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# 多层聚吡咯-铂复合膜电极的甲醇电催化氧化

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**摘要:** 应用循环伏安法电沉积多层聚吡咯-铂复合膜电极, 研究该电极的甲醇电催化氧化性能. 循环伏安和计时安培法测试表明, 该复合膜电极具有更好的甲醇电催化活性和抗毒性. 铂量增加, 电极反应控制步骤将由 CO 氧化转化为甲醇的吸附脱氢.

**关键词:** 甲醇氧化; 电化学催化; 聚吡咯; 循环伏安; 电沉积

**中图分类号:** O646

**文献标识码:** A

直接甲醇燃料电池(DMFC)是便携式、小型化能源存储器件之一, 有较高的能量转换效率, 但甲醇的电化学氧化速率较慢<sup>[1-2]</sup>. 铂是甲醇氧化有效的催化剂, 然而价格昂贵, 且易毒化<sup>[3]</sup>. 对此, 人们广泛开展了有关铂基二元或多元复合催化剂的研究<sup>[4-5]</sup>. 此外, 铂、铂基合金还可与导电聚合物复合, 制得复合催化剂. 利用低电位下 OH<sup>-</sup> 的生成, 促进甲醇的氧化<sup>[6-10]</sup>. 本文构建金属铂和聚吡咯(Ppy)复合膜, 研究甲醇在该电极上的电催化氧化. 结果表明, 多层聚吡咯-铂复合膜电极具有更好的甲醇电催化活性和抗毒性.

## 1 实验部分

### 1.1 试剂与仪器

吡咯(Sigma公司, 蒸馏提纯); 氯铂酸(上海试剂一厂)及其余试剂均为分析纯. 水(18.3 MΩ cm)由 Milli-Q 装置净化得到.

电化学测试使用 CHI630 电化学分析仪(上海辰华). 常规三电极体系, 工作电极为玻碳电极(GC)( $\phi$  3 mm), 对电极为螺旋型铂丝, 参比电极 Ag/AgCl/KCl(饱和). 玻碳电极使用前依次用 0.3, 0.05 和 0.01  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> 粉抛光至呈镜面, 然后用无水乙醇, 蒸馏水反复超声清洗.

### 1.2 实验

#### 1) Ppy/GC 电极

以抛光处理的玻碳电极作基底, 电解液为 0.1 mol · L<sup>-1</sup> 的吡咯和 0.5 mol · L<sup>-1</sup> 的 KNO<sub>3</sub> (pH = 1.08), 在 0.0 ~ 0.7 V 电位区间内多圈循环扫描(扫速 50 mV · s<sup>-1</sup>), 聚吡咯沉积电量达 8.24 × 10<sup>-3</sup> C 即可.

#### 2) Pt/Ppy/GC 电极

电沉积后的 Ppy/GC 电极经蒸馏水冲洗干净, 置于 0.1 mol · L<sup>-1</sup> 的氯铂酸溶液, 在 -0.2 ~ 0.5 V 电位区间内循环扫描多圈(扫速 50 mV · s<sup>-1</sup>), 制得的 Pt/Ppy/GC 电极铂电沉积电量分别为 0.1 C, 0.4 C, 0.6 C 的 Pt/Ppy/GC 电极.

#### 3) 多层 Pt/Ppy/GC 电极

将以上 Pt/Ppy/GC 电极洗净、重复多次沉积即可得多层 Pt/Ppy/GC 电极.

## 2 结果与讨论

### 2.1 聚吡咯-铂电极硫酸溶液的电化学性能

图 1 示出循环伏安电沉积聚吡咯膜的 SEM 照片. 从图看出, 聚吡咯膜呈多孔结构, 比表面较大. Pt/GC 电极、Pt/Ppy/GC 及多层复合膜电极的循环伏安曲线如图 2 所示. 图中 A, A' 峰分别表征电极上氢的吸脱附, B, B' 峰则分别对应于铂氧化物(PtO, Pt<sub>2</sub>O<sub>2</sub>) 的还原与氧化<sup>[11]</sup>. 如图, 氢的吸脱附电流和铂氧化还原电流依多层 Pt/Ppy/GC > Pt/Ppy/GC > Pt/GC 顺序增加, 表现出在同量铂沉积

情况下,前二者氢吸脱附电流和铂氧化还原电流均大于 Pt/GC 电极. 这是由于多孔结构的聚吡咯基底可提供更大的比表面. 同时,多层膜使铂更分散,从而使氢脱吸附和铂氧化还原电流达最大.

