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Article

N-doped carbon modified Pt/CNTs synthesized by atomic layer deposition with enhanced activity and stability for methanol electrooxidation

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ARTICLE INFO

Article history:

Received 28 December 2017

Accepted 20 February 2018

Published 5 June 2018

Keywords:

Atomic layer deposition

Methanol electrooxidation

Platinum

Nitrogen-doped carbon

ABSTRACT

A Pt/CNTs catalyst coated with N-doped carbon (xNC-Pt/CNTs) is synthesized by atomic layer deposition (ALD) and applied in methanol electrooxidation reaction. Pt nanoparticles and polyimide (PI) are sequentially deposited on carbon nanotubes (CNTs) by ALD. After annealing at 600 °C in H₂ atmosphere, the PI is carbonized to produce porous N-doped carbon. Upon coating with a moderately thick layer of N-doped carbon, the optimized 50NC-Pt/CNTs show higher activity, better long-term stability, and improved CO resistance towards methanol electrooxidation compared with Pt/CNTs and commercial Pt/C (20 wt%). X-ray photoelectron spectroscopy characterization result indicates that the Pt–CO bond is weakened after N-doped carbon coating and CO adsorption on the Pt surface is weakened, leading to superior electrocatalytic performance.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted great attention as a reliable power source for electric vehicles and portable devices due to its high energy conversion, high power density, and environmental friendliness [1,2]. However, the widespread commercial application of DMFCs is not yet achieved because of the limiting electrocatalytic materials. Conventional Pt-based materials are the most effective catalysts for the methanol oxidation reaction (MOR) compared to other noble metals such as Ru, Pd, Au, Ag, etc. [3,4]. However, Pt-based catalysts suffer from several issues including (1) poor abundance and high cost, (2) low catalytic efficiency, and (3) catalyst poisoning originating from the strong interaction between intermediate CO species and Pt active sites [5–7].

Tremendous efforts have been devoted to developing catalytic materials with excellent activity, good stability, and high CO tolerance. Ultrafine Pt particles can effectively enhance the catalytic efficiency due to their high surface area and large number of edges and corners [8,9]. Alloying Pt with a second metal such as Pd, Ru, Fe, Co, Ni, etc. also remarkably improves the catalytic activity and CO tolerance with an accompanying reduction in cost [10–13]. Exploiting supports with advanced structures and surface properties can also increase the electrocatalytic performance of DMFCs [14]. For example, doping nitrogen into carbon materials accelerates the nucleation and growth of Pt NPs into small particles with uniform dispersion [15,16]. Doping also improves the intrinsic properties of carbon materials, which increases the catalyst efficiency [17,18]. However, N-doped carbon materials are usually prepared at

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This work was supported by the National Natural Science Foundation of China (21403272, 21673269) and the Natural Science Foundation of Shanxi Province (2015021046).

DOI: 10.1016/S1872-2067(18)63066-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 6, June 2018

extremely high temperatures, high pressures, and in an ammonia atmosphere; such harsh conditions increase the preparation difficulty and cost [19].

The interface between the metal nanoparticles and the support plays an important role in catalysis. The rational design and engineering of metal-support interfaces is crucial in developing highly efficient catalysts [20,21]. Atomic layer deposition (ALD) is a thin-film deposition technique based on sequential surface reactions by alternately injecting gaseous precursors and reactants. The self-limiting character of the procedure allows the synthesis of ultrafine nanoparticles and ultrathin films on the atomic scale [22]. ALD can be used to modify the surface of metal nanoparticles by coating the surface with nanofilms. The film thickness can be precisely controlled, allowing for the optimization of the interface between the metal particles and the coating [22]. In our previous work, Pt nanoparticles were easily deposited on an inert CNT surface using O_3 as the reactant gas and $MeCpPtMe_3$ as the Pt precursor [23,24], and porous N-doped carbon nanofilms were obtained by pyrolyzing PI films deposited by molecular layer deposition (MLD)[25].

