

Final Report for AOARD Grant “

Research Title: Nanostructured Electrocatalysts for Fuel Cells

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Abstract:

For the development of high performance of direct methanol fuel cell (DMFC), a major key point is to enhance the cathode oxygen reduction reaction (ORR). For the purpose, designing a 3-dimensional nanostructured electrode materials for catalysts to enhance electrochemical activities is the target. Thus, careful construction of the nanoparticle/support assembly for high surface reactivity, facile transport of oxygen, good electron conductivity and proton conductivity would enhance ORR activities while decreasing cathode overpotential. Here, we present a novel ordered mesoporous carbon film, which showed perpendicular channels and the unique short pore length as called thin film carbon (TFC). In our electrochemical device, the results show that specific activities ($0.073 \text{ mA/cm}^2_{\text{metal}}$) of Pt/TFC catalyst (20 wt% Pt on TFC) gave higher value than that ($0.069 \text{ mA/cm}^2_{\text{metal}}$) of commercial Pt/C catalyst (20 wt% Pt on Vulcan XC-72 carbon; E-TEK)(Johnson Matthey) at 0.8 V relative to RHE at 25°C, while the metal loading on a glassy carbon rotating disk electrode (GC-RDE) was $40.8 \mu\text{g/cm}^2$. In addition, the mass activities ($0.060 \text{ mA}/\mu\text{g}_{\text{metal}}$) of 20 wt% Pt/TFC gave higher value than that ($0.056 \text{ mA}/\mu\text{g}_{\text{metal}}$) of commercial Pt/C catalyst. In summary, it was presented that ORR activities were improved by TFC as novel supported carbon for hosting electrocatalysts. Thus, it is suggested that TFC is a promising material in substitution for commercial Vulcan XC 72 carbon (E-TEK).

Introduction:

For the development of high performance of DMFC, a major key point is necessary to enhance oxygen reduction reaction (ORR) activities in cathode.¹ For the purpose, designing 3-dimensional nanostructured electrode materials for catalysts is efficient to enhance electrochemical activities.² Thus, careful construction of the nanoparticle/support assembly for high surface reactivity, facile transport of oxygen, good electron conductivity and proton conductivity would enhance ORR activities and to decrease the cathode overpotential.

Nanostructured carbon materials synthesized by casting manipulation of ordered porous silica templates³ are of great interest in many applications such as catalyst supports⁴ and adsorbents. Ordered mesoporous carbon (OMC) has the advantages of high surface area, tunable pore size, interconnected pore network, and tailorable surface properties. Recently, OMC as support for metal nanocatalysts for electrode materials in low-temperature fuel cells has been attracting much attention.⁵ In particular, the CMK-3 mesoporous carbon, casted from SBA-15, possesses a structure of a hexagonally assembled array of interconnected long carbon rods (usually more than 500 nm).⁶ With the deposition of Pt or Pt-based nanoparticles on its internal and external surfaces, the materials have been used as anode materials in direct methanol fuel cell (DMFC).^{7,8,9} However, the synergy feature between catalyst and carbon support for cathode is less explored. In this research, we presented a novel carbon support with very short channels to increase dispersion of precious metal and to facilitate the transport of oxygen as called thin film carbon (TFC). The basic operating principle of the DMFC with TFC supported precious metal electrocatalysts is shown in Fig 1. At the anode, methanol and water are converted to carbon dioxide, protons and electrons. The protons are transferred to the cathode side through a polymer electrolyte membrane (PEM). The electrons are transported through the external circuit, where they can be used to perform work. At the cathode, the protons and electrons reduce oxygen (from air) to form water.

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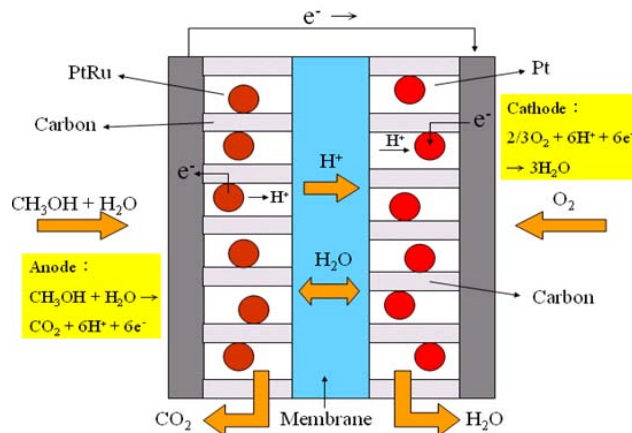


Fig. 1. The basic operating principle of the DMFC with TFC supported precious metal of electrocatalysts.

