

Mesoporous Carbon Supported Bifunctional Pt-M (M = Ru, Fe, Mo, Sn) Catalysts for Applications in DMFC at Anode

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Abstract

Pt-based catalysts supported on porous carbons have been widely used as electrocatalysts for direct methanol fuel cell (DMFC) both at anode and cathode. It has been shown that the addition of a secondary metal (e.g. Ru) helps to modify the structural, electronic, and chemical properties of the bifunctional alloy catalyst, leading to better stability in terms of resistance to CO-poisoning during methanol oxidation reaction (MOR). However, in view of the cost effectiveness of the electrocatalyst, reducing the amount of noble metals used in the electrocatalyst remains as one of the critical issue. In continuation of our research endeavor, we report herein the synthesis of bifunctional Pt-M (M = Ru, Fe, Mo, Sn) electrocatalysts. Their structural and physicochemical properties have been characterized by a variety of different analytical and spectroscopic techniques, such as XRD, TEM, gas adsorption, and cyclic voltammetry (CV) etc. It was found that the alloy metal-incorporated ordered mesoporous carbons (OMCs) so obtained possess high specific surface areas ($> 1000 \text{ m}^2/\text{g}$), uniform pore size distributions (ca. 3 nm), and average particle sized (2 ~ 4 nm). Further electrocatalytic tests by CV revealed that the MOR activities of the electrocatalysts follow the order: PtRu-OMC $>$ PtMo-OMC $>$ PtFe-OMC $>$ PtSn-OMC. Although the PtRu-OMC catalyst has the best performance than the others, it is less compelling in terms of cost and the observed current density per unit metal. It is noteworthy that the PtFe-OMC catalyst shows a superior electrocatalytic performance during MOR at anode than the

other Pt-M-OMCs.

Keywords: Electrocatalyst, DMFC, methanol oxidation reaction, supported Pt-based catalyst, ordered mesoporous carbons.

1. Introduction

DMFC has been regarded the most potential, clean, high-efficiency energy conversion devices, in which noble metal (Pt, Ru)-based catalysts supported on porous carbons have been widely used as electrocatalysts both at anode and cathode. It has been shown [1] that the addition of a secondary metal (e.g. Ru) helps to modify the structural, electronic, and chemical properties of the bifunctional alloy catalyst, leading to better stability in terms of resistance to CO-poisoning during methanol oxidation reaction (MOR). Previously, we have introduced a facile synthesis route to fabricate OMC supported mono- (Pt) [2] and bi-functional (PtRu) [3] catalysts with superior electrocatalytic performances and stability using a direct replicate synthesis method. However, in view of the cost effectiveness of the electrocatalyst, developments of low-noble metal or non-noble metal electrocatalysts remain as one of the critical issued. While a variety of non-Pt catalysts have been developed [4,5], their catalytic activities were unsatisfactory and need to be further improved. In terms of anodic catalyst, it has been shown [4,5] that alloying of Pt with a secondary transition-metal may significantly enhance the electrocatalytic activities and tolerance to CO-poison. Frelink et al. [6] showed that the addition of a foreign metal tends to provoke a bifunctional mechanism, which in turn, modify the configural, electronic, and

chemical properties of the catalyst to improve stability, efficiency, and cost in terms of resistance to CO-poisoning and reduction in noble metal usage in the Pt amount, hence reducing the overall cost of the materials.

Previously, we have reported [2,3] a facile synthesis route, utilizing mesoporous silica (e.g., SBA-15) as the hard template, furfural alcohol and trimethylbenzene as the primary carbon sources, and organic metal (such as platinum/ruthenium acetylacetonates) as the primary metal precursor as well as the subsidiary carbon sources. The OMC supported mono- (Pt) [2] and bi-functional (PtRu) [3] catalysts so synthesized using a direct replicate synthesis method were found to have high specific surface area and well-dispersed PtRu nanoparticles (2-3 nm). The catalysts so fabricated were also found to possess high electrocatalytic activities and excellent stability in terms of resistance to CO-poisoning during MOR [7]. Nonetheless, both species are precious metals, it is therefore desirable to seek for a replacement metal that is more cost-effective while capable of sustaining a good electrocatalytic performance.

