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氟硼酸镀液二氧化铅电沉积

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摘要: 研究了在氟硼酸或其掺杂镀液中于 Pt 基底电沉积 PbO₂ 镀层的电化学和结构性质. 循环伏安测试、XRD 分析和 SEM 形貌观察表明, BF₄⁻ 可提高二氧化铅电沉积速率; 电沉积的 PbO₂ 晶型为 β-PbO₂; F⁻、Fe³⁺ 共掺杂影响晶体生长的择优取向及镀层形貌, 电沉积的 FB/F-Fe-PbO₂ 镀层整齐致密; 电沉积过程增大电流密度可改变生长晶面取向.

关键词: 二氧化铅; 电沉积; 氟硼酸; 掺杂离子

中图分类号: TQ153

文献标识码: A

二氧化铅阳极材料具有较高析氧过电位、价格低廉、性能稳定, 已广泛应用于铅酸电池^[1]、有机合成^[2-3]、臭氧制备^[4]、废水处理^[5]、传感器分析^[6]等.

然而有关 PbO₂ 阳极的基底结合力、寿命及电催化活性还有待进一步改进和提高. 国内外大量研究均致力于电沉积过程工艺条件的优化、基材材料的选择以及掺杂改性等方面^[7-10]. Pamplin K L^[11]报道, 掺 Bi³⁺ 二氧化铅电极对 Cr³⁺ 电催化氧化表现出很高的选择性. Velichenko A B 等^[10]指出: 掺 Fe³⁺ 或掺 Fe³⁺ + F⁻ 的二氧化铅电极物性与纯二氧化铅电极明显不同. Mathato 等^[12]认为 β-PbO₂ 电极中掺杂入 Ni²⁺ 后, 可降低析氧过电位. 美国专利^[13]指出, 镀液中加入 Ni²⁺ 后, 可使表面光滑, PbO₂ 晶粒细化. 上述研究均采用硝酸介质.

本文以四氟硼酸作介质电沉积制备 PbO₂ 电极, 研究掺杂离子对电沉积过程的影响.

1 实验部分

1.1 电极制备

试剂: 四氟硼酸、四氟硼酸铅、氢氧化铁和氢氟酸等均为分析纯. 镀液由二次去离子水配制.

Pt 盘电极 (Φ8 mm) 经抛光后, 浸入 H₂SO₄ (98%) + H₂O₂ (30%) (1: 1 by volume) 配置的混合液中 2 min, 然后去离子水冲洗干净备用.

以铂盘基底电极, 饱和甘汞参比电极和铂丝对电极组成三电极体系, 在镀液 0.02 mol · L⁻¹ Pb(BF₄)₂ + 0.1 mol · L⁻¹ HBF₄ (25 °C) 中. 恒电流电沉积 30 min, 得到电极 FB/PbO₂. 另由 0.02 mol · L⁻¹ Pb(NO₃)₂ + 0.1 mol · L⁻¹ HNO₃ 镀液制得 N/PbO₂; 四氟硼酸镀液中添加 0.002 mol · L⁻¹ Fe³⁺ + 0.06 mol · L⁻¹ F⁻ 制得 FB/F-Fe-PbO₂ 电极.

1.2 测试与表征

循环伏安法测试使用 IM6ex 电化学工作站. X-射线衍射仪 (XRD, D8 Advanced 型) 分析镀层物相结构, 辐射源为 CuKα (λ = 0.15406 nm), 管压 40 kV, 管流 40 mA. 扫描电子显微镜 (SEM, Inspect S 型) 观察电极表面形貌.

2 结果与讨论

2.1 PbO₂ 电沉积

图 1 示出在硝酸或四氟硼酸镀液中 PbO₂ 于铂基底上电沉积的 CV 曲线. 由图可见, 正向扫描时, 于电位 1.5 V 处开始电流急剧增大, 而反向扫描则在 1.0 V 左右出现还原峰, 显示此时 PbO₂ 已在基底表面发生沉积. 图中 3 种镀液 (a ~ c) 的 CV 曲线形状并无明显差别, 可认为 BF₄⁻ 的存在并不改变 PbO₂ 的电沉积过程, 仅是提高了它的还原电流. 比较镀液 b 和 c, 其还原峰面积分别为 7.89 mC

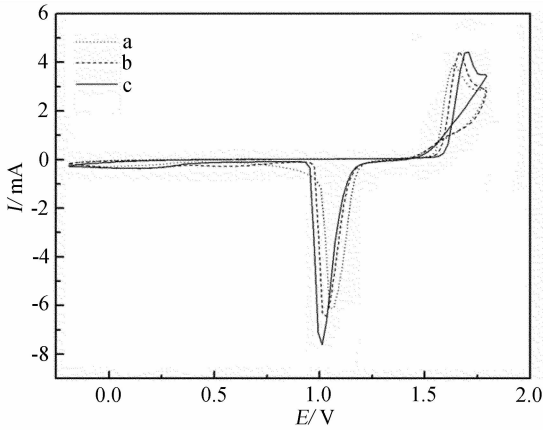


图1 Pt 基底在 3 种不同镀液中的循环伏安曲线

Fig. 1 Cyclic voltammograms of the Pt-electrode in three different solutions

- a. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{NO}_3)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HNO}_3$,
 - b. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{NO}_3)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4$,
 - c. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4$,
- scan rate: 100 mV/s

