Ordered Mesoporous Carbon/Titanium Carbide Composites as Support Materials for Platinum Catalysts

Gang Zhao, Tianshou Zhao,* Xiaohui Yan, Lin Zeng, and Jianbo Xu[a]

Introduction

New carbon materials, including carbon nanofibers,[1] carbon nanotubes,[2] carbon aerogels,[3] and mesoporous carbons,[4] have been studied as support materials for platinum (Pt) catalysts in fuel cells owing to their good electrical conductivities, high corrosion resistances, and high specific surface areas. Among these materials, ordered mesoporous carbon (OMC) is one of the most promising because of its high specific surface area, unique textural structure, and narrow pore size distribution.

OMC was first synthesized by Ryoo et al. in 1999,[5] using a mesoporous silica molecular sieve (MCM-48) as the hard-template agent and sucrose as the carbon source. After that, Joo et al. used a similar method to prepare OMC by employing another mesoporous silica molecular sieve (SBA-15) as the template and furfuryl alcohol as the carbon source.[6] Platinum supported on OMC showed a much higher activity than platinum on carbon black. In 2006, Meng et al. reported the synthesis of OMC from an organic–organic assembly of triblock copolymers with phenolic resin precursors by an evaporation induced self-assembly (EISA) strategy.[7] Different from the hard-template methods above, this so-called soft-template method does not involve the extra step of removing the hard template, making it more economical. Since then, OMC has been receiving increasing attention as a support material in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).[4a,c,8]

However, despite the advantageous ordered mesoporous structure of OMC, there are some disadvantages to use OMC as the support material for platinum catalysts. Firstly, OMC prepared by either soft- or hard-template methods contains few oxygen-containing groups to act as the anchoring sites for platinum catalysts. Although functionalization can furnish OMC with these groups, the textural structure of the OMC is prone to collapse as well.[9] Secondly, the normally low carbonization temperature (<1000°C) of OMC would inevitably lead to low degrees of graphitization, resulting in low electrical conductivity and low resistance to the corrosion.[10]

Titanium carbide (TiC) is reported to have a high electrical conductivity and good resistance to corrosion, and the potential of using TiC as a support material has been demonstrated.[11] Nevertheless, the specific surface area of TiC is rather low, due to its large molecular weight.[12] In this sense, the titanium carbide can be formed in the skeleton of OMC, the electrical conductivity and corrosion resistance of this composite may improve significantly, while the high specific surface area and the pore structure are still maintained. Furthermore, titanium atoms can work as the anchoring sites for platinum particles, so that the functionalization step on OMC can be avoided.

Herein, we describe the synthesis of ordered mesoporous carbon/titanium carbide (OMC/TiC) composites with a high specific surface area and narrow pore size distribution by a soft-template method. After that, platinum catalysts are prepared by reducing platinum particles in the pores of the OMC/TiC composite by an impregnation method, using ethylene glycol (EG) as the reducing agent. Compared to platinum supported on pure OMC (Pt/OMC) and commercial Pt/C, platinum supported on OMC/TiC (Pt/OMC/TiC) shows higher activity towards the methanol oxidation (MOR) and the methanol oxygenation reaction (ORR), as well as better stability.

[a] G. Zhao, T. Zhao, X. Yan, L. Zeng, J. Xu
Department of Mechanical and Aerospace Engineering
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong SAR (PR China)
E-mail: metzhao@ust.hk
Results and Discussion

Characterization of OMC and OMC/TiC composites

X-ray diffraction (XRD) patterns of the OMC/TiC composite and pure OMC are shown in Figure 1a. As can be seen, a broad diffraction peak centered at $2\theta \approx 43.8^\circ$ of the pure OMC corresponds to the [100] reflection of graphitic carbon. For the as-prepared OMC/TiC composite, five resolved diffraction peaks are observed at $2\theta \approx 36.2^\circ$, 42.00°, 60.70°, 72.60°, and 76.70°, indexed to the [111], [200], [220], [311], and [222] reflections of the cubic titanium carbide phase, according to the standard powder diffraction file (PDF) 38-1420, which confirms the formation of nanocrystals of TiC.

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ure 2c,d), and the TiC nanocrystals with sharp contrast are well demonstrated. It is noted that some TiC particles are so large that the ordered mesoporous structure undergoes a severe distortion, which explains the inferior regularity of the OMC/TiC. The lattice fringes of the nanocrystals observed in the inset high-resolution TEM (HRTEM) image (Figure 2d) further confirms the formation of a TiC cubic phase in the carbon framework.

