Applied Surface Science 317 (2014) 496–504

Contents lists available at ScienceDirect

Applied Surface Science

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

# Pt catalysts on PANI coated WC/C nanocomposites for methanol electro-oxidation and oxygen electro-reduction in DMFC

Maryam Yaldagard[a,b,*], Mohsen Jahanshahi[b], Naser Seghatoleslami[a]

[a] Department of Chemical Engineering, Ferdowsi University of Mashhad, P.O. Box 91775-1111, Iran
[b] Nanotechnology Research Institute, School of Chemical Engineering, Babol University of Technology, Iran

ARTICLE INFO

*Article history:*
Received 28 May 2014
Received in revised form 22 August 2014
Accepted 24 August 2014
Available online 3 September 2014

*Keywords:*
Methanol electro-oxidation
Oxygen electro-reduction
PANI
WC/C nanocomposites
Activity and stability
Microwave heating

ABSTRACT

In the present study a Pt/PANI/WC/C electrocatalyst was developed to increase the methanol electro-oxidation and oxygen electro-reduction activity and stability of commercial Pt/C electrocatalyst. WC/C was coated with protonated polyaniline (PANI) in situ during the polymerization of aniline. Fourier transform infrared (FTIR) results illustrate the presence of PANI in the composite. The conductivity of PANI coated – WC/C has been compared with the conductivity of the corresponding mixtures of WC/C and Vulcan XC-72. X-ray diffraction results showed that Pt particles were dispersed on the support with mean particle size of about 10.56 nm. Transition electron microscopy images showed that the nanosized WC/C were successfully coated by PANI. Based on the electrochemical properties characterized by cyclic voltammetry, CO stripping and rotating disk electrode measurements it was found that the as prepared Pt/PANI/WC/C electrocatalyst exhibited a comparable activity for methanol oxidation reaction and oxygen reduction reaction with respect to the commercial one. A significant reduction in the potential of CO electro-oxidation peak from 0.75 V for Pt/C to 0.52 V for Pt/PANI/WC/C electrocatalyst indicates that an increase in the activity for CO electro-oxidation is achieved by replacing the carbon support by PANI coated WC/C. Chronoamerometry results also showed, in the presence of methanol the Pt/PANI/WC/C electrocatalyst still maintains a higher current density than Pt/WC/C and Pt/C.



## 1. Introduction

A direct methanol fuel cell (DMFC) is an electrochemical device that converts a chemical energy into electricity using methanol and oxygen as the anode and cathode reactants, respectively. The usage of a liquid fuel is a superior characteristic in that it allows easy handling of fuel with very high specific energy density [1]. High energy density requires the utilization of high concentration of methanol [2]. However, the usage of concentrated methanol in fuel cell applications causes several problems such as low catalytic activity at the anode electrode and methanol cross-over to the cathode electrode [1,3]. Pt is most widely used catalyst for both of anode and cathode sections. However, it suffers from high cost, low catalytic activity for oxygen reduction reaction (ORR) and CO poisoning caused by methanol that crossed-over from the anode [1]. The methanol adsorbs on the Pt sites at the cathode, and a mixed potential, resulting from the oxygen reduction and methanol oxidation occurring simultaneously, reduces the cell voltage [3]. Since the catalytic capability of tungsten carbide (WC) has been shown to be analogous to that platinum [4–6] extensive research has been devoted to its application in incorporation into Pt catalyst and support material in recent years [7,8]. This means that tungsten carbides are expected to be used as electrocatalysts in incorporation by Pt or as catalyst supports, which might promote catalytic activity through synergistic effects. Meanwhile, it has also been found that the introduction of WC into electrocatalysts has positive effect on hydrogen evolution [9,10], and alcohol electro-oxidation [11–14]. Moreover Tungsten carbide has an important advantage – an especially strong resistance to catalytic poisons, such as carbon monoxide, hydrocarbons, and hydrogen sulfide [4] and insolubility in acid solutions [1]. However, the electrocatalytic activity and effective surface area of WC are much less than that of platinum metal and carbon black support, respectively. The commercial WC is very low in surface area (about 2 $m^2 g^{-1}$) with in micrometer size. Therefore, methods to improve the catalytic activity and effective surface area of WC in nanometer size, so that its activity approaches that of platinum and carbon black support, are a key area of interest. The early studies showed that

* Corresponding author. Tel.: +98 5138816840; fax: +98 5138816840.
*E-mail addresses:* m_yaldagard@yahoo.com, ma_ya371@stu-um.ac.ir (M. Yaldagard), mjahan@nit.um.ac.ir (M. Jahanshahi), Slami@um.ac.ir (N. Seghatoleslami).

http://dx.doi.org/10.1016/j.apsusc.2014.08.148
0169-4332/