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Peng LI

Yue-min ZHAO

Li-zhang WANG

School of Environment and Spatial Informatics, China University of Mining and Technology, Xuzhou 22116, Jiangsu, China; wzh0731@126.com

Yan-le ZHANG

Zhao-qing LU

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β -PbO₂/Sb-SnO₂/Ti 电极的苯酚电催化性能研究

李 鹏¹, 赵跃民², 王立章^{1*}, 张延乐³, 芦兆青¹

- (1. 中国矿业大学环境与测绘学院环境工程专业, 江苏 徐州 221116;
2. 中国矿业大学化学化工学院矿物加工专业, 江苏 徐州 221116;
3. 徐州市工程咨询中心, 江苏 徐州 221116)

摘要: 采用刷涂热解-电镀工艺制得了 β -PbO₂/Sb-SnO₂/Ti 电极. 采用 X 射线衍射(X-ray Diffraction, XRD)和扫描电镜(Scanning Electron Microscope, SEM)进行物相组成分析与微观形貌观察. Sb-SnO₂ 中间层抑制 PbF₂ 的生成, NaF 促进二氧化铅晶粒的成型与分散, 消除了 β -PbO₂ 团聚. 据谢乐公式(Scherrer)计算晶粒尺寸为 25.2 nm, 电极表面结晶度高达 100%. 极化测试显示, β -PbO₂/Sb-SnO₂/Ti 电极扩散段电位区、析氧电位和 Tafel 斜率分别为 1.85 ~ 2.15 V、2.08 V 和 0.84, 优于 β -PbO₂/Ti 电极的 1.40 ~ 1.80 V、1.75 V 和 0.36. 使用 β -PbO₂/Sb-SnO₂/Ti、 β -PbO₂/Ti 电极在 9 mA·cm⁻² 电流密度对苯酚模拟废水处理 240 min, 前者 COD(Chemical Oxygen Demand)去除率、电流效率(Instant Current Efficiency)高达 90.1%和 63.28%, 优于后者 66.9%和 44.96%. 强化寿命测试表明, β -PbO₂/Sb-SnO₂/Ti 电极与 β -PbO₂/Ti 电极相比延长 10 倍, 工业寿命可达 8.6a, 有较高的工程应用价值.

关键词: Sb-SnO₂ 中间层; β -PbO₂/Ti; 极化特性; 电流效率; 加速寿命测试

中图分类号: TQ050.4; X703

文献标识码: A

电镀钛基二氧化铅电极(β -PbO₂/Ti)因其有高析氧电位、高催化活性和低制备成本等优势而成为电化学废水处理技术的理想阳极材料^[1-6]. 然而, PbO₂/Ti 阳极极化过程中 Ti 基底与 PbO₂ 镀层间易形成裂缝, 使 TiO₂ 生成机率增加, 因 TiO₂ 和 PbO₂ 晶粒尺寸差异致使镀层脱落, 降低其电催化性能而失活^[7-10]. Sn-SnO₂ 中间层的应用是 PbO₂/Ti 阳极保护的主要途径^[11-13]. 梁镇海等^[14]采用刷涂热解-电镀法制得了 PbO₂-SnO₂-Sb/Ti 电极, 1000 A·m⁻² 电流密度下工业使用寿命可长达 8a, 但存在电极表面孔径较多, 活性物质分布不均问题. Duan 等^[15]采用相同方法制得 PbO₂-SnO₂-Sb/Ti 阳极, 在 10 mA·cm⁻² 电流密度下对自配苯酚进行电催化降解实验, 电解 6 h 其苯酚 COD 去除率和电流效率仅分别为 34.3%和 26.5%. 另外, Vicent 和 An 等^[16-17]研究了掺锡量和添加 NaF 分散剂对 PbO₂-SnO₂-Sb/Ti 电极形貌和性能的影响.

本文在前人研究基础上优化钛基二氧化铅电极制备工艺, 制得了锡锑掺杂 PbO₂/Ti 阳极

(β -PbO₂/Sb-SnO₂/Ti) 以期提高其电催化氧化苯酚废水的 COD 去除率及电流效率, 延长阳极使用寿命.