Characterization of Pt/OMC and Pt/OMC/TiC

XRD patterns of platinum catalysts supported on the OMC and OMC/TiC composite are illustrated in Figure 3a. Four resolved diffraction peaks can be clearly observed in both samples at $2\theta \approx 39.8^\circ$, $46.2^\circ$, $68.3^\circ$, and $81.3^\circ$, indexed to the [111], [200], [220], and [311] reflections of the typical face-centered cubic platinum. For the Pt/OMC/TiC, the reflections of the nanocrystal of TiC seem to be covered by the signals of platinum; however, a small diffraction peak of Pt/OMC/TiC could be seen at $2\theta \approx 61.0^\circ$, corresponding to the [220] reflection of crystallized TiC, implying the existence of TiC nanocrystals. To calculate the average particle size of platinum by Scherrer equation, we choose the [220] reflection peaks of platinum at $2\theta \approx 68.3^\circ$, in order to avoid the influence of carbon and TiC. The average platinum particle size of Pt/OMC/TiC composite is 2.8 nm, much smaller than that of Pt/OMC (3.5 nm).

In order to determine the amount of platinum, TG measurements for the as-prepared Pt/OMC and Pt/OMC/TiC in air are illustrated in Figure 3b. In the first stage, when the temperature is below 300°C, both samples show a small weight loss, which can be ascribed to some residue of organic materials, such as ethylene glycol, glycolic acid, and so on. The significant weight losses occur at around 400°C, indicating a collapsed carbon framework caused by burning out in air. The different behaviors of Pt/OMC and Pt/OMC/TiC manifest exactly the same trend as shown in Figure 1b. Therefore, combined with Figure 1b, the weight ratios of platinum in Pt/OMC and Pt/OMC/TiC are 13.5% and 18.2%, respectively. The actual weight ratios of platinum in Pt/OMC and Pt/OMC/TiC may get a little higher, if the weight losses in the beginning stage are considered.

From the above XRD and TG results, it is found that the platinum catalyst supported on OMC/TiC has a smaller average particle size and higher weight ratio than that supported on OMC. This can be explained by the fact that the oxygen-containing groups of OMC after heat treatment are so few that not enough anchoring sites are provided for platinum. As to the Pt/OMC/TiC, titanium atoms in the framework of OMC can act as the anchoring points for platinum. Furthermore, the molar ratio between titanium and platinum is larger than 3:2, implying that sufficient anchoring sites are provided.

TEM images of the as-prepared Pt/OMC and Pt/OMC/TiC are illustrated in Figure 3c,d. Domains of ordered hexagonal arrays can be observed in both samples, suggesting that the unique pore structure is preserved after supporting platinum catalysts. Platinum particles are mostly deposited inside the pores of the supporting materials, including OMC and OMC/TiC composite, but not on the outside surface, indicating high utilization of the surface area of the supporting materials. However, the agglomeration of platinum particles seems more severe in Pt/OMC than in Pt/OMC/TiC, despite the fact that TG curves show the amount of platinum in Pt/OMC is much lower than in Pt/OMC/TiC. The reason is that TiC can offer anchoring sites for platinum particles, which helps the dispersion and deposition of platinum particles on the surface of OMC/TiC. However, in Pt/OMC, due to insufficient anchoring sites, platinum particles are liable to agglomer-
Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed to investigate the electrocatalytic behavior of the as-prepared Pt/OMC and Pt/OMC/TiC in nitrogen-saturated 0.5 m HClO$_4$ solution, compared to a commercial 20% Pt/C sample on Vulcan XC-72 from E-TEK. All the samples demonstrate a behavior typical of platinum catalysts in an acid environment, with hydrogen adsorption/desorption in the potential range of 0–0.35 V (vs. RHE, the same as following), as indicated in Figure 4a. The double electric layers of the Pt/OMC and Pt/OMC/TiC are referred to in nitrogen-saturated 0.5 m HClO$_4$ solution (a), and calculated values of $S_{ECSA}$ for the as-prepared Pt/OMC and Pt/OMC/TiC, compared with the commercial 20% Pt/C.