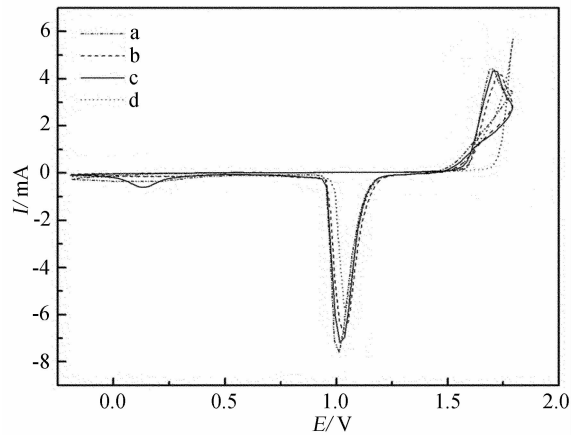


图2 在 4 种不同掺杂的镀液中铂电极的循环伏安曲线

Fig. 2 Cyclic voltammograms of the Pt-electrode in four doped solutions

- a. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4$,
- b. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$,
- c. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+}$,
- d. $0.1 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+} + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$

和 7.97 mC . 还原峰面积随 BF_4^- 浓度增加而增大, 表明 BF_4^- 具有加快电沉积速率的作用.

图2为在掺杂 F^- 或 Fe^{3+} 或二者共掺杂的 4 种氟硼酸镀液中 PbO_2 于铂基底电沉积的循环伏安曲线. 由图看出, 各曲线形状相似, 但掺杂却使阴极还原峰面积减小, 降低电沉积速率. Fe^{3+} 掺杂反向扫描出现了两个还原峰, 另在 0.2 V 处还出现一微小的还原峰, 这可能是由于掺杂 Fe^{3+} 使起始沉积的二氧化铅形成了数量相当的两种同素异型的二氧化铅晶体 ($\alpha\text{-PbO}_2$ 和 $\beta\text{-PbO}_2$)^[14-15].

2.2 PbO_2 的 XRD 谱图

图3给出了在 3 种不同镀液中电沉积生成的 N/PbO_2 (a), FB/PbO_2 (b), FB/F-Fe-PbO_2 (c) 镀层的 XRD 谱图. 图中可见, 3 种镀层均由 $\beta\text{-PbO}_2$ 组成, 其中由 F^- 和 Fe^{3+} 共掺电沉积生成的镀层并未明显改变 PbO_2 的晶相组成. N/PbO_2 (a) 的 $\beta(110)$, $\beta(101)$ 和 $\beta(211)$ 峰均大于 $\beta(202)$ 峰. 而 FB/PbO_2 (b) 的 $\beta(202)$ 峰则明显大于 $\beta(110)$, $\beta(101)$ 和 $\beta(211)$ 的峰, 表明 FB/PbO_2 的优先生长晶面为 $\beta(202)$. 与 FB/PbO_2 相比, 镀层 FB/F-Fe-PbO_2 (c) 的 $\beta(110)$, $\beta(101)$, $\beta(211)$ 和 $\beta(301)$ 峰均有所增强, $\beta(202)$ 的峰则稍小. 可见 F^- 与 Fe^{3+} 共掺对晶体生长取向产生了较大影响. 因为 F^- 和 O^{2-} 离子半径相似, F^- 易取代 O^{2-} 的点位而进入 $\beta\text{-PbO}_2$ 晶格, 而 Fe^{3+} 也容易取代 Pb^{4+} 进入 $\beta\text{-PbO}_2$

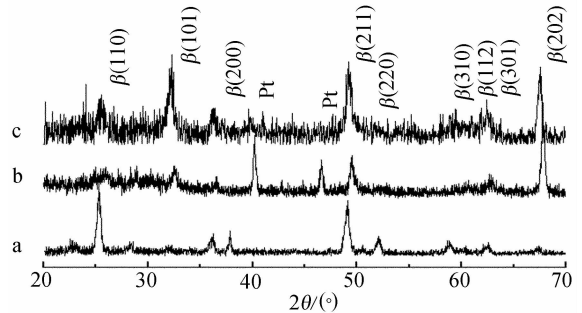


图3 3 种不同镀液中电沉积 PbO_2 膜的 XRD 谱图

Fig. 3 X-ray diffractograms of the PbO_2 films deposited in three doped solutions

- a. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{NO}_3)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HNO}_3$,
- b. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4$,
- c. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+} + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$

晶格.

