



Enhanced oxygen reduction reaction stability on platinum nanoparticles photo-deposited onto oxide-carbon composites

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ARTICLE INFO

Article history:

Received 26 September 2015
Received in revised form 10 January 2016
Accepted 12 January 2016
Available online 14 January 2016

Keywords:

Platinum nanoparticles
Strong metal-support interaction
Oxide-carbon composite
Oxygen reduction reaction

ABSTRACT

Oxide-Carbon composites (TiO₂-C) and yttrium-doped TiO₂-C (Y:TiO₂-C), synthesized via sol-gel route, were used as supports to photo-deposit platinum nanoparticles (Pt NPs). The physical-chemical properties of these materials were investigated by Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD). The TEM images showed that Pt NPs were agglomerated and deposited onto oxide sites of the composites. Pt face-centered cubic, and TiO₂ Anatase phases were identified on both Pt/TiO₂-C and Pt/Y:TiO₂-C samples. The particle size, stacking fault and micro-strain of Pt NPs were estimated by Williamson-Hall method. Compared with Pt/TiO₂-C, similar stacking faults as well as increased crystallite sizes and micro-strain values could be observed for Pt/Y:TiO₂-C sample, indicating a minimum impact of the rare earth element on Pt. Pt/C was prepared by the same method, and used as a reference catalyst. The strong-metal/support interaction (SMSI) effect induced by the photo-deposition method, in Pt/TiO₂-C and Pt/Y:TiO₂-C samples, was probed by CO-stripping, and associated to the enhanced stability toward the oxygen reduction reaction (ORR) in acid medium.

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1. Introduction

Although the proton exchange membrane fuel cells (PEMFCs) is one of the most promising candidates in clean energy sources, the cathode catalyst issue is still a great challenge for its large-scale commercialization because of the following reasons: (1) the low efficiency of the electrochemical reaction at the catalytic centre [1,2]; (2) the degradation of the carbon black, used as a popular support, a major cause of loss of the cell performance during long-term operation [3]. Since oxygen reduction reaction (ORR) at the cathode is more difficult than the oxidation of fuels (*i.e.* hydrogen, formic acid) at the anode, it is the key to improve the efficiency of PEMFCs. Although Pt-based materials are proven as the best electrocatalyst, the cathodic performance toward durability in fuel cells is still insufficient [4]. Therefore, a number of alternative electrocatalysts has been proposed to enhance the ORR kinetics on Pt-based catalysts, such as: Pt-Ln₂O₃/C (Ln = Y and Gd) [5], Pt-M/C (M = Fe, Co and Cr) [6], Pt-Pd alloy nanoflowers [7], as well as their stability on carbon supports [8,9]. Regarding the deterioration of ORR activity, it was reported that the agglomeration of nanoparticles derived from electrochemical corrosion of supports lead to the

degradation of electrocatalysts in acid and alkaline environments [10,11]. Such an agglomeration of Pt nanoparticles, induced by the corrosion of the support, can be actually reduced by applying a corrosion-resistant support [12–14]. The oxide-carbon composite is a good candidate since Pt electronic modification can be induced, *via* strong metal-support interaction (SMSI) [12,14–16] and finally improving the ORR activity and/or stability. Additionally, supports with suitable porosity (mesoporous material), with high conductivity, high surface area, and resistant to oxidation will favor the catalytic performance of Pt active site towards ORR [3].

Conversely, the photo-deposition method has been exploited to deposit metals nanoparticles on semiconductor materials [13,17–20]. Titanium dioxide (TiO₂, Anatase phase) was selected to prepare oxide-carbon composite as support for nanoparticles. It is a large band-gap ($E_g = 3.2$ eV) semiconductor, that plays an important role in photocatalysis [21,22] allowing for the photo-deposition of metal NPs, *e.g.* Pt [13] via UV-irradiation. Its photoactivity can be tuned depending on the nature of the dopants, *e.g.* transition metals [23–26] or rare earth (RE) elements such as Cerium (Ce) [27] and Yttrium (Y) [28]. The Y:TiO₂ material presents a reasonable photoactivity to be applied for the degradation of organic molecules. Therefore, RE-doped TiO₂ (Anatase phase) should be a promising support for Pt NPs. Herein, we report Y-doped TiO₂ and carbon composite (Y:TiO₂-C), prepared via sol-gel route, applied as supporting materials for Pt NPs. This latter was photo-deposited mainly onto

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the oxide sites to prepare Pt/Y:TiO₂-C catalyst. The electro-catalytic performance towards ORR kinetics, and stability in acid medium were investigated and compared to Pt/TiO₂-C and Pt/C catalyst, synthesized by the same method.