![Figure 4. CV curves in nitrogen-saturated 0.5 m HClO$_4$ solution (a), and calculated values of $S_{ECSA}$ for the as-prepared Pt/OMC and Pt/OMC/TiC, compared with the commercial 20% Pt/C.](image)

and Pt/OMC/TiC in the potential range of 0.35–0.6 V are much thicker than that of the commercial 20% Pt/C, implying much higher specific surface areas of the two home-made platinum catalysts than that of the commercial Pt/C, caused by the high specific surface areas of the OMC and OMC/TiC composite, used as the support materials for platinum catalysts. By integrating the charge ($Q_H$) in the hydrogen desorption region ranging from 0–0.35 V, deducting the effect of double-layer charging, the electrochemical surface area ($S_{ECSA}$) can be obtained using Equation (1):

$$S_{ECSA} = \frac{Q_H}{Q_{H\text{tot}}}$$

where $Q_{H\text{tot}}$ is a constant and assumed to be 0.21 mCcm$^{-2}$. By calculation, the value of $S_{ECSA}$ of the Pt/OMC/TiC is 100.5 m$^2$g$^{-1}$, larger than that of the Pt/OMC (79.9 m$^2$g$^{-1}$) and the commercial Pt/C (75.0 m$^2$g$^{-1}$), as indicated in Figure 4b. The probable reason is that the average platinum particle size of Pt/OMC/TiC may be smaller than that of the Pt/OMC, in addition to the platinum particles being well-dispersed in the pore structures, according to the Figure 3c,d, implying an approved efficiency with respect to platinum utilization. Compared to the commercial Pt/C, the unique pore structure of OMC seems to improve the value of $S_{ECSA}$ by facilitating the transportation.

Linear sweeping voltammmograms (LSVs) were conducted to further understand the ORR performance of the as-prepared Pt/OMC and Pt/OMC/TiC, which was performed in an oxygen-saturated 0.5 m HClO$_4$ solution with a flow rate of 20 mLmin$^{-1}$ and at a rotation speed of 1600 rpm and a scan rate of 10 mV s$^{-1}$. As shown in Figure 5a, all the as-prepared platinum catalysts demonstrate an activity for ORR performance. Specifically, the onset potentials for the Pt/OMC/TiC and Pt/OMC are 1.01 V and 0.99 V, slightly more positive compared to that of the commercial Pt/C (0.98 V). To evaluate the mass activity of the platinum catalyst for ORR, the kinetics current density ($j_k$) at the potential of 0.9 V vs. RHE is widely accepted as a standard for comparison, which can be calculated from the Koutecky–Levich (K–L) Equation (2):

$$j^{-1} = j_k^{-1} + j_a^{-1}$$

where $j$, $j_k$, and $j_a$ are the measured, kinetic-limiting, and diffusion-limiting current density, respectively. By calculation, the Pt/OMC/TiC had the highest value of $j_k$ (260 mA mg$^{-1}$), much larger than that of Pt/OMC (196 mA mg$^{-1}$) and commercial Pt/C (186 mA mg$^{-1}$), as shown in Figure 5b, implying the best mass activity of Pt/OMC/TiC for ORR. This result is consistent with the comparison of $S_{ECSA}$ for the three platinum catalysts, indicating that the improvement for ORR can be ascribed to the enlargement of the value of $S_{ECSA}$.

Other than the ORR, a CV measurement of the methanol oxidation reaction (MOR) was also conducted in a mixture of 1 m methanol and 0.5 m HClO$_4$ solution. Figure 6a reveals that for all samples, methanol oxidation produces anodic peaks at around 0.8 V in the positive scan, while in the negative one, anodic peaks appear at around 0.7 V, due to the oxidation of the incompletely oxidized carbonaceous species dissociated from methanol molecules formed in the positives scan. For the as-prepared Pt/OMC and the commercial Pt/C, the onset potentials for MOR are similar. However, the peak MOR current densities are different. By calculation, we correct peak current density in the CV curves by the amount of platinum used ($j_{p,\text{mass}}$). As seen in Figure 6b, the value of
OMC/TiC is shifted negatively by about 80 mV, compared to in the latter. The peak potential of CO oxidation on Pt/OMC/TiC composite is the negative shift of the CO oxidation peak most notable difference between Pt/OMC and the Pt/OMC/TiC. Furthermore, the value of \( j_{p,max} \) for the Pt/OMC/TiC is 780 mAmg\(^{-1}\)\(\text{Pt} \), which is the largest of the three samples. This could be ascribed to not only the smaller particle size and the highly ordered pore structure, but also a synergetic effect of TiC on platinum.\(^{[15]}\) Platinum is easily poisoned by CO-like intermediate products of the MOR process. However, this poisonous effect could be significantly alleviated by the synergetic effect of TiC, due to the formation of CO stripping voltammetry measurement. As shown in Figure 7a, a distinct peak, referred to as the CO oxidation reaction, could be observed for all of the samples. However, the most notable difference between Pt/OMC and the Pt/OMC/TiC composite is the negative shift of the CO oxidation peak in the latter. The peak potential of CO oxidation on Pt/OMC/TiC is shifted negatively by about 80 mV, compared to that on Pt/OMC, indicating that the formation of TiC in the OMC framework reduced the overpotential for CO oxidation. Therefore, the Pt/OMC/TiC has an improved CO tolerance.