图4是在 $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+} + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$ 镀液中不同电流密度下电沉积 FB/F-Fe-PbO_2 的 XRD 谱图. 由图看出, 在 $2 \sim 60 \text{ mA/cm}^2$ 电流密度范围内, 电沉积形成的镀层均为 $\beta\text{-PbO}_2$, 无其它晶相出现. 而各晶面峰都随电流密度增加而增强, 并以 $\beta(202)$ 晶面峰增强最多. 显然在电沉积过程中

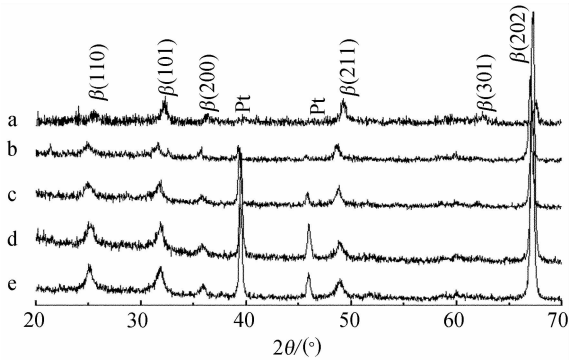


图4 不同电流密度下电沉积二氧化铅的 XRD 谱图

Fig. 4 X-ray diffractograms of the PbO_2 films deposited in $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+} + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$ solution with different current density current density $a \sim e/\text{mA} \cdot \text{cm}^{-2}$: 2, 10, 20, 40, 60

增大电流密度,更有利于 $\beta(202)$ 晶面的生长。

2.3 表面形貌

图5示出 FB/PbO_2 (b), $\text{FB}/\text{F-Fe-PbO}_2$ (c) 镀层及通常的二氧化铅镀层 N/PbO_2 (a) 的 SEM 照片。由图可知,二氧化铅形貌很大程度上取决于镀液组成。 N/PbO_2 (a) 结晶粗大、不匀; FB/PbO_2 (b) 表面分布均匀致密;而 $\text{FB}/\text{F-Fe-PbO}_2$ (c) 晶粒则呈半球形,排布均匀堆积紧密,无明显的裂缝。由此

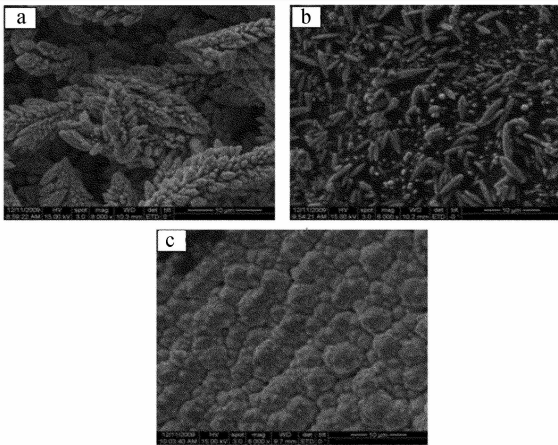


图5 3种不同镀液中电沉积 PbO_2 的 SEM 照片

Fig. 5 SEM of the PbO_2 films deposited from three different solutions

a. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{NO}_3)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HNO}_3$, b. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4$, c. $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Pb}(\text{BF}_4)_2 + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HBF}_4 + 0.002 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+} + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{F}^-$

可见,镀液中 F^- 与 Fe^{3+} 共掺对电沉积过程 $\beta\text{-PbO}_2$ 晶体生长的择优取向的确产生了相当的影响,改变了晶胞形貌。

3 结 论

BF_4^- 离子能够提高二氧化铅电沉积速率,且所得镀层为 $\beta\text{-PbO}_2$ 晶型,在四氟硼酸镀液中掺杂 F^- 、 Fe^{3+} 或 F^- 与 Fe^{3+} 二者共掺均可降低二氧化铅电沉积速率。所得 $\text{FB}/\text{F-Fe-PbO}_2$ 镀层整齐致密,在 $2 \sim 60 \text{ mA}/\text{cm}^2$ 电流密度范围内,电流密度增加,并不改变电沉积二氧化铅晶型,只改变晶体生长的择优取向。

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Electrodeposition of Lead Dioxide from Fluoroborate Solutions

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Abstract: The PbO_2 anodes were prepared on platinum from fluoroborate media and its doped solutions by electrodeposition technique. Electrochemical and physicochemical properties of these PbO_2 films were studied by cyclic voltammetry methods, XRD and SEM. The results showed that the presence of BF_4^- increased PbO_2 electrodeposition rate; the prepared lead dioxide consisted of $\beta\text{-PbO}_2$; the preferential orientation of crystals and surface morphology were affected a lot by doping F^- and Fe^{3+} . The FB/F-Fe- PbO_2 electrode exhibited regular-shaped layers with compact morphology. Furthermore, increasing current density also change the preferential orientation of PbO_2 crystals.

Key words: PbO_2 ; electrodeposition; fluoroborate; doping-ions