1 实验

1.1 材料与试剂

材料: 钛板(2 cm×3 cm)、316# 不锈钢(4×4 cm).

试剂: 五水合结晶四氯化锡、三氯化锑、正丁醇、氟化钠、硝酸铜、草酸、氢氧化钠、硫酸、硝酸、苯酚均为分析纯. 溶液由去离子水配制.

1.2 电极制备

在 SbCl₃(0.42 g) + 正丁醇(4 mL)溶液中, 加入 SnCl₄·5H₂O(4.2 g), 并滴加 2 mL 浓盐酸以防四氯化锡水解, 搅拌使药品完全溶解(半透明乳白溶液), 将涂液均匀刷涂在打磨、刻蚀处理的钛基底^[18](均匀麻灰色)表面, 室温晾干 10 min, 放入干燥箱 130 °C 烘干 15 min, 转入马弗炉 500 °C 热解 20 min. 上述操作重复 10 次, 最后在马弗炉中 500 °C 煅烧 1 h, 自然冷却后取出.

以预处理钛基体或 Sb-SnO₂/Ti 做阳极(2 cm ×

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3 cm), 不锈钢为阴极(4 × 4 cm), 0.5 mol · L⁻¹ Pb(NO₃)₂、0.2 mol · L⁻¹ Cu(NO₃)₂、0.1 mol · L⁻¹ HNO₃ 和 0.04 mol · L⁻¹ NaF 电镀液, 电磁搅拌(转速 250 r · min⁻¹), 在 2.3 V 恒电位电镀(60 °C)2 h, 可得 PbO₂/Ti 电极和 PbO₂/Sb-SnO₂/Ti 电极.

1.3 测试方法

使用 X 射线衍射仪(Bruker Corp, D8 Advance)和扫描电子显微镜(FEI Corp, Quanta250)表征电极的物相特征、观察其微观形貌; 使用电化学工作站(Zahner Corp, IM6)测试电极的极化曲线; 测试电极寿命使用 HYL-A 型恒压/恒流源.

1.4 苯酚电催化

以 β-PbO₂/Ti、β-PbO₂/Sb-SnO₂/Ti 作阳极, 钛基体为阴极, 室温条件下电催化降解 200 mg · L⁻¹ 含酚废水(Na₂SO₄ = 3% (ω/ω)). 反应器尺寸 10 cm × 10 cm × 3 cm, 极板间距 3 cm, 电流密度 9 mA · cm⁻². 定时取样, 用重铬酸钾回流法测定 COD 值, 并计算去除率(X%).

1.5 分析方法

电极表面晶粒尺寸(*D*, nm) 可据谢乐公式计算^[19]:

$$D = \frac{k\lambda}{FW(S) \cdot \cos\theta} \quad (1)$$

式中, *k* 为常数, 取 0.89; λ 为 X 射线波长, 1.5482 nm; *FW(S)* 为试样宽化, nm; θ 为衍射角, Rad.

苯酚电催化降解瞬时电流效率(ICE)^[20]:

$$ICE = \frac{[\text{COD}_0 - \text{COD}_t]}{8 \cdot I \cdot \Delta t} \cdot F \cdot V \quad (2)$$

式中, COD₀、COD_{*t*} 分别为初始和 *t* 时刻含酚废水 COD 值 (g (O₂) · L⁻¹); *I* 为电流值 (A); *t* 反应时间 (s); *F* 为法拉第常数 (96485 C · mol⁻¹); *V* 电解液体积 (L).

使用下式进行阳极实用寿命与工业寿命转换^[21]:

$$t = \left[\frac{A_1}{A} \right]^2 \cdot t_1 \quad (3)$$

*A*₁ 为实验电流密度 (A · m⁻²); *A* 为工业应用电流密度 (1000 A · m⁻²); *t*₁ 为实验使用寿命 (h); *t* 为工业使用寿命 (h).

