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High Utilization AuPt Nanoparticles Supported on MWCNTS for Methanol Electro-oxidation in Alkaline Medium

Xun GUO

Dao-jun GUO

Xin-ping QIU

Li-quan CHEN

Wen-tao ZHU

高利用率多壁碳纳米管负载金铂合金纳米粒子催化剂在碱性溶液中的甲醇电催化氧化性能研究

郭　勋[1]，郭道军[1,2]，邱新平[1*]，陈立泉[1]，朱文涛[1]

(1. 清华大学 有机光电子与分子工程教育部重点实验室,化学系,北京 100084;
2. 曲阜师范大学化学与化工学院,山东 曲阜 273165)

摘要： 使用乙二醇还原法合成了一系列高利用率多壁碳纳米管负载的金铂双金属纳米粒子电催化剂,在碱性溶液中由循环伏安和计时电流法测试该 AuPt催化剂对于甲醇氧化反应的电催化活性.透射电子显微镜、X射线衍射与 X射线能谱观测催化剂形貌,表征催化剂结构.结果表明,金铂双金属纳米粒子均匀分散在碳纳米管上,催化剂具有良好甲醇电氧化性能.实验表明 Au/Pt/MW CNTs比为 10:8:32(by mass)时,该催化剂具有最高甲醇电氧化峰电流密度与最负起始氧化电位.

关键词： 甲醇电氧化；乙二醇还原；金铂纳米粒子；多壁碳纳米管；直接甲醇燃料电池

中图分类号： O646; TM911　　　　**文献标识码：** A

直接甲醇燃料电池被认为是一种理想可移动的燃料电池系统,相对于其它类型的燃料电池系统,在质量、体积、能量密度、工作环境要求等方面具有一定的优势[1-3],但也遇到技术难题,如贵金属催化剂的高载量、催化剂低电氧化活性[4-5]、甲醇在质子交换膜的渗透[6-7]、中间产物的毒化[1,8-10]以及二氧化碳与水的管理[11]等.钌[12]和锡[13]加入可以有效增加铂的利用率,降低类一氧化碳中间产物的毒化[14].

Hanuta等证明纳米级金催化剂对于一氧化碳氧化反应具有很高的催化活性[15-17].并且金对铂基催化剂催化甲醇电氧化还具有助催化作用[18-23].合成金铂催化剂方法,如浸渍法、协同浸渍法和沉积沉淀法等,但是这些方法都比较复杂.乙二醇还原是一种简单有效的碳纳米管负载铂催化剂的制备方法[25].本文利用改进的简化一步乙二醇还原法制备多壁碳纳米管负载的金铂纳米粒子催化剂相关研究尚未见报道,AuPt/MW CNTs与 Pt/MW CNTs相比,预期对在甲醇电氧化有更高的活性.

1 实 验

1.1 AuPt/MW CNTs催化剂

载体碳纳米管使用前先用浓盐酸处理,之后为了增加其亲水性再用浓硝酸回流处理.将适量的 HAuCl·4H₂O 乙二醇溶液 (0.02 mol/L) 和 H₂PtCl·6H₂O乙二醇溶液 (0.02 mol/L)加入到 150 mL NaOH乙二醇溶液 (0.1 mol/L)中 (二乙醇被用作稳定剂和还原剂).再于混合溶液中加入处理后的多壁碳纳米管,超声分散 (15 min).加热该溶液 (130～140℃),反应 3 h冷却至室温,依次滴入 100 mL KNO₃ (0.1 mol/L)和 100 mL HCl(0.5 mol/L),搅拌 (过夜),使 AuPt纳米粒子充分负载在多壁碳纳米管载体上.产物抽滤分离,去离子水和乙醇数次清洗,真空烘干 (70℃)过夜,制得 AuPt/MW CNTs催化剂.

1.2 电化学性能测试

取上述催化剂 0.5 mg放在 15 μL Nafion乙二醇混合液 (20% Nafion、80% 乙二醇, by volume)和 65 μL去离子水中超声分散 (15 min).然后将浆料均匀涂在抛光的金片 (面积 1 cm²)上,80℃ 烘

干(2 h),制成工作电极,并与对电极铂片和参比电极饱和硫酸亚汞电极(文中所有电位均相对于此而言)组成三电极体系. 使用 PARSTAT 2273恒电位仪(PowerSuite 软件控制)测试催化剂电化学活性.