The stability of the platinum catalysts was examined by an accelerated degradation test (ADT), as depicted in the Experimental section. As Figure 7b shows, all the platinum catalysts demonstrate a decreasing trend of \( S_{ECSA} \) with an increase of the number of cycles. For the commercial Pt/C and the Pt/OMC, the decreasing rates of \( S_{ECSA} \) are similar, which reduce by half after 6000 cycles. While that for Pt/OMC/TiC is only about 28% reduction, indicating a better stability. ORR and MOR performances after the ADT further confirm the improvement of the corrosion resistance of Pt/OMC/TiC (Figure 7c, d). Notably, the commercial Pt/C and Pt/OMC illustrate similar slopes in the ORR tests, showing the similar degradation rates after 6000 cycles (about 50% reduction of \( j_k \) for both the commercial 20% Pt/C and the Pt/OMC). A slower corrosion rate could be observed for the Pt/OMC/TiC on ORR performance after 6000 cycles (24% reduction). For MOR, the value of \( j_{p,max} \) decreases by about 52%, 47%, and 14% for the commercial Pt/C, the Pt/OMC, and the Pt/OMC/TiC, respectively. Overall, the above data imply that the commercial Pt/C and the Pt/OMC have a similar degradation rate. However, the Pt/OMC/TiC has a slower degradation rate. As we know, the degradation of Pt/C catalysts is mainly caused by carbon corrosion, leading to the agglomeration of platinum particles and a reduction in platinum utilization, resulting in performance degradation.\(^{[16]}\) For this reason, the formation of TiC in the OMC framework can improve the corrosion resistance of the OMC/TiC composite, and platinum catalysts supported on a OMC/TiC composite shows an enhanced stability.

**Conclusions**

Ordered mesoporous carbon/titanium carbide composite (OMC/TiC) has been successfully synthesized by using Pluronic F127 and titanium isoproxide as the structure-directing agent and the titanium precursor. The as-prepared OMC/TiC exhibits a large surface area of 535.55 m\(^2\)g\(^{-1}\) and a narrow pore size distribution, and the weight ratio of TiC is as high as 9.3%. Platinum supported on the as-prepared OMC/TiC composite demonstrates a smaller average particle size and higher loading. In addition, Pt/OMC/TiC shows superior mass activities for MOR and ORR to those of the Pt/OMC and commercial Pt/C. For ORR, the mass activity of the as-prepared Pt/OMC/TiC is 260 mAmg\(^{-1}\)\(\text{Pt} \), much higher than that of the Pt/OMC (196 mAmg\(^{-1}\)\(\text{Pt} \)) and the commercial Pt/C (186 mAmg\(^{-1}\)\(\text{Pt} \)). For MOR, the as-prepared Pt/OMC/TiC has a more negative onset potential and higher value of \( j_{p,max} \) (780 mAmg\(^{-1}\)\(\text{Pt} \)), compared to that of the Pt/OMC (452 mAmg\(^{-1}\)\(\text{Pt} \)) and the commercial Pt/C (358 mAmg\(^{-1}\)\(\text{Pt} \)). Furthermore, the ADT test demonstrated that the formation of TiC in the composites improves the corrosion resistance of the support material. Therefore, OMC/TiC has a great po-
tential to be used as a support material for platinum catalysts in PEMFCs and DMFCs.

### Experimental Section

#### Preparation of OMC/TiC composite

A resin solution, obtained from phenol and formaldehyde according to the previously reported procedures, was used as the carbon precursor. For a typical preparation, 1.0 g of phenol and 0.21 g of NaOH (20 wt%) were mixed and stirred, then 1.7 g of formaldehyde solution (37 wt%) was dropped into this solution. The mixture was heated at 75 °C for 1 h and cooled. The pH value of the mixture was adjusted to 7.0 by using dilute HCl solution, and water in the mixture was reduced through vacuum distillation. Ethanol was added to form a resin solution (20 wt%).

