INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 3229–3237

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Tungsten carbide hollow microspheres as electrocatalyst and platinum support for hydrogen evolution reaction

*Chaoyun Tang, Dezhi Wang, Zhuangzhi Wu, Bohua Duan**

Key Laboratory of Ministry of Education for Non-ferrous Materials Science and Engineering, School of Materials Science and Engineering, Central South University, Yuelu Road, Changsha, Hunan 410083, PR China

ARTICLE INFO

Article history:
Received 10 March 2014
Received in revised form
20 December 2014
Accepted 24 December 2014
Available online 28 January 2015

Keywords:
Tungsten carbide
Hollow microspheres
Platinum support
Hydrogen evolution reaction

ABSTRACT

Tungsten carbide with special spherical hollow microstructure was synthesized and tested as an electrocatalyst or electrocatalysts support for platinum. Both bulk WC and as-synthesized WC supported Pt were evaluated as hydrogen evolution catalysts. It was found that the synthesis temperature is crucial to the compositions and surface states of products, and has direct influence on HER activity. The WC possesses spherical micro-morphology with a high specific surface area, and its hollow and cracked structural features are considered to be beneficial for its electrocatalytic ability and potential as electrocatalysts support. The bulk WC hollow microspheres displayed excellent HER activity. The 20% Pt/WC also exhibited better electrocatalytic performance than the commercial 20% Pt/C: the current density has obviously increased, and the kinetic parameters such as Tafel slope and exchange current density have obvious improvement as well. The investigations indicated that the as-synthesized WC could be considered as a potential electrocatalyst and electrocatalyst support.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is considered to be an ideal fuel in the future, because it is clean, energetic and could be produced from renewable energy sources [1]. Nowadays, although water electrolysis from renewable energy sources (i.e. PV solar, wind energies) is less competitive when compared to hydrocarbons reforming which is currently practiced in industry, it has been proposed to represent a truly sustainable route for H_2. The efficiency of water electrolysis critically depends on cathode materials, especially in proton exchange membrane (PEM) based electrolyzers [2,3]. Supported Pt electrocatalysts are the most popular cathode material for hydrogen evolution reaction (HER) [4,5]. However, high loadings of expensive noble metals, which lead to high capital costs, proposed an urgent need to develop high efficient and less expensive materials to replace these noble metals or reduce their usage [6].

Tungsten carbides (WC) have been widely known since Levy and Boudart discovered its Pt-like catalysis for several chemical reactions [7–9]. Since then, researchers have found that WC exhibits high activities, which is similar to those of noble metal catalysts for a number of reaction including hydrogen evolution reaction [10] and oxygen reduction

* *Corresponding author*. Tel.: +86 073188877221.
E-mail address: msewml@csu.edu.cn (B. Duan).
http://dx.doi.org/10.1016/j.ijhydene.2014.12.105
0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

reaction (ORR) [11]. Although the performance of WC is inferior in direct comparison to platinum, its other outstanding advantages such as lower price, high resistance to both carbon monoxide and bisulfide poisoning [12,13], enhanced resistance to surface oxidation in acidic solution and comparable stability in neutral/alkaline solution [14], drive people to consider it as an interesting alternative to noble metal catalyst. However, tungsten carbide alone can't be directly used for HER due to its high overpotential, which is consequently leading to the high electricity consumption [15]. Nowadays, most researchers prefer to study WC as an electrocatalyst substrate combined with platinum nanoparticles because it is generally believed to have a synergistic effect which makes Pt/WC electrocatalysts possess a higher intrinsic activity. But which element was playing the leading role is still unknown, people are trying to reduce the usage of Pt in Pt/WC [16]. Many studies focused on the relationship between the micro-morphology and the catalytic activity of WC, and tried to design an optimal nanostructure to enhance its catalytic ability [17]. However, there is no widely accepted theory about the catalytic active site until now. Calculation results [18,19] through theoretical Density Functional theory (DFT) didn't give researchers acceptable and instructional theory yet. Some researchers [20–24] have successfully prepared WC with special morphology such as microspheres, nanowires or nanofibers etc, and have conducted measurements toward their electrocatalytic property as well. The results exhibited that WC possess excellent electrocatalytic abilities, but there are still a lot of unsolved problems need people to study.