1.3　仪　器

透射电子显微镜(TEM, JEOL model JEM-2011, 200 keV)观察催化剂表面形貌. 使用含扫描电子显微镜(SEM, JEOL model JEM-6301F, 15 keV)装备的 X射线能谱仪(EDS)及带铜放射源的 Rigaku X-ray衍射仪(2θ角度区间为 10°到 90°,扫速为 8°/min 步进为 0.02°)分析催化剂元素组成结构.

2　结果与讨论

2.1　透射电子显微镜

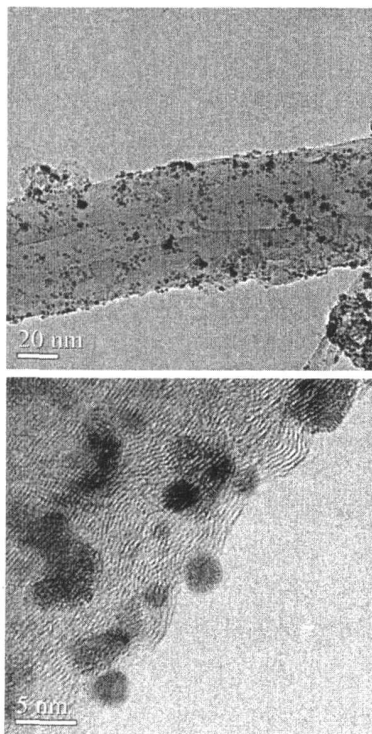图 1示出 AuPt/MWCNTs催化剂(成分见表 1的 No 6)透射电子显微镜照片. 可看出,该 AuPt催化剂形成了粒径 2~4 nm双金属纳米粒子,均匀分散在多壁碳纳米管载体上,因而具有较高的活性比表面.

图 1　AuPt/MWCNTs催化剂(表 1-No 6)透射电子显微镜照片
Fig 1　TEM images of Au/Pt/MWCNTs (Table 1-No 6)

2.2　X射线衍射图

图 2示出不同 Au、Pt配比的 AuPt/MWCNTs催化剂的 XRD图谱. 如图,在 26.2°处显示多壁碳纳米管石墨结构的特征峰,没有观测到 Au和 Pt的氧化物衍射峰. 在 38.6°、44.8°、65.6°和 78.8°处出现的衍射峰,分别与单质金(38.3°、44.6°、64.7°和 77.5°)和单质铂(39.7°、46.2°、67.4°和 81.2°)面心立方相结构相近,而且介于 Au、Pt二者的衍射峰之间,这说明 AuPt纳米粒子之形成并非金与铂之简单的混合,而确实形成了双金属纳米粒子[26-27].
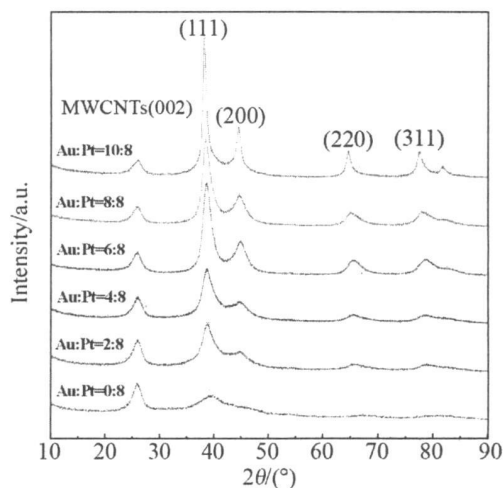
图 2　AuPt催化剂 X射线衍射图谱
Fig 2　XRD patterns of AuPt/MWCNTs catalysts
　　　Au:Pt (by mass): 10:8, 8:8, 6:8, 4:8, 2:8, 0:8

2.3　AuPt/MWCNTs催化剂电化学性能

图 3示出 AuPt/MWCNTs在 0.5 mol/L KOH溶液中的循环伏安曲线. 一般而言,可根据伏安曲线的脱附峰积分面积评价该催化剂的电化学活性. 图 3示明,不含 Au的 Pt/MWCNTs其氢脱附峰积分面积比 Au/Pt=10:8或 8:8的 AuPt/MWCNTs的小. 可见,一定量 Au的加入可在一定程度上提高该催化剂的活性,同时也增大了 Pt的利用率. 图 4同样给出在 0.5 mol/L KOH+0.5 mol/L CH₃OH溶液中,上述两种组分的 AuPt/MWCNTs催化剂,其对甲醛的电催化氧化作用(表现在氧化峰电流上)也比 Pt/MWCNTs的高. 说明,Au在这一过程中,具有很明显的助催化作用. 如上,对 AuPt/MWCNTs其 Au:Pt以 10:8为最佳.

