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One-Step Synthesis of PANI/NiHCF Hybrid Film Using Unipolar Pulse Electrodeposition and Its Electrocatalytic Reduction Performance for H₂O₂ Detection

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单极脉冲一步合成聚苯胺/铁氰化镍杂化膜 及其过氧化氢电催化还原活性

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摘要: 采用单极脉冲法在铂基体表面一步合成聚苯胺/铁氰化镍 (PANI/NiHCF) 有机-无机杂化膜, 并分析了杂化膜高电势静电吸引沉积机理. 高电压聚合杂化膜避免了 $\text{Fe}(\text{CN})_6^{3-}$ 的还原, 并形成单一“不可溶”结构 NiHCF. 用扫描电镜 (SEM)、X 射线能谱仪 (EDS) 和傅立叶变换红外 (FT-IR) 光谱研究了杂化膜表面形貌及组成, 并考察了不同单极脉冲电压制得杂化膜的电化学性能. 结果表明, 单极脉冲电压 1.0 V 制得的 PANI/NiHCF 杂化膜有最佳的电活性和良好的稳定性. 使用计时电流法考察了杂化膜电极的过氧化氢 (H_2O_2) 电催化还原活性, 在 $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ KCl} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$ 电解液中, PANI/NiHCF 杂化膜电极过氧化氢催化还原电流与其浓度 ($4.0 \times 10^{-4} \sim 1.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$) 呈良好的线性关系, 相关性系数 $R = 0.9991$, 检出限为 $6.09 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, 灵敏度为 $1075 \text{ mA} \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^2$.

关键词: 单极脉冲; 聚苯胺; 铁氰化镍; 杂化膜; 过氧化氢

中图分类号: O657.1

文献标识码: A

铁氰化镍 (NiHCF) 过渡金属铁氰化物在钾离子溶液中表现出良好的结构稳定性及电化学特性, 其制备方法对结构及电化学性能有很大影响^[1]. 镍基体阳极氧化可合成单一“不可溶”结构的铁氰化镍, 而阴极还原沉积及化学沉积通常制得“可溶”和“不可溶”两种结构的铁氰化镍^[1-3]. 作者课题组^[4]曾通过单极脉冲法制备单一“不可溶”结构的铁氰化镍. 夏兴华等^[5-6]通过循环伏安法和界面电动势法制得单一“不可溶”结构的铁氰化镍, 与混合结构相比具有更好的电催化性能. 然而单一的铁氰化镍材料, 在中性溶液^[7]或含 Na^+ 水溶液中^[8]稳定性较差、电荷传递速率较低^[9-10]. PANI 有机导电高聚物有高电导率、良好的氧化还原稳定性^[11-14], 若通过化学或物理的方法合成 PANI/NiHCF 有机-无机杂化膜, 则既有有机聚合物的坚韧性、伸缩性, 同时又保留了无机固体材料的优良的力学性能、化学稳定性. 杂化膜中带正电的 PANI 与带负电的 NiHCF 之间通过静电吸引紧密地结合可显示出快速的离子传递能力和良好的化学稳定性^[9]. 此

前曾通过循环伏安法将 PANI/NiHCF 杂化膜沉积于碳纳米管修饰的铂基体上^[13,15], 但该方法很难得到单一结构的铁氰化镍. 单极脉冲电沉积已广泛应用于制备铁氰化镍^[16]、聚苯胺膜^[4,11,17]. 若用单极脉冲电聚合可避免三价铁的还原和一定程度的聚苯胺水解, 从而三价的铁氰根 ($\text{Fe}(\text{CN})_6^{3-}$) 与镍离子 (Ni^{2+}) 反应仅生成单一“不可溶”结构的铁氰化镍^[4].

本文采用单极脉冲一步合成法在铂基体上制得单一“不可溶”NiHCF 结构的 PANI/NiHCF 杂化膜, 分析了其可能成膜机理, 考察了不同单极脉冲电压制得的杂化膜的电化学性能, 并探讨其过氧化氢电催化还原活性.

