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Article

Pt/MoO₃-WO₃/CNTs catalyst with excellent performance for methanol electrooxidation

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ABSTRACT

A composite Pt-based catalyst was prepared by loading MoO₃ and WO₃ nanoparticles onto carbon nanotubes (Pt/MoO₃-WO₃/CNTs). There was a uniform nanoparticle distribution with small particle sizes. This was achieved through an *in situ* self-assembly method using poly(diallyldimethylammonium chloride) as a linker and through subsequent immobilization of the Pt using ethylene glycol as a reducing agent. The total amount of oxide in the CNTs was 10 wt%, and when the molar ratio of MoO₃ to WO₃ was 1:0.5, Pt/MoO₃-WO₃/CNTs showed the highest activity for the electrocatalytic oxidation of methanol with forward peak current of 835 A/g_{Pt}. Because MoO₃ and WO₃ improve the electrocatalytic activity for methanol, CO oxidation ability, and the durability of the catalyst, the Pt/MoO₃-WO₃/CNTs catalyst exhibited excellent performance for the electrocatalytic oxidation of methanol.

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1. Introduction

Direct methanol fuel cells (DMFCs) are clean and highly efficient electrochemical energy conversion system. DMFCs have the advantages of being quick to recharge, high energy density, easy to carry, and environmentally friendly and thus have great potential in the portable power field [1–3]. As the anode catalyst of DMFCs, Pt-based alloy catalysts have shown better electrocatalytic activity and stability than pure Pt catalysts [4–7]. However, Pt is scarce and expensive, and so it is important to improve the electrocatalytic activity and usage ratio of Pt-based catalysts.

In recent years, metal oxide-modified Pt based catalysts such as Pt-RuO₂ [8], Pt-SnO₂ [9], Pt-CeO₂ [10], Pt-WO₃ [11], and Pt-MoO₃ [12] have drawn attention as they can improve catalyst stability and enhance electrocatalytic oxidation activity for

methanol. Among these oxide-modified catalysts, MoO₃- or WO₃-modified Pt can improve hydrogen and CO overflow from Pt to MoO₃ or WO₃. This allows the exposure of the active sites occupied by hydrogen to take part in the methanol oxidation reaction, which enhances the electrocatalytic activity in methanol oxidation [13–15]. Moreover, MoO₃ can also improve the catalyst's resistance to poisons, such as CO, through the dual functional effect [16]. However, it is difficult to synthesize oxide nanoparticles with a uniform distribution on a carbon support, especially for WO₃ and MoO₃ because of the difficulty of adsorbing the anion precursors onto a negative carbon support due to the dissociation of the functional groups attached onto the carbon support. There is a need for a simple way to prepare a WO₃- and MoO₃-modified Pt-based anode catalyst to improve the performance of Pt-based catalysts in the electrocatalytic oxidation of methanol.

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Recently, an *in situ* self-assembly technique using poly(diallyldimethylammonium chloride) (PDDA) as a linker has shown to have many advantages for catalyst preparation [17–19]. The positive charge on the surface of the PDDA modified carbon material allowed for negatively charged metal anion precursors to be adsorbed easily onto the carbon support. He *et al.* [20] prepared a high dispersion Pt/graphene catalyst with the average particle size of the Pt of 1.9 nm using the *in situ* self-assembly technology.

In this work, MoO₃ and WO₃ nanoparticles were immobilized uniformly onto carbon nanotubes (CNTs) by PDDA self-assembly. This was followed by the loading of Pt onto the nanoparticles modified CNTs through the use of ethylene glycol as a reducing agent to obtain the Pt/MoO₃-WO₃/CNTs. The morphology, structure, and electrocatalytic performance for methanol oxidation of this composite were investigated.

2. Experimental

2.1. Catalyst preparation

Carbon nanotubes were purchased from Shenzhen Nanotechnology Port with the purity of 95% and diameter 40–60 nm and length 5–15 μm . All of the solutions were prepared with deionized water with a resistivity of at least 18 M Ω cm. All of the other reagents used in this work were of analytic grade and were used without any further treatment.

