



Pt modified tungsten carbide as anode electrocatalyst for hydrogen oxidation in proton exchange membrane fuel cell: CO tolerance and stability



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ABSTRACT

Pt supported on tungsten carbide-impregnated carbon (Pt/WC/C) is evaluated for hydrogen oxidation reaction in hydrogen/oxygen polymer electrolyte fuel cell at two different temperatures (85 and 105 °C), in absence and presence of 100 ppm CO. Carbon supported PtW, prepared by a formic acid reduction method is also evaluated for comparison. At 85 °C, the initial hydrogen oxidation activity in the presence of 100 ppm CO is higher for Pt/WC/C, showing a CO induced overpotential of 364 mV for 1 A cm⁻² of current density as compared to an overpotential of 398 mV for PtW/C. As expected, an increase in CO tolerance is observed with the increase in cell temperature for both the catalysts. The increased CO tolerance of Pt/WC/C catalyst is in agreement with CO stripping experiments, for which the CO oxidation potentials occurred at lower potentials at three different temperatures (25, 85 and 105 °C) in comparison to PtW/C. The stability of both electrocatalysts is evaluated by an accelerated stress test and the results show a better stability for Pt/WC/C catalyst. On the basis of cyclic voltammograms and polarization curves, it is concluded that Pt/WC/C is more stable than PtW/C and can be used as alternative anode catalyst in PEMFC, especially at high temperatures.

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1. Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs) have been recognized as the most feasible power source for low/zero-emission electric vehicles and stationary applications [1]. In such type of fuel cells, H₂ is used as fuel and O₂/air as oxidant [2]. Utilization of pure hydrogen as fuel is the simplest and most efficient way for PEMFCs, but the infrastructure required is limited due to the production cost and storage difficulties. Alternatively, hydrogen may be obtained from reformed fuels, such as steam-reformed methanol, ethanol or natural gas. A potential problem which arises from this system is the production of small amount of impurities particularly carbon monoxide, which strongly adsorb on the Pt catalyst, usually employed in the anode [3], blocking the sites for the hydrogen adsorption and oxidation. Therefore, Pt is modified with other elements such as Ru or Mo for the PEMFCs so as to search for enhanced CO tolerant materials [4,5]. Unfortunately, the relative high cost and insufficient durability of these

elements still hinder the large scale commercialization of PEMFCs. For example, Antolini [6] observed the dissolution of Ru from the Pt–Ru anode catalyst and its presence in the cathode side. Other studies have shown the dissolution of Mo from the Pt–Mo anode and its transfer through the electrolyte membrane to the cathode side [7,8]. Therefore, most robust materials are required to provide not only stability to the anode catalysts, but also ability to tolerate trace amounts of CO. Because the catalytic properties of transition metal carbides have been found to be similar to those of precious metals like Pt [9], extensive studies have been carried out using transition metal carbides, particularly WC, as catalyst supports to improve the catalytic performance and minimize usage of precious metals. As electrocatalysts, they are also known to be highly resistant to CO poisoning and stable in acidic and basic solutions [10]. This is most probably due to the active surface of WC toward the dissociation of H₂O to produce surface hydroxyl group [11], which are critical for the subsequent oxidation of CO. If used as support, WC helps to increase the dispersion of precious metals [12].

There have been recent studies to evaluate the use of tungsten carbide as catalyst for fuel cells and it has been shown that Pt supported on tungsten carbide presents superior activity for both, the methanol electro-oxidation and oxygen reduction

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reactions [13,14]. In the work performed by Chhina et al. [15] a higher activity and stability for oxygen reduction reaction before and after 100 oxidation cycles was shown by the Pt/WC as compared to Pt/C. In another study, it has been observed that Pt supported on tungsten carbide shows higher activity for electrochemical oxidation of methanol than a commercial carbon supported PtRu electrocatalyst [16]. Lee et al. [17] reported that Pd/WC shows improved activity for the electro-oxidation of methanol as compared to a Pd/C catalyst in an alkaline media. Similarly, in the work conducted by Moon and co-workers [18], it has been demonstrated that Pd supported on mesoporous tungsten carbide showed a more negative peak potential compared to Pd/C in the CVs for methanol electrooxidation. They also evaluated the stability of these electrocatalysts in alkaline solution containing methanol and reported only 2.2% decrease in current density for Pd/meso-WC after stability test compared to a decrease of 26% for Pd/C. In a subsequent study, it has been shown that tungsten carbide alone has low activity for the methanol and hydrogen oxidations [19]. The hydrogen oxidation activity of WC-based anode in absence of noble metals was also evaluated by Yanga and Wang [20]. They observed that WC has very low activity toward hydrogen oxidation. However, the activity could be improved significantly by adding a small amount of Pt to tungsten carbide [21,22]. Hence, in the work performed by Ham and co-workers, the Pt/WC catalyst showed two times higher activity per mass of Pt for hydrogen oxidation compared to a commercial Pt/C [23].

Similarly, Kelly et al. [24] investigated the hydrogen evolution activity of Pd supported on tungsten and molybdenum carbide. In their work a superior activity was noted for Pd/C in contrast to bare carbides. Nevertheless, only the addition of monolayer of Pd to these carbides doubled the values of corresponding current density for the resultant carbide based electrocatalysts. Furthermore, the activity and stability of Pt supported on tungsten carbide has been tested for hydrogen evolution and oxidation reaction by Liu and Mustain [25]. Although they found a very little difference in the activity of Pt/WC and Pt/C catalysts for hydrogen evolution reaction, the stability of Pt/WC was far better than that of Pt/C. A loss of only 4% in activity was observed for Pt/WC which was very small in comparison to loss in activity of more than 20% for Pt/C.

