



Pt Catalyst Supported within TiO₂ Mesoporous Films for Oxygen Reduction Reaction



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ARTICLE INFO

Article history:

Received 17 September 2013
Received in revised form 18 February 2014
Accepted 20 February 2014
Available online 12 March 2014

Keywords:

Oxygen reduction reaction
Catalyst
Electrochemical deposition
Interfacial charge transfer
Mesoporous film.

ABSTRACT

In this study, dispersed Pt nanoparticles into mesoporous TiO₂ thin films are fabricated by a facile electrochemical deposition method as electro-catalysts for oxygen reduction reaction. The mesoporous TiO₂ thin films coated on the fluorine-doped tin oxide glass by screen printing allow a facile transport of reactants and products. The structural properties of the resulted Pt/TiO₂ electrode are evaluated by field emission scanning electron microscopy, energy dispersive X-ray spectrometry, X-ray diffraction, and X-ray photoelectron spectroscopy. Cyclic voltammetry measurements are performed to study the electrochemical properties of the Pt/TiO₂ electrode. Further study demonstrates the stability of the Pt catalyst supported within TiO₂ mesoporous films for the oxygen reduction reaction.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted great attention as alternative clean energy technologies for transportation vehicles and portable electronic devices, with the advantages of high efficiency and low emission of pollutants [1,2]. However, the practical commercialization of the PEMFCs still faces several fundamental challenges. As far as the oxygen reduction reaction (ORR) is concerned, the major challenges for PEMFCs are to retain a sufficient performance of the catalysts and ensure the durability of the system under the dynamic load operation [3]. A large variety of ORR catalysts have been developed and tested in order to improve the catalytic property and stability. The catalyst materials for operation in acidic environment are mainly based on noble metals, in particular Pt and its alloys. Support materials have received somewhat less attention and most examples rely on different variety of carbon-based materials. An ideal support should have good electrical conductivity, high surface area, corrosion resistance and good adhesion of catalyst particles onto its surface. It was found that the interaction between Pt nanoparticles (NPs) and supports has a strong influence on the performance of the catalyst and

the access of electrons and reactants to the active sites on the Pt NPs surface [4–6]. Synergistic effects between precious metal NPs and a wide variety of oxides [7–9] as well as polymer supports [10] have been reported.

Thus far Pt nanoparticles (NPs) loaded on carbon black with high surface area have been the most commonly used catalysts for ORR. The Pt/C catalysts exhibit desirable kinetic properties leading to ‘counterbalance behavior’ in acid or alkaline condition needed for the efficient functioning of fuel cells, which is catalytically active enough to reduce oxygen with four-electron pathway at potentials that are as close as possible to the formal potential of the oxygen electrode [11,12]. This behavior has rendered the Pt/C system to be the present ‘candidate of choice’ in the initial commercial application of PEMFC. Various methods to deposit Pt nanoparticles on carbon-based substrates have been documented. Among these methods, electrochemical deposition has the advantages of low-energy consumption and easy control of the loading mass of Pt [13–15]. Though the Pt/C catalyst shows remarkable performance in the PEMFC, there is an ongoing quest to find suitable alternatives of the support due to a number of reasons: the oxidation of carbon materials during fuel cell operation degrades the cell performance. The corrosion and collapse of carbon supports lead to Pt NP agglomeration resulting in a lower Pt utilization and loss of the electrochemical surface area (ECSA) [16–18].

The need to support catalysts with high ECSA is one of the driving forces for the development of mesoporous materials with an enormous internal surface area and an efficient mass transport

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at the same time. Nanocrystalline TiO_2 as catalyst support has received increasing attention due to its inherent stability in the electrochemical environment and commercial availability [19–22]. An appropriate integration of Pt NPs with TiO_2 would produce a hybrid nanocomposite that combines desirable properties of two nanoscaled materials and allows for fine-tuning of the properties of Pt NPs [23]. For example, a novel electro-catalyst based on mesoporous TiO_2 -supported Pt NP was reported by Popov *et al.* [19]. It showed a high stability under accelerated stress test conditions and an activity comparable to the commercial Pt/C catalyst [19]. Leung *et al.* investigated the influence of the reductive treatment on structural properties of TiO_2 -supported Pt NPs and their catalytic activity for formaldehyde oxidation [24]. The enhanced performance was attributed to a uniform dispersion Pt NPs and the interaction between Pt and TiO_2 . Nb- TiO_2 mesoporous microsphere and nanofiber-supported Pt catalysts were synthesized for high temperature PEM fuel cells, showing an improved electrochemical ORR stability compared to that of a commercially available Pt/C catalyst [25]. TiO_2 has also been decorated with Pt catalysts for photoelectrochemical water splitting. For example, Yu *et al.* reported that hydrogen production could be significantly enhanced by photocatalytic water splitting over Pt/ TiO_2 nanosheets with exposed (001) facets [26]. Several methods have been applied in the preparation of metal NPs deposited on TiO_2 substrates, such as under-potential deposition [27], hydrothermal treatment [21], photo-assisted reduction [28], and vacuum deposition [29]. Electrodeposition would be a simple and straightforward approach for the synthesis of Pt NPs onto the surface of TiO_2 , which is highly needed for production of complex electrode architectures in fuel cells.

In this contribution, we report a facile method for synthesis of Pt NPs with good adhesion into mesoporous TiO_2 thin film (Figure S1). Herein the nanostructured mesoporous TiO_2 thin film was used as support for electro-catalysts. The physicochemical properties of the resulted Pt/ TiO_2 electrode were evaluated by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) measurements were performed to study the electrochemical properties of the Pt/ TiO_2 electrode, which showed remarkable electrochemical activity and stability towards the oxygen reduction reaction.