The novel carbon supported material is based on the mesoporous carbon CMK-3 of film morphology with short channels (less than 100 nm) perpendicular to the film surface. Because of eliminating the transport hindrance effect caused by long distance migration is a criterion in 3-dimensional nanostructured electrode materials. Thus, the novel TFC support simultaneously not only improved its electric contact area with film shape but also mass transport of oxygen in and water out of the short channels. In addition, the particle size of electrocatalysts could be suppressed the growth by nano-pore size of channel during DMFC operation.

In this work, we made the composite metal nanoparticles as the electrocatalysts by various Pt and Au molar ratios on depositing TFC support, and found the optimum ORR activities by electrochemical measurements. In addition, the structure and the composition of the electrocatalysts, e.g. particle size, and alloying degree, were measured by TEM, XRD to observe the intrinsic effects in enhancing ORR activities.

Experiment:

Syntheses SBA-15 ⊥:

A ternary surfactant system: cetyltrimethylammonium bromide (C₁₆TMAB, Acrôs), sodium dodecylsulfate (SDS, Acrôs), and Pluronic 123 (EO₂₀PO₇₀EO₂₀, Aldrich) was used to synthesize the mesoporous silica platelets with short vertical channels. A chemical composition of 0.75 g C₁₆TMAB, 0.89 g SDS, and 0.70 g Pluronic 123 was mixed in 150 ml H₂O at 45°C and pH = 4.5. Then the mixture was directly poured into a 150 ml dilute solution of sodium silicate (S.S, Aldrich), with [SiO₂] = 80.0 mM, at 45°C and pH = 4.5. The precipitates formed within seconds were hydrothermally treated at 100°C for 24 h, filtered, washed with water, and calcined at 560°C for 6 h. The product was ground and denoted as SBA-15 thin film template (SBA-15 ⊥).

Syntheses TFC:

To have thin film carbon (TFC) from inverse replicated SBA-15 ⊥ template. First, 0.5 g SBA-15 ⊥ template was mixed into a solution composed of 0.625 g sucrose (Acrôs), 0.07 g concentrated sulfuric acid and 5 g deionized water. After stirring for 1 h, the mixture was dried at 100°C for 6 h and then at 160°C for another 6 h. The sample turned dark brown during heat treatment, the sucrose in the channel pores became partially polymerized and carbonized. With further addition of 0.4 g sucrose, 0.045 g concentrated sulfuric acid, the sample was treated again at 100°C and 160°C. The carbonization was completed with the heating rate 2.5°C/min and kept at 900°C for 6 h under N₂ atmosphere. The silica-carbon composite was then washed with 10 wt% hydrofluoric acid solution. The product was filtered, washed with deionized water, and dried. The product was ground and denoted TFC.

Syntheses PtAu/TFC :

The PtAu composite electrocatalysts were deposited on the TFC supports by using a wet chemical reduction method. A 0.1 g TFC was added in a solution containing a desired amount of 0.01 M H₂PtCl₆ (Acrôs) and 0.01 M HAuCl₃ (Acrôs). Then, an excess of 0.1 M NaBH₄ (Aldrich) was added

into the mixture drop by drop and stirred for 1 h, the solid was recovered by centrifugation, and extensively washed with deionized water. The product was dried and denoted as Pt/TFC or PtAu(mole ratio)/TFC catalyst, while 20 weight percent of Pt and Au on TFC.

Electrochemical device:

The oxygen reduction reaction (ORR) activity were analyzed by cyclic voltammetry (CV) using an Autolab PGSTAT 30 Potentiostat equipped with a rotatory disk electrode (RDE). A conventional three-compartment electrochemical cell consisting of the glassy carbon (GC) electrode with an area of 0.196 cm² as the working electrode, Pt flat as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode was used. In addition, 0.1 M HClO₄ was used as an electrolyte solution and kept at 25°. All potentials were converted to values with reference to a reversible hydrogen electrode (RHE).

Preparation of working electrode:

The working electrode was prepared by the following steps: first, ca. 3 mg of PtAu/TFC catalyst was added into 1.5 mL of deionized water, followed by ultrasonic treatment for 0.5 h. Next, ca. 20 μ L of the resultant suspension mixture was withdrawn and injected onto the GC electrode, followed by drying in air at room temperature for 2 h. Finally, 15 μ L of 1% Nafion (DuPont) solution was added as a binder.