Summarizing, there has been some research data in the literature on the use of tungsten carbide as anode materials, either for hydrogen oxidation/evolution or for methanol oxidation. However, the CO tolerance and stability of this material as anode electrocatalyst in a real fuel cell environment has not been studied in detail. Thus in this work, carbon supported tungsten carbide prepared by a simple impregnation method was used as Pt catalyst supports in the anode of a PEMFC. The Pt was supported on this carbide by a formic acid reduction method. The resulting catalyst was first tested for hydrogen oxidation in the presence of pure hydrogen and hydrogen containing CO and then its stability was evaluated by an accelerated stress test [26], applying an electrode potential cycling, from a low to a high potential. The results obtained were compared with carbon supported PtW catalyst, which was also prepared by formic acid reduction method.

2. Experimental

2.1. Electrocatalysts preparation

Tungsten carbide supports with different W/C wt. percentages (10, 20 and 30) were prepared by a simple impregnation method [27]. Briefly, the tungsten precursor (WCl_6 , Aldrich) and carbon black (Vulcan XC-72) were added in to ethanol and then the composite was impregnated for 3 h at room temperature. The mixture was then heated at 70 °C, until the ethanol was

evaporated completely. The resultant solid was transferred in to a quartz reactor, placed in a tubular furnace and heat treated under CH_4/H_2 atmosphere at 800 °C for 3 h to give the tungsten carbide, which was passivated using a 1% O_2/Ar mixture for at least 3 h, prior it was taken outside the quartz reactor. Pt (20 wt.%) was deposited on these carbide supports by the formic acid reduction method, which consisted of the reduction of dihydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich), in the presence of the prepared tungsten carbide, using formic acid as reducing agent [7,8,28]. These catalysts were then designated as Pt/WC/C10, Pt/WC/C20 and Pt/WC/C30, where the numbers represent the W/C wt.% ratios. For the purpose of comparison, PtW/C (60:40 atomic proportions) was prepared by the same formic acid method, maintaining the metal content at 20 wt.%. Pt supported on Vulcan XC-72 carbon also with 20 wt.% metal/C was supplied by E-TEK. The Pt and PtW loading in all electrocatalysts was maintained at 20 wt.%.

2.2. Physical characterizations

The real tungsten content of the WC/C supports, as well as the metal loadings (Pt and W) of the catalysts were estimated by energy dispersive x-ray spectroscopy (EDX) in a scanning electron microscope LEO, 440 SEM-EDX system (Leica-Zeiss, DSM-960) with a microanalyzer (Link analytical QX 2000) and a Si (Li) detector, using a 20 keV incident electron beam. X-ray diffraction (XRD) analyses of the materials were conducted using a RIGAKU XRD RU200B diffractometer ($\text{Cu } K_\alpha$ radiation), in the 2θ range from 10 to 90°. X-ray photoelectron spectroscopy (XPS) measurements were conducted for the investigation of surface oxidation state of the catalysts. XPS studies were conducted at the National Synchrotron Light Laboratory (LNLS) on a SPECS (spectrometer-Phoibos HSA3500 MCD9 150) equipped with a InSb (1 1 1) monochromator and X-rays with energy of 1840 eV. The energy was calibrated to give a binding energy of 84 eV for the gold 4f 7/2 region. The instrument was programmed for the passage of 20 eV energy, with the energy step of 0.1 eV and acquisition time of 200 ms. Particle size distributions of Pt and PtW nanoparticles were determined by transmission electron microscopy (TEM, JEOL 2100 transmission electron microscope). The average crystallite sizes of Pt in the catalysts were determined by the Scherrer equation [29], using the Pt (2 2 0) diffraction peak and were compared with the results from TEM.

2.3. Electrochemical measurements

The electrochemical measurements were conducted in a single cell, using membrane electrode assemblies (MEAs) prepared with Nafion 115 membranes (DuPont, USA) in the middle and electrodes formed by gas diffusion and catalyst layers on both sides of the membrane. The method of preparation of MEAs can be found in literature [30]. Fuel cell polarization measurements were carried out galvanostatically with the cell at two different temperatures (85 and 105 °C). For 85 °C the gases were saturated with water at 100 °C and 2 atm for the anode and at 90 °C and 1.7 atm for the cathode, whereas at 105 °C the gases were saturated at 120 °C and 3 atm for the anode and 110 °C and 2.7 atm for the cathode. The system was first maintained at an initial potential of 0.7 V in pure H_2 , for 2 h, and then at 0.8 V in $\text{H}_2/100$ ppm CO, also for 2 h, to reach the steady state before the data acquisition at both the temperatures. In these experiments the cathode was constantly fed with O_2 . *On line* mass spectrometry (Pfeiffer Vacuum GSD 301 Omnistar, quadrupole QMS 200 Prisma, W filament 70 eV electron energy with SEM 1000 V common voltage) measurements at the anode outlet was used to monitor the formation of CO_2 as a function of the cell potential. In these experiments the anode was fed with either H_2 or $\text{H}_2/100$ ppm CO, whereas the cathode was constantly fed with O_2 , keeping the cell at the condition of open circuit potential.

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