When preparing OMC/TiC, triblock copolymer Pluronic F127, the resin solution, and titanium isoproxide were dissolved in ethanol to form a solution. The solution was transferred to dishes and evaporated at room temperature for 8 h to remove the solvent, followed by heating at 100 °C for 24 h for thermopolymerization. The product was heated at 350 °C for 3 h to remove F127 and 1200 °C for 2 h for the carbothermal reaction in argon flow. The heating rate was 1 °C min⁻¹ below 600 °C and then increased to 5 °C min⁻¹ above 600 °C. For comparison, OMC was prepared, and the preparation procedure was similar to that of the OMC/TiC composite without adding titanium isoproxide.

#### Preparation of supported platinum catalysts

Platinum catalysts supported on OMC/TiC composite and pure OMC were prepared by impregnation with ethylene glycol (EG) as the reducing agent and platinum loadings were both set at 20 wt%.

In a typical preparation of Pt/OMC/TiC, 3.38 mL of chloroplatinic acid EG solution (7.4 mgPt mL⁻¹) and 100 mg of OMC/TiC were mixed in a certain amount of EG. The pH value of the mixture was adjusted to about 12 by using 1 M NaOH EG solution. The mixture was heated to 140 °C for 3 h, and then cooled. The final catalyst (Pt/OMC/TiC) was obtained after filtering, washing, and drying at 80 °C for 10 h in a vacuum oven. For comparison, Pt/OMC was also synthesized in the same procedure, with the difference that pure OMC was used instead of the OMC/TiC composite. Commercial 20% Pt/C on Vulcan XC-72 carbon was also used for comparison.

#### Physical characterization

X-ray diffraction (XRD) patterns were recorded with an X’pert Pro (PANalytical) with nickel-filtered CuKα radiation. Thermogravimetric (TG) analyses were measured on a TGAQ5000 from room temperature to 900 °C under air flow with a ramp rate of 5 °C min⁻¹. Nitrogen sorption isotherms were measured with a Beckman Coulter SA3100 Surface Area Analyzer. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were utilized to calculate the specific surface area (S_{BET}) and the pore size distribution. Transmission electron microscopy (TEM) experiments were conducted on a TEM 2010F (JEOL). The samples for TEM measurements were suspended in ethanol and dropped onto a holey carbon film supported on a copper grid. The electrical conductivity measurements were done according to literature reports. Briefly, the sample was pressed to a pellet, and then placed between two gold plates. The electrical conductivity was measured by impedance spectroscopy. For comparison, the electrical conductivity of Vulcan XC-72 carbon was also measured.

### Electrochemical measurement

All electrochemical measurements were carried out using an Autolab instrument. A three-electrode system was used, in which a platinum mesh was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was made as follows: 2.0 mg of catalyst was dispersed in 2 mL of ethanol and ultrasonicated for 20 min, and then 20% Nafion solution was added and ultrasonicated for another 20 min. 20 μL of the above-prepared catalyst ink was injected onto a polished glassy carbon electrode by a microsyringe and dried at ambient conditions. Cyclic voltammetry (CV) measurements were conducted under nitrogen saturated 0.5 M HClO₄ solution. Linear sweep voltammetry (LSV) measurements were conducted under oxygen saturated 0.5 M HClO₄ solution with a rotating speed of 1600 rpm to examine the oxygen reduction reaction (ORR) performance, and CV measurements were conducted under nitrogen saturated 0.5 M HClO₄ + 1 M CH₃OH solution for methanol oxidation reaction (MOR). CO stripping voltammetry were measured to examine the CO tolerance for the as-prepared samples in 0.5 M HClO₄ solution. Accelerated degradation test (ADT) was conducted to evaluate the stability of the catalysts, by continuous cycling for 6000 cycles between 0 V and 1.2 V vs. RHE in 100 mVs⁻¹ in 0.5 M HClO₄ solution at room temperature. The S_{ECSA}, the J_{max} for MOR, and the J_{c} for ORR were measured and calculated every 2000 cycles during ADT.

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### Keywords:

- carbons
- composites
- fuel cells
- platinum
- titanium carbide

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In need of some TiC: Composites of ordered mesoporous carbon and titanium carbide (OMC/TiC) are prepared, and used as support material for platinum catalysts (Pt/OMC/TiC). Electrochemical measurements reveal that Pt/OMC/TiC has superior activity towards the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR), which confirms that OMC/TiC composite offers great potential as a support material for platinum catalysts in fuel cells.