Electrochemical measurements:

The CV curves was measured with a scan rate of 50 mV/s between 0 and 1.0 V under a saturated-N₂ electrolyte solution, subsequently, the electrochemically active surface area (ECSA) was derived from hydrogen-ion desorption integrated area of CV curves. The linear sweep voltammogram (LSV) curves was measured at a scan rate of 10 mV/s between 0.2 and 1.2 V with working electrode rotated in 1,600 rpm under a saturated-O₂ electrolyte solution, subsequently, the kinetic current was calculated based on the following equation (Koutecky-Levich equation):

$$\frac{1}{I_{\text{measured}}} = \frac{1}{I_{\text{kinetic}}} + \frac{1}{I_{\text{diffusion}}}$$

Then, the specific activities and mass activities was calculated from the kinetic current, which was derived from the measured current at 0.8V and the diffusion current at 0.3 V.

Results and Discussion:

In Fig 2.(a), the TEM image shows the perpendicular channels of thin film carbon (TFC), composed of well-ordered hexagonal rod array with narrow pore could be seen clearly. In Fig 2.(b), the Pt nanocatalysts were well-dispersed inside the vertical channel network assembled by carbon rods of TFC support.

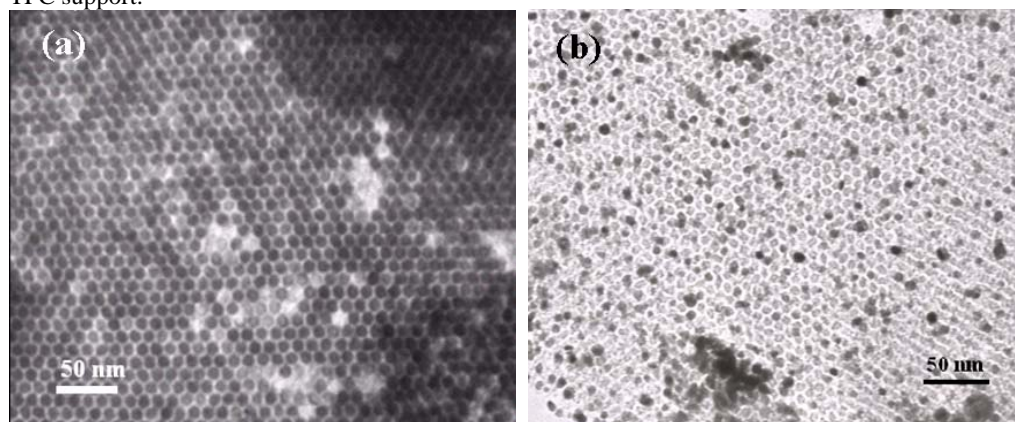


Fig. 2. TEM images of (a) the TFC support, and (b) the Pt/TFC catalyst.

The ICP-MS analysis over the PtAu composite electrocatalysts were shown in Table 1. The composition of the electrocatalysts was converted to normalized theoretical composition for comparison with analyzed composition. The analyzed value (mol%) of Pt or Au to all electrocatalysts remained about original 90% content. The similar loss of about 10 mol% was believably ascribed to centrifugation and extensively washed with deionized water. In other words, it was suggested that Pt or Au through synthesized process was stable to hold in an acceptable level.

Table 1. The ICP-MS analysis over the PtAu composite electrocatalysts.

Theoretical composition	Normalized theoretical composition	Pt (mol%)		Au (mol%)		Pt-Au	
		Anal.	Theor.	Anal.	Theor.	atomic ratio%	ratio
Pt/C(J.M.)	Pt ₁	88.1	100.0	-	-	88.1 - 0	-
Pt/TFC	Pt ₁	86.3	100.0	-	-	86.3 - 0	-
PtAu(11:1)/TFC	Pt _{0.916} Au _{0.083}	80.7	91.6	6.7	8.3	92.4-7.6	12.1
PtAu(8:1)/TFC	Pt _{0.888} Au _{0.111}	77.3	88.8	8.8	11.1	89.8-10.2	8.8
PtAu(5:1)/TFC	Pt _{0.833} Au _{0.166}	71.7	83.3	13.2	16.6	84.5-15.5	5.4
PtAu(3:1)/TFC	Pt _{0.750} Au _{0.250}	64.5	75	19.5	25.0	86.8-23.2	3.3

The XRD patterns of the PtAu/TFC catalyst were shown in Fig 3. All of the PtAu/TFC catalyst displayed similar diffraction profiles of face-centered cubic (fcc) structure of Pt or Au, indicating that two phases of Pt and Au showed at about 40° by different peak of Pt(111) and Au(111). However, it was a unexpected result that the PtAu composite electrocatalysts displayed poor alloying. Thus, suggesting that the Pt nanoparticle was major factor of oxygen reduction reaction (ORR) instead of the Au nanoparticle. In addition, the nanoparticle size of Pt was smaller than that of Au in comparison with peak intensity.