We report herein the synthesis of bifunctional Pt-M (M = Ru, Fe, Mo, Sn) electrocatalysts. Their structural and physicochemical properties were characterized by a variety of different analytical and spectroscopic techniques, such as XRD, TEM, ICP-MS, and gas adsorption, and cyclic voltammetry (CV). In addition, their electrocatalytic properties during MOR were examined by cyclic voltammetry (CV).

2. Experimental

The SBA-15 mesoporous silica, which was used as hard template for preparation of OMC, was synthesized according to a known recipe [10]. Subsequent syntheses of PtM-OMCs (M = Ru, Mo, Fe, and Sn) were achieved by direct replication method, which was developed by this group earlier [2,3].

2.1. Catalyst preparation

First, ca. 0.5 g calcined SBA-15 was dehydrated at 673 K for 3 h under vacuum. Meanwhile, known amounts of Pt(acac)₂ and/or M_x(acac)_x were dissolved in furfuryl alcohol and trimethylbenzene mixed solution (volume ratio

was 2:3), along with oxalic acid to catalyze polymerization of FA under ultrasonic environment. The mixture solution, which serves as the carbon source as well as metallic precursor is then infiltrated in SBA-15 at room temperature (298 K) by conventional incipient wetness impregnation method, followed by polymerization in air at 333 K, then at 353 K for 12 h, respectively. Subsequently, the composite was subjected to graphitization treatment. This is carried out by first treating the composite at 423 K for 3 h, then, ramped to 573 K (ca. 5 K/min), finally increased to 1073 K (ca. 10 K/min) and maintained at the temperature for 4 h. It is noteworthy that the above carbonization procedure was performed under N₂ environment. The black powders so obtained was leached by HF (1.5wt%) aqueous solution for at least 24 h to remove the silica hard template. Finally, the PtM-OMC was washed with deionized water and alcohol several times, then dried at 373 K for 8 h.

2.2. Characterization Methods

X-ray diffraction (XRD) patterns of all samples were recorded on a PANalytical (X'Pert PRO) instrument using Cu K α radiation (λ = 0.1541 nm). The compositions of various PtM-OMC catalysts were measured by energy dispersive X-ray analysis (EDX, JEOL JEM-2100F). The specific surface areas of the samples were evaluated by the Brunauer-Emmett-Teller (BET) method using the adsorption branch of the N₂ adsorption/desorption isotherm obtained at relative pressure (P/P₀) within 0.05 ~ 0.2. Likewise, their total pore volumes were estimated at P/P₀ of 0.99. Whereas the pore size distributions of the samples are derived from the adsorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) equation. N₂ adsorption-desorption isotherms were measured at 77 K on a Quantachrome autosorb-1-MP-P adsorption analyzer. For transmission electron microscopy (TEM) experiments, sample was dissolved in alcohol (95 vol%) under ultrasonication, then allow to precipitate on a lacey carbon grid. All TEM images were obtained at room temperature using an electron microscope (JEOL JEM-2100F) operating at 200 kV.

2.3. Electrochemical Measurements

The electrochemical properties of various samples were probed by a three-electrode electrochemical cell using a

rotating disk electrode setup with an Ag/AgCl reference electrode and a Pt wire counter electrode (Autolab, PGSTAT30). The working electrode (rotating disk electrode) is prepared by applying the ink to the glassy carbon disk (5 mm diameter). The ink is prepared by supersonically dispersing 10 mg sample in 5 mL deionized water for 30 min. An aliquot of 20 μL catalyst suspension was then pipetted onto the disk, followed by drying in air at 333 K for 30 min. Subsequently, 7.5 μL of a 1 wt% Nafion[®] solution was pipetted onto the sample then waited for ca. 5 min. For MOR activity test, the working electrode was immersed in N_2 purged 0.5 M H_2SO_4 and 1.0 M methanol. Cyclic voltammetry (CV) profile was recorded throughout the oxidation process from -0.2 to 1.0 V at 10 mVs^{-1} , and a disk rotating rate of 1600 rpm.