Prior to the preparation of the catalyst, the CNTs were treated with nitric acid at 140 °C for 2 h to increase their hydrophilicity. A dispersion comprising 200 mg of pretreated CNTs, 200 mL of 0.5 wt% PDDA solution, and 1.0 g NaCl was prepared in a 500 mL round bottom flask. After ultra-sonication for 2 h, the dispersion was stirred continuously for 24 h. The dispersion was washed three times with deionized water and collected by filtering to obtain PDDA/CNTs. The pre-fixed proportion of phosphotungstic acid solution (10 mg/mL) and phosphomolybdic acid solution (6 mg/mL) was added to the PDDA/CNTs (40 mg) in 30 mL of deionized water, and the mixture was stirred continuously for 5 h. The suspension was centrifuged and dried after washing three times with deionized water. The precipitate was calcined at 600 °C under Ar for 2 h in a tube furnace. The sample obtained was the MoO₃-WO₃/CNTs.

For the subsequent deposition of Pt, the MoO₃-WO₃/CNTs and a hexachloroplatinic acid solution (16.4 mmol/L) were dispersed in 50 mL of ethylene glycol using ultra-sonication for 15 min. After adjusting the pH to 8.5 with a KOH/ethylene glycol solution (0.04 mol/L), the slurry was refluxed at 140 °C for 2 h. The slurry was cooled to room temperature, filtered and washed with copious amounts of deionized water. The resulting catalyst paste was dried at 70 °C in a vacuum oven overnight to obtain the Pt/MoO₃-WO₃/CNTs.

For comparison, Pt/MoO₃/CNTs and Pt/WO₃/CNTs were also prepared using the same method as that of the Pt/MoO₃-WO₃/CNTs with the addition of either MoO₃ or WO₃. The Pt content was 15 wt%, and the amount of the metal oxides was at 10 wt% in all of the catalysts.

2.2. Catalyst characterization

The morphology of the catalysts was characterized using transmission electron microscopy (TEM, JEOL, JEM 2010) operating at 200 kV. Structural characterization of the catalyst was carried out using X-ray diffraction (XRD, D/max2 IIIA spectrometer). The chemical composition of Pt, Mo, and W in the prepared catalyst was analyzed using X-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD). The spectra were corrected using the C 1s binding energy of 284.6 eV as a reference.

2.3. Electrochemical measurements

All of the electrocatalytic performance was evaluated using a computer-controlled Autolab PGSTAT30 electrochemical analyzer (Eco Chemie B. V., Utrecht, Netherlands). The catalyst-modified glassy carbon (GC) electrode ($\Phi = 4$ mm) was used as the working electrode. The preparation of the working electrode was described in our previous paper [21]. A Ag/AgCl electrode saturated with KCl and a Pt electrode were used as the reference and the counter electrodes, respectively. Cyclic voltammetry (CV) was carried out in 0.5 mol/L H₂SO₄ solution with 1.0 mol/L CH₃OH at a scan rate of 0.1 V/s from –0.1 to 0.9 V. The CO oxidation ability was tested through a CO-stripping experiment using an H₂SO₄ electrolyte with a concentration of 0.5 mol/L. Values were recorded from –0.245 to 0.9 V with a sweep rate of 0.1 V/s. The chronopotentiometry response (CP) was measured in 0.5 mol/L H₂SO₄ solution with 1.0 mol/L CH₃OH at a current density of 1.6 mA/cm². Chronoamperometric response (CA) was measured at 0 V for 2 min, and then the voltage was increased to 0.6 V for a period of 2 h. All of the electrochemical experiments were performed at 30 °C.

3. Results and discussion

Figure 1 shows the TEM images of the Pt/CNTs prepared using different conditions and the corresponding histograms of particle size distribution. The average particle sizes of the Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs were 2.62, 2.10, and 2.41 nm, respectively. The particle size distributions for these samples were more uniform on the surface of the CNTs than on the Pt/CNTs that had an average particle size of 2.72 nm. This suggests that the introduction of WO₃ and MoO₃ improves the dispersion of the Pt particles, which in turn improves the utilization rate of the Pt.

In all of the XRD patterns (Fig. 2), there was a characteristic peak of the CNTs at 26°. The peaks at $2\theta \approx 39.8^\circ$, 46.3° , 67.5° , and 81.3° were attributed to the (111), (200), (220), and (311) crystal planes of Pt, respectively [22,23]. No diffraction peaks for MoO₃ and WO₃ could be observed, indicating that they are amorphous [14,24].