2 结果与讨论

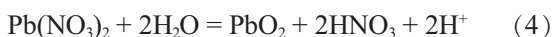
2.1 X 射线衍射

β-PbO₂/Ti 与 β-PbO₂/Sb-SnO₂/Ti 电极 XRD 谱图如图 1 所示. 从图 1 可以看出, β-PbO₂/Ti 与

β-PbO₂/Sb-SnO₂/Ti 电极 XRD 谱图的峰位和峰高相似, 说明中间层添加前后两电极表面物相组成和结晶化度基本相同; 据 PDF 标准卡 (65-2826#) 25.354°、31.936°、36.190°、49.070°、52.068°、54.231°、58.763°、60.676° 处呈现了明显的 β-PbO₂ 衍射峰, 其衍射强度较强, 即两电极表面均附着较多 β-PbO₂; 同时 31.65°、49.23°、62.50° 处的衍射峰(参照标准卡 13-0509#) 可判断 PbF₂ 的存在. β-PbO₂/Sb-SnO₂/Ti 电极 XRD 谱图中的 PbF₂ 峰明显降低, 添加 Sb-SnO₂ 抑制了 PbF₂ 的生成, 这将有助于电沉积过程 PbO₂ 的生成; 添加中间层前后电极表面结晶化度分别为 96% 和 100%, 电极表面均有较好的结晶度, 这主要归因于 NaF 浓度的优化使其电极表面活性物质分散更加均匀, 有利于金属氧化物的结晶成型, 而适量锡锑掺杂, 使 β-PbO₂/Sb-SnO₂/Ti 电极表面更致密、均匀, 结晶化度优于 β-PbO₂/Ti 电极; 据谢乐公式 Sb-SnO₂ 掺杂前后, 电极表面 PbO₂ 晶粒大小分别为 16.8 nm 和 25.2 nm.

β-PbO₂/Sb-SnO₂/Ti 和 β-PbO₂/Ti 两电极的 XRD 图谱中均未呈现 Pb(II)^[22]、Pb(III)^[23] 衍射峰, 这主要是由于在高电位电镀过程中添加 Cu(NO₃)₂, 抑制了 Pb²⁺ 向 PbO/Pb₃O₄ 转化, 电极二氧化铅活性层纯度得以提高. 电极反应如下:

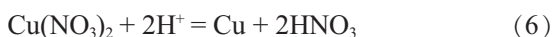
阳极:



副反应:



阴极:



2.2 扫描电镜照片

图 2 给出 β-PbO₂/Ti 与 β-PbO₂/Sb-SnO₂/Ti 电极的扫描电镜照片. 从照片看出, 添加中间层前后电极表面的微观形貌基本相同, 两电极表面颗粒分布均匀. 氟化钠促进了二氧化铅晶格的成型和分散. 再者, 锡锑复合电极表面活性层颗粒间结合更加紧密, 孔隙率明显降低, 结晶程度高(无细小晶粒堆积), 这与 XRD 谱图中电极表面结晶化度较高相对应. Sb-SnO₂ 掺杂后, 电极表面活性层晶粒尺寸略有增大, 亦与 XRD 晶粒计算结果相符.

