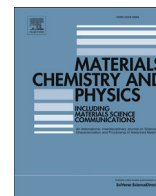




Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Catalytic activity of tungsten carbide-carbon (WC@C) core-shell structured for ethanol electro-oxidation

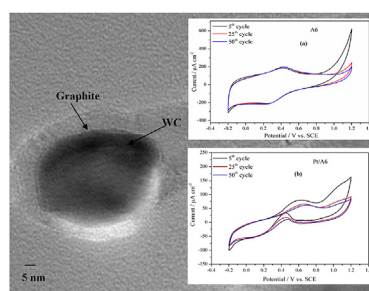
Gourav Singla, K. Singh, O.P. Pandey*

School of Physics and Materials Science, Thapar University, Patiala, Punjab, India

HIGHLIGHTS

- Tungsten carbide nano powder was synthesized using acetone as carbon source.
- *In-situ* produced outer carbon layer increase the surface area of materials.
- Mesoporous WC with surface areas 52.6 m²/g obtained.
- Pt modified WC powder showed higher electrochemical stability.
- Better CO-tolerance for ethanol oxidation after the deposition of Pt nano particles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 August 2015

Received in revised form

15 June 2016

Accepted 9 July 2016

Available online xxx

Keywords:

Tungsten carbide

Core-shell

Ethanol oxidation

Catalyst support

ABSTRACT

In this study, carbon coated WC (WC@C) was synthesized through solvothermal reactions in the presence of reducing agent magnesium (Mg) by employing tungsten oxide (WO₃) as a precursor, acetone (C₃H₆O) as a carbon source. The formation of WC@C nano particles is confirmed by X-ray diffraction and Transmission electron microscopy. The thermal stability of the synthesized powder examined in air shows its stability up to 550 °C. In this method, *in-situ* produced outer carbon layer increase the surface area of materials which is 52.6 m² g⁻¹ with pore volume 0.213 cm³ g⁻¹. The Electrocatalytic activity of ethanol oxidation on a synthesized sample with and without Pt nano particles have been investigated using cyclic voltammetry (CV). The CV results show the enhancement in oxidation stability of WC@C in acidic media as well as better CO-tolerance for ethanol oxidation after the deposition of Pt nano particles as compared to without Pt nano particles.

© 2016 Published by Elsevier B.V.

Nowadays, almost every aspect of human life at least in developed countries is strongly depended on availability of energy provided by fossil fuel. However, the limited sources of fossil energy put restrictions on the economic development of any country. Hence, after looking the crisis of energy resources most of the research has now shifted towards development of new energy

sources like fuel cells, which works on the principle of electrocatalysis for energy conversion [1–3]. In fuel cells, alcohol like ethanol which is produced by biological conversions of carbohydrates (wheat, maize, etc.) is used as fuel [1,4]. It converts chemical energy of fuel into electrical energy through an electrochemical reaction [5]. In order to enhance the efficiency of fuel cell a catalyst layer such as platinum (Pt) is used, which provide a conducive environment for electrochemical reactions [6]. However, Pt as a catalyst suffers from several drawbacks, including slow kinetics, low efficiency, high cost, and limited lifetime [7,8]. So, in order to expedite the usage of fuel cells one of the most important

* Corresponding author.

E-mail addresses: g Singhla@gmail.com (G. Singla), k Singh@thapar.edu (K. Singh), oppandey@thapar.edu (O.P. Pandey).

challenges is to supplement the high-cost metal catalyst with high surface area materials which show similar type of catalytic activity.

In recent years, the carbon supported Pt catalysts (Pt/C) have been studied extensively [8,9]. However, due to the higher operating temperature with variable thermal cycle carbon support catalysts corrode rapidly [10,11]. Furthermore, this carbon oxidation/corrosion can result Pt catalyst agglomeration and this degrading the fuel-cell performance significantly [12]. The current research is focused on the development of new non carbon-based support catalyst material, which have low cost, high performance, stability, and high durability.

Among the non-carbon support candidates, tungsten carbide (WC) appears to be an important material that shows good electronic conductivity, chemically inert, low cost and tolerance to CO poisoning [8,13–15]. However, the experimental results showed that at ambient conditions WC is oxidized at around 600 °C [16,17], which is much higher than the required operating temperature of the low temperature fuel cells. In addition, the Pt like catalytic behavior of WC could result in a cooperative effect with the metal catalyst, leading to enhancement in the catalytic activity [18]. Hence, most of the authors have synthesized tungsten carbide by different methods, used it as Pt supported catalysts (Pt/WC) and reported its two main electrochemical reactions viz oxygen reduction reaction (ORR)/hydrogen evolution reaction (HER) as well as alcohol (methanol/ethanol) oxidation [8,10,15,19–21]. Moreover, as far as the oxidative stability of WC is concerned, the presence of Pt seems to improve the corrosion resistance of the carbide [22].