The XPS spectra of Pt/MoO₃-WO₃/CNTs are presented in Fig. 3. In the Pt 4f XPS spectrum, the strong doublet at 71.6 and 74.8 eV is characteristic of metallic Pt, and the weak doublet near 72.6 and 76.0 eV was assigned to Pt(II) oxides, such as PtO or Pt(OH)₂ [25]. The peak area of metallic Pt was much larger

Fig. 1. TEM images and the corresponding histograms of particle size distribution of Pt/CNTs (a), Pt/MoO₃/CNTs (b), Pt/WO₃/CNTs (c), and Pt/MoO₃-WO₃/CNTs (d).

than that of Pt(II) oxide, which indicated that most of the Pt was in the metallic state [26]. In the Mo 3d XPS spectrum from Pt/MoO₃-WO₃/CNTs, the single pair of peaks located at about 232.4 and 235.3 eV were assigned to Mo (Mo⁶⁺) oxide (MoO₃) [16]. In the W 4f XPS spectrum from Pt/MoO₃-WO₃/CNTs, the only pair of peaks located at 35.5 and 37.5 eV were assigned to W (W⁶⁺) oxide (WO₃) [27,28]. The XPS peak intensities of W and Mo were weak as they were covered by Pt [29].

The cyclic voltammograms from the Pt/WO₃-MoO₃/CNTs with different molar ratios of MoO₃ to WO₃ (with a total concentration of 10 wt%) for the electrocatalytic oxidation of methanol are shown in Fig. 4. As shown in the figure, adding a small amount of WO₃ into Pt/MoO₃/CNTs improved the elec-

Fig. 2. XRD patterns of Pt/CNTs (1), Pt/MoO₃/CNTs (2), Pt/WO₃/CNTs (3), and Pt/MoO₃-WO₃/CNTs (4) catalysts.

Fig. 3. XPS spectra of Pt 4f, Mo 3d, and W 4f for Pt/MoO₃-WO₃/CNTs.

Fig. 4. CV curves of Pt/MoO₃-WO₃/CNTs with the MoO₃ to WO₃ molar ratios of 1:0.5 (1), 1:1 (2), 1:1.5 (3), and 1:2 (4) and the comparison with that of Pt/CNTs (5), Pt/MoO₃/CNTs (6), and Pt/WO₃/CNTs (7) in 0.5 mol/L H₂SO₄ and 1.0 mol/L CH₃OH solution.

Table 1

Results of electrochemical measurements from Pt/CNTs, Pt/MO₃/CNTs, Pt/WO₃/CNTs and Pt/MoO₃-WO₃/CNTs.

Sample	$I_f/(A/g_{Pt})$	E_{CO}/V	$EAS/(m^2/g_{Pt})$	t_{CP}/s
Pt/CNTs	335	0.52	20	15
Pt/MoO ₃ /CNTs	709	0.37	89	512
Pt/WO ₃ /CNTs	580	0.51	64	142
Pt/MoO ₃ -WO ₃ /CNTs	835	0.33	92	331

trocatalytic activity of methanol oxidation. The Pt/WO₃-MoO₃/CNTs catalyst showed the optimum electro-catalytic activity for methanol oxidation with the molar ratio of MoO₃ to WO₃ of 1:0.5. The forward peak current of Pt/MoO₃-WO₃/CNTs for the oxidation of methanol was 835 A/gPt, which was 18%, 44%, and 149% higher than that of Pt/MoO₃/CNTs (709 A/gPt), Pt/WO₃/CNTs (580 A/gPt), and Pt/CNTs (335 A/gPt), respectively. The results are listed in Table 1.

To further evaluate the CO electro-oxidizing ability of the four catalysts, the CO-stripping test was carried out as shown in Fig. 5. The electrochemical active surface (EAS) area based on

Fig. 6. Chronopotentiometry response recorded with Pt/CNTs, Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs in 0.5 mol/L H₂SO₄ and 1.0 mol/L CH₃OH solution at a current density of 1.6 mA/cm².

the area of the CO desorption peak (Q_{CO}) was obtained using the equation $EAS = Q_{CO}/([Pt] \times 0.484)$ [30]. The EAS areas of the four catalysts are listed in Table 1. The onset potentials of Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs for CO electrooxidation were 0.37, 0.51, and 0.33 V, respectively, indicating that MoO₃ improved the CO electro-oxidation more efficiently than WO₃. The EAS areas of Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs were 89, 64, and 92 m²/g, which are 4.45, 3.2, and 4.6 times that of Pt/CNTs (20 m²/g), respectively.