2. Experimental

2.1. Synthesis of Y:TiO₂-C and TiO₂-C composites

The Y-doped TiO₂-C (Y:TiO₂-C) composites were prepared by mixing carbon Vulcan (XC-72) with titanium isopropoxide and YCl₃ in isopropanol solvent on ice/water bath (ca. 4 °C) [13]. To synthesize 20 wt.% Y:TiO₂, 31.4 mg YCl₃ (99.9%, Alfa-Aesar) was dissolved with isopropanol (99.9%, Alfa-Aesar) also on ice/water bath for 4 h. A volume of 189.1 μL of titanium isopropoxide (TIP, 99.9%, Sigma-Aldrich) was added to have a ratio of Ti/Y = 7 mol/3 mol at ca. 4 °C and mixed further for 16 h. Afterwards, 200 mg of carbon (preheated at 400 °C under N₂ for 4 h) was incorporated in the suspension and stirred for 1 more hour. One mL of ultra-pure water (18.2 MΩ-cm, MilliQ) was added to hydrolyze TIP and produce Y:TiO₂ further stirred for 4 h in ice/water bath. Subsequently, the isopropanol solvent was evaporated at 100 °C. The as-prepared material was rinsed by ultra-pure water and then dried at 60 °C, overnight. Finally, the sample was heat-treated at 400 °C for 1 h under nitrogen (99.99%, Air Liquide) atmosphere. Same procedure was carried out for the synthesis of TiO₂-C (20 wt.% TiO₂). The synthesis of the oxides Y:TiO₂ and TiO₂ was also done.

Preparation of Pt/TiO₂-C and Pt/Y:TiO₂-C via photo-deposition method (PD Method). Pt NPs were deposited by irradiation as follows. To produce 20 wt.% Pt, 25 mL deionized water with 100 mg of Y:TiO₂-C or TiO₂-C composites was mixed ultrasonically for 20 min in a photo-reactor [29]. The system was saturated with nitrogen for another 20 min. Then, 6 mL of isopropanol solution containing 66.4 mg of H₂PtCl₆ + 6H₂O (99.9%, Alfa-Aesar) was added into the photo-reactor and kept under constant stirring for 3 h. For reference purposes, Pt NPs (20 wt.% Pt) supported on C and TiO₂ were prepared with the same protocol. Carbon-supported Pt NPs (20 wt.% Pt) was also prepared by carbonyl chemical route (CCR) and heat-treated at 300 °C for 3 h in nitrogen atmosphere. The source of ultraviolet (UV-vis) radiation used for the experiments was a Xe lamp (159 W) provided with a water filter.

2.2. (Photo)-electrochemical and electrochemical measurement

The (photo)-electrochemical measurements were performed using a potentiostat in a three-electrode standard electrochemical cell (EC) and photo-electrochemical cell (PEC). For EC, a carbon rod and reversible hydrogen electrode (RHE) were used as a counter and reference electrode, respectively. A gold disk electrode with 3 mm (0.07 cm²), polished to a mirror-like finish with a 0.05-μm alumina suspension before each experiment, was used for the catalyst ink deposit. The latter was prepared by dispersing 5 mg of electrocatalyst in 710 μL of water-isopropanol solution (3:1 vol.) and 40 μL Nafion® (5 wt.% Nafion®). The suspension was mixed and ultrasonicated for 1 h on a water bath at room temperature. A drop of 3 μL of the ink was deposited onto gold surface of a rotating disk electrode (RDE) and dried at a rotating rate of 300 rpm in air for at least 30 min. Prior to electrochemical measurements, in order to stabilize the current-potential signals, the working electrode was activated in 0.1 M HClO₄ solution with 20 potential CVs cycles from 0.05 to 1.2 V/RHE at scan rate of 50 mV s⁻¹. Before CO-stripping, two CVs cycles from 0.05 to 1.2 V/RHE was performed at 5 mV s⁻¹ to assure the steady-state conditions. CO was adsorbed at 0.1 V/RHE in CO-saturated electrolyte (99% CO) for 3 min, and further purged for 30 more min with nitrogen. Two potential cycles