2.3 极化曲线

图 3 是 β-PbO₂/Ti 和 β-PbO₂/Sb-SnO₂/Ti 电极在 1 mol · L⁻¹ H₂SO₄ 溶液的极化曲线. 从图 3 看出,

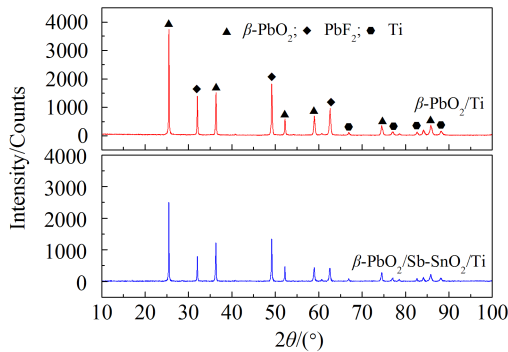


图 1 β -PbO₂/Ti 与 β -PbO₂/Sb-SnO₂/Ti 电极的 X 射线衍射谱图

Fig. 1 XRD patterns of β -PbO₂/Ti and β -PbO₂/Sb-SnO₂/Ti electrodes

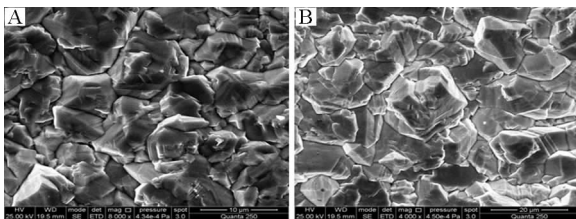


图 2 β -PbO₂/Ti (A) 与 β -PbO₂/Sb-SnO₂/Ti (B) 电极的扫描电镜照片

Fig. 2 SEM images of β -PbO₂/Ti (A) and β -PbO₂/Sb-SnO₂/Ti (B) electrodes

β -PbO₂/Ti 和 β -PbO₂/Sb-SnO₂/Ti 电极的极化曲线可分为三段. 第一阶段(a, a') 电流密度随电位线性变化, 电极的电荷传输遵循欧姆扩散模式, 两电极的电位宽度分别为 1.06 V ~ 1.4 V、1.01 V ~ 1.85 V, 锡铋复合电极能在较宽的电位范围内保持电荷传输的欧姆极化. 第二阶段(b, b') 电流密度随电位的增加呈对数形式变化, 系扩散控制阶段. β -PbO₂/Sb-SnO₂/Ti 电极电位为 1.85 V ~ 2.15 V 较 β -PbO₂/Ti 电极 1.40 V ~ 1.80 V 大, 内置图中 β -PbO₂/Ti 电极极限扩散电流^[24]电位区间为 1.72 ~ 1.80 V, 同理可得 β -PbO₂/Sb-SnO₂/Ti 电极极限扩散电流电位区间为 1.86 V ~ 1.89 V, 使得 β -PbO₂/Sb-SnO₂/Ti 电极具有较快的电子传递速率, 原因在于 SnO₂ 可有效地降低复合电极的界面电阻, 适量的 Sb 原子, 促使 5 价 Sb 原子取代了 SnO₂ 晶格中 4 价 Sn 原子余下的一个电子进入导带, 提高 SnO₂ 电导性, 当掺 Sb 量过多则增加了 SnO₂ 晶格的无序性, 甚至使其晶格遭到破坏, 其电导性反而迅速下降; 含 SnO₂-Sb 中间层电极析氧电位更高(2.08 V). 第三阶段(c, c')

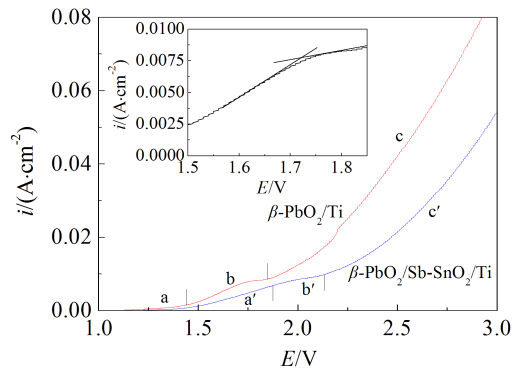


图 3 β -PbO₂/Ti (a, b, c) 和 β -PbO₂/Sb-SnO₂/Ti (a', b', c') 在 1 mol·L⁻¹ H₂SO₄ 溶液的极化曲线, 扫描速率 10 mV·s⁻¹

Fig. 3 Polarization curves of β -PbO₂/Ti (a, b, c) and β -PbO₂/Sb+SnO₂/Ti (a', b', c') in 1 mol·L⁻¹ sulfuric acid solutions Scan rate 10 mV·s⁻¹

电流密度随电位呈指数变化, 而 β -PbO₂/Sb-SnO₂/Ti 电极在较高电位下能够保持较强的稳定性.

将两电极的 E -lgi 曲线参数列于表 1, β -PbO₂/Sb-SnO₂/Ti 电极的过电位较小, 而交换电流较大.

表 1 β -PbO₂/Ti 与 β -PbO₂/Sb-SnO₂/Ti 电极的 Tafel 参数
Tab. 1 Tafel parameters of β -PbO₂/Ti and β -PbO₂/Sb-SnO₂/Ti electrodes

Electrode	a/V	b/V	i ₀ /(A·cm ⁻²)
β -PbO ₂ /Ti	1.79	0.36	1.06 × 10 ⁻⁵
β -PbO ₂ /Sb+SnO ₂ /Ti	0.93	0.84	7.81 × 10 ⁻²

2.4 苯酚电