

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article

Pyrolyzed titanium dioxide/polyaniline as an efficient non-noble metal electrocatalyst for oxygen reduction reaction

Zhijuan Zou ^a, Hao Cheng ^a, Jingyu Wang ^{a,b,*}, Xijiang Han ^{a,#}^a Department of Chemistry, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China^b Key Laboratory for Large-Format Battery Materials and System (Ministry of Education), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China

ARTICLE INFO

Article history:

Received 13 July 2014

Accepted 4 September 2014

Published 20 March 2015

Keywords:

Polyaniline

Titania

Pyrolyzation

Cathode catalyst

Oxygen reduction reaction

ABSTRACT

To overcome the prohibitive cost and poor durability of conventional Pt-based catalysts, TiO₂/C was prepared by pyrolyzing a novel titanium dioxide/polyaniline (TiO₂/PANI) composite. The prepared catalysts were characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, cyclic voltammetry (CV), and linear sweep voltammetry. Interaction between PANI and TiO₂ was found to inhibit the aggregation of TiO₂ and its transformation from anatase to rutile. The catalytic activity of the TiO₂/C first increased with increasing PANI content and then decreased; the optimum was achieved when the PANI/TiO₂ mass ratio was 35/100. CV and *i-t* curves showed that the prepared composite has a good catalytic stability.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The preparation of low-cost, efficient, and stable catalysts as fuel cell cathode materials is currently a hot research topic. Groups 4 and 5 metal oxide compounds have been regarded as promising candidates for polymer electrolyte fuel cell (PEFC) cathode catalysts because they are insoluble in acid media [1]. The use of oxides of zirconium [2–6], tantalum [5–10], niobium [6], titanium [1,5], and hafnium [11–13] as cathode catalysts in oxygen reduction studies has been reported, with varied synthesis methods employed. In particular, TiO₂ is a promising photocatalyst that has received widespread interest [14,15]. Thorough research has been conducted regarding its synthesis, morphology and crystal phase control, modification, and combination with other materials to prepare composite materials.

TiO₂ is often used as the base material for catalysts because of its good stability. Recently, TiO₂ has also been examined as a fuel cell cathode catalyst because it can improve the stability [16] and methanol resistance of cathode catalysts and the selectivity and catalytic activity of 4-electron reactions [17,18]. Non-stoichiometric TiO₂ has also been used as a base material for cathode catalysts [19].

Notably, TiO₂ is an oxygen reduction catalyst. Zhang et al. [20] prepared a cathode catalyst via the hydrolysis of TiCl₄ followed by heat treatment and used the resulting product in zinc–air batteries. Dam et al. [21] used TiO₂ as a precursor to prepare a titanium carbonitride matrix after calcination at high temperature, and the resulting TiCNO product was a mixture of TiO₂ and TiCN catalysts. The initial oxygen reduction potential and the carrying current of the titanium carbonitride catalyst

* Corresponding author. Tel: +86-451-86413702; Fax: +86-451-86418750; E-mail: jingyu.wang@163.com# Corresponding author. Tel: +86-451-86413702; Fax: +86-451-86418750; E-mail: hanxijiang@hit.edu.cn

This work was supported by the National Natural Science Foundation of China (21001037, 21071037, and 91122002), the Special Fund for Harbin Technological Innovation Talent (2013RFLXJ011), and the Research Fund for Talent Introduction of Huazhong University of Science and Technology (2014036).

DOI: 10.1016/S1872-2067(14)60223-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 3, March 2015

were significantly improved compared with those of pure TiO₂. Additionally, Chisaka et al. [1] prepared a cathode catalyst, in which the main component was rutile TiO₂, by heat treatment of TiCN. Their studies showed that the residual carbon did not integrate into the TiO₂ lattice to form impurity defects. During heat treatment at elevated temperatures, C was instead incorporated into graphene, which then coated the surface of the TiO₂; the coating played a role in the oxygen reduction electron transfer process. Although part of the N and Ti formed TiN, the N atoms did not influence the oxygen reduction activity because they were not integrated into the TiO₂ lattice. Conversely, both oxygen defects generated in TiO₂ during heat treatment at high temperatures and doped N are known to significantly affect the activity of TiO₂ towards oxygen reduction. Recent studies have indicated that the (110) plane of TiO₂ [1] is more conducive to the adsorption of oxygen. Thus, the (110) facets are favorable for oxygen reduction reactions. Despite the research results achieved to date, further investigations are required to adequately determine the mechanism of oxygen reduction over TiO₂ and its performance as a catalyst or catalyst support.

