

Pt/PMo₁₂/PEDOT/GC 电极的制备 及其甲醇电氧化性能

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摘要: 将磷钼酸(PMo₁₂)修饰到电化学聚合制得的聚 3,4-乙 烯二氧噻吩(PEDOT) (PEDOT/GC)膜表面 (PMo₁₂/PEDOT/GC), 随后电沉积 Pt 得 Pt/PMo₁₂/PEDOT/GC 电极. 研究了 PMo₁₂ 和 PEDOT 对电极氧化甲醇性能的影响. 结果表明, PMo₁₂ 改变了电极上负载 Pt 的形态和结构, 导致 Pt 纳米结构边缘产生尖锐的刺状结构. Pt/PMo₁₂/PEDOT/GC 和 Pt/PEDOT/GC 电极有较好的甲醇氧化电催化活性, 而前者尤佳. PEDOT 不仅提高甲醇氧化的电流, 还使甲醇的起始氧化电位负移. 进一步修饰 PMo₁₂ 后, 可明显增大甲醇氧化的电流.

关键词: 聚 3,4-乙 烯二氧噻吩; 磷钼酸; 燃料电池; 阳极催化剂; 甲醇电氧化

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聚-3,4-乙 烯二氧噻吩(PEDOT)具有良好的热与电化学稳定性^[1-5]. Patra 等^[3]以 PEDOT 覆盖的碳纸为载体恒电位沉积 Pt 制得 Pt-PEDOT/C 催化剂, PEDOT 的存在有利于改善沉积 Pt 颗粒的分散度, 从而对甲醇氧化表现出高的电催化活性和稳定性. Tintula 等^[5]以介孔碳(MC)-PEDOT 复合材料为载体化学还原制得 Pt/PEDOT-MC 催化剂, 该催化剂提高了聚合物电解质燃料电池(PEFCs)的寿命.

杂多酸是含有氧桥的多核高分子配合物、类似于分子筛的笼型结构, 易不可逆吸附于碳和金属等固体材料表面^[6-8]. 有关杂多酸修饰催化剂已有报道, 如杂多酸修饰多壁碳纳米管(MWCNTs)^[7,9]和纳米 Pt^[6,8,10]. 本文将磷钼酸(PMo₁₂)吸附于电聚合制得的 PEDOT 膜表面(PMo₁₂/PEDOT/GC), 并电沉积 Pt 得 Pt/PMo₁₂/PEDOT/GC 电极, 研究了该电极的甲醇电催化氧化性能.

1 实 验

1.1 试剂与仪器

3,4-乙 烯二氧噻吩(EDOT)(Aldrich, 分析纯); 硫酸、甲醇(分析纯); 高氯酸锂(分析纯); 乙腈(色谱纯); 磷钼酸(分析纯). 溶液均由三次蒸馏水配

制. Quanta 200 场发射环境扫描电镜 (SEM, 荷兰 Philips-FEI)配置 EDX 系统.

1.2 电 极

玻碳基底 (GC, $\phi = 5\text{ mm}$), 分别用 5、1、0.3 μm Al₂O₃ 研磨粉研磨抛光, 三次蒸馏水超声清洗, 置于 0.01 mol·L⁻¹ EDOT 与 0.01 mol·L⁻¹ 高氯酸锂的乙腈溶液中 1.5 V 电聚合 (10 min) 即得 PEDOT 膜(PEDOT/GC). 而后, 将 PEDOT/GC 电极分别置于 1、3、5、7 或 10 mmol·L⁻¹ PMo₁₂ + 0.5 mol·L⁻¹ H₂SO₄ 溶液 (5 min) 获得 PMo₁₂/PEDOT/GC, 又将该电极置于 5 mmol·L⁻¹ H₂PtCl₆ 溶液 -0.25 V 恒电位沉积 (10 min) 可得 Pt/PMo₁₂/PEDOT/GC 电极. 通过对不同 PMo₁₂ 浓度制得 Pt/PMo₁₂/PEDOT/GC 电极对甲醇氧化的活性进行比较, 发现 3 mmol·L⁻¹ PMo₁₂ 所得电极性能最佳, 本文中 Pt/PMo₁₂/PEDOT/GC 电极均在此 PMo₁₂ 浓度下制得.

