INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–12

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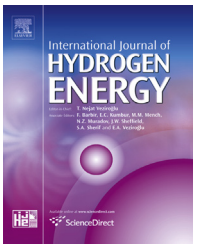

# Effect of different structures of carbon supports for cathode catalyst on performance of direct methanol fuel cell

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ARTICLE INFO

*Article history:*
Received 19 August 2015
Received in revised form
6 November 2015
Accepted 19 November 2015
Available online xxx

*Keywords:*
Direct methanol fuel cell
Carbon support
Cathode catalyst layer
Compression ratio
Mass transport

ABSTRACT

Carbon black (CB), multiwalled carbon nanotubes (MWNTs), reduced graphene oxide (rGO) are used as the cathode catalyst supports to investigate the effect on direct methanol fuel cell (DMFC) performance by using rotating disk electrode and fuel cell testing. The results of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) show that the electrocatalytic activity sequence for oxygen reduction reaction (ORR) is Pt/rGO > Pt/MWNTs > Pt/C catalysts. The single cell tests results show that the maximum power densities of DMFC with Pt/C, Pt/MWNTs and Pt/rGO cathode catalysts are 74.0, 74.2 and 3.3 mW $cm^{-2}$, respectively. The experimental results indicate that the performance of DMFC is substantially influenced by the structures of cathode catalyst supports. The significant differences in DMFCs performance are due to the compression ratios and hydrophilic/hydrophobic properties of catalyst layers with different structures of carbon supports, which strongly affect electrochemical active sites and mass transport in cathode catalyst layers. Long-term testing of DMFCs indicates that Pt/MWNTs exhibits superior stability. Considering the factors of the power and lifetime comprehensively, MWNTs is optimal candidate among the three investigated carbon supports.



## Introduction

Direct methanol fuel cells (DMFCs) have been extensively studied as a promising candidate for portable power sources over the past few decades due to their unique features such as easy fuel storage and transportation, high energy density and environmental friendliness [1–7]. However, there are a few fundamental challenges on the cathode of DMFC: the sluggish oxygen reduction reaction (ORR) kinetics, the methanol

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http://dx.doi.org/10.1016/j.ijhydene.2015.11.103

crossover and the poor long-term durability [5,8]. The value of low open circuit voltage (OCV) is about 0.7 V. The high degree of irreversibility of ORR and the methanol crossover result in lower cell voltage by 0.3 V, which incurs above 50% of the total performance losses in the cell [9–12]. Hence, the increasement of catalyst loading of DMFC cathode is of great importance [13]. Unfortunately, the cathode catalyst layer (CCL) with a high Pt loading would be so thick as to cause a significant mass transfer limitation when carbon supported catalyst is used in DMFC, which leads to degrade the performance of DMFC [13,14].

In DMFC cathode, carbon-supported Pt catalyst is still considered to be the most effective cathode catalyst at present. Carbon supports are necessary to obtain a high dispersion and a narrow distribution of Pt nanoparticles, which is the prerequisite to prepare high performance catalysts. More importantly, catalyst supports interplay with catalytic metals and influence the catalytic activity and durability of the electrocatalyst [15,16]. So far, carbon black (CB) is widely used as catalyst support. Nevertheless, carbon black is easily corroded and gasified, which results in Pt catalyst agglomeration and the change of catalyst surface hydrophobic property to decrease fuel cell performance under the long operation conditions [17]. In recent years, one dimensional (1D) carbon nanotubes (CNTs) is the most investigated carbon material as carbon black alternative for catalyst supports in low temperature fuel cells because of their unique structure and properties [18,19]. Since the use of graphene as fuel cell catalyst support in about 2009, two dimensional (2D) graphene has also been demonstrated as one of promising candidate supports for low-temperature fuel cell catalysts [19]. A substantial portion of the published work has been focused on effect of these carbon materials as support on the performance of catalyst [10,20–23]. The physical properties of carbon support can greatly affect the properties of catalyst with metal particle size, morphology, durability and electrocatalytic activity. Moreover, controversial results regarding the effect of carbon supports on the performance of catalyst have been reported by half-cell measurements [10,23–26].