2. Experimental

2.1. Chemicals

Titanium iso-propyloxyde, ethyl cellulose and K_2PtCl_4 were purchased from Sigma-Aldrich. Acetic acid, nitric acid, sulfuric acid and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Fluorine-doped tin oxide (FTO) glass with a sheet resistance of $15 \Omega \text{ sq}^{-1}$ was purchased from Nippon Sheet Glass Co. Ltd. All chemicals were used as received. Deionized water ($18.2 \text{ M}\Omega \text{ cm}$) was produced by a Millipore-Q purification system and used throughout all experiments. Mesoporous TiO_2 colloids and its screen-printing paste were prepared according to the reported procedure [30].

2.2. Preparation of Pt/ TiO_2 /FTO electrode

The FTO glass was firstly ultrasonicated in ethanol and acetone for 10 min, respectively. After rinsing with deionized water and drying in high-purity nitrogen stream, one layer of the prepared TiO_2 paste was coated on the FTO glass plate by screen printing. The TiO_2 /FTO electrode was heated in an air atmosphere

at 112°C (15 min), 150°C (10 min), 325°C (10 min), 425°C (10 min) and 500°C (30 min). The thickness of the TiO_2 mesoporous film was controlled to around $2.5 \mu\text{m}$ as measured using a profilometer. After cooling down, the as-prepared TiO_2 /FTO electrode was used as working electrode for electrochemical deposition of Pt NPs. The annealing progress not only introduces the mesoporous structure, but also improves the conductivity of TiO_2 , which is beneficial for the electrochemical deposition of Pt NPs. Adhesive tape was used to cover the bare FTO glass around TiO_2 film to prevent the direct deposition of Pt onto the FTO glass, which is not our interest. The uncovered area at one of the ends was used to take electrical contact, and the rest of its length was used as working electrode. The Pt NPs were deposited into TiO_2 film at -445 mV (versus SCE) in an aqueous solution of $5 \text{ mM K}_2\text{PtCl}_4 + 0.1 \text{ M K}_2\text{SO}_4$ with the magnetic stirring. Finally, the electrode was rinsed with pure water and dried for surface characterization and electrochemical study. The as-prepared Pt NPs on nanocrystal TiO_2 film (coded as Pt/ TiO_2 /FTO electrode) are stable and very difficult to remove from the electrode surface.

2.3. Instruments and measurements

The FESEM micrographs and EDX of as-prepared mesoporous TiO_2 thin film and TiO_2 -supported Pt NPs were performed with a Sirion 200 (FEI Company from Holland). XRD patterns were recorded by an X'pert PRO diffractometer (PANalytical B.V.) with $\text{Cu K}\alpha$ radiation as the X-ray source for excitation operating at 40.0 kV and 40.0 mA within the 2θ ranges from 20 to 70 . X-ray photoelectron spectroscopy (XPS) was carried out on a VG Multilab 2000 XPS instrument (Thermo Electron Co.) with $\text{Al K}\alpha$ radiation as for excitation. The binding energy of the XPS was referenced to the $\text{C}1\text{s}$ spectrum of carbon tape at 284.60 eV .

The catalytic activity and electrochemical performance of the Pt/ TiO_2 electrodes were evaluated in a conventional three-electrode electrochemical cell. The fabricated Pt/ TiO_2 electrodes were used as the working electrode, twisted platinum wire as the auxiliary electrode, and saturated calomel electrode (SCE) as reference electrode. An electrolyte of $0.5 \text{ M H}_2\text{SO}_4$ was used to examine the hydrogen adsorption and desorption behaviors and investigate the oxygen reduction activity of Pt/ TiO_2 electrodes. The ECSA of Pt was evaluated based on the hydrogen desorption peaks appearing between -0.295 and 0.105 V , by assuming a charge of $210 \mu\text{C cm}^{-2}$ for the electro-active Pt surface [20]. The electrolyte was purged with oxygen or nitrogen for 15 min prior to any electrochemical measurements. In order to evaluate the electrochemical stability and performance of Pt/ TiO_2 /FTO electrodes, cyclic voltammetry was carried out for 1000 cycles in $0.5 \text{ M H}_2\text{SO}_4$ at the scan rate of 100 mV s^{-1} in the range of -0.295 V to 1.155 V . The catalyst stability was assessed by monitoring the ECSA of Pt in the 1^{st} , 200^{th} , 400^{th} , 600^{th} , and 800^{th} cycles.

3. Results and discussion

Fig. 1a shows an FESEM image (top view) of a nanocrystalline TiO_2 film with an average particle size of about 20 nm . The specific surface area, the average pore size and porosity of the mesoporous TiO_2 film were estimated to be about $80 \text{ m}^2 \text{ g}^{-1}$, 30 nm , and 78% by the Brunauer-Emmett-Teller (BET) analysis, respectively. The mesoporous TiO_2 film has a surface area available for catalysts adsorption over a thousand times larger than the geometric area of the screen printed regions. In addition, the mesoporous TiO_2 film favors an easy penetration of the electrolyte with the Pt precursors ($[\text{PtCl}_4]^{2-}$). In this study, electrochemically deposition of Pt nanoparticles into TiO_2 mesoporous films under potentiostatic conditions (-0.445 V vs. SCE) was obtained in

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