1 实 验

1.1 试剂与仪器

试剂为优级纯或分析纯, 超纯水 (Millipore, $18.2 \text{ M}\Omega \cdot \text{cm}$). 使用 EC-Lab 软件控制的多通道 Princeton VMP3 恒电位仪测试电极电化学性能; 使用岛津 IRAffinity-1 工作站分析 PANI/NiHCF 杂化膜红外光谱; 使用美国 Kevex.Sigama 型能谱仪对

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杂化膜进行 EDS 与 SEM 分析。

1.2 电极预处理

将铂片(1 cm×1 cm)用氧化铝打磨成镜面,绝缘胶带固定铂片的单面(接触面积 0.5 cm²,计时电流和过氧化氢催化活性测试所用铂片有效工作面积为 4.5 mm²)。将铂电极置于 1.0 mol·L⁻¹ H₂SO₄ 溶液电化学清洗,以扫描速率 50 mV·s⁻¹ 在 -275 ~ 1675 mV 电压范围循环扫描 50 周期清洁表面,纯水冲洗晾干备用。

1.3 杂化膜的制备

在铂片工作电极、饱和甘汞电极(SCE)参比电极、铂丝对电极及含 0.005 mol·L⁻¹ NiCl₂、0.1 mol·L⁻¹ KCl、0.005 mol·L⁻¹ KHCF、0.05 mol·L⁻¹ 苯胺、0.1 mol·L⁻¹ HCl 电解液的三电极体系调控单极脉冲一步共聚,脉冲电压分别为 0.8、0.9、1.0 和 1.1 V,脉冲时间 0.4 s,占空比 50%,聚合周期 1200 次。

单一 PANI、NiHCF 膜也采用相同参数制备。单一 PANI 制膜电解液:0.1 mol·L⁻¹ KCl、0.05 mol·L⁻¹ 苯胺、0.1 mol·L⁻¹ HCl; 单一 NiHCF 制膜电解液:0.005 mol·L⁻¹ NiCl₂、0.1 mol·L⁻¹ KCl、0.005 mol·L⁻¹ KHCF、0.1 mol·L⁻¹ HCl。所制薄膜用超纯水冲洗干净,晾干备用。

1.4 杂化膜性能测试

PANI/NiHCF 杂化膜电极与饱和甘汞电极参比电极、铂片对电极,在 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 混合溶液测试循环伏安特性及其过氧化氢催化还原活性。在恒定转速搅拌条件下,采用计时电流法对杂化膜电极检测过氧化氢的灵敏度与检出限进行电流响应测试。

2 结果与讨论

2.1 NiHCF/PANI 膜制备

图 1 为调控 PANI/NiHCF 膜的瞬时电位(电流密度)-时间曲线(A:初始,B:平衡)。单极脉冲电压 0.9 V,脉冲时间 0.4 s,占空比 50%,脉冲次数 1200。脉冲初始瞬间,电极表面尚未电沉积 PANI/NiHCF,电极表面液/固界面双电层电容快速放电,电解池两极电压迅速下降到 0.51 V。第 1 个导通时间 t_{on} 内,苯胺单体氧化成二聚体,峰电流值瞬间增大至 0.75 mA·cm⁻²,PANI 膜开始形成。同时,在高电位静电吸引下阴离子 Fe(CN)₆³⁻ 吸附于 PANI 周围。而后,第一个截断时间 t_{off} 内,阴离子 Fe(CN)₆³⁻ 与阳离子 Ni²⁺ 反应生成铁氰化镍,由于消除额外施加电压,电压从 0.9 V 降至 0.75 V。随着膜的生长,开路电压逐渐升高至 0.83 V,并趋于稳定,而峰电流值迅速减小至 0.04 mA·cm⁻² 并趋于平稳。制备后期,电解液单体浓度降低,反应基本结束,整个体系仅为电容器充放电过程,所得的杂化膜较为均匀。

图 2 为单极脉冲调控 PANI/NiHCF 杂化膜的电沉积原理示意图。如图所示,脉冲初始瞬间铂基体聚集大量正电荷,苯胺单体被氧化成单体自由基,与此同时由于静电吸引 Fe(CN)₆³⁻ 阴离子附着于铂基体表面。随之脉冲电压持续作用下,苯胺单体自由基与苯胺单体反应形成二聚体,二聚体与其它苯胺单体自由基反应生成聚苯胺。在截断时间 t_{off} ,电极表面无施加额外电压,此时 K⁺、Ni²⁺ 阳离子聚集于电极表面与 Fe(CN)₆³⁻ 阴离子反应生成 NiHCF,此过程 Fe(CN)₆³⁻ 不被还原,而生成了单一“不可溶”结构的 NiHCF。作者课题组^[18]曾报道单一“不可溶”结构 NiHCF 相比其他结构有更优的