CP measurements are another useful approach to study the anti-poisoning ability of catalyst for the electrocatalytic oxidation of methanol. CP measurements were carried out in 0.5 mol/L H₂SO₄ and 1.0 mol/L methanol solution as shown in Fig. 6. The sustained times before the electrode potential increased to a higher value (t_{CP}) for the different catalysts are also listed in Table 1. The t_{CP} increased in the order Pt/CNTs < Pt/WO₃/CNTs < Pt/MoO₃-WO₃/CNTs < Pt/MoO₃/CNTs, indicating that MoO₃ and WO₃ can both improve the anti-poisoning ability of the Pt

Fig. 5. CO-stripping curves of Pt/CNTs, Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs in 0.5 mol/L H₂SO₄ solution.

Fig. 7. Chronoamperometric response of Pt/CNTs, Pt/MoO₃/CNTs, Pt/WO₃/CNTs, and Pt/MoO₃-WO₃/CNTs in 0.5 mol/L H₂SO₄ and 1.0 mol/L CH₃OH solution at 0.6 V.

catalyst. Additionally, MoO₃ showed more of an improvement than the WO₃. These results are in quite good agreement with the CO-stripping measurements.

The durability of the catalysts was evaluated by CA recorded at 0.6 V in 0.5 mol/L H₂SO₄ and 1.0 mol/L methanol solution as shown in Fig. 7. Although Pt/MoO₃/CNTs had a higher current density in the initial stage than Pt/WO₃/CNTs, the current density declined more quickly than that of Pt/WO₃/CNTs. This indicates that the durability of Pt/MoO₃/CNTs is inferior to that of Pt/WO₃/CNTs because WO₃ is resistant to acid [31]. Because MoO₃ can improve catalytic activity and WO₃ can improve durability, the Pt/MoO₃-WO₃/CNTs catalyst showed the highest electrocatalytic activity for the oxidation of methanol and had excellent durability.

4. Conclusions

MoO₃ and WO₃ were immobilized on CNTs by an *in situ* self-assembly technique. Pt was loaded by an ethylene glycol reduction method to prepare the Pt/MoO₃-WO₃/CNTs composite. From TEM, the Pt/MoO₃-WO₃/CNTs catalyst showed a uniform nanoparticle distribution with a smaller size than the other catalysts tested. CO adsorption voltammetric tests showed that MoO₃ can promote CO oxidation more effectively to improve the poison resistance ability of the catalyst. The introduction of WO₃ improves the durability of the catalyst by promoting acid resistance. As MoO₃ can improve the electrocatalytic activity for methanol oxidation and also CO oxidation ability, and WO₃ can improve the catalyst durability, the Pt/MoO₃-WO₃/CNTs catalyst exhibited excellent performance for the electrocatalytic oxidation of methanol. It is therefore an excellent anode catalyst for DMFCs.

References

- [1] Zhang J, Tang S H, Liao L Y, Yu W F. *Chin J Catal* (张洁, 唐水花, 廖龙渝, 郁卫飞. 催化学报), 2013, 34: 1051
- [2] Ji K, Chang G, Oyama M, Shang X Z, Liu X, He Y B. *Electrochim Acta*, 2012, 85: 84
- [3] Chu Y Y, Wang Z B, Cao J, Gu D M, Yin G P. *Fuel Cells*, 2013, 13: 380
- [4] Hsieh C T, Lin J Y. *J Power Sources*, 2009, 188: 347
- [5] Lin M L, Lo M Y, Mou C Y. *Catal Today*, 2011, 160: 109
- [6] Suntivich J, Xu Z C, Carlton C E, Kim J, Han B H, Lee S W, Bonnet N, Marzari N, Allard L F, Gasteiger H A, Hamad-Schifferli K, Shao-Horn Y. *J Am Chem Soc*, 2013, 135: 7985
- [7] Long N V, Thi C M, Yong Y, Nogami M, Ohtaki M. *J Nanosci Nanotechnol*, 2013, 13: 4799
- [8] Zhou C M, Peng F, Wang H J, Yu H, Yang J, Fu X B. *Fuel Cells*, 2011, 11: 301