负载 Pt 的量可由下式计算^[11]:

$$W_{\text{Pt}} = \frac{Q_{\text{Pt}} M_{\text{Pt}}}{Fz} \quad (1)$$

式中, Q_{Pt} 为沉积 Pt 的电量, M_{Pt} 为 Pt 原子量, F 为法拉第常数 ($9.65 \times 10^4\text{ C} \cdot \text{mol}^{-1}$), z 为 4 (Pt 电子转

移数). Pt/PMo₁₂/PEDOT/GC、Pt/PEDOT/GC 和 Pt/GC 电极的 Pt 载量分别为 0.199、0.152 和 0.115 mg·cm⁻².

1.3 电化学测试

使用 CHI660C 型电化学工作站测试电极性能. 由覆有催化层的 GC 基底工作电极、铂片对电极、饱和甘汞电极(SCE)参比、0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ 混合电解液组成三电极体系, 通氮除氧 10 min. 循环伏安测量电位扫描速率 50 mV·s⁻¹.

2 结果与讨论

2.1 扫描电镜(SEM)表征

图 1 给出 PEDOT/GC、PMo₁₂/PEDOT/GC、Pt/PEDOT/GC、Pt/PMo₁₂/PEDOT/GC 和 Pt/GC 样品的 SEM 照片. 从照片可以看出, GC 基底聚合的 PEDOT 膜呈现多孔的网状结构(图 1A), 有利于 PMo₁₂ 的吸附(图 1B)和 Pt 的沉积(图 1C), 不同基底负载 Pt 其形貌均有明显差异(图 1C、D、E). 无 PMo₁₂ 时 Pt 粒子聚集在 PEDOT 表面, 形成了一定的层状结构; 有了 PMo₁₂ 后 Pt 纳米结构边缘呈现出明显的刺状结构; 而直接沉积于 GC 基底上的 Pt 则显示不规则颗粒状纳米结构. 图 2 为 Pt/PMo₁₂/

PEDOT/GC 的 EDX 面扫描分布图, 由图可知 Pt 在样品中的分布均匀, 样品包含 Pt、S、Mo 和 O 等元素(图 2B).

2.2 电化学表征

图 3 分别为 Pt/GC、Pt/PEDOT/GC 和 Pt/PMo₁₂/PEDOT/GC 电极在 0.5 mol·L⁻¹ H₂SO₄ 溶液中的循环伏安曲线. 从图中可以看出, 三种电极 -0.2 ~ 0.05 V 电位范围均有明显的氢吸脱附电流, 显示 Pt 负载的特征. 修饰 PEDOT 后, 电极背景电流明显增大, 氢吸脱附特征发生变化. 曲线 c 在 0.17、0.34 和 0.46 V 附近有 3 对较明显的氧化还原峰, 这归属于 PMo₁₂ 不同价态 Mo 之间的氧化还原^[7-8], 说明电极表面业已吸附 PMo₁₂. Pt/PMo₁₂/PEDOT/GC、Pt/PEDOT/GC 和 Pt/GC 电极的氢吸脱附电量(Q_H)分别为 3.4、3.8 和 0.6 mC, 按下式估算其电化学活性表面积^[11]:

$$EASA = \frac{Q_H}{0.21W_{Pt}} \quad (2)$$

式中, W_{Pt} 为 Pt 载量 (mg·cm⁻²). 据上式计算得到 Pt/PMo₁₂/PEDOT/GC、Pt/PEDOT/GC 和 Pt/GC 电极的 EASA 分别为 8.13、11.83 和 2.63 m²·g⁻¹, 表明相同 Pt 载量的 PEDOT 可明显增大其活性表面积.

