TiO_2/SWNTs/Pt/C Catalyst for Methanol Electro-Oxidation

ตัวเร่งปฏิกิริยาชนิดไทเทเนียมไดออกไซด์/ท่อนาโนคาร์บอนชนิดผนังชั้นเดียว/แพลตินัม/คาร์บอนสำหรับปฏิกิริยาออกซิเดชันของเมทานอล

Chonlada Theerakarunwong[1,*], Zi-Feng Ma[2] and Sukon Phanichphant[3]

Abstract

Electro-oxidation of methanol in sulfuric acid solution was investigated using titanium dioxide/single-walled carbon nanotubes (TiO_2/SWNTs) composite with platinum/carbon (Pt/C) catalyst. The TiO_2/SWNTs/Pt/C composite electrocatalysts activity was studied by cyclic voltammetry (CV) at 17°C and it was found that the TiO_2/SWNTs/5wt%Pt/C showed good activity for methanol oxidation. Moreover, the performance of catalyst for methanol oxidation was enhanced by the SWNTs. The study on morphology of $^1TiO_2$/SWNTs/Pt/C was also investigated by using TEM.

Keywords: Electro-oxidation, titanium dioxide, single wall carbon nanotube

[1] Department of Science, Faculty of Science and Technology,Rajabhat Nakhon Sawan University, Nakhon Sawan 60000, Thailand

**corresponding author:, e-mail: chonlada.dechakiatkrai@gmail.com*

บทคัดย่อ

ทำการศึกษาปฏิกิริยาออกซิเดชันของเมทานอลในสารละลายกรดซัลฟิวริกโดยใช้ไทเทเนียมไดออกไซด์/ท่อนาโนคาร์บอนชนิดผนังชั้นเดียวกับแพลตินัม คาร์บอนเป็นตัวเร่งปฏิกิริยา โดยศึกษาประสิทธิภาพการย่อยสลายเมทานอลโดยเทคนิคไซคลิก โวลแทรมเมตรีที่อุณหภูมิ 17 องศาเซลเซียส จากผลการทดลองพบว่าตัวเร่งปฏิกิริยาชนิดนี้ให้ประสิทธิภาพในการศึกษาการออกซิเดชันของเมทานอลอยู่ในเกณฑ์ที่ดี และพบว่าการเจือท่อนาโนคาร์บอนในตัวเร่งปฏิกิริยาไทเทเนียมไดออกไซด์นาโนทิวป์ยังเป็นการเพิ่มประสิทธิภาพการย่อยสลายเมทานอล นอกจากนี้ยังศึกษาสัณฐานวิทยาของตัวเร่งปฏิกิริยาผสมสำหรับปฏิกิริยาออกซิเดชันของเมทานอลโดยใช้กล้องจุลทรรศ์อิเล็กตรอนแบบส่องผ่าน

คำสำคัญ: การออกซิเดชัน, ไทเทเนียมไดออกไซด์, ท่อนาโนคาร์บอนชนิดผนังชั้นเดียว

Introduction

Direct methanol fuel cells (DMFCs) have been considered as promising high-efficiency for portable electronic devices and automobiles (Gang *et al.*, 2007). DMFCs have great potential for lithium-ion batteries and lithium polymer batteries due to their high energy and power density (Weijiang *et al.*, 2007). Platinum (Pt) is widely used for DMFCs catalyst because of its properties for promoting the adsorption/dissociation of methanol in acid media. High efficiency of methanol oxidation on platinum makes this metal a perfect catalyst for DMFCs anode (Wang wt *et al.*, 2007). Pt based methanol oxidation catalyst is significantly affected by the supporting materials, and the nature of supporting materials can be crucial in determining the electrochemical performance of the electrode catalysts. One of the supporting materials, titanium dioxide (TiO_2), has been widely used in the field of photocatalytic oxidation because of its strong oxidizing power, physical and chemical stability (Song *et al.*, 2008, Dechakiatkrai *et al.*, 2007). TiO_2, however will not attract considerable interest since their low conductivity, resulting in a poor rate capability.

Cabon nanotubes (CNTs) have attracted interest since their discovery because of their unique properties, including high surface area, high electrical conductivity, and significant mechanical strength, integrating carbon nanotubes with TiO_2 nanoparticles should result in

changes in morphology and enhanced properties in particular electrical conductivity of TiO_2. (Dechakiatkrai et al 2007, 2009).