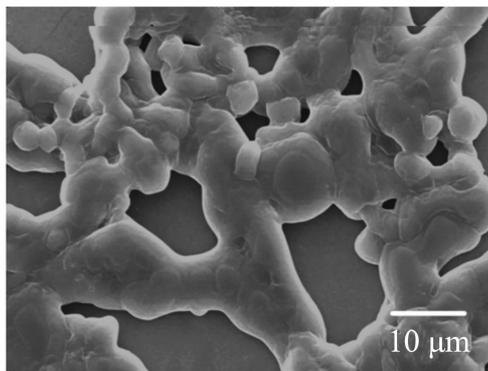


图1 Ppy 膜扫描电镜照片

Fig. 1 SEM image of Ppy film

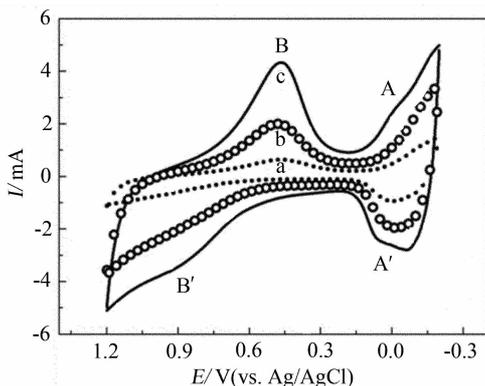


图2 Pt/GC, Pt/Ppy/GC 和多层 Pt/Ppy/GC 电极在  $\text{H}_2\text{SO}_4$  溶液中的循环伏安曲线

Fig. 2 Cyclic voltammograms of the Pt/GC (dotted line, a), Pt/Ppy/GC (circle line, b), and Pt/Ppy/Pt/Ppy/GC (solid line, c) electrode in  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$

the deposition charges for Pt and Ppy controlled at  $0.1 \text{ C}$  and  $8.24 \times 10^{-3} \text{ C}$ , scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$

## 2.2 多层 Pt/Ppy/GC 电极的甲醇电催化性能

图3 给出  $2 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  溶液中,3 种不同电极的循环伏安曲线. 从图看出,正向扫描时,在  $0.7 \sim 0.8 \text{ V}$  处呈现甲醇的氧化峰. 其中,以多层 Pt/Ppy/GC 电极的氧化电流最大, Pt/Ppy/GC, Pt/GC 电极的次之. 其氧化电位

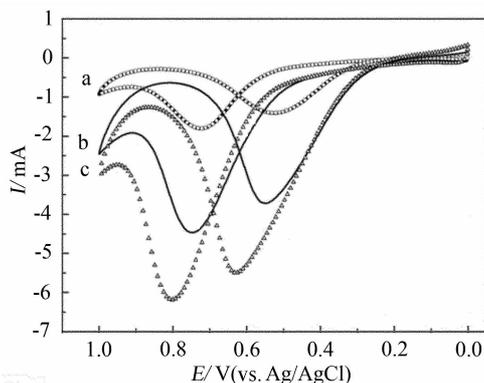


图3 Pt/GC (a), Pt/Ppy/GC (b) 和多层 Pt/Ppy/GC (c) 电极在  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  溶液中的循环伏安曲线

Fig. 3 Cyclic voltammograms of the Pt/GC (a), Pt/Ppy/GC (b), and Pt/Ppy/Pt/Ppy/GC (c) electrode in  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  (scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$ )

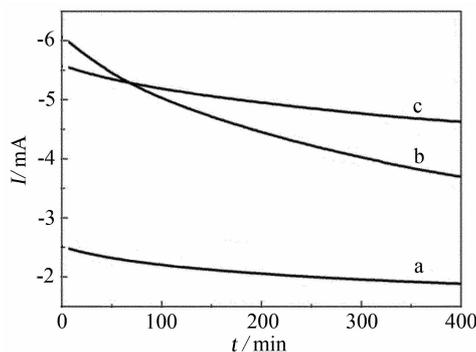


图4 Pt/GC (a), Pt/Ppy/GC (b) 和 Pt/Ppy/Pt/Ppy/GC (c) 电极在  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  溶液中  $700 \text{ mV}$  (vs. Ag/AgCl) 下的计时安培曲线