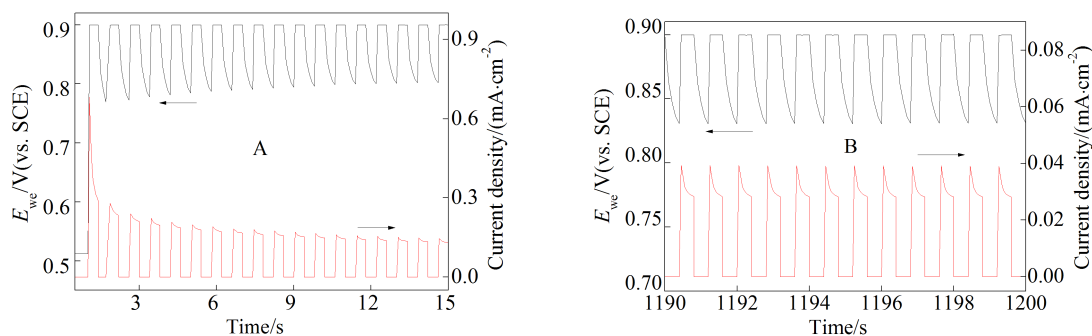


图 1 单极脉冲调控 PANI/NiHCF 膜的瞬时电位(电流密度)-时间曲线(A:初始,B:稳定)

Fig. 1 Potential (current density)-time transients of unipolar pulsed deposition of PANI/NiHCF hybrid film (A: initial period, B: stable period) in a solution of 0.005 mol·L⁻¹ NiCl₂ + 0.1 mol·L⁻¹ KCl + 0.005 mol·L⁻¹ KHCF + 0.05 mol·L⁻¹ aniline + 0.1 mol·L⁻¹ HCl. The pulse conditions include 0.9 V pulse potential, 0.4 s on-time and the duty cycles of 50%.

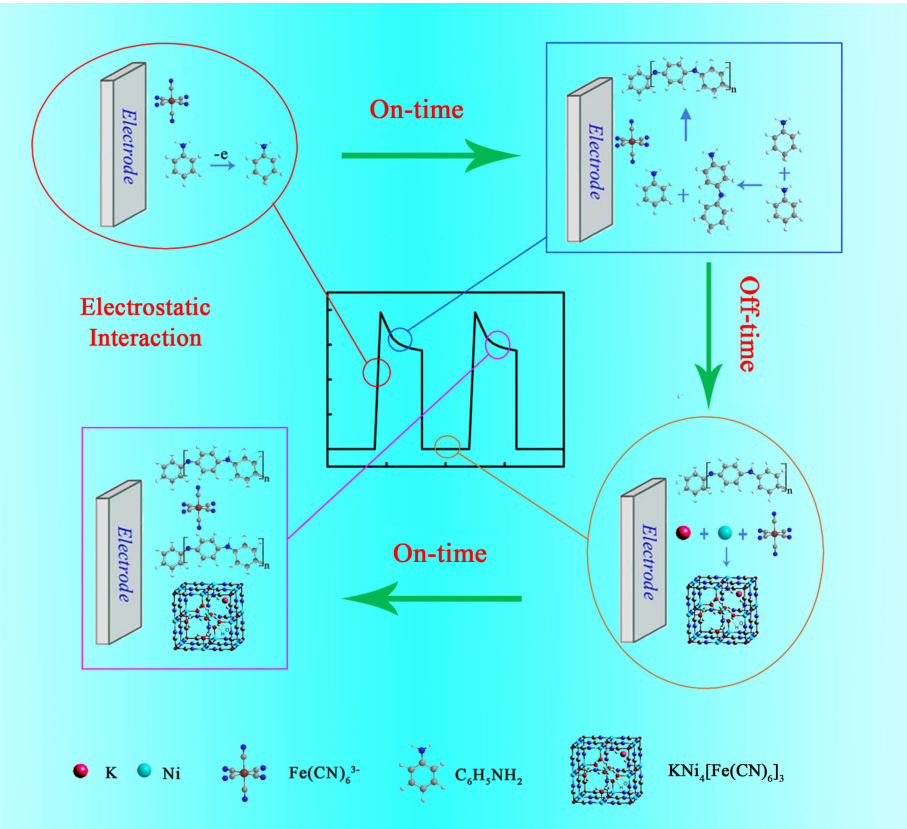


图 2 单极脉冲法调控 PANI/NiHCF 杂化膜的电沉积机理示意图

Fig. 2 Schematic representation for the deposition of PANI/NiHCF hybrid film using unipolar pulsed method

H₂O₂ 电催化活性.