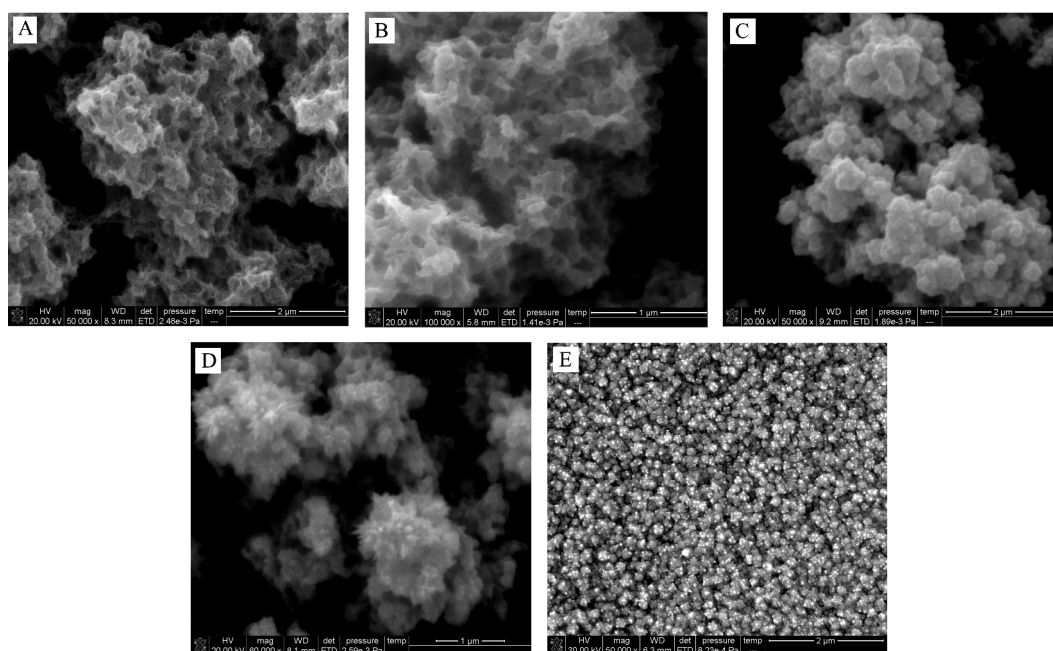


图 1 PEDOT/GC (A)、PMo₁₂/PEDOT/GC (B)、Pt/PEDOT/GC (C)、Pt/PMo₁₂/PEDOT/GC (D)和 Pt/GC (E)电极的 SEM 照片

Fig. 1 SEM images of PEDOT/GC (A), PMo₁₂/PEDOT/GC (B), Pt/PEDOT/GC (C), Pt/PMo₁₂/PEDOT/GC (D) and Pt/GC (E) electrodes

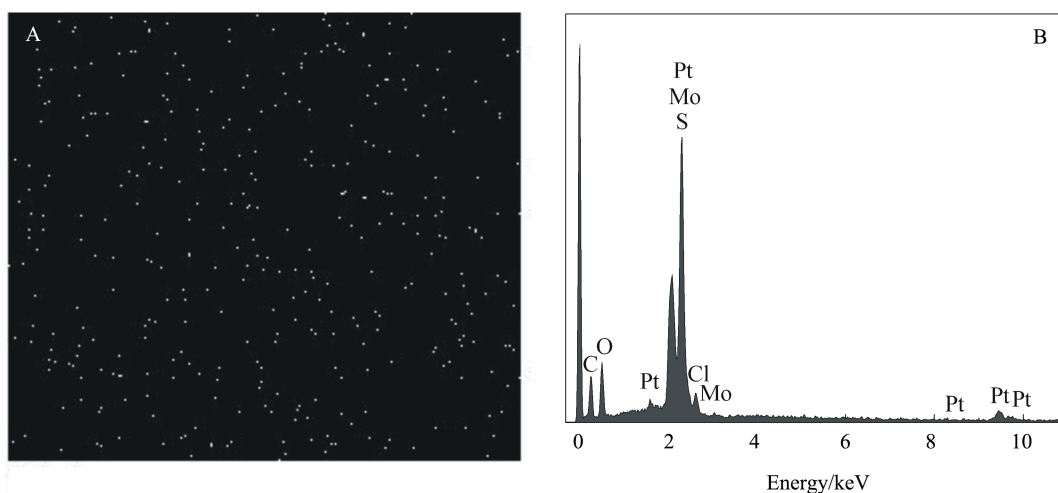


图 2 Pt/PMo₁₂/PEDOT/GC 电极的 EDX 面扫描分布图(A)及其 EDX 能谱(B)