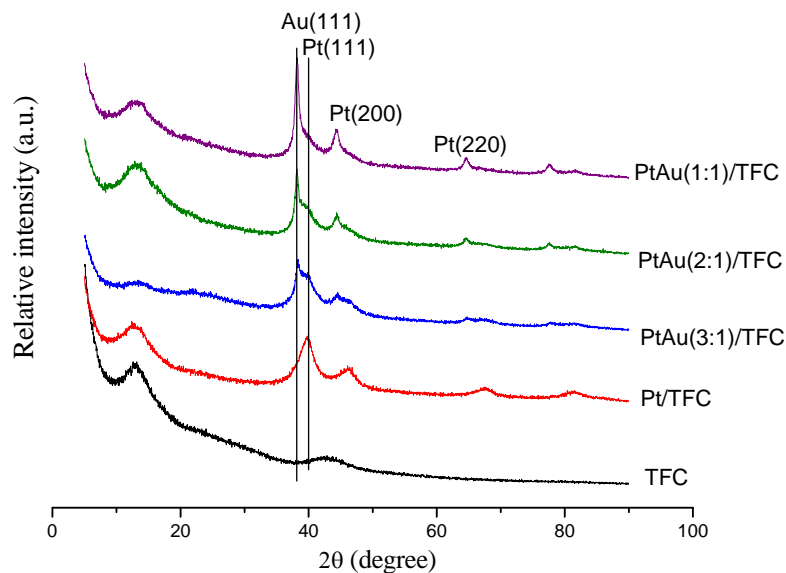


Fig. 3. The XRD patterns of the PtAu/TFC catalyst.

The particle size of Pt over the electrocatalyst was shown in Table 2. As can be seen, the particle size by Scherrer equation was suggested to agreement with the TEM result. In addition, the particle size of Pt increased slightly with increasing the amount of Au by Scherrer equation (i.e., 4.3 nm for Pt/TFC and 5.4 nm for PtAu(8:1)/TFC), indicating that the fact of the slight alloying degree of Au.

Table 2. The particle size of Pt over the electrocatalyst.

the electrocatalyst	θ (°)	β (°)	D (nm)	TEM (nm)
PtAu(3:1)/TFC	-	-	-	8±6
PtAu(5:1)/TFC	-	-	-	8±6
PtAu(8:1)/TFC	39.74	1.89	5.4	-
PtAu(9:1)/TFC	39.78	2.03	5.0	-
PtAu(10:1)/TFC	39.79	2.12	4.8	-
PtAu(11:1)/TFC	39.74	2.61	4.7	5±3
Pt/TFC	39.78	2.39	4.3	6±2
Pt/C (J.M.)	39.78	3.17	3.2	2±1

a. θ is the diffraction angle of maximum intensity.

b. β is the full width at half maximum intensity of the peak.

c. D is the particle size of the electrocatalyst by Scherrer equation.

The LSV curves over various catalysts were shown in Fig 4. All the curves showed reduced current from 0.9V to 0.6V, namely a mixture of kinetic and diffusion current. As can be seen, the Pt/TFC catalyst exhibited slight higher the diffusion current over commercial Pt/C catalyst (Johnson Mathey). However, the reduced current of the other PtAu/TFC catalyst were lower in comparison with the Pt/TFC catalyst. Thus, the addition of Au to Pt for the electrocatalyst could not be enhanced the reduced current of the ORR. The results were ascribed that the poor alloying of Pt and Au could not be enhanced the utilization of Pt.