Herein, ALD is used to synthesize porous N-doped carbon coated Pt/CNTs catalysts. The size of the Pt particles and the thickness of the N-doped carbon film are highly controlled by adjusting the number of ALD cycles. The activity of the optimized sample is 2.7-times higher than that of commercial Pt/C (20 wt% Pt). Moreover, the long-term stability and CO resistance of the catalyst are also considerably improved.

2. Experimental

2.1. Materials

CNTs with a specific surface area of 40–70 $m^2 g^{-1}$ and diameters in the 40–60 nm range were purchased from Shenzhen Nanotech Port Co. Ltd, China. $MeCpPtMe_3$, pyromellitic dianhydride (PMDA), and 4,4'-diaminodiphenyl ether (ODA) were obtained from J&K Scientific Ltd. All the materials were used as received.

2.2. Preparation of the catalyst

Typically, 8 mg of CNTs were dispersed in ethanol, dropped onto a quartz wafer (10 cm $\times$ 10 cm), and dried in air. Then, the quartz wafer was transferred to a homemade ALD chamber for Pt ALD. The CNTs were sequentially exposed to $MeCpPtMe_3$ and O_3 . The pulse, exposure, and nitrogen purge times were 0.5, 8, and 20 s for $MeCpPtMe_3$ and 1, 8, and 20 s for O_3 , respectively. The temperature of the chamber was maintained at 280 °C. $MeCpPtMe_3$ was maintained at 60 °C to provide enough vapor pressure. The number of cycles of Pt deposition was 20 for all samples. PI deposition was carried out after Pt deposition. The sample was sequentially exposed to PMDA and ODA. The pulse, exposure, and nitrogen purge times were 5, 10, and 30 s for PMDA and 3, 8, and 30 s for ODA, respectively. The temperature of the chamber, PMDA, and ODA was maintained at 160, 155, and 140 °C, respectively. The number of cycles of PI depo-

sition was 40, 50, 60, and 70 to produce different samples. Finally, the as-prepared samples were transferred into a furnace and calcined in H_2/N_2 (5%) to pyrolyze the PI. During the pyrolysis process, the temperature was first raised from rt. to 600 °C at a rate of 3 °C min^{-1} , maintained at 600 °C for 2 h, and then lowered. The prepared samples were denoted as xNC-Pt/CNTs, where x is the number of cycles of PI deposition. For comparison, a catalyst with no PI coating (denoted as Pt/CNTs) was also prepared.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a CHI 760D electrochemical workstation and a three-electrode cell at room temperature. The working electrode was prepared as follows. 1 mg of catalyst, 1 mL of ethanol, and 20 μL of Nafion solution (5 wt%, Aldrich) were mixed ultrasonically for at least 30 min. Then 10 mL of the ink was transferred onto a freshly polished glassy carbon (GC, 5 mm diameter) electrode and dried in air. A Pt foil served as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. Cyclic voltammetric (CV) and chronoamperometric measurements were carried out in an N_2 -saturated aqueous solution of 1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} CH_3OH . A CO stripping test was conducted by immersing the as-prepared electrode in a CO-saturated 1 mol L^{-1} H_2SO_4 solution for 20 min and bubbling N_2 into the electrolyte for 30 min.

2.4. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a JEOL-2100F microscope operated at 200 kV. The Pt loading of the catalyst was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) on a Thermo Icap6300 apparatus. X-ray photoelectron spectra (XPS) were collected using an ESCALAB-250 X-ray photoelectron spectrometer with an Al K_{α} source (1486.6 eV).