Fig. 2 EDX mapping of Pt on PMo₁₂/PEDOT/GC support (A) and EDX spectrum of Pt/PMo₁₂/PEDOT/GC (B)

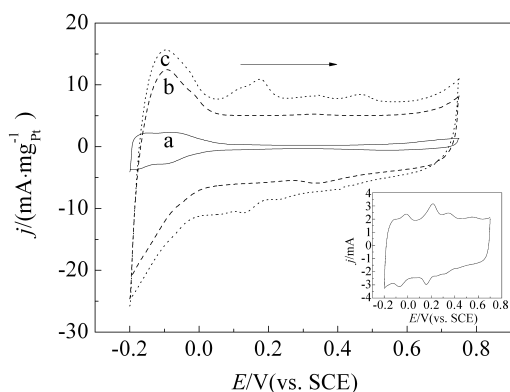


图 3 Pt/GC (a)、Pt/PEDOT/GC (b)和 Pt/PMo₁₂/PEDOT/GC (c)电极在 0.5 mol·L⁻¹ H₂SO₄ 溶液中扫描速率为 50 mV·s⁻¹ 的循环伏安曲线(插图是 PMo₁₂/PEDOT/GC 的循环伏安曲线)

Fig. 3 Cyclic voltammograms of Pt/GC (a), Pt/PEDOT/GC (b) and Pt/PMo₁₂/PEDOT/GC (c) electrodes in 0.5 mol·L⁻¹ H₂SO₄ solution at the scan rate of 50 mV·s⁻¹ (the inset is cyclic voltammogram of PMo₁₂/PEDOT/GC)

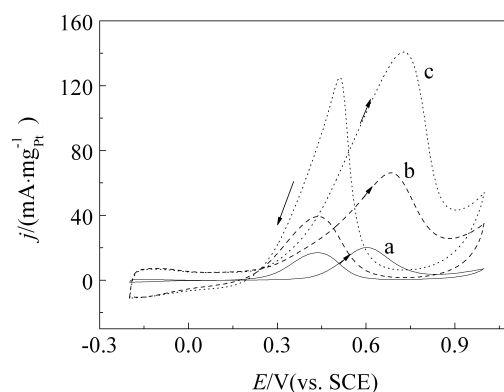


图 4 Pt/GC (a)、Pt/PEDOT/GC (b)和 Pt/PMo₁₂/PEDOT/GC (c)电极在 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ 溶液中的循环伏安曲线(扫描速率: 50 mV·s⁻¹)

Fig. 4 Cyclic voltammograms of Pt/GC (a), Pt/PEDOT/GC (b) and Pt/PMo₁₂/PEDOT/GC (c) electrodes in 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ solution (scan rate: 50 mV·s⁻¹)

2.3 电化学性能

图 4 分别给出 Pt/GC、Pt/PEDOT/GC 和 Pt/PMo₁₂/PEDOT/GC 电极在 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ 溶液中的循环伏安曲线. 由图可知, 甲醇氧化的活性顺序为: Pt/PMo₁₂/PEDOT/GC (143.3 mA·mg⁻¹) > Pt/PEDOT/GC (66.5 mA·mg⁻¹) > Pt/GC (20.6 mA·mg⁻¹). Pt/PMo₁₂/PEDOT/GC 和 Pt/PEDOT/GC 电极的甲醇起始氧化电位相近(0.17

V), 与 Pt/GC 电极上的起始氧化电位(0.34 V)相比负移了 170 mV. 表明 PEDOT 能明显提高电极的甲醇氧化活性, 而 Pt/PMo₁₂/PEDOT/GC 电极的甲醇氧化活性更优异.

图 5 给出控电位 0.5 V 时 Pt/GC、Pt/PEDOT/GC 和 Pt/PMo₁₂/PEDOT/GC 电极在 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ 溶液中的计时电流曲线. 从图 5 中可以看出, 双电层的充电电流引起初始锐电流峰, 随之电流迅速衰减, 并趋于稳定. Pt/PMo₁₂/PEDOT/GC 电极的甲醇氧化电流密度

(24.9 mA·mg⁻¹)为 Pt/PEDOT/GC 电极(9.4 mA·mg⁻¹)的 2.6 倍,为 Pt/GC 电极(1.2 mA·mg⁻¹)的 20.8 倍,其甲醇氧化活性最佳。