3. Results and discussion

3.1. Physicochemical characterization

As shown in Fig. 1a, the small-angle XRD patterns observed for all PtM-OMC samples exhibit a main diffraction peak (100) at $2\theta \sim 1.0^\circ$, indicating the existence of mesoporous structure with a long-range order with two-dimensional hexagonal symmetry similar to that of the carbon mesoporous material CMK-3 [2,3].

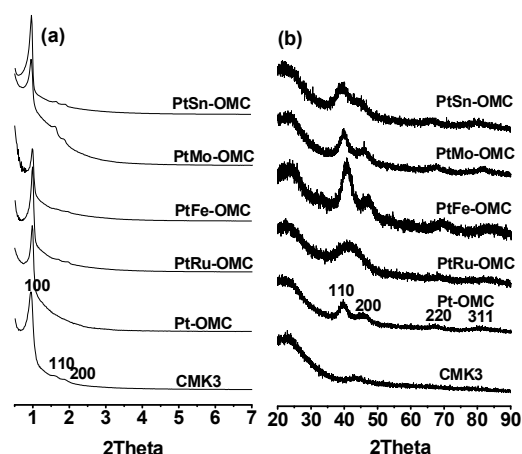


Fig. 1. (a) Small-angle and (b) wide-angle PXRD patterns of CMK-3 and various PtM-OMC samples.

The wide-angle XRD patterns of PtM-OMC (Fig. 1b) show distinct (111), (200), (220), and (311) diffraction peaks at $2\theta \sim 39.6, 45.7, 67.4,$ and 81.3° , respectively, indicating that the Pt particles have a face-centered cubic structure.

Table 1. Physical properties of CMK-3 and PtM-OMC samples

Sample	Pt:M ^a	S (m^2/g) ^b	D (nm) ^c	V (cc/g) ^d
CMK3	---	1319	3	1.0
Pt-OMC	10.3:0	1034	3.3	1.0
PtRu-OMC	7.8:4.1	1181	3.1	0.9
PtFe-OMC	18.1:5.2	955	2.7	0.8
PtMo-OMC	7:3.4	1195	3.3	1.1
PtSn-OMC	12.2:7.4	971	3	0.8

^a Metal atomic ratios (wt%:wt%) from ICP results.

^b Brunauer-Emmet-Teller (BET) surface areas.

^c Pore diameters calculated by the Barrett-Joyner-Halenda (BJH) method using the adsorption branches.

^d Total pore volumes calculated as the amount of N_2 adsorbed at a relative pressure of 0.99.

The textural properties of various samples are summarized in Table 1. In brief, all metal supported samples were found to possess high surface areas ($> 900 \text{ m}^2/\text{g}$), an uniform pore size distribution ($\sim 3 \text{ nm}$), and total volume close to 1 cc/g . Figs. 2 and 3 show the typical TEM images of PtM-OMC. It is indicative that the PtRu-OMC, PtFe-OMC, PtMo-OMC, and PtSn-OMC samples exhibit an ordered array of mesoporous carbon nanorods dispersed with uniform metal nanoparticles (NPs) of average sizes 2.5, 2.3, 2.9, and 1.1 nm, respectively. No evidence of metal aggregation was found, indicating that the NPs are confined in the carbon pores. As shown in histograms in Figs. 2 and 3, the metal NPs has a relatively narrow particle size distribution of ca. 1-5 nm, except for PtFe-OMC and PtSn-OMC. The former catalyst has a larger average particle size and a broader distribution. The above results are in agreement with that of wide-angle XRD data. On the other hand, PtSn-OMC has a narrower distribution of metal NPs of ca. 0.5-2 nm. An earlier study by Maillard *et al.* [12] reported that, average metal particle sizes exceeding 5 nm and smaller than 2 nm are unfavorable for MOR.