3. Results and discussion

The activity of the catalyst for methanol electrooxidation was measured by CV curves in a N_2 -saturated aqueous solution of 1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} CH_3OH (Fig. 1). All CV curves present hydrogen adsorption and desorption peaks in the potential range of -0.2 to 0.1 V. The electrochemical activity can be described by the forward peak current density (i_f), which is generally regarded as the electrooxidation of methanol [26]. Zhang et al. [14] modified multiwalled carbon nanotubes with N-doped carbon quantum dots as Pt catalyst support, which achieved a current density of methanol electrooxidation of 0.42 A mg_{Pt}^{-1} . Zhang et al. [27] synthesized TiN@nitrogen-doped carbon-supported Pt nanoparticles as high-performance anode catalysts for methanol electrooxidation and obtained a current density of 0.626 A mg_{Pt}^{-1} . Zhao et al. [28] used a 3D porous N-doped graphene aerogel as support on which Pt nanoparticles were loaded, which achieved a current density of 0.544 A

Fig. 1. Cyclic voltammetric curves of commercial Pt/C and of the prepared samples at a scan rate of 50 mV s^{-1} in a $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ aqueous solution.

$\text{mg}_{\text{Pt}}^{-1}$. Zhan et al. [29] prepared titanium cobalt nitride/CNT hybrid materials on which Pt nanoparticles were anchored, and the obtained current density reached $0.92 \text{ A mg}_{\text{Pt}}^{-1}$. Herein, the I_f of the Pt/CNTs is $0.43 \text{ A mg}_{\text{Pt}}^{-1}$, which is higher than that of commercial Pt/C ($0.28 \text{ A mg}_{\text{Pt}}^{-1}$). In the N-doped carbon modified samples, the methanol electrooxidation activity first increases and then decreases as the number of PI ALD cycles increases. Particularly, the I_f of 50NC-Pt/CNTs is $0.76 \text{ A mg}_{\text{Pt}}^{-1}$, which is 2.7 times higher than that of commercial Pt/C and 1.7 times higher than that of Pt/CNTs, demonstrating a great improvement of the catalytic activity.

The Pt and N contents were measured, and the results are shown in Table 1. The Pt content is about 4 wt% in each sample. The N content increases from 0.87 to 1.51 wt% as the number of PI ALD cycles increases from 40 to 60.

The results are shown in Fig. 2. In all samples, the current density rapidly decays in the initial stage and then reaches an apparent steady state at 3600 s. This phenomenon can be explained by the poisoning of the Pt active sites by the generated intermediate species (for example, CO), and thus, methanol oxidation is largely hindered [30,31]. During the experiment, the current density of the 50NC-Pt/CNTs is always higher than that of the commercial Pt/C and Pt/CNTs catalysts. The current density of the commercial Pt/C and Pt/CNTs catalysts decreases by 91% and 96% after 3600 s, respectively, while that of the 50NC-Pt/CNTs sample decreases by 79%, implying a higher tolerance to the poisonous species generated during the methanol oxidation process.

Table 1

Physicochemical characteristics of all samples.

Sample	Pt ^a (wt%)	N ^b (wt%)
Pt/CNTs	4.38	–
40NC-Pt/CNTs	4.17	0.9
50NC-Pt/CNTs	4.16	1.08
60NC-Pt/CNTs	4.16	1.51

^a Measured by ICP-OES. ^b Measured by XPS. The long-term stability of the catalysts was investigated by chronoamperometric measurements at a constant potential of 0.6 V in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$.

Fig. 2. Chronoamperometric curves of commercial Pt/C, Pt/CNTs, and 50NC-Pt/CNTs in a $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ aqueous solution at a constant potential of 0.6 V.

The morphology and microstructure of the Pt/CNTs and 50NC-Pt/CNTs catalysts are examined by TEM. As seen in Fig. 3(a), the Pt nanoparticles are uniformly deposited on the CNTs, with a diameter of 2–3 nm for the Pt/CNTs sample. The 50PI-Pt/CNTs sample was prepared by 50 PI deposition cycles, and the PI films uniformly coat the outer face of the catalyst. The thickness of the PI films is approximately 13 nm. The PI-coated Pt/CNTs sample is then treated with a 5% H_2/N_2 mixture at 600°C . During the treatment, the PI films are pyrolyzed to form N-doped carbon nanofilms, eventually providing the 50NC-Pt/CNTs catalysts. The HRTEM image of the 50NC-Pt/CNTs sample shows that the Pt particles are covered by an N-doped carbon film with a thickness of about 1 nm. In our previous work, it revealed that the PI films shrunk extensively after pyrolysis to produce N-doped carbon nanofilms

Fig. 3. TEM images of Pt/CNTs (a), 50PI-Pt/CNTs (b), and 50NC-Pt/CNTs (c, d).