PEDOT 降低了 Pt 纳米粒子的尺寸,增大了其活性表面,PEDOT 和 PMo₁₂ 均具有优异的电子和离子导电性,两者的协同效应更利于该电极的导电性促进电子转移反应。PMo₁₂ 的修饰导致 Pt 边缘产生了尖锐的刺状结构,该结构可能含有高密度的原子台阶,而表现出较高的甲醇电催化氧化活性^[12-13]。PMo₁₂ 的存在增强了电极表面的亲水性,利于与甲醇等极性分子相互作用,可能起着预活化作用,扩大了电极反应活性区域^[14]。PMo₁₂ 的强氧化性有利于促进毒性中间产物(CO_{ad})的氧化,增强了抗 CO 毒化能力^[7]。

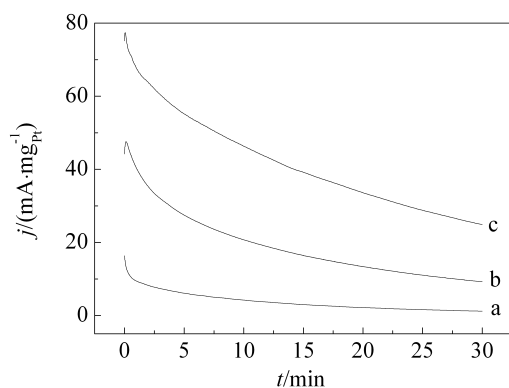


图 5 Pt/GC (a)、Pt/PEDOT/GC (b) 和 Pt/PMo₁₂/PEDOT/GC (c) 电极控电位 0.5 V 时在 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ 溶液中的计时电流曲线

Fig. 5 Chronoamperometric curves of Pt/GC(a), Pt/PEDOT/GC (b) and Pt/PMo₁₂/PEDOT/GC (c) electrodes at 0.5 V in 0.5 mol·L⁻¹ CH₃OH + 0.5 mol·L⁻¹ H₂SO₄ solution

3 结 论

将 PMo₁₂ 吸附于以玻碳(GC)为基底、电化学聚合制得的 PEDOT/GC 表面,随之又负载 Pt 制得 Pt/PMo₁₂/PEDOT/GC 电极。PMo₁₂ 改变了 Pt 的形态和结构,使其边缘产生尖锐的刺状结构。Pt/PMo₁₂/PEDOT/GC 和 Pt/PEDOT/GC 电极有较好的甲醇氧化电催化活性,而以前者尤佳。PEDOT 不仅增强了甲醇氧化的电流,还负移了甲醇的起始氧化电位。PMo₁₂ 也会增大甲醇氧化的电流。该研究对进一步改善燃料电池阳极过程催化剂的性能具有一

定的指导意义。

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Preparation and Methanol Electrooxidation of Pt/PMo₁₂/PEDOT/GC Electrodes

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Abstract: Modification of phosphomolybdic acid (PMo₁₂) on poly(3,4-ethylenedioxythiophene) (PEDOT) film (PEDOT/GC) obtained through the electrochemical polymerization was performed using adsorption method (PMo₁₂/PEDOT/GC), followed by electrodepositing Pt on PMo₁₂/PEDOT/GC, to prepare Pt/PMo₁₂/PEDOT/GC electrode. Effects of PMo₁₂ and PEDOT on the methanol oxidation performance of electrode were investigated. Results showed that PMo₁₂ obviously changed the morphology and structure of Pt loaded on the electrode, leading to the formation of sharp thorns at the edge of Pt nanostructures. Cyclic voltammetry and chronoamperometry data demonstrated that the catalytic activities of methanol electrooxidation on the Pt/PMo₁₂/PEDOT/GC and Pt/PEDOT/GC electrodes were higher than that on Pt/C, and the former exhibited the best performance. It was found that the presence of PEDOT not only increased the current, but also lowered the onset potential towards methanol oxidation. After further modification of PMo₁₂, the current of methanol oxidation was significantly increased, while the onset potential of methanol oxidation remained unaffected.

Key words: poly(3,4-ethylenedioxythiophene); phosphomolybdic acid; fuel cells; anode catalysts; methanol electrooxidation