2.2 PANI/NiHCF 杂化膜的组成和微观形貌分析

图 3 显示了 PANI/NiHCF 杂化膜的 SEM 图 (A)和 EDS 能谱图(B). 由图 3A 可知,杂化膜由比较均一的复合颗粒堆积而成, 构成了三维多孔结

构,暗示其具有较大的比表面积,降低了离子扩散阻力. 杂化膜 EDS 能谱中谱峰 6.39 keV 来自 Fe,谱峰 7.47 keV 来自 Ni,0.269 keV 和 0.494 keV 则可分别归因于 C 和 N, 说明杂化膜中含有 NiHCF 和 PANI 组分. 另外, 谱峰 3.30 keV 和 2.09 keV 可分别归因于电解液中 K 离子和 Pt 基体.

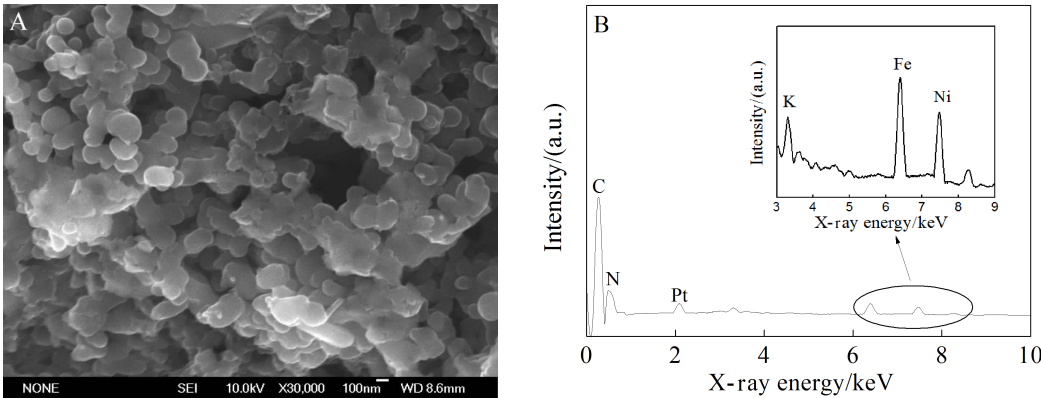


图 3 PANI/NiHCF 杂化膜的电子扫描电镜图(A)和 EDS 能谱图(B)

Fig. 3 Typical SEM image (A) and EDS spectrum (B) of PANI/NiHCF hybrid film

图 4 示出了 PANI/NiHCF 杂化膜的红外光谱图。由图可知,其 2090 cm^{-1} 峰对应于 NiHCF 的 —CN— 伸缩振动^[6]; 3440 cm^{-1} 峰对应于苯胺 N—H 伸缩振动^[19]; 833 cm^{-1} 处的吸收峰是苯环的 C—H 面外弯曲振动^[20]; 1126 cm^{-1} 处是质子化的 PANI 特征峰^[21]; 1304 cm^{-1} 和 1396 cm^{-1} 峰均对应于苯胺的 C—N 伸缩振动^[11]; 1627 cm^{-1} 和 1497 cm^{-1} 处分别对应于醌环和苯环的 C=C 键伸缩振动吸收峰^[17]; 2924 cm^{-1} 处对应于 C—H 伸缩振动^[22]。红外表征结果显示存在着 PANI 和 NiHCF 的特征峰,进一步证明杂化膜中二者同时存在。