Fig. 4. CO stripping cyclic voltammetric curves of commercial Pt/C, Pt/CNTs, and 50NC-Pt/CNTs catalysts at a scan rate of 50 mV s⁻¹ in a 1 mol L⁻¹ H₂SO₄ aqueous solution.

with numerous micropores and mesopores [25]. The porous structure allows the underlying Pt NPs to be accessible to reactant molecules.

To investigate the CO tolerance ability of 50NC-Pt/CNTs, a CO stripping test was carried out. In Fig. 4, the hydrogen desorption region (−0.2 to 0.1 V) disappears in the forward scan due to the adsorption of CO molecules on the Pt surface, and a remarkable CO oxidation peak is observed (0.5 to 1 V). The onset potential of CO electrooxidation on 50NC-Pt/CNTs is shifted negatively by about 116 mV, and the peak potential shifted negatively by about 157 mV compared with the Pt/CNTs and commercial Pt/C catalysts. The lower onset potential indicates that CO is more easily removed from the catalyst surface [7]. The lower peak potential implies better activity toward CO oxidation, and thus the CO tolerance is enhanced.

The ECSA (m² g_{Pt}⁻¹) of a catalyst is estimated from the CO stripping test according to the equation $ECSA = Q_{CO} / (0.42 [Pt])$, where [Pt] represents the Pt loading (mg cm⁻²) on the electrode, Q_{CO} is the total charge for CO oxidation (mC cm⁻²), and the constant 0.42 represents the charge required to oxidize a mon-

olayer of CO on a Pt surface. The ECSA of the Pt/CNTs sample (184 m² g_{Pt}⁻¹) is higher than that of commercial Pt/C (80 m² g_{Pt}⁻¹) due to the ultrafine Pt nanoparticles synthesized by ALD. After modification with N-doped carbon, the ECSA of 40NC-Pt/CNTs, 50NC-Pt/CNTs, and 60NC-Pt/CNTs decreases to 126, 93, and 81 m² g_{Pt}⁻¹, respectively. Moreover, as the thickness of the N-doped carbon films increases, the ECSA decreases owing to the occupation of the Pt surfaces by the N-doped carbon films. Though the ECSA decreases on the 40NC-Pt/CNTs and 50NC-Pt/CNTs samples, the activity for methanol electrooxidation is largely improved compared to Pt/CNTs, implying that the interface between Pt and the N-doped carbon films plays an important role in methanol electrooxidation. The N-doped carbon film in the 60NC-Pt/CNTs sample is too thick, causing the catalytic activity to decrease.

To further study the atomic composition and chemical states of the catalyst surface, XPS measurements were conducted. The N 1s spectrum of 50NC-Pt/CNTs is shown in Fig. 5(a). The N content calculated from the XPS measurement is 1.08 wt%, and the spectrum is fitted into three main peaks. The peaks near 401.5, 400.5, and 398.7 eV are assigned to quaternary N, pyrrolic N, and pyridinic N, respectively [32].

To investigate the electronic structure of Pt, the Pt 4f region of the Pt/CNTs and 50NC-Pt/CNTs samples was measured, and the corresponding XPS spectra are shown in Fig. 5(b). The Pt 4f XPS spectrum contains two peaks corresponding to the Pt 4f_{7/2} and 4f_{5/2} states from the spin-orbit splitting. The peak intensity of the 50NC-Pt/CNTs sample is lower than that of the Pt/CNTs sample, which is due to the N-doped carbon occupying the Pt surface. Moreover, the interaction between Pt and the N-doped CNTs reduces the electron density of the Pt atoms, causing the Pt 4f peaks to shift to a higher binding energy. The σ-π bond of Pt-CO, which depends on electron back-donation from Pt, is thus weakened in the 50NC-Pt/CNTs [33,34]. In other words, CO adsorption on Pt in the 50NC-Pt/CNTs sample is not as strong as that in the Pt/CNTs sample. Therefore, the CO molecules can be more easily removed, and the activity and stability of the 50NC-Pt/CNTs catalyst is enhanced.