TiO₂ is a semiconductor, and as such its low conductivity limits its application in terms of oxygen reduction. Based on first-principle calculations, Zheng et al. [22] reported that for low-conductivity materials, the electron transfer efficiency is low, the reaction is limited to a small area on the material interface, and oxygen reduction tends to occur via a two-electron mechanism. The accumulation of the resulting products, H₂O₂ and HO₂⁻ ions, is unfavorable for the reaction to continue. Conversely, the introduction of conductive carbon favors the reduction of oxygen via a four-electron mechanism, thereby improving the oxygen reduction performance of the material. These conclusions have been experimentally confirmed [22]. Chisaka et al. [1] studied TiO₂ prepared via heat treatment of titanium carbonitride at high temperatures in N₂ and H₂ atmospheres. The resulting material exhibited oxygen reduction activity; C was not incorporated into the lattice of TiO₂ but was instead present as a single layer of graphite on the surface of the TiO₂. C played a primary role in electron transportation [23], and the oxygen defects formed during the heat treatment process had a decisive role in improving the performance of the oxygen reduction catalyst.

In this study, we first prepared a novel TiO₂/polyaniline (PANI) complex via a hydrothermal route, and a TiO₂/C catalyst was obtained via subsequent pyrolysis. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the crystal phase composition and morphology of the TiO₂/C, and its electrochemical performance was assessed. Moreover, the influence of the mass ratio of PANI to TiO₂ and the pyrolysis temperature on the oxygen reduction performance of the catalyst was examined to establish optimum synthesis conditions to provide a reference for the future study of oxygen reduction TiO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

First, 2.282 g ammonium persulfate (APS, AR, Tianjin Damao Chemical Reagent Factory, Tianjin, China) was dissolved in HCl (36%, AR, Beijing Chemical Plant, Beijing, China) solution (0.1 mol/L) and held in an ice-water bath. Then, 0.3411 g of cetyltrimethylammonium chloride (CTAC, AR, Tianjin Guangfu Chemical Plant, Tianjin, China) dissolved in HCl solution (0.1 mol/L) was added to a three-necked flask. After adding 0.92 mL aniline (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), the mixture was mechanically stirred in an ice-water bath for 1 h to ensure uniform dispersion of the aniline monomers. The polymerization of the aniline monomers was initiated by the addition of the pre-cooled APS solution. The total volume of HCl solution (0.1 mol/L) used was 100 mL. The reaction solution was kept in an ice-water bath under mechanical stirring for 24 h. After the reaction, the product was centrifuged and washed three times with industrial ethanol, distilled water, and absolute ethanol (AR, Sinopharm) in turn. Finally, the product was redispersed in 80 mL absolute ethanol before use. The 20 mL of polyaniline (PANI) ethanol dispersion was centrifuged and dried in a vacuum dryer at 60 °C for 6 h, and the concentration of the PANI nanofiber dispersion (11.46 mg/mL) was calculated by weighing the resulting solid powder. The yield of PANI was found to be about 97.6%.

Next, 3 mL of tetrabutyl titanate (AR, Sinopharm) was mixed with a certain amount of ethanol. After ultrasonic dispersion, the PANI ethanol dispersion was added, and the mixture was ultrasonically dispersed for another 10 min. The total volume of the ethanol dispersion was set at 30 mL. Then, under magnetic stirring, 10 mL of distilled water was added dropwise to the above mixture. The mixture was stirred at 70 °C for a further 30 min to ensure complete hydrolysis. The resulting precipitate was centrifuged, washed three times with distilled water, and then dispersed into 60 mL of aqueous HCl solution (1 mol/L). The mixture was transferred to a 250 mL three-necked flask and mechanically stirred at 70 °C for 4 h. The resulting solution was then transferred to a 35 mL autoclave and hydrothermally treated at 150 °C for 18 h. The precipitated powder was centrifuged, washed three times each with industrial ethanol and distilled water, and dried at 60 °C. Finally, the obtained solid was ground and calcined in a tube furnace at 800 °C under flowing N₂ to generate the TiO₂/C catalyst.

2.2. Catalyst characterization

XRD measurements were performed with a Rigaku D/Max-RB X-ray diffractometer (Japan) using Cu K_α radiation at a tube voltage of 40 kV and operating current of 30 mA. The morphologies of the samples were analyzed with a field emission scanning electron microscope (FE-SEM; Philips FEI-Sirion 200) and a transmission electron microscope (TEM; FEI TECNAI G2). Raman spectra were collected with a Renishaw inVia Raman spectrometer using a He-Ne laser (0.1 mW) at 633 nm. Fourier transform infrared spectra (FT-IR) were collected using a Nicolet Avatar 360 spectrometer (USA). X-ray photoelectron spectroscopy (XPS) measurements were performed with a ULVAC PHI5700ESCA spectrometer. Thermal analysis of the samples was carried out using an SDT Q600 thermogravi-

Download English Version:

<https://daneshyari.com/en/article/59948>

Download Persian Version:

<https://daneshyari.com/article/59948>

[Daneshyari.com](https://daneshyari.com)