Graphical Abstract

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Pt/MoO₃-WO₃/CNTs catalyst with excellent performance for methanol electrooxidation

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Pt/MoO₃-WO₃/CNTs with uniform nanoparticle distribution was prepared with poly(diallyldimethylammonium chloride). Incorporating MoO₃ and WO₃ to improve the electrocatalytic activity, CO oxidation, and durability, the Pt/MoO₃-WO₃/CNTs catalyst showed excellent performance for the electrocatalytic oxidation of methanol.

- [9] Guo D J, You J M. *J Power Sources*, 2012, 198: 127
- [10] Lin R, Cao C H, Zhang H Y, Huang H B, Ma J X. *Int J Hydrogen Energy*, 2012, 37: 4648
- [11] Cui Z M, Feng L G, Liu C P, Xing W. *J Power Sources*, 2011, 196: 2621
- [12] Guillen-Villafuerte O, Garcia G, Rodriguez J L, Pastor E, Guil-Lopez R, Nieto E, Fierro J L G. *Int J Hydrogen Energy*, 2013, 38: 7811
- [13] Cui X Z, Shi J L, Chen H R, Zhang L X, Guo L M, Gao J H, Li J B. *J Phys Chem B*, 2008, 112: 12024
- [14] Vellacheri R, Unni S M, Nahire S, Kharul U K, Kurungot S. *Electrochim Acta*, 2010, 55: 2878
- [15] Zhang J, Tu J P, Du G H, Dong Z M, Su Q M, Xie D, Wang X L. *Electrochim Acta*, 2013, 88: 107
- [16] Shin J K, Jeong S M, Tak Y, Baeck S H. *Res Chem Intermed*, 2010, 36: 715
- [17] Zhang Y F, Bo X J, Luhana C, Guo L P. *Electrochim Acta*, 2011, 56: 5849
- [18] Zhu C Z, Fang Y X, Wen D, Dong S J. *J Mater Chem*, 2011, 21: 16911
- [19] Zhang S, Shao Y Y, Yin G P, Lin Y H. *Appl Catal B*, 2011, 102: 372
- [20] He W, Jiang H J, Zhou Y, Yang S D, Xue X Z, Zou Z Q, Zhang X G, Akins D L, Yang H. *Carbon*, 2012, 50: 265
- [21] Wang H J, Yu H, Peng F, Lv P. *Electrochim Commun*, 2006, 8: 499
- [22] Wang J S, Deng X Z, Xi J Y, Chen L Q, Zhu W T, Qiu X P. *J Power Sources*, 2007, 170: 297
- [23] Huang H J, Sun D P, Wang X. *J Phys Chem C*, 2011, 115: 19405
- [24] McLeod E J, Birss V I. *Electrochim Acta*, 2005, 51: 684
- [25] Hsieh C T, Chen W Y, Chen I L, Roy A K. *J Power Sources*, 2012, 199: 94
- [26] Peng F, Zhou C M, Wang H J, Yu H, Liang J H, Yang J. *Catal Commun*, 2009, 10: 533
- [27] Chhina H, Campbell S, Kesler O. *J Electrochem Soc*, 2007, 154: B533
- [28] Wu F, Liu Y H, Wu C. *J Wuhan Univ Technol-Mater Sci Ed*, 2011, 26: 377
- [29] Zhou C M, Wang H J, Liang J H, Peng F, Yu H, Yang J. *Chin J Catal* (周春梅, 王红娟, 梁家华, 彭峰, 余皓, 杨剑. 催化学报), 2008, 29: 1093
- [30] Zhou C M, Wang H J, Peng F, Liang J H, Yu H, Yang J. *Langmuir*, 2009, 25: 7711
- [31] Lebedeva N P, Rosca V, Janssen G J M. *Electrochim Acta*, 2010, 55: 7659