Fig. 5. XPS spectra of N 1s of 50NC-Pt/CNTs (a) and Pt 4f of Pt/CNTs and 50NC-Pt/CNTs (b).

4. Conclusions

We have successfully synthesized N-doped carbon modified Pt/CNTs by ALD. The thickness of the N-doped carbon films can be precisely controlled by adjusting the number of ALD cycles. The catalyst exhibits superior activity and long durability in the methanol electrooxidation reaction. The interface between Pt and the N-doped carbon films plays an important role in methanol electrooxidation. Furthermore, the interaction between Pt and the N-doped carbon weakens the Pt-CO bond, and CO adsorption on Pt surface is weakened. Therefore, both the activity and durability of the catalyst for the methanol electrooxidation reaction are significantly improved. Modifying the surface of the Pt particles and adjusting the electronic environment of the Pt atoms through ultrathin coating by ALD can be extended to other catalysts.

References

- [1] J. Y. Cao, X. J. Yin, L. D. Wang, M. W. Guo, J. Xu, Z. D. Chen, *Int. J. Hydrogen Energy*, **2015**, 40, 2971–2978.
- [2] M. Winter, R. J. Brodd, *Chem. Rev.*, **2004**, 104, 4245–4269.
- [3] S. Mondal, S. Malik, *J. Power Sources*, **2016**, 328, 271–279.
- [4] M. Wang, Z. W. Wang, L. Wei, J. W. Li, X. S. Zhao, *Chin. J. Catal.*, **2017**, 38, 1680–1687.
- [5] M. M. Liu, Y. Z. Lu, W. Chen, *Adv. Funct. Mater.*, **2013**, 23, 1289–1296.
- [6] A. U. Nilekar, K. Sasaki, C. A. Farberow, R. R. Adzic, M. Mavrikakis, *J. Am. Chem. Soc.*, **2011**, 133, 18574–18576.
- [7] L. X. Ding, A. L. Wang, G. R. Li, Z. Q. Liu, W. X. Zhao, C. Y. Su, Y. X. Tong, *J. Am. Chem. Soc.*, **2012**, 134, 5730–5733.
- [8] B. E. Hayden, *Acc. Chem. Res.*, **2013**, 46, 1858–1866.
- [9] Y. N. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.*, **2009**, 48, 60–103.
- [10] S. An, J. H. Park, C. H. Shin, J. Joo, E. Ramasamy, J. Hwang, J. Lee, *Carbon*, **2011**, 49, 1108–1117.
- [11] B. Choi, W. H. Nam, D. Y. Chung, I. S. Park, S. J. Yoo, J. C. Song, Y. E. Sung, *Electrochim. Acta*, **2015**, 164, 235–242.
- [12] J. Y. Cao, M. W. Guo, J. Y. Wu, J. Xu, W. C. Wang, Z. D. Chen, *J. Power Sources*, **2015**, 277, 155–160.
- [13] P. P. Patel, M. K. Datta, P. H. Jampani, D. Hong, J. A. Poston, A. Manivannan, P. N. Kumta, *J. Power Sources*, **2015**, 293, 437–446.
- [14] J. J. Zhang, Z. B. Wang, C. Li, L. Zhao, J. Liu, L. M. Zhang, D. M. Gu, *J. Power Sources*, **2015**, 289, 63–70.
- [15] T. B. Zhou, H. Wang, J. Key, S. Ji, V. Linkov, R. F. Wang, *RSC Adv.*, **2013**, 3, 16949–16953.
- [16] X. F. Jiang, X. B. Wang, L. M. Shen, Q. Wu, Y. N. Wang, Y. W. Ma, X. Z. Wang, Z. Hu, *Chin. J. Catal.*, **2016**, 37, 1149–1155.
- [17] Z. H. Sheng, L. Shao, J. J. Chen, W. J. Bao, F. B. Wang, X. H. Xia, *ACS Nano*, **2011**, 5, 4350–4358.
- [18] S. U. Lee, R. V. Belosludov, H. Mizuseki, Y. Kawazoe, *Small*, **2009**, 5, 1769–1775.
- [19] T. Susi, A. Kaskela, Z. Zhu, P. Ayala, R. Arenal, Y. Tian, P. Laiho, J. Mali, A. G. Nasibulin, H. Jiang, G. Lanzani, O. Stephan, K. Laasonen, T. Pichler, A. Loiseau, E. I. Kauppinen, *Chem. Mater.*, **2011**, 23, 2201–2208.
- [20] M. H. Wang, Z. Gao, B. Zhang, H. M. Yang, Y. Qiao, S. Chen, H. B. Ge, J. K. Zhang, Y. Qin, *Chem. Eur. J.*, **2016**, 22, 8438–8443.
- [21] Z. Gao, M. Dong, G. Z. Wang, P. Sheng, Z. W. Wu, H. M. Yang, B. Zhang, G. F. Wang, J. G. Wang, Y. Qin, *Angew. Chem. Int. Ed.*, **2015**, 54, 9006–9010.
- [22] J. L. Lu, B. S. Fu, M. C. Kung, G. M. Xiao, J. W. Elam, H. H. Kung, P. C. Stair, *Science*, **2012**, 335, 1205–1208.
- [23] J. W. Li, B. Zhang, Y. Chen, J. K. Zhang, H. M. Yang, J. W. Zhang, X. L. Lu, G. C. Li, Y. Qin, *Catal. Sci. Technol.*, **2015**, 5, 4218–4223.
- [24] J. K. Zhang, C. Q. Chen, S. Chen, Q. M. Hu, Z. Gao, Y. Q. Li, Y. Qin,