In this present work, the TiO_2 nanotubes composite with SWNTs/Pt/C was investigated on a photocatalytic performance of methanol electro-oxidation. Compared with the bare TiO_2, SWNTs/Pt/C and TiO_2/SWNTs, the TiO_2/SWNTs/Pt/C electrode exhibits good cell performance for direct methanol oxidation. It has been proved that TiO_2/SWNTs/Pt/C composite could be the hopeful catalysts in the direct oxidation methanol fuel cells (DMFCs). These studies also suggest that titania together with suitability functionalized SWNTs could potentially be used in photocatalytic activity of methanol electro-oxidation. The step involved in dry method presents an ideal opportunity to introduce nanotube and Pt/C into practically useful structure.

Experimental

Materials

All chemicals, single wall CNTs (SWNTs, HiPCO produced from CNI, standard 20%Pt/C was obtained from Johnson Matthey. Methanol (Univar, Ajax Finechem) and H_2SO_4 (Univar, Ajax Finechem) were used as received. TiO_2 nanoparticles were synthesized using a modified sol-gel method (Wetchakul and Phanichphant *et al.*, 2006) The TiO_2/SWNTs composite was prepared following the procedure according to previous study (Dechakiatkrai *et a*l., 2007).

Preparation of TiO_2-based electrocatalysts

TiO_2-based electrocatalysts were prepared by milling of TiO_2, TiO_2/SWNTs with Pt/C. The mixed powder were mechanical blended using Variable Speed Rotor Mill (Germany) at 300 rpm, for 2h. 3 different ratios of Pt/C as 1wt%, 3wt% and 5wt% were prepared to make a composite with TiO_2-based electrocatalyst.

Ink catalyst preparation

Ink catalyst was prepared by mixing 5 mg of catalyst with 0.5 ml DI water and 50 μl of 5wt%nafion solution followed by ultrasonication for 30 min. 10 μl of the ink was dropped onto the surface of grassy carbon working electrode and left at room temperature for 30 min to allow the ink solution dry.

Electrochemistry of TiO_2-based electrocatalyst for methanol oxidation

A three electrode used for electrochemical testing comprised of working (glassy carbon), reference (SCE standard calomel) and counter electrode (platinum wire). 0.5 M MeOH/0.5 M

H_2SO_4 was used as supporting electrolyte. The supporting electrolyte was purged with N_2 for 30 min before methanol oxidation measurement. The cyclic voltammograms were recorded by applying a various scan rate (0.2, 0.1, 0.05 and 0.01 Vs^{-1}) between 0-0.9 V at room temperature ($17^{o}C$).

Results and discussions

Electrochemical performance of TiO_2-based electrocatalyst in 0.5 M MeOH/0.5 M H_2SO_4

The electrochemical performance of the TiO_2-based composite catalyst was tested for methanol oxidation in 0.5 M MeOH/0.5 M H_2SO_4. As shown in Fig. 1, the typical CV curve of standard Pt/C showed 2 methanol oxidation peaks at +0.73 V on the forward scan and +0.45 V on the reverse scan. The catalytic performance of TiO_2/SWNTs/5wt%Pt/C was investigated using cyclic voltammetry in 0.5 M MeOH/0.5 M H_2SO_4 supporting electrolyte.

Fig. 2 shows the cyclic voltammograms observed from TiO_2/SWNTs/5wt%Pt/C and TiO_2/5wt%Pt/C for methanol oxidation in 0.5 M MeOH/0.5 M H_2SO_4. The catalysts without SWNTs had a lower activity than catalysts containing SWNTs whereas a bare TiO_2 had a lowest activity (data not shown), which is about 1.5-2.0 times higher than those of TiO_2/5wt%Pt/C and Pt/C electrode. Due to TiO_2 being a semiconductor, the current obtained was lowest whereas the TiO_2/5wt%Pt/C showed the current signals higher than Pt/C electrode catalyst. The catalytic performance of TiO_2/SWNTs/5wt%Pt/C was improved by the incorporation of SWNTs into TiO_2/5wt%Pt/C because of the excellent properties of SWNTs such as high electrical conductivity and high surface area that may increase the charge transfer process (Xiong and Mathiram, 2004). The less activity for methanol oxidation obtained from TiO_2 may due to the structure of TiO_2 nanotubes are not completely obtained during the preparation process in the autoclave as evidenced by TEM analysis (will be discussed in later part). Fig. 3 summarized the results obtained by using TiO_2 based catalyst with 5wt%Pt/C. The highest catalyst activity was obtained from standard Pt/C while TiO_2/SWNT/5wt%Pt/C and TiO_2/5wt%Pt/C show similar current output.