Colloidal carbon spheres are widely applied as catalyst support and template due to its hydrophilic surface and regular spherical micro-morphology, and usually synthesized by using hydrothermal methods [25,26]. Some researchers [27–29] have already combined this technique to prepare WC-contained compounds. Their products have regular spherical micro-morphology and are easy to load other materials. Further studies indicated that this spherical WC possessed high electrochemical activity and electrochemical stability, especially effective as Pt catalyst support. Although the spherical WC possesses those advantages mentioned above, most of their researches mainly focused on the ORR field of WC, and rarely discussed about the HER field. They also haven't deeply investigated about the influence of preparation condition on electrochemical ability. For those purposes, we adopted hydrothermal and reduction methods, successfully synthesized WC with special hollow structure, and investigated it's HER ability as bulk catalyst and Pt electrocatalysts support. What's more, we managed to study the relationship among electrochemical ability, phase composition and surface states at different synthesis conditions, and obtained an optimal preparation condition. We hope this study could give some instructive advices for WC synthesis.

Experiment

Sample preparation

Excessive amount of Ammonium Metatungstate (AMT) and glucose were dissolved in 60 ml de-ionized water and completely scattered through ultrasonic oscillations for a half hour. Then the transparent solution were transferred into a sealed 100 ml Teflon-lined stainless autoclave, heated up to 200 °C and sustained for 10 h. After cooled down naturally to room temperature (25 °C), the product should be filtered, subsequently washed by de-ionized water and ethanol in order for several times. At last the sediment was collected and dried out in a vacuum oven at 80 °C for 8 h to get the loose powder precursor. The precursor comprised tungsten containing species and carbonized polymer, presented spherical particles in scanning electron microscope. The formation of this complex precursor can be attributed to the poly-condensation process of glucose. When the glucose molecules dehydrated and carbonized into carbon spheres, its hydrophilic groups could complex with the Amino-groups or tungstic acid groups of AMT. Therefore, the tungsten species were fixed into the spherical particles and this spherical structure precursor can form special spherical morphology in later processing. In order to remove those unexpected elements and finally synthesize the bulk WC, the scattered precursor was slowly heated up to setting temperature at the rate of 1 °C per minute and then carbonized for 3 h in presence of purity argon flow in tube furnace. At last for the sake of removing amorphous carbon, it was treated at pure hydrogen flow for about 1 h at the same temperature then cooled down to room temperature in pure argon protection.

WC-supported 20% Pt electrocatalyst was prepared by using microwave-assisted ethylene glycol process [30,31]. Above all, 0.1 g WC sample synthesized before was placed in 100 mL beaker with 25 mL ethylene glycol. After stirred 20 min to form an uniform suspension liquid, certain amount of $H_2PtCl_6 \cdot 6H_2O$ were dropped into this solution and completely mixed. Then 0.4 mol L^{-1} KOH solutions were slowly added and mixed until the solution's PH value reach 10. Nest the mixture solution was ultrasound oscillated for 10 h. At last, the mixture were placed into a domestic microwave oven and heated for 1 min at the power 700 W the sample was repeatedly washed by deionized water and collected by centrifuge.

Sample characterizations

X-ray diffraction (XRD) patterns were recorded by using D/max-2500 system with a Cu Kα irradiation source (λ = 0.154 nm) and crystallite size were calculated using scherrer equation. The micro-morphology and microstructure were studied by scanning electron microscope (SEM, FEI Sirion 200) and transmission electron microscope (TEM, Tecnai $G^2$20). Specific surface areas (BET) were determined by N_2 adsorption at 77 K with the BET method using a volumetric unit (Quadrasorb SI-3MP). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) were also used to investigate the surface composition of samples.

Electrochemical measurements

0.5 M H_2SO_4 solutions were freshly prepared from deionized water prior to all electrochemical measurements. 1 mg sample was mixed with 800 uL deionized water, 200 uL absolute ethyl alcohol and 80 ml Nafion ionomer dispersion, then the mixture were ultrasonic dispersed for 30 min in order to

Download English Version:

https://daneshyari.com/en/article/1272018

Download Persian Version:

https://daneshyari.com/article/1272018

Daneshyari.com