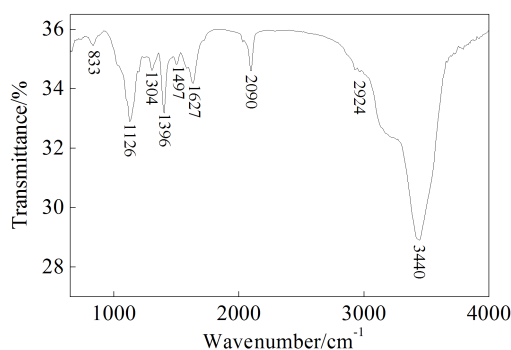


图 4 PANI/NiHCF 杂化膜的红外光谱图

Fig. 4 FT-IR spectrum of PANI/NiHCF hybrid film

2.3 PANI/NiHCF 杂化膜电化学性能

1) 膜电极循环伏安曲线

图 5 示出各膜电极在 $0.5\text{ mol}\cdot\text{L}^{-1}\text{ KCl} + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ 电解液, $50\text{ mV}\cdot\text{s}^{-1}$ 扫描速率, $-0.20 \sim 0.75\text{ V}$ 电位区间的循环伏安曲线。从图 5 看出,杂化膜在 $0.22/0.16\text{ V}$ (1) 和 $0.53/0.5\text{ V}$ (2) 左右出现两对氧化还原峰,其中峰 1 对应着 PANI 由完全还原态 (Leucoemeraldine State) 向半氧化态 (Emeraldine State) 的转化,峰 2 则对应着 NiHCF 与 PANI 的氧化还原峰电位的重叠,证明 PANI/NiHCF 杂化膜已电沉积于铂基体上。杂化膜峰电流比单一 PANI 膜和单一 NiHCF 膜的更高, PANI 与 NiHCF 之间的协同效应可明显提高杂化膜的电化学活性。

2) 脉冲电压

图 6 是不同单极脉冲电压下电沉积的 PANI/NiHCF 杂化膜电极的循环伏安曲线。单极脉冲电压 $0.8 \sim 1.0\text{ V}$ 范围内,峰电流随脉冲电压增加而逐增,单极脉冲电压高于 1.0 V 时,峰电流急剧下降。这是由于在一定单极脉冲电压范围,其单

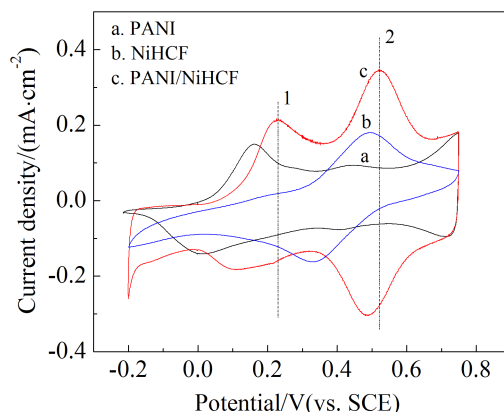


图 5 PANI、NiHCF 和 PANI/NiHCF 杂化膜电极在 $0.5\text{ mol}\cdot\text{L}^{-1}\text{ KCl} + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ 溶液中的循环伏安曲线,扫描速率: $50\text{ mV}\cdot\text{s}^{-1}$

Fig. 5 Cyclic voltammograms of different films in a solution of $0.5\text{ mol}\cdot\text{L}^{-1}\text{ KCl} + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$, scan rate: $50\text{ mV}\cdot\text{s}^{-1}$

a. PANI film; b. NiHCF film; c. PANI/NiHCF hybrid film

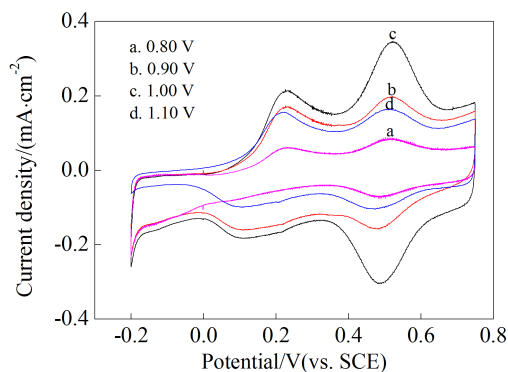


图 6 不同单极脉冲电压 (0.8 V 、 0.9 V 、 1.0 V 、 1.1 V) 电沉积的 PANI/NiHCF 杂化膜电极在 $0.5\text{ mol}\cdot\text{L}^{-1}\text{ KCl} + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ 电解液中的循环伏安曲线,扫描速率: $50\text{ mV}\cdot\text{s}^{-1}$