3.2. Electrochemical performance

Figure 4 shows the electrocatalytic activities of various PtM-OMC catalysts during MOR. All CV curves were obtained in a potential range between -0.2 and 1.2 V in 1.0 M CH_3OH and 0.5 M H_2SO_4 with a scanning rate of 10 mV/s . Among them, the PtRu-OMC catalyst exhibits the highest anodic peak intensity (0.52 A). For the rest of PtM-OMCs, the following trend was observed: PtMo-OMC (0.31 A) \sim PtFe-OMC (0.30 A) $>$ Pt-OMC (0.2 A) \gg PtSn-OMC (0.05 A). It is indicative that the electrocatalytic performance of the catalyst appears to be

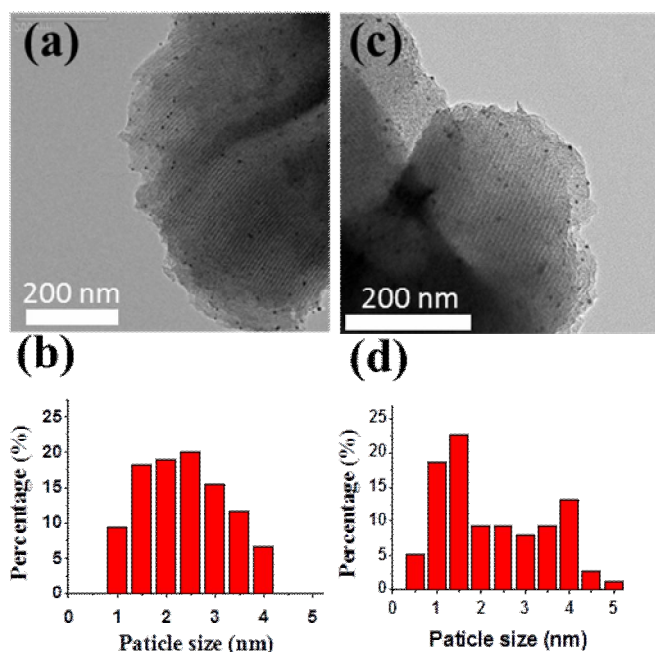


Fig. 2. TEM images and histograms of metal particle size distribution of (a-b) PtRu-OMC, and (c-d) PtFe-OMC.

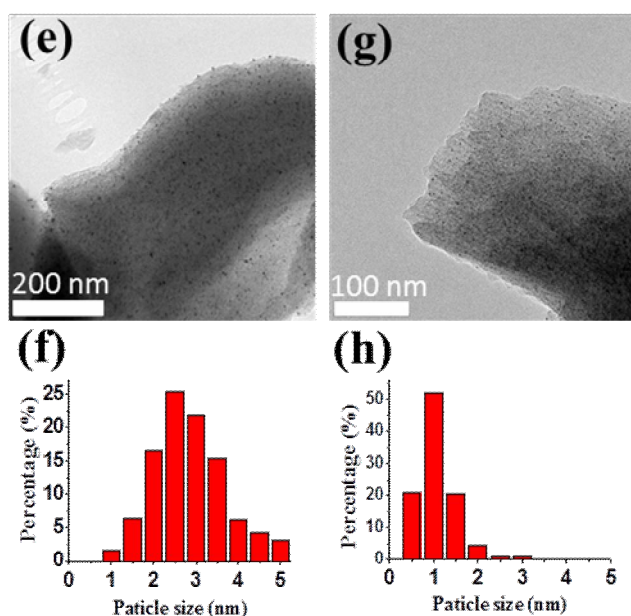


Fig. 3. TEM images and histograms of metal particle size distribution of (e-f) PtMo-OMC and (g-h) PtSn-OMC.

highly dependent with the size of the metal particle. For example, the PtSn-OMC catalyst possesses the smallest particle size (< 2 nm) than the other samples.