From a practical point of view, the single cell testing is the ultimate evaluation criterion for electrocatalyst materials [27]. The membrane electrode assembly (MEA) is the key component of a fuel cell, which is usually fabricated by hot-pressing process to obtain a good interface between the electrodes and the membrane [28,29]. However, the porosity and the performance of MEA are evidently changed with the hot-pressing process [29,30], especially in DMFC with a thicker CCL. In fabrication of microstructure controlled CCLs, hot-pressing parameters have been investigated to improve the performance of DMFC [28,31–35]. In addition to hot-pressing parameters factors, the properties of catalyst layer are strongly influenced by various carbon supports in the same hot-pressing condition. Wang and coworkers [30] reported that DMFC using PtRuNi supported on carbon-containing large mesopores as anode catalyst exhibited significantly higher power density than that using PtRuNi/C catalyst under same operation condition. Jha and coworkers [25] reported that DMFC using the mixture of MWNTs and graphene as cathode catalyst support offered a higher power density than that using graphene. Carbon supports play a very important role in DMFC performance, but effect of their structures on the performance of DMFC has not been intensively studied.

In this work, CB, MWNTs and rGO sheets, which are commonly used as the catalyst supports, are chosen to analyze the effect of different structures of carbon supports for cathode catalyst on DMFC performance. The performances of DMFCs are strongly influenced by the compression ratios and hydrophilic/hydrophobic properties of catalyst layer, which are closely related to the structures effect of carbon supports. The thicknesses and the hydrophilic/hydrophobic properties of the catalyst layers are observed by scanning electron microscopy (SEM) and the contact angle, respectively. The performances of DMFCs are characterized by cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and polarization curves.

## Experimental

### *Catalyst preparation*

MWNTs with pristine specific surface areas of 250 $m^2\ g^{-1}$ (Chengdu Corp.) were functionalized by conventional mixed acid treatment method, detailed method was provided in our previous work [36]. Graphene oxide (GO) was prepared from natural graphite (XF Nano. Inc) using a modified Hummers method [37]. Carbon black (Vulcan XC-72, Cabot, 254 $m^2\ g^{-1}$), MWNTs and GO (reduced GO, 281 $m^2\ g^{-1}$) were used as the supports of three cathode catalysts, respectively. All catalysts (metal loading of 40 wt.%.) were prepared through the microwave-assisted polyol process (MAPP) as reported by our team [38]. In detail, the required amounts of carbon support was dispersed in the mixture of ethylene glycol (EG) and isopropanol (V/V = 4:1) in 100 mL beaker and ultrasonicated for 30 min to form a uniform ink, into which adding the calculated volume of $H_2PtCl_6$–EG solution with the subsequent mixing process for 3 h. Then the pH value of the suspension was adjusted to 12.00 with dropwise addition of 1 mol $L^{-1}$ NaOH–EG solution. The beaker was subjected to consecutive heating for 55 s in a microwave oven (Galanz Ltd., 800 W) under flowing argon gas to form catalyst. The solution was allowed to cool down to room temperature, then 0.1 mol $L^{-1}$ $HNO_3$ solution was added into the cooled solution to adjust pH value of the solution to about 3. The product was washed repeatedly with hot ultrapure water (Millipore, 18.25 MΩ cm). The obtained catalyst was dried for 3 h at 80 °C. PtRu/C was prepared similarly through the MAPP method [39].

### *MEA fabrication*

MEA was fabricated by the gas diffusion layer (GDL)-based method [40,41]. The active area of the MEA was 5 $cm^2$. Anode catalyst was homemade PtRu/C. Cathode catalysts were Pt/C and Pt/MWNTs, Pt/rGO, respectively. The uniform catalyst ink was made from the catalyst mixed with 5 wt.% Nafion ionomer solution (DuPont), water and isopropyl alcohol, stirred in an ultrasonic bath continuously at 25 °C. The Nafion content was 20 wt.% and the metal loading of anode and cathode was 2.5 mg $cm^{-2}$. Then the catalyst ink was brushed onto the gas diffusion layer. The carbon paper (Toray paper TGPH 090) was

Please cite this article in press as: Liu J, et al., Effect of different structures of carbon supports for cathode catalyst on performance of direct methanol fuel cell, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.11.103