Fig. 6 Cyclic voltammograms of PANI/NiHCF film at different voltages in a solution of $0.5\text{ mol}\cdot\text{L}^{-1}\text{ KCl} + 0.5\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$, scan rate: $50\text{ mV}\cdot\text{s}^{-1}$

a. 0.80 V ; b. 0.9 V ; c. 1.0 V ; d. 1.1 V

极脉冲电压增加可有效地提高苯胺单体的氧化聚合速率,也相应提高了在截断时间 t_{off} 时 $\text{Fe}(\text{CN})_6^{3-}$ 阴离子由于静电吸引与氧化态的 PANI 的复合速率。由图 6 可知,在 1.0 V 下制得的杂化膜的复合峰 ($0.53/0.5\text{ V}$) 与 PANI 氧化峰 ($0.22/0.16\text{ V}$) 的峰面积及峰面积比值均为最大,说明在此电位下杂化

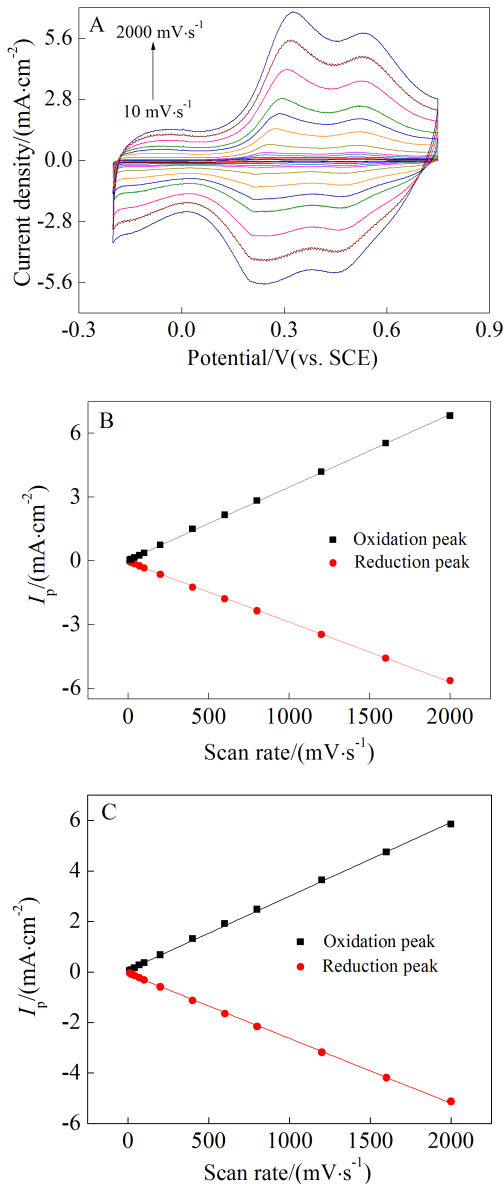


图 7 PANI/NiHCF 杂化膜电极在 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中不同扫描速率 (mV·s⁻¹: 10, 20, 40, 70, 100, 200, 400, 600, 800, 1200, 1600, 2 000) 下的循环伏安曲线 (A) 和氧化还原电位峰电流 *I_p*-*v* 曲线 (B. 低电位峰电流; C. 高电位峰电流)

Fig. 7 Cyclic voltammograms of PANI/NiHCF films at different scan rates (A) and plots of the anodic and cathodic peak currents (*I_p*) versus scan rate (B. low potential; C. high potential) Scan rates increase along with the arrow: 10, 20, 40, 70, 100, 200, 400, 600, 800, 1200, 1600, 2000 mV·s⁻¹, in 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl electrolyte solution

膜中沉积了更多的 NiHCF 和 PANI,且二者复合杂化更为充分,表现出更优异的电化学活性. 但是过

高的单极脉冲电压易使聚苯胺过氧化, 导致杂化膜电化学活性急剧下降, 故单极脉冲电压调控于 1.0 V 为宜.

3)扫描速率

图 7A 为 PANI/NiHCF 杂化膜在 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中不同扫描速率下 (10~2000 mV·s⁻¹) 的循环伏安曲线, 电位范围 -0.2~0.75 V. 由图可见, 当扫描速率加快其电流响应增加, 峰电位 (0.22/0.16 V 和 0.53/0.5 V) 基本不发生偏移, 表明杂化膜表面和内部可以发生快速的氧化还原反应, 且可逆性良好, 具有良好的离子和电子传递性能, 更利于提高杂化膜的灵敏度^[23]. 杂化膜氧化还原峰电流与扫描速率呈线性关系, 如图 7B、C 所示, 说明 PANI/NiHCF 杂化膜电子传递为表面控制过程^[24].