That the forward methanol oxidation peak observed for the PtRu-OMC (0.58 V) is smaller than that of the other catalysts (0.6 V), indicating that the latter require a higher potential

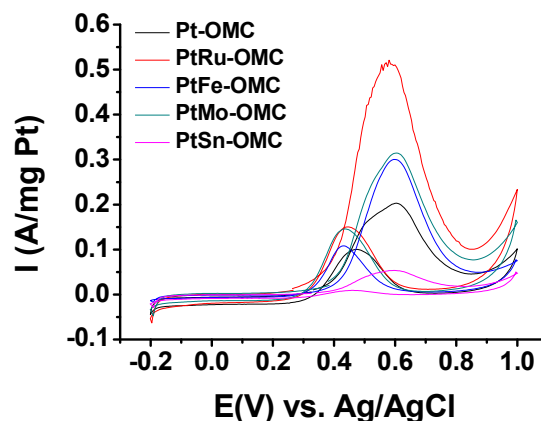


Fig. 4. CV curves of various PtM-OMC catalysts under 0.5 M H_2SO_4 and 1 M CH_3OH with a scanning rate of 10 mV/s.

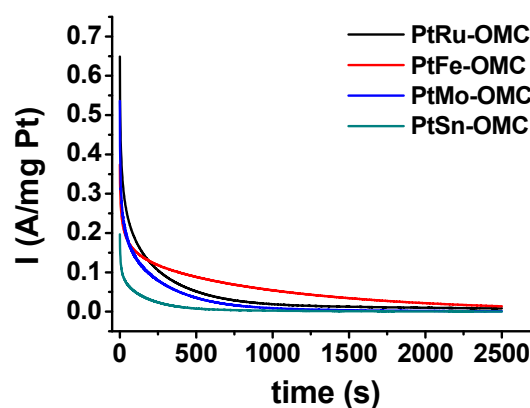


Fig. 5. CA curves of various PM-OMC catalysts under 0.5 M H_2SO_4 and 1 M CH_3OH at 0.6 V.

for MOR. To further assess steady state catalyst performance with respect to methanol electrooxidation, we have carried out chronoamperometry (CA) tests at steady potential, as shown in Fig. 5. It appears that the PtFe-OMC catalyst exhibits the best durability and lifetime as compared to the other PtM-OMCs in despite of the significant current decays of the latter due to undesirable poisoning by CO as well as the formation of reaction intermediates during MOR.

4. Conclusions

A facile synthesis route is reported to fabricate bimetallic PtM-OMC ($M = \text{Ru}, \text{Fe}, \text{Mo}, \text{Sn}$) via direct replication method using mesoporous silica as the hard template and by co-feeding carbon sources and metal precursors during synthesis process. One of the major advantages of this

synthesis method is that it allows for confinement of metal nanoparticles of ca. 2-3 nm in the carbon mesopores, and hence avoiding particle aggregation during catalytic reactions. As a result, these bifunctional PtM-OMC catalysts were found to have superior electrocatalytic properties and stabilities compared to the mono-metal Pt-OMC catalysts during the oxidation of methanol. In terms of MOR activity over various catalysts, the following trend may be inferred: PtRu-OMC > PtMo-OMC ~ PtFe-OMC > Pt-OMC >> PtSn-OMC. Although the PtRu-OMC exhibits the best activity, the use of transition-metal as the secondary metal may still be beneficial in terms of the cost. Among them, PtFe-OMC appears to be an excellent candidate for future applications as anodic electrocatalyst in DMFCs.

Acknowledgment

The financial support of this work from the National Science Council, Taiwan (NSC98-2113-M-001-017-MY3 to SBL) is gratefully acknowledged.

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