durability tests (ADT) of $\mathrm{Pt}_{50}\mathrm{Co}_{50}$/OMC and JM-Pt/C samples were performed by cycling the electrode potential between −0.2 and 1.0 V vs. Ag/AgCl at a scanning rate of 50 mV/s for 1000 cycles in a nitrogen-saturated atmosphere over a period of 13 h.

Single cell tests were carried out in a 5 cm^2 cross-sectional catalyst area (2.25 cm × 2.25 cm). Various catalyst inks containing Nafion ionomer (DuPont, 5 wt.% solution), electrocatalysts, and isopropyl alcohol were applied on carbon cloth substrates (APWOS1002). Pt loading was 0.2 and 0.4 mg/cm^2 for the anode and cathode, respectively. A Nafion 212 membrane (DuPont) was inserted between the anode and cathode layers by hot pressing at 398 K under a pressure of 50 kg/cm^2. The hydrogen and air were used as the fuels with the flow rates of 300 and 2000 mL/min, respectively. The gases were humidified at a relative humidity of 100%. The cells were operated at 353 K and the operating pressure was atmospheric. Prior to the measurement, cells were activated