图 3　AuPt催化剂在 0.5 mol/L KOH 电解液中的循环伏安
　　　曲线图 扫描速率: 50 mV·s^{-1}

Fig 3　Cyclic voltammograms (CV) of AuPt/MWCNTs in 0.5 mol/L KOH　scan rate: 50 mV·s^{-1}

图 4　AuPt催化甲醇氧化 E～I曲线
　　　扫描速率: 50 mV·s^{-1}

Fig 4　Cyclic voltammograms (CV) of AuPt/MWCNTs　scan rate: 50 mV·s^{-1}, electrolyte: 1 mol/L CH$_3$OH in 0.5 mol/L KOH

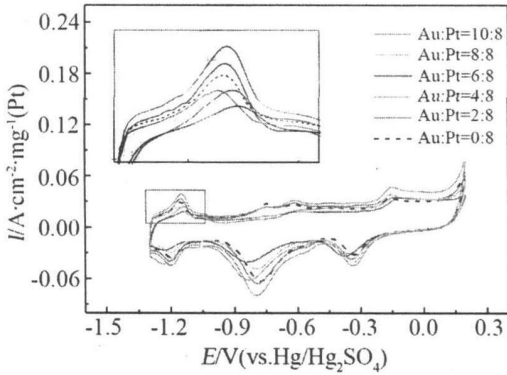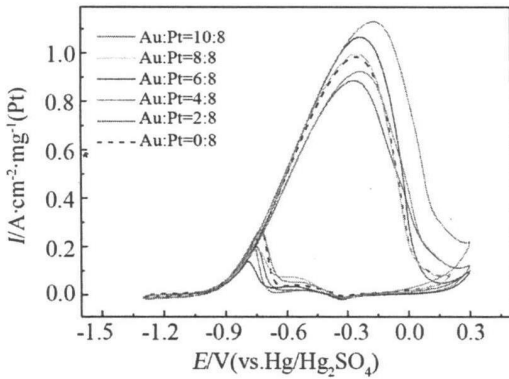图 5示出,不同 Au、Pt配比的 AuPt/MWCNTs/MwCNTs在氮饱和的 0.5 mol/L KOH ＋ 1.0 mol/L CH$_3$OH溶液中恒电位 −0.55 V计时电流曲线. 如图,在电流衰减整个过程 (1 h)中, AuPt/MWCNTs 催化剂的电流都比 Pt/MWCNTs 的更高. 说明 AuPt/MWCNTs具有更好的抗类一氧化碳中间产物 (CO$_{ads}$, CH$_3$OH$_{ads}$ and CHO$_{ads}$等)中毒的能力[28].

图 6示出,不同 AuPt配比 (by mass)的 AuPt/MWCNTs催化剂甲醇电氧化峰电流密度和起始电位的变化曲线 (见表 1).

可以看出,加入 Au形成双金属纳米粒子的催化剂可降低甲醇电氧化反应的起始电位,一定程度上提高峰电流密度.

AuPt催化剂抗类一氧化碳中间物中毒和甲醇电催化氧化的双功能反应机理[21]可表示如下:
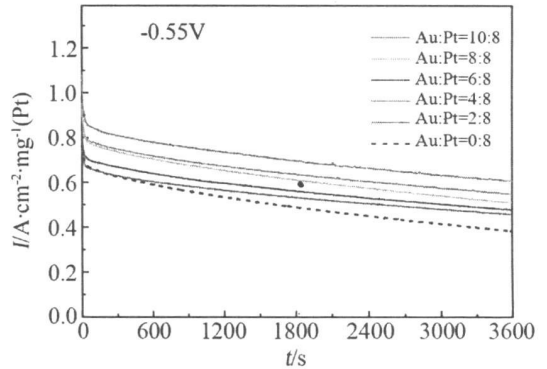
图 5　AuPt催化剂在 0.5 mol/L KOH ＋ 1 mol/L CH$_3$OH
　　　溶液中的计时电流曲线

Fig 5　Chronoamperometry curves for AuPt/MWCNTs in 1 mol/L CH$_3$OH＋0.5 mol/L KOH at −0.55 V

表 1　AuPt催化剂甲醇氧化峰电流密度和起始电位
Tab 1　Methanol electro-oxidation data of the AuPt/MWCNTs catalysts