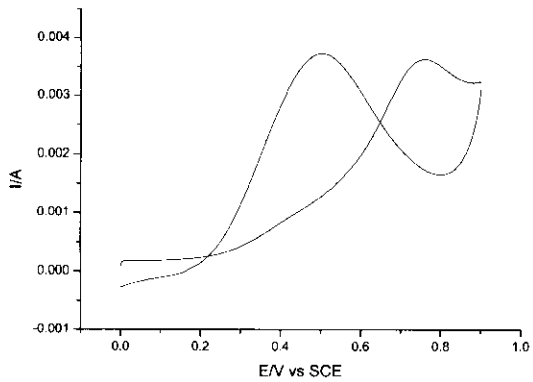

Fig 1. Cyclic voltammogram of standard Pt/C in 0.5 M MeOH/0.5 M H_2SO_4 with scan rate of 0.05 V/s

Stability of the catalyst

Figs. 4 and 5 show the first five scan cyclic voltammograms for TiO_2/SWNTs/ 5wt%Pt /C in 0.5 M MeOH/0.5 M H_2SO_4 at the scan rate of 0.05 V/s. The current output was decreased with increasing cycle number which may due to the operation temperature (17°C) (Wei *et al.*, 2002). These data indicated that temperature control for DMFCs is known to affect the methanol oxidation activity. It was found that the current decreased with increasing the cycle number. These data confirmed that the temperature control and sample preparation become important factors to determine anode material for methanol oxidation.

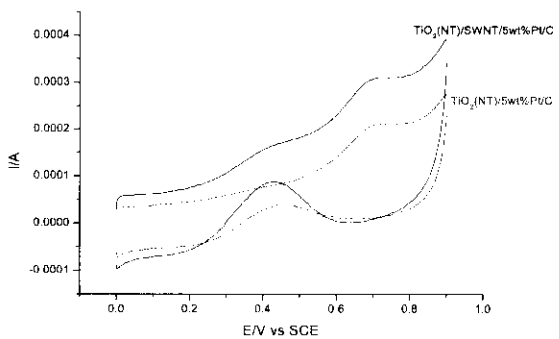

Fig 2. Cyclic voltammograms of (black) TiO_2/SWNTs/5wt%Pt/C and (red) TiO_2/5wt%Pt/C in 0.5 M MeOH/0.5 M H_2SO_4 with scan rate of 0.05 V/s

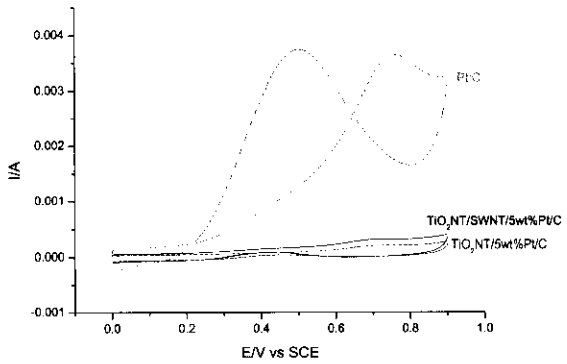

Fig 3. Cyclic voltammograms of (red) TiO_2/5wt%Pt/C, (black) TiO_2/SWNTs/5wt%Pt/C and (green) Pt/C in 0.5 M MeOH/0.5 M H_2SO_4 with scan rate of 0.05 V/s

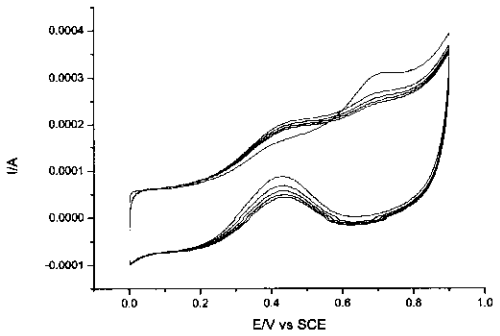

Fig. 4 Cyclic voltammograms of TiO_2/SWNTs/5wt%Pt/C in 0.5 M MeOH/0.5 M H_2SO_4 with scan rate of 0.05 V/s