4)PANI/NiHCF 杂化膜电极的过氧化氢电催化性能

图 8 为 PANI/NiHCF 杂化膜在 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中添加 H₂O₂ 前后的循环伏安曲线. 由图 8 可知, 当电解液中加入 3.5 × 10⁻³ mol·L⁻¹ H₂O₂ 后还原电流明显降低, 表明杂化膜对 H₂O₂ 具有明显的催化还原活性.

图 9 为 PANI/NiHCF 杂化膜电极在 40 mL 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中连续滴加 4.0 × 10⁻⁴ 或 2.0 × 10⁻³ mol·L⁻¹ H₂O₂ 的计时电流曲线

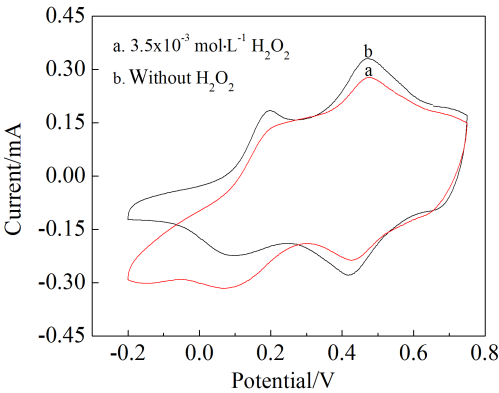


图 8 PANI/NiHCF 杂化膜电极在 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中添加 3.5 × 10⁻³ mol·L⁻¹ H₂O₂ 前(b)后(a)的循环伏安曲线

Fig. 8 Voltammetric responses of PANI/NiHCF hybrid film with (a) and without (b) the addition of 3.5 × 10⁻³ mol·L⁻¹ H₂O₂ in a solution of 0.5 mol·L⁻¹ + 0.5 mol·L⁻¹ HCl at a scan rate of 50 mV·s⁻¹

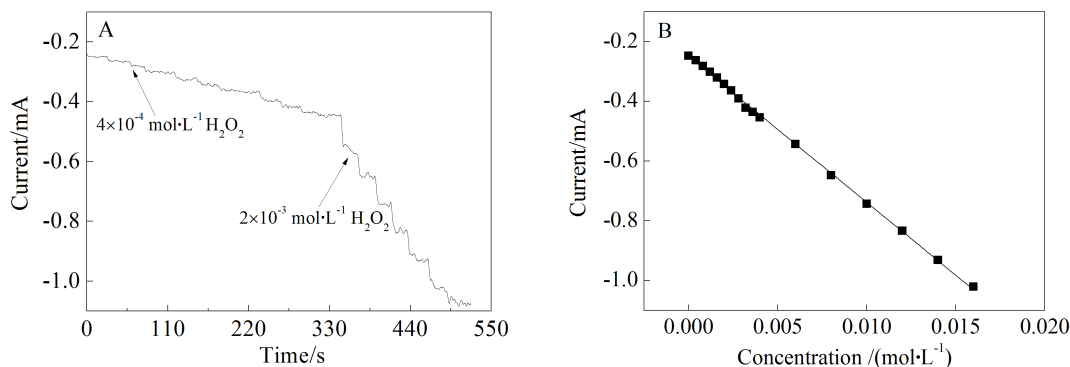


图 9 PANI/NiHCF 杂化膜电极在 40 mL 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl 电解液中连续滴加 4.0×10⁻⁴ 或 2.0×10⁻³ mol·L⁻¹ H₂O₂ 的计时电流曲线(A)和响应电流与过氧化氢浓度的校准曲线(B) 电极电位: -0.2 V(vs. SCE)

Fig. 9 Amperometric responses of the PANI/NiHCF film (A) and the calibration curve for H₂O₂ detection (B) upon successive additions of H₂O₂ (4.0×10⁻⁴ or 2.0×10⁻³ mol·L⁻¹) to the solutions of 40 mL 0.5 mol·L⁻¹ KCl + 0.5 mol·L⁻¹ HCl at an applied potential of -0.2 V (vs. SCE)