Catalyst	No	Mass ratios	Methanol electro-oxidation	
			Peak current density/ A·cm^{-2}·mg^{-1}(Pt)	Onset potential/ V (vs Hg/Hg$_2$SO$_4$)
Au/Pt/MWCNTs	1	0:8:32	0.984	−1.01
	2	2:8:32	0.886	−1.03
	3	4:8:32	0.923	−1.02
	4	6:8:32	1.065	−1.04
	5	8:8:32	0.996	−1.05
	6	10:8:32	1.130	−1.06

$$CH_3OH + Pt \longrightarrow Pt\text{-}CO_{ads} + CO_3^-$$

$$Pt\text{-}CO_{ads} + Au \longrightarrow Au\text{-}CO_{ads} + Pt$$

$$Au + OH^- \longrightarrow Au\text{-}OH_{ads} + e^-$$

$$Pt + OH^- \longrightarrow Pt\text{-}OH_{ads} + e^-$$

$$Pt\text{-}CO_{ads} + Pt\text{-}OH_{ads} \longrightarrow CO_3^- + Pt + e^-$$

$$Pt\text{-}CO_{ads} + Au\text{-}OH_{ads} \longrightarrow CO_3^- + Pt + Au + e^-$$

$$Au\text{-}CO_{ads} + Au\text{-}OH_{ads} \longrightarrow CO_3^- + Au + e^-$$

图 6　Au/Pt 于催化剂在 0.5 mol/L KOH ＋ 1 mol/L CH$_3$OH 溶液中伏安扫描的峰电流和起始氧化电位随 Au，Pt 组成比的变化

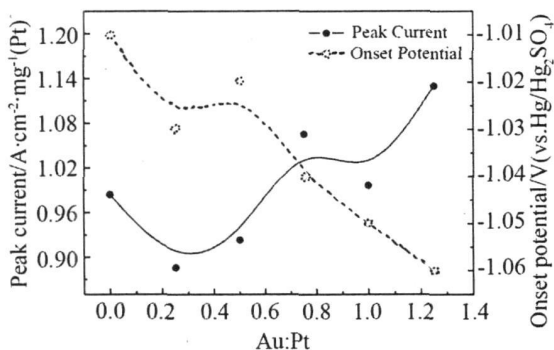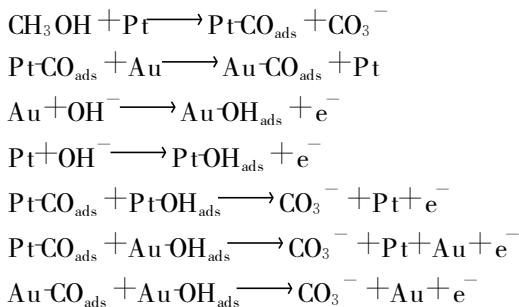Fig 6　The effect of the Au/Pt mass ratios on the peak current density and onset potential of AuPt/MWCNTs in 0.5 mol/L KOH ＋ 1 mol/L CH$_3$OH solutions catalyst Au：Pt (by mass)：10：8, 8：8, 6：8, 4：8, 2：8, 0：8

3　结　论

利用乙二醇 (稳定剂和还原剂) 液相一步合成法制备多壁碳纳米管负载 AuPt 双金属纳米粒子催化剂. AuPt/MWCNTs 催化剂具有较高的甲醇氧化峰电流密度、较低的起始电位和较好的抗类一氧化碳中间物中毒能力. 最佳催化剂 Au/Pt/MWCNTs 各元素比为 10：8：32 (by mass).

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High Utilization AuPt Nanoparticles Supported on MWCNTS for Methanol Electro-oxidation in Alkaline Medium

GUO Xun[1], GUO Dao-jun[1,2], QIU Xin-ping[1*], CHEN Li-quan[1], ZHU Wen-tao[1]

(1. Key Laboratory of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China; 2. School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China)

Abstract: We synthesized gold-platinum electrocatalysts supported on multi-walled carbon nanotubes (MWCNTs) with high utilization by a simple one-step method. A high Pt loading series of bimetallic AuPt/MWCNTs catalysts were prepared by the improved ethylene glycol reduction method, and then were compared in terms of the electrocatalytic activity for methanol electro-oxidation using cyclic voltammetry (CV) and chronoamperometry in alkaline solutions. The structure of AuPt/MWCNTs was characterized by the transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS). The results showed that the AuPt/MWCNTs catalysts had high Pt utilization, uniform AuPt nanoparticles size and good electrocatalytic activity for methanol electro-oxidation. The effect of Au/Pt mass ratio on electrocatalytic activity was also investigated. The highest peak current and lowest onset potential for methanol electro-oxidation appeared at the Au/Pt/MWCNTS mass ratio of 10:8:32.

Key words: methanol electro-oxidation; ethylene glycol reduction; AuPt nanoparticles; multi-walled carbon nanotubes; direct methanol fuel cell