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A combined physicochemical and electrocatalytic study of microwave synthesized tungsten mono-carbide nanoparticles on multiwalled carbon nanotubes as a co-catalyst for a proton-exchange membrane fuel cell

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ABSTRACT

Tungsten mono-carbide (WC) nanoparticles supported on multiwalled carbon nanotube (MWCNT) was synthesized by a microwave-assisted solid-state carburization. The prepared samples were used as a co-catalyst to prepare Pt-WC/MWCNT catalyst for a proton-exchange membrane fuel cell. MWCNTs with and without oxidative pretreatments were characterized as the starting precursors. The influence of the carbide formation conditions on the physico-chemical characteristics of the final product were extensively investigated. According to the results, surface pretreatment of the MWCNTs can improve the yield of carbide formation. Furthermore, carburization process can improve the catalyst utilization due to increasing the number of surface defects of the MWCNT supporting materials which can be interpreted as structural effect of the carburization process. It is believed that the superior performance of electrodes modified with tungsten carbide is mostly due to the structural effect of the carburization process and synergistic effect between the electrocatalytic activity of WC and Pt.

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Introduction

Fuel cell technology has attracted an increasing amount of attention in recent decades due to the greater demand for energy, the eventual depletion of fossil fuels, and the rise of environmental pollution throughout the world [1–4]. Proton-exchange membrane fuel cells (PEMFC) are considered to be the next generation of energy conversion devices for a wide range of applications in portable, stationary and transportation markets due to their high power density and relatively low operation temperatures [2,3]. Currently, Pt–Ru and Pt are the most effective catalyst materials for anode and cathode of DMFC-PEMFC, respectively [5]. However, in addition to the limited resources and high cost of Pt and Ru which hindering the wider commercialization of PEMFC fuel cells, it has been shown that the catalytic activity of both Pt and Ru are easily susceptible to poisoning by the adsorption of several intermediate products, especially on the anode side of the fuel cell [6]. Therefore, development of new alternative catalysts is necessary to reduce or replace expensive Pt and Pt–Ru bimetallic catalysts. Over the past several years, considerable efforts have been made to increase the performance of the catalyst materials used in PEMFCs. It has been reported that transition metal carbides show some Pt-like behavior for fuel cell reactions [7,8]. Many studies have investigated the surface science and electrochemical performance of transition metal carbides as alternative electrocatalysts. Among these, tungsten carbide has received considerable attention and has been proposed as one of the most promising materials for various catalytic reactions in PEMFC [6]. In the 1960s, Binder et al. [9] for the first time reported the hydrogen oxidation on tungsten carbide electrodes in an H_2SO_4 aqueous solution. Since that time, considerable efforts have been made to increase the use of tungsten carbide in the catalyst layers of PEMFC. It has been reported that the catalytic activity of tungsten carbide is attributed to its Pt-like electron state, which is induced by the filling of the d-states at the Fermi level of tungsten by an alloying carbon [10,11]. Some investigators have studied the electrocatalytic properties of tungsten carbide for hydrogen electrooxidation [12–16]. Although the electrocatalytic activity of tungsten carbide for fuel cell applications remains low, the results of investigations show that the application of tungsten carbide as a Pt co-catalyst or catalyst support can promote the catalytic performance in terms of the activity, durability and poisoning effects [17–21]. Recently, carbon nanotubes (CNT) have attracted increasing attentions as an effective catalyst support due to their unique properties, such as their high current carrying ability, chemical stability, thermal conductivity and mechanical strength [22–26]. Recent studies have revealed that modification of the CNT with tungsten carbide could be an effective approach to improve its performance as a catalyst support [27–33]. Several investigations have been conducted to study the electrocatalytic properties of tungsten carbide decorated on the outside surface of CNT [27,28]. Recently, the present authors investigated the electrocatalytic activity of tungsten carbide decorated on directly grown multiwalled carbon nanotube (MWCNT) as a co-catalyst for methanol oxidation [34]. It was concluded that the synergistic effect between Pt nanoparticles

and tungsten carbide, in addition to the unique structural effect of the MWCNT, could significantly enhance the methanol electro-oxidation performance. However, because CNT basal planes are chemically inert, it is necessary to utilize an adequate preparation technique to ensure the good dispersion of the catalyst nanoparticles on the external walls of the CNT with good control over the particle size and distribution. It has been reported that the nature and concentration of surface functional groups besides CNT surface defects plays an important role in catalyst utilization because they can serve as anchoring sites for catalyst metals. On the other hand, carbide formation arises between tungsten-containing species and CNT supporting materials at high temperatures under reductive environments. Thus, the carburization condition can have a strong influence on the characteristics of the carbides produced and on the structure and surface properties of the CNT supporting material [35,36]. To the best of our knowledge, there has been no systematic study on the influence of the carbide formation conditions on the surface and physicochemical characteristics of the MWCNT supported tungsten mono-carbide (WC) nanoparticles. The aim of the present research was to investigate the influence of the carbide formation conditions on the physicochemical and electrocatalytic performance of the microwave-synthesized WC nanoparticles supported on MWCNT as a co-catalyst for PEMFC electrodes.

Experimental

Preparation of WC/MWCNT and Pt-WC/MWCNT

WC-MWCNT was synthesized using a microwave carburization technique. MWCNT particles with a nanotube diameter of 10–15 nm and a purity level of ~ 96% (Hanwha Nanotech Corp., Korea) with and without oxidative pretreatment were used as the supporting material for the WC/MWCNT synthesis process. An $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid solution was used for the oxidative pretreatment. To investigate the effect of the oxidative pretreatment, MWCNT particles were activated by refluxing in a mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (1:1) acid solution and then were washed with a copious amount of distilled deionized water. Prior to microwave heating, tungsten powder (1 g, 99.9%, Aldrich) was completely dissolved in 20 ml of an 8 wt.% H_2O_2 aqueous solution using a hot-plate magnetic-stirrer. It was then mixed with 5 ml of 2-Propanol and MWCNT (1 g) and stirred for 24 h to give a uniform suspension. Finally, the suspension was boiled dry and used as a tungsten carbide precursor. In order to form WC, the precursor in an alumina crucible was placed inside a Pyrex beaker which was purged with pure argon for 10 min and then heated in a household microwave oven (Magic MWO-20M8, 800 W, 2.45 GHz) with an intermittent heating procedure of 15 s on with a 5 s pause. This was done twenty times. The Pyrex beaker was sealed from the atmosphere with an outlet air-locked through a bubbler to limit back-diffusion of air into the cell.

Pt/MWCNT and Pt-WC/MWCNT electrocatalysts were synthesized by a microwave-assisted improved aqueous impregnation technique which described elsewhere [37]. In

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