具有优异甲醇催化氧化性能的Pt/MoO₃-WO₃/CNTs催化剂

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摘要: 以聚二烯丙基二甲基胺盐酸盐(PDDA)为连接剂, 采用原位自组装方式将MoO₃和WO₃负载到碳纳米管(CNTs)上, 然后通过乙二醇还原法负载Pt纳米颗粒, 得到Pt纳米颗粒均匀分布的Pt/MoO₃-WO₃/CNTs催化剂. 当氧化物总量控制在10 wt%, MoO₃与WO₃摩尔比为1:0.5时, Pt/MoO₃-WO₃/CNTs催化剂催化甲醇氧化活性最高, 甲醇氧化峰电流 I_p 高达835 A/g_{Pt}. WO₃和MoO₃的加入提高了催化剂的甲醇氧化活性、抗CO中毒能力和稳定性, 使得Pt/MoO₃-WO₃/CNTs催化剂表现出优异的甲醇电催化氧化性能.

关键词: 直接甲醇燃料电池; 阳极催化剂; 铂; 氧化钼; 氧化钨; 碳纳米管; 甲醇电催化氧化; 一氧化碳氧化

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1. 前言

直接甲醇燃料电池(DMFC)作为清洁、高效的电化学能源转换系统, 具有方便、快速充电、能量密度高、携带方便和绿色环保等优点, 在移动电源领域具有广阔的应用前景^[1-3]. 作为DMFC的阳极催化剂, Pt基合金催化剂表现出较高的催化活性和较好的稳定性^[4-7]. 但是Pt资源稀缺, 价格昂贵, 因此提高Pt基催化剂的活性和利用率尤为重要.

近年来, 金属氧化物修饰的Pt催化剂, 如Pt-RuO₂^[8], Pt-SnO₂^[9], Pt-CeO₂^[10], Pt-WO₃^[11]和Pt-MoO₃^[12]等, 由于具有高的稳定性和明显的甲醇电催化氧化促进作用, 引起了越来越多的关注. 在这些氧化物中, MoO₃和WO₃修饰的Pt催化剂能改善氢和CO的溢流, 使得Pt暴露更多的活性位, 从而提高催化剂的甲醇电催化氧化活性^[13-15].

此外, MoO₃能通过双功能机理提高催化剂抗CO中毒能力^[16]. 然而, 对于氧化物, 特别是WO₃和MoO₃, 由于来源于阴离子前驱物磷酸根和磷钼酸根, 因而很难使它们均匀分散于带负电荷的碳载体上. 因此, 寻找一种简单的制备WO₃和MoO₃修饰的Pt催化剂来提高甲醇电催化氧化性能显得非常重要.

近来, 采用聚二烯丙基二甲基胺盐酸盐(PDDA)作为连接剂的原位自组装技术在催化剂制备方面的优势逐渐显现出来^[17-19]. 通过PDDA修饰的碳材料表面带正电荷, 带负电荷的金属阴离子容易吸附到碳材料表面, 从而实现原位自组装. He等^[20]采用这种原位自组装技术制备出以石墨烯为载体的高度分散的Pt催化剂, Pt的平均粒径达到1.9 nm.

本文采用PDDA修饰碳纳米管(CNTs), 然后通过原位自组装的方式制备出MoO₃-WO₃/CNTs, 再通过乙二

醇还原法负载Pt纳米颗粒, 制备出Pt/MoO₃-WO₃/CNTs 催化剂, 并对其形貌、结构和甲醇电催化氧化性能进行了详细研究。

2. 实验部分

2.1. 催化剂制备

CNTs (纯度95%, 直径20–40 nm, 长度5–15 μm) 购于深圳纳米港; 其它化学试剂均为分析纯, 无需纯化直接使用; 所有水溶液均用去离子水配制。