Fig. 4 Chronoamperometric curves of the Pt/GC (a), Pt/Ppy/GC (b), and Pt/Ppy/Pt/Ppy/GC (c) electrodes in  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  at  $700 \text{ mV}$  (vs. Ag/AgCl)

无明显变化,表明在相同的铂载量下, Pt/ppy/GC 电极有较好的电催化活性,这得益于聚吡咯的多孔结构,它为金属铂提供了更大的比表面,表现出聚吡咯与铂对甲醇电催化的“协同效应”. 可以推测多层的聚吡咯为金属铂提供了三维结构的载体,使其电催化性能最佳. 图4 给出3种电极计时安培法的  $I \sim t$  曲线. 如图,其甲醇氧化电流的衰减也有与图3 相似的变化趋势. 这或许可以进一步说明多层聚吡咯构建的铂电极具有更好的抗毒化作用<sup>[12]</sup>.

## 2.3 铂载量对多层聚吡咯-铂电极电催化性能的影响

图 5 示出不同铂载量的多层聚吡咯-铂电极的甲醇循环伏安曲线. 从图中看出: 甲醇氧化起始电位提前, 并在 0.6 ~ 0.8 V 和 0.8 ~ 1.0 V 的氧化峰电流随着铂载量的增加而增大, 当铂电量达 0.6 C (d) 时, 此两氧化峰也消失. 根据铂催化氧化甲醇的反应机理推断, 0.6 ~ 0.8 V 处的氧化峰是甲醇吸附中间产物的氧化, 而 0.8 ~ 1.0 V 处的氧化峰可指认为甲醇氧化, 因生成的一氧化碳及中间产物吸附在电极表面, 致使甲醇氧化更难, 电极反应步骤由 CO 的氧化转化为甲醇的吸附脱氢<sup>[13]</sup>.

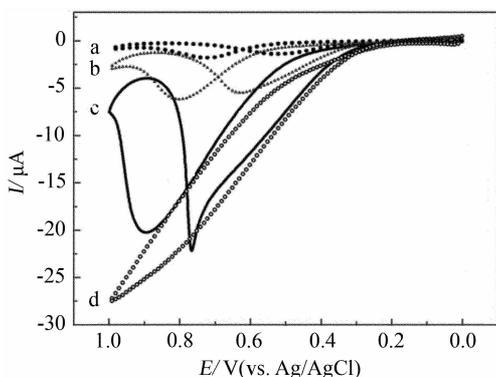


图 5 Pt/GC (a, 0.1 C) 和不同 Pt 沉积量的多层 Pt/Ppy/GC (b, 0.1 C; c, 0.4 C; d, 0.6 C) 在  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  溶液中的循环伏安曲线

Fig. 5 Cyclic voltammograms of the Pt/GC electrode (a) and Pt/Ppy/Pt/Ppy/GC electrode (b, c, d) with different monolayer depositions in  $2.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  solution charges of Pt 0.1C (a), 0.1C (b), 0.4C (c) and 0.6C (d) (scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$ )

## 3 结 论

多层聚吡咯-铂复合膜电极有更好的甲醇催化活性和抗毒化性. 铂量增加, 电极反应的控制步骤由 CO 的氧化转化为甲醇吸附脱氢.

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# Electrooxidation of Methanol on Multilayer Films of Polypyrrole-Platinum Electrode

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**Abstract:** Multilayer films of polypyrrole-platinum electrode were fabricated by cyclic voltammetric technique. Electro-oxidation of methanol on this electrode was investigated with the aid of cyclic voltammetry and chronoamperometry. Results demonstrated that the multilayer of polypyrrole-platinum electrode behaved better electrocatalytic performance for electro-oxidation of methanol and better poison resistant. Furthermore, with the increase of deposited platinum loadings, the rate controlling step on electro-oxidation reaction of methanol was changed from CO oxidation to sorption-desorption of hydrogen.

**Key words:** methanol electro-oxidation; electrocatalysis; polypyrrole; cyclic voltammetry; electrodeposition