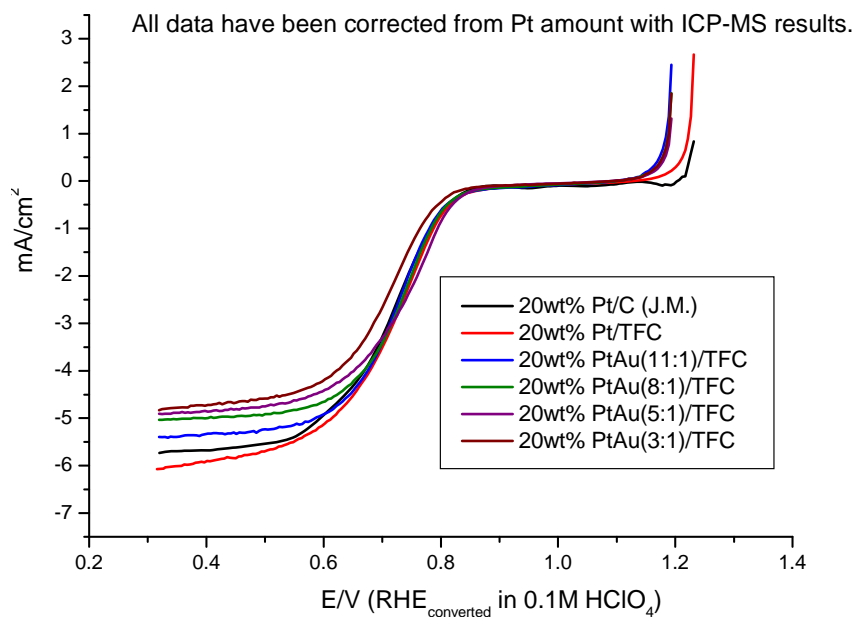


Fig 4. The LSV curves over various catalysts. All data have been corrected from Pt amount with ICP-MS results.

The ORR activities of the electrocatalyst are summarized in Table 3. All of the electrocatalysts on working electrode surface have the same metal loading weight of $40.8 \mu\text{g}/\text{cm}^2$. Two kinds of ORR activities were based on different units derived from the kinetic current over the electrochemically active surface area (ECSA), and over the metal loading weight. As can be seen, the specific activity ($0.073 \text{ mA}/\text{cm}^2_{\text{metal}}$) of the Pt/TFC catalyst showed higher value than that ($0.069 \text{ mA}/\text{cm}^2_{\text{metal}}$) of commercial Pt/C catalyst. At the similar results, the mass activity ($0.060 \text{ mA}/\mu\text{g}_{\text{metal}}$) of the Pt/TFC catalyst showed higher value than that ($0.056 \text{ mA}/\mu\text{g}_{\text{metal}}$) of commercial Pt/C catalyst. Thus, our TFC support provides a reasonably high dispersion for Pt nanoparticle (i.e., $42.8 \text{ m}^2/\text{g}_{\text{metal}}$ for Pt/TFC versus $36.4 \text{ m}^2/\text{g}_{\text{metal}}$ for Pt/C), despite their slightly large particle size was shown in Table 2 (i.e., 4.3 nm for Pt/TFC versus 3.2 nm for Pt/C). On the contrary, the ORR activities of the other PtAu/TFC catalysts decreased obviously with increasing the amount of Au. The factor illustrated the poor alloying without the utilization of Pt.

Table 3. the ORR activities of the electrocatalyst at 0.8 V.

the electrocatalyst	$\mu\text{g}/\text{cm}^2$	ECSA ($\text{m}^2/\text{g}_{\text{metal}}$)	specific activities ($\text{mA}/\text{cm}^2_{\text{metal}}$)	mass activities ($\text{mA}/\mu\text{g}_{\text{metal}}$)
Pt/C (J.M.)	40.8	36.4 (33.4)	0.069 (0.047)	0.056 (0.040)
Pt/TFC	40.8	42.8 (37.3)	0.073 (0.056)	0.060 (0.045)
PtAu(11:1)/TFC	40.8	35.8 (32.9)	0.064 (0.042)	0.052 (0.041)
PtAu(8:1)/TFC	40.8	29.9 (26.8)	0.059 (0.040)	0.047 (0.038)
PtAu(5:1)/TFC	40.8	27.2 (24.1)	0.055 (0.038)	0.037 (0.030)
PtAu(3:1)/TFC	40.8	24.4 (21.8)	0.049 (0.034)	0.031 (0.025)

All data have been corrected from Pt amount with ICP-MS results.

All data in parentheses were based on theoretical composition before correction.

Conclusion:

Mesoporous thin film carbon (TFC) with perpendicular channels and the unique short pore length was successfully synthesized in our lab. The Electrochemical oxygen reduction of the TFC supported Pt (Pt/TFC) catalyst showed higher catalytic activity than that of commercial Pt/C catalyst (Johnson Mathey) for improvement. Our Pt/TFC catalyst perform at about the same level as commercial catalyst with lot of rooms for facile transport of oxygen and the improvement of metal dispersion. Thus, it is suggested that the TFC support is a promising material in substitution for commercial Vulcan XC 72 supported carbon (E-TEK). In the future work, the alloying of Pt and Au may be performed for the enhancement of utilization of Pt.

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List of Publications: Please list any publications, conference presentations, or patents that resulted from this work.

1. Meng-Liang Lin, Man-Yin Lo, Chung-Yuan Mou, “ PtRuP nanoparticles supported on mesoporous carbon thin film as highly active anode materials for direct methanol fuel cell” *Catal Today*, 160, 109-115. (2011)

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