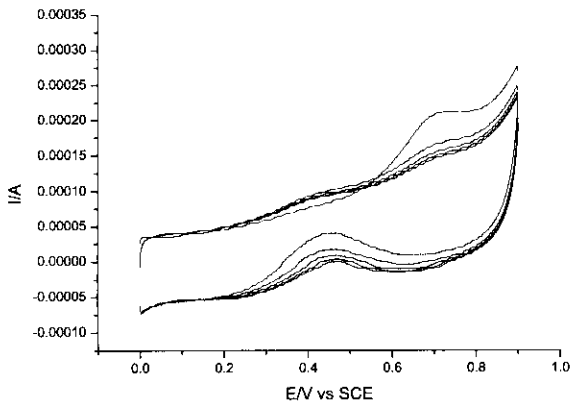

Fig 5. Cyclic voltammograms of TiO_2/5wt%Pt/C in 0.5 M MeOH/0.5 M H_2SO_4 with scan rate of 0.05 V/s

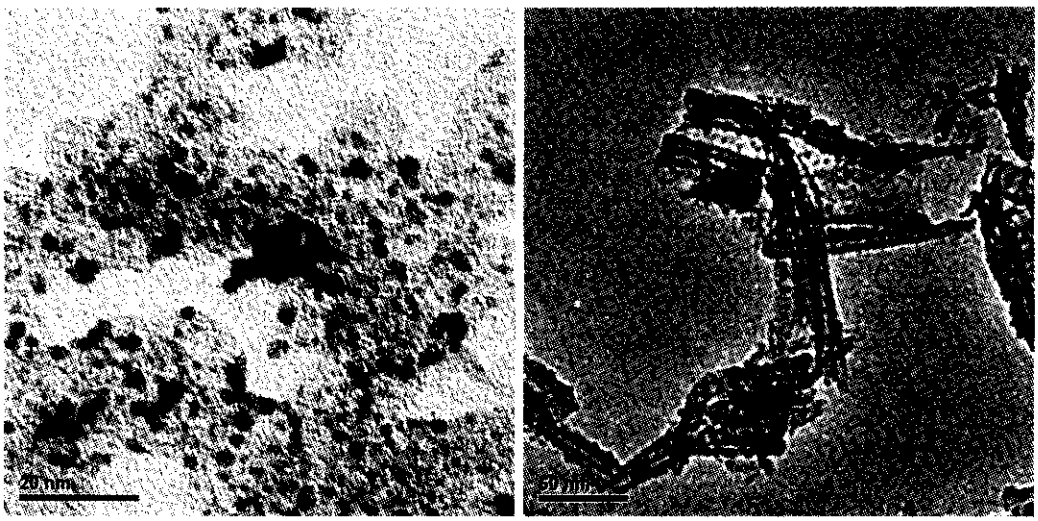

Fig 6. TEM imaging of TiO_2/SWNT/Pt/C (a) and SWNT/TiO_2 nanotube (b)

TEM analysis

Fig. 6 presents typical TEM images of the Pt/C nanoparticles supported on SWNTs/TiO_2 nanotubes. It was found that the Pt particle dispersed with SWNTs/TiO_2 (Fig. 6(a)) was remarkably uniform and Pt nanoparticles on the SWNTs are well dispersed. The particle size of the obtained Pt/C catalyst has a relatively less than 20 nm and the aggregation of the Pt/C nanoparticles is minimal. TEM imaging of the composite showed that in Fig. 6(b) , the TEM images of the TiO_2 show that it contains some large aggregated of both TiO_2 particles and tubes. These may related the un-completely transformation from particle to nanotubes during the fabrication method. Also, it can be seen that these particles and tubes have quite uniform morphologies. Most of the nanotubes are close ended. However, some open-ended nanotubes are observed occasionally.

Conclusion

Preliminary studies of the TiO_2 nanotubes were carried out to investigate the methanol eletro-oxidation activity. The performance of TiO_2/SWNTs with Pt/C as the anode catalyst was much better than those of TiO_2/SWNTs and Pt/C electrodes. The performance of the DMFCs anode material with Pt/C was greatly improved compared to those previously reported. Clearly, doping SWNTs and TiO_2 to Pt/C is valuable way to improve the catalytic activity of methanol oxidation and TiO_2/SWNTs/Pt/C is a promising anode catalyst for DMFCs.

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