Graphical Abstract

Chin. J. Catal., 2018, 39: 1038–1043 doi: 10.1016/S1872-2067(18)63066-9

N-doped carbon modified Pt/CNTs synthesized by atomic layer deposition with enhanced activity and stability for methanol electrooxidation

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Uniform polyimide films are deposited on the outer face of a Pt/CNTs catalyst by atomic layer deposition. After pyrolysis, polyimide films are converted to porous N-doped carbon films. By precisely adjusting the thickness of the polyimide films, the optimized 50NC-Pt/CNTs catalyst shows 1.7-fold enhancement in activity in the methanol electrooxidation reaction.

- Catal. Sci. Technol.*, **2017**, 7, 322–329.
- [25] P. Yang, G. Z. Wang, Z. Gao, H. Chen, Y. Wang, Y. Qin, *Materials*, **2013**, 6, 5602–5612.
- [26] X. L. Sui, Z. B. Wang, C. Z. Li, J. J. Zhang, L. Zhao, D. M. Gu, S. Gu, *J. Mater. Chem. A*, **2015**, 3, 840–846.
- [27] J. Zhang, L. Ma, M. Y. Gan, S. Fu, Y. Zhao, *J. Power Sources*, **2016**, 324, 199–207.
- [28] L. Zhao, X. L. Sui, J. L. Li, J. J. Zhang, L. M. Zhang, Z. B. Wang, *Catal. Commun.*, **2016**, 86, 46–50.
- [29] G. H. Zhan, Z. G. Fu, D. L. Sun, Z. C. Pan, C. M. Xiao, S. K. Wu, C. Chen, G. H. Hu, Z. G. Wei, *J. Power Sources*, **2016**, 326, 84–92.
- [30] X. W. Teng, X. Y. Liang, S. Rahman, H. Yang, *Adv. Mater.*, **2005**, 17, 2237–2241.
- [31] W. L. Xu, T. H. Lu, C. P. Liu, W. Xing, *J. Phys. Chem. B*, **2005**, 109, 14325–14330.
- [32] Y. Chen, Z. Gao, B. Zhang, S. C. Zhao, Y. Qin, *J. Power Sources*, **2016**, 315, 254–260.
- [33] H. Igarashi, T. Fujino, Y. M. Zhu, H. Uchida, M. Watanabe, *Phys. Chem. Chem. Phys.*, **2001**, 3, 306–314.
- [34] H. H. Wang, S. M. Chen, C. D. Wang, K. Zhang, D. B. Liu, Y. A. Haleem, X. S. Zheng, B. H. Ge, L. Song, *J. Phys. Chem. C*, **2016**, 120, 6569–6576.