首先, 在140 °C下用硝酸对CNTs处理2 h以提高其亲水性。取200 mg处理后的CNTs, 200 mL PDDA溶液(0.5 wt%) 和1.0 g NaCl加入到500 mL圆底烧瓶中, 超声2 h后磁力搅拌24 h; 然后过滤, 并用去离子水洗三次, 之后干燥, 研磨, 得PDDA/CNTs。称取40 mg PDDA/CNTs, 加入相应量的10 mg/mL磷酸钼溶液、6 mg/mL磷酸钨溶液和30 mL去离子水, 磁力搅拌5 h, 离心并用去离子水洗三次, 烘干, 然后放置于管式炉中, 以Ar为保护气600 °C焙烧2 h, 得到样品MoO₃-WO₃/CNTs。将MoO₃-WO₃/CNTs与氯铂酸溶液(16.4 mmol/L)加入到50 mL乙二醇溶液中, 超声15 min, 用KOH/乙二醇溶液(0.04 mol/L)调节体系的pH值到8.5, 然后在140 °C下回流2 h, 冷却至室温后, 进行过滤、洗涤和70 °C真空干燥过夜, 得到Pt/MoO₃-WO₃/CNTs催化剂。

为便于比较, 同法制备了Pt/CNTs, Pt/MoO₃/CNTs和Pt/WO₃/CNTs。四种催化剂中Pt含量控制在15 wt%; Pt/MoO₃/CNTs, Pt/WO₃/CNTs 和 Pt/MoO₃-WO₃/CNTs 三种催化剂中金属氧化物的总量均控制在10 wt%。

2.2. 催化剂表征

催化剂形貌采用透射电镜(TEM, JEOL, JEM 2010)表征, 操作电压为200 kV。催化剂结构采用X射线衍射仪(XRD, D/max2 IIIA)表征。催化剂中元素的价态采用X射线光电子能谱(XPS, Kratos Axis Ultra-DLD)表征, 以C的1s键合能284.6 eV作为参比。

2.3. 电化学测试

所有的电化学性能采用Autolab PGSTAT30 (Eco Chemie B. V., Utrecht, 荷兰)电化学工作站以经典三电极体系在30 °C进行评价。以涂有催化剂的玻璃碳电极(Φ = 4 mm)为工作电极, KCl饱和的Ag/AgCl为参比电极, 铂丝为对电极。工作电极制备方法详见文献^[21]。催化剂的甲醇氧化活性测试主要通过循环伏安法和计时电流法在含甲醇的硫酸溶液(0.5 mol/L H₂SO₄ 和 1.0 mol/L CH₃OH)中进行。其中循环伏安测试条件为: 扫描电势

范围-0.1至0.9 V, 扫描速率0.1 V/s; 计时电流测试条件为: 在0 V下运行2 min后阶跃至0.6 V下运行2 h。催化剂抗中毒性能测试主要通过计时电位法和预吸附CO氧化法进行。在含甲醇的硫酸溶液(0.5 mol/L H₂SO₄和1.0 mol/L CH₃OH)中于1.6 mA/cm²的电流密度下进行计时电位法测试。预吸附CO氧化法测试在0.5 mol/L的H₂SO₄溶液中进行, 电势扫描范围-0.245至0.9 V, 扫描速率0.1 V/s。

3. 结果与讨论

图1为四种催化剂的TEM照片和相应的粒径分布图。由图可见, Pt/MoO₃/CNTs, Pt/WO₃/CNTs和Pt/MoO₃-WO₃/CNTs催化剂的平均颗粒粒径分别为2.62, 2.10和2.41 nm, 小于Pt/CNTs的2.72 nm, 且颗粒更为均匀。这表明MoO₃和WO₃的引入能提高Pt颗粒的分散程度, 从而有效地提高Pt的利用率。

图2是四种催化剂的XRD谱。由图可见, 所有催化剂在26°处均显示CNTs的特征衍射峰, 在 2θ = 39.8°, 46.3°, 67.5°和81.3°处出现明显的对应于Pt(111), (200), (220)和(311)晶面的特征衍射峰^[22,23]。另外, 在Pt/MoO₃/CNTs, Pt/WO₃/CNTs和Pt/MoO₃-WO₃/CNTs中并未出现MoO₃和WO₃的特征衍射峰, 表明MoO₃和WO₃可能处于无定形态^[14,24]。