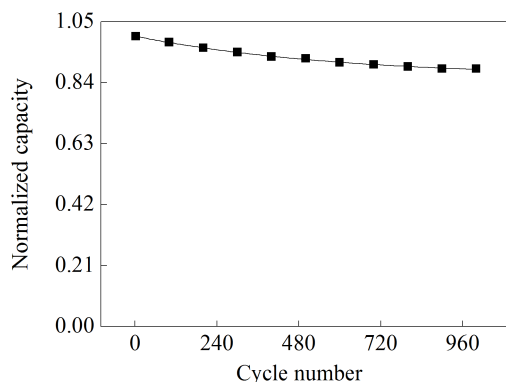


图 10 PANI/NiHCF 杂化膜电极在 0.2 mol·L⁻¹ PBS + 0.2 mol·L⁻¹ KNO₃ 电解液的循环稳定性曲线

Fig. 10 Electrochemical stability of the PANI/NiHCF film.

The data were obtained from the cyclic voltammograms of the electrode in a solution of 0.05 mol·L⁻¹ KCl + 0.05 mol·L⁻¹ PBS (pH 6.5) at a scan rate of 50 mV·s⁻¹. The capacity values were normalized by their corresponding initial capacity

(A),控制电极电位为 -0.2 V.滴入 H₂O₂,PANI/NiHCF 杂化膜电极电流变化非常显著,其响应电流与过氧化氢浓度有较好的线性关系(B),相关性系数 $R = 0.9991$,在 5 s 内其电流基本达到稳定,在 4.0×10⁻⁴ ~ 1.6×10⁻² mol·L⁻¹ 浓度范围与电流呈很好的线性关系,灵敏度为 1075 mA·(mol·L⁻¹)⁻¹·cm⁻²,检出限为 6.09×10⁻⁵ mol·L⁻¹.

5)PANI/NiHCF 杂化膜电极的稳定性与重现性

图 10 是 PANI/NiHCF 杂化膜电极的循环稳定性曲线.循环扫描 1000 周期,其电容量衰减了约

12%.在 4 组 PANI/NiHCF 杂化膜电极平行样品上滴加相同浓度 H₂O₂ 溶液,其电流响应值相近,RSD 1.5%,有较好的稳定性与重现性^[21].

3 结 论

单极脉冲一步在铂片电极上制得单一“可溶”NiHCF 结构的 PANI/NiHCF 杂化膜,在 4.0×10⁻⁴ ~ 1.6×10⁻² mol·L⁻¹ 范围内,H₂O₂ 浓度与响应电流呈线性关系,灵敏度 1075 mA·(mol·L⁻¹)⁻¹·cm⁻²,检出限 6.09×10⁻⁵ mol·L⁻¹.该杂化膜对过氧化氢有较好的电活性.

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One-Step Synthesis of PANI/NiHCF Hybrid Film Using Unipolar Pulse Electrodeposition and Its Electrocatalytic Reduction Performance for H₂O₂ Detection

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Abstract: Organic-inorganic hybrid films composed of polyaniline/nickel hexacyanoferrate (PANI/NiHCF) were fabricated on platinum substrates using unipolar pulse one-step electrodeposition. The deposition mechanism of hybrid film was proposed: Due to high potential of unipolar pulse electrodeposition, which avoided the reduction of $\text{Fe}(\text{CN})_6^{3-}$, the films with high electrocatalytic property and “insoluble” form of NiHCF were achieved. The morphology and composition of PANI/NiHCF hybrid film were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Fourier transform infrared spectroscopy (FT-IR). The effect of pulse potential on the electrochemical performance of hybrid film was investigated in detail. Results showed that pulse potential had a major impact on electroactivity and stability of the film, and the optimal deposition potential was 1.0 V. The hybrid films exhibited high electrocatalytic activity, eligible sensitivity and low detection limit in detecting hydrogen peroxide (H₂O₂). The linear range for the detection of H₂O₂ was from 4.0×10^{-4} to $1.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ with a correlation coefficient of 0.9991, a sensitivity of $1075 \text{ mA} \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^{-2}$ and a detection limit of $6.09 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$.

Key words: unipolar pulse; polyaniline; nickel hexacyanoferrate; hybrid film; hydrogen peroxide