from 0.05 to 1.2 V/RHE was recorded at $v = 5 \text{ mV s}^{-1}$. The ORR polarization curves were recorded at scan rate of 5 mV s⁻¹ in O₂ (99.99%, Air Liquide) saturated electrolyte, with rotating speeds of 400, 900, 1600 and 2500 rpm. For the accelerated stability test (AST) analyses, the working electrode was cycled at 50 mV s⁻¹ from 0.6 to 1.0 or to 1.2 V/RHE in N₂-saturated electrolyte. After each 500 potential cycles, the working electrode was activated at 50 mV s⁻¹ in N₂-saturated electrolyte.

For photo-electrochemistry, the working photo-electrodes were prepared by spin coating (at 3000 rpm) using a suspension of the oxides in 15 mg mL⁻¹ of ethanol (99.9%, Alfa-Aesar) and deposited on SnO₂:F (FTO) support of 0.35 cm². After ejection and evaporation of the solvent, a porous adhering thin film was formed. The samples were sintered afterwards, in air at 450 °C for 1 h. The photoelectrochemical cell (PEC) was provided with a quartz window and was placed on an optical table on a support that allowed the displacement of all the system in X-, Y- and Z-directions. The measurement was carried out under UV-vis illumination and in the darkness. The UV-vis source of light was from a Xenon lamp, Spectral products ASB-XE-175. Current-potential curves were performed in N₂-saturated electrolyte, from 0.05 to 1 V/RHE.

The electrical conductivity of powders was determined using a homemade four-probe cell [30] via impedance spectroscopy. The system consists of a hollow cylinder constructed with a Plexiglas material, in which two metallic cylinders served as electrodes. Two wires penetrating ca. 1 mm into the sample chamber, were assembled. The sample chamber was submitted to 25 lb in⁻² (172.4 kPa).

2.3. X-ray diffraction, TEM and ICP analysis

The nanoparticle sizes for all samples were evaluated by TEM on a JEOL microscope (JEM-2001). The samples were dispersed in ethanol and then a drop of such solution was placed on a copper grid covered by carbon film and the solvent was evaporated. For all electrocatalysts, the diameter of particles from TEM images was evaluated by the free ImageJ software. Particle-size-distribution histograms were done by counting 30 particles in different TEM images. The stoichiometric composition of all electrocatalysts was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2000 DV, PerkinElmer). The powder X-ray diffraction (pXRD) was performed on an Empyrean Panalytical X-ray diffractometer using Cu-Kα radiation ($\lambda = 0.15406 \text{ nm}$). The pXRD patterns were obtained, using high resolution, with step-scanning mode, slit at 1/16°, and counting time of 240 s/0.05° in the range of 20°–95°. Using the Joint Committee on Powder Diffraction Standard International Centre for Diffraction Data (JCPD-ICDD), the structural phase in pXRD pattern was identified. The instrumental broadening was corrected by the standard pattern of LaB₆. Prior to analysis of pXRD patterns of Pt-based catalysts, XRD pattern of support was used to calibrate the background contribution. The lattice parameter, a , of catalyst was estimated using Eq. (1) [31].

$$2\theta_{hkl} = 2\sin^{-1} \left(\frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2} \right) \quad (1)$$

where λ = Cu-Kα radiation, θ angle Bragg diffraction in radians, and hkl Miller indices. In PD method, each Bragg diffraction peak was fitted with Pearson VII function. In Pt/C CCR, Pearson VII and Pseudo-Voigt functions were used for deconvolution of the contribution on each Bragg diffraction peak. These functions aid to obtain the parameters such as a , θ_{hkl} and full-width at half-maximum (FWHM, β_f), Eqs. (2)–(6).

$$I_C = \frac{I_{hkl}}{(1 + \kappa * \Delta\theta^2)^m} \quad (2)$$

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