图3为Pt/MoO₃-WO₃/CNTs催化剂中Pt 4f, Mo 3d及W 4f的XPS谱。在Pt 4f的XPS图中存在相对强度较大的一对峰, 结合能位于71.6和74.8 eV, 归属于单质Pt; 结合能位于72.6和76.0 eV的一对相对强度较弱的峰则归属于Pt氧化态, 如PtO和Pt(OH)₂等^[25], 金属态的峰面积明显大于氧化态的, 说明Pt主要以金属态存在于催化剂中^[26]。在Mo 3d的谱图中只存在一对峰, 位于232.4和235.3 eV, 归属于Mo氧化态(Mo⁶⁺)^[16]。在W 4f的XPS图中也只存在一对峰, 位于35.5和37.5 eV, 归属于W的氧化态(W⁶⁺)^[27,28], 由于后负载的Pt的包覆, W和Mo的XPS信号相对较弱^[29]。

图4为不同MoO₃与WO₃摩尔比的Pt/MoO₃-WO₃/CNTs样品的循环伏安图。可以看出, 向Pt/MoO₃/CNTs中添加少量WO₃有利于提高催化剂的甲醇氧化活性, 且当MoO₃与WO₃的摩尔比为1:0.5时, Pt/MoO₃-WO₃/CNTs催化剂活性最高。此时, 甲醇催化氧化的正向峰电流可达835 A/g_{Pt}, 分别较Pt/MoO₃/CNTs (709 A/g_{Pt}), Pt/WO₃/CNTs (580 A/g_{Pt})和Pt/CNTs (335 A/g_{Pt})提高了18%, 44%和149% (表1)。

为评价四种催化剂的抗CO中毒能力,进行了CO的预吸附氧化循环伏安测试,结果见图5. 根据公式 $EAS = Q_{CO}/([Pt] \times 0.484)^{[30]}$,基于CO脱附峰面积(Q_{CO})可算得电活性面积(EAS, 表1). 由图5可见, Pt/MoO₃/CNTs, Pt/WO₃/CNTs和Pt/MoO₃-WO₃/CNTs的CO氧化起始电位分别为0.37, 0.51和0.33 V, 表明在CO催化氧化过程中MoO₃的促进作用较WO₃更为明显. Pt/MoO₃/CNTs, Pt/WO₃/CNTs和Pt/MoO₃-WO₃/CNTs的电化学活性面积分别为89, 64和92 m²/g, 分别是Pt/CNTs (20 m²/g)的4.45, 3.2和4.6倍.

图6为四种催化剂在1.6 mA/cm²电流密度下在含甲醇的硫酸溶液中的计时电位曲线. 四种催化剂在电势跳跃到0.6 V前的持续时间 t_{cp} 见表1. 可以看出, t_{cp} 按以下顺序逐渐增加 Pt/CNTs < Pt/WO₃/CNTs < Pt/MoO₃-WO₃/CNTs < Pt/MoO₃/CNTs, 说明向催化剂中添加MoO₃和WO₃都能增强催化剂的抗中毒能力, 并且MoO₃对抗中毒能力的增强优于WO₃. 这与预吸附CO氧化循环伏安曲线的结果吻合较好.

采用含甲醇的硫酸溶液, 在0.6 V电位下的计时安培

测试评价了四种催化剂的稳定性, 结果见图7. 可以看出, 对于Pt/MoO₃/CNTs, 尽管在初始阶段显示出比Pt/CNTs和Pt/WO₃/CNTs更高的电流密度, 但是其下降速度明显高于Pt/WO₃/CNTs催化剂, 表明Pt/MoO₃/CNTs的稳定性不如Pt/WO₃/CNTs. 这可能是由于WO₃具有更优异的抗酸性能^[31]. 对于Pt/MoO₃-WO₃/CNTs, 由于MoO₃提高了其催化活性, WO₃提高了其稳定性, 因而该催化剂表现出最高的甲醇电催化氧化活性和优异的稳定性.

4. 结论

采用原位自组装方法制备MoO₃-WO₃/CNTs, 再通过乙二醇还原法负载Pt, 制备了Pt/MoO₃-WO₃/CNTs催化剂. 结果表明, 所制催化剂的粒径更小, 分布更加均匀. CO预吸附氧化伏安测试表明, MoO₃能在较低电位下促使CO氧化, 有效地提高了催化剂的抗中毒能力; 引入WO₃后, Pt/MoO₃-WO₃/CNTs催化剂的稳定性明显增加. 因此, Pt/MoO₃-WO₃/CNTs催化剂表现出最高的甲醇电催化氧化活性和优异的稳定性, 成为性能优异的DMFC阳极催化剂.