原子层沉积制备掺氮碳膜修饰的 Pt/CNTs 实现甲醇高效电催化氧化

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摘要: 甲醇燃料电池作为一种清洁、高效的能源转化形式广受关注。贵金属 Pt 是甲醇燃料电池阳极催化剂不可缺少的活性组分, 但 Pt 价格昂贵, 易与 CO 等中间体强相互作用而中毒失活, 从而限制了甲醇燃料电池的广泛应用。因此, 如何提高 Pt 的利用率成为一个关键问题。研究表明, 在碳材料载体中掺杂氮元素, 改变了载体本身的表面结构和电子性质, 有利于 Pt 颗粒的成核和生长, 可获得尺寸小、分布均匀的 Pt 纳米颗粒, 能显著提升催化反应活性和 Pt 利用率。然而, 传统的氮掺杂方法需要在高温、高压及氨气条件下进行, 增加了催化剂制备难度和成本。

原子层沉积技术是逐层超薄沉积技术, 能够在原子级别精确控制膜的厚度, 既可制备尺度均一、高度可控的纳米粒子, 也能实现材料表面的可控超薄修饰。本课题组利用原子层沉积技术优势, 首先在碳纳米管表面沉积了直径 2 nm 左右的 Pt 纳米颗粒, 然后在 Pt 纳米颗粒外表面超薄修饰聚酰亚胺膜, 通过后处理得到多孔掺氮碳膜修饰的 Pt/CNTs 催化剂。碳膜的厚度可简单通过调控聚酰亚胺膜的沉积厚度来控制。结果表明, 适当厚度的碳膜修饰 Pt/CNTs 催化剂可显著提升其甲醇电氧化性能, 电流密度可达商业 20% Pt/C 的 2.7 倍, 催化剂稳定性也显著改善。然而碳膜修饰过厚会导致催化活性降低。通过计算催化剂电化学活性表面积发现, 超薄修饰碳膜后催化剂活性表面积有所降低, 这是由于碳膜的覆盖导致表面 Pt 原子数减少。修饰前后催化剂颗粒尺度变化不大, 推测催化活性的提高与形成了有利于催化反应的 Pt-碳膜界面有关。然而, 当碳膜修饰层过厚时, 会导致反应物分子难以扩散到 Pt 颗粒表面, 使催化活性降低。预吸附单层 CO 溶出实验结果表明, 多孔掺氮碳膜超薄修饰 Pt/CNTs 催化剂后, CO 氧化峰的起始电位和峰值电位都向低电位处偏移, 这表明 Pt 表面吸附的 CO 在较低电位下即可被氧化, CO 更容易从 Pt 表面移除, 从而提高了催化剂的抗 CO 毒化能力。X 射线光电子能谱实验结果进一步表明, 经多孔掺氮碳膜修饰后, Pt 的 4f 电子向高结合能处偏移, 表明 Pt 原子周围的电子密度减小, 从而弱化了 Pt 对 CO 吸附的 $\sigma-\pi$ 键反馈作用, 即减弱了 Pt 原子对 CO 的吸附, 这是导致掺氮碳膜修饰后催化剂活性及稳定性都大幅提高的原因。

关键词: 原子层沉积; 甲醇电氧化; 铂纳米粒子; 氮掺杂碳

收稿日期: 2017-12-28. 接受日期: 2018-02-20. 出版日期: 2018-06-05.

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基金来源: 国家自然科学基金 (21403272, 21673269); 山西省自然科学基金 (2015021046).

本文的电子版全文由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).