For better catalytic activity high surface area having highly active sites are required; which depends on particle morphology and the existing porosity [23,24]. However, these characteristics are achieved during synthesis of WC by optimizing the chemical composition and reduction as well as carburization temperature of oxide precursors [25]. Hence in this paper, we present an approach to prepare WC@C nano powder by solvothermal method using tungsten trioxide as tungsten raw materials and magnesium with acetone as reducing agent and carbon resource respectively. The Pt nanoparticles are deposited on the higher electrocatalytic synthesized powder sample to prepare Pt/WC catalyst and examine its electrocatalytic activity in the ethanol oxidation.

1. Experimental procedure

1.1. Preparation

1.1.1. Synthesis of tungsten carbide

For the synthesis of carbon coated WC (WC@C) nano particle; WO₃ (2.314 g), Mg (2.304 g) as reducing agent and Acetone (30 ml) as a source of carbon were added into a specially designed stainless steel autoclave. The autoclave was sealed from the top and the entire assembly was put inside the furnace at room temperature. The temperature of the furnace was raised from room temperature to desired temperature slowly (500 °C, 600 °C, 700 °C and 800 °C) and maintained at that temperature for 10 h. After that the autoclave was allowed to cool to room temperature. The resultant product was collected and washed by dilute HCl (1:1) to remove MgO. After leaching the powder was washed with distilled water several times to remove HCl. Finally, the obtained product was washed with acetone and then dried in vacuum at 100 °C. The samples so obtained are denoted as A5, A6, A7 and A8 corresponding to their reaction temperature.

1.1.2. Deposition of Pt

Pt nano particles were deposited on synthesized WC by dispersing 40 mg of WC powder in 20 ml of ethanol in ultrasonic

bath and then 100 μL hexachloroplatinic acid (H₂PtCl₆) aqueous solution was added to ultrasonicated solution. In the mixture of metal salt and WC support, appropriate amount of 0.05 M NaOH/ethanol was added to maintain the pH~10. The precipitate was washed with high purity water and then dried at 80 °C.

1.2. Characterization of synthesized nanopowder

1.2.1. Physical characterization of synthesized powder

The X-ray diffraction study of the product phase was done at room temperature between 20° ≤ 2θ ≤ 80° to identify crystalline phases. The XRD of the samples was performed using PANalytical Xpert-Pro with CuKα radiation (λ = 1.54 Å) obtained from the copper target using an inbuilt Ni filter. During XRD experiment, scan speed was 5 °C/min. Crystallite size of synthesized WC was determined by XRD profile technique. The phase analyses were done by Rietveld structural refinement of the XRD profiles using FullProf version 2.05. The Williamson-Hall equation as given in equation (1) was used to calculate the crystallite size.

$$\beta_{hkl} \cos \theta_{hkl} = [K\lambda/t] + [4\epsilon \sin \theta_{hkl}] \quad (1)$$

Where β(2θ) is the full width at half maximum (FWHM), λ is the X-ray wavelength, t is the crystallite mean size and ε is strain. Thermo gravimetric analysis (TGA) was done to find out the thermal stability of the samples. The TGA experiment was done at heating rate of 5 °C/min from room temperature to 1000 °C in air atmosphere. Raman spectra of powder sample was recorded using Renishaw via Raman spectrometer with the 514.5 nm line of an Ar⁺ laser at 20 mW power. The morphology, particle size and distribution of the samples were studied by high-resolution transmission electron microscope (HRTEM, JEOL 2100F) operating at 200 kV.

1.2.2. Electrochemical characterization of WC@C powder

The electrochemical measurement was performed at Bio-Logic EC Lab SP300. A standard three compartment electrochemical cell was used with glassy carbon electrode (GCE), Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All the measurement was carried out at room temperature in 0.5 M H₂SO₄.

The top surface of GCE rod having 6 mm diameter was pre cleaned with emery paper. Typically 4 mg of synthesized powder sample was mixed with 1 mL of ethanol. The mixture was treated ultrasonically for 20 min for uniform dispersion. 10 μL of mixture was then dropped onto the surface of the GCE. Finally a drop of 10 μL of Nafion[®] 117 solution (Sigma Aldrich) was dropped onto the top surface and left in air for overnight drying.

2. Results and discussion

2.1. X-ray diffraction analysis (XRD)

Fig. 1 show the XRD pattern of the product phase obtained after acid treatment of samples synthesized at 500, 600, 700 and 800 °C for 10 h holding time periods. A typical XRD pattern of the synthesized black powder taken after acid leaching clearly confirms the presence of tungsten carbide (WC) without any kind of impurities such as tungsten oxide or even pure tungsten metal in the synthesized samples. The presence of lower tungsten carbide (W₂C) in spite of the presence of excess carbon level may be due to C accumulation in the surface layer in sample A5. It occurs due to relatively fast surface diffusion of carbon in the freshly reduced highly reactive nano structured W as compared to bulk diffusivity at low temperatures [26–28]. Moreover, the existence of W₂C in this case suggests that system pressure plays an important role in

Download English Version:

<https://daneshyari.com/en/article/5448461>

Download Persian Version:

<https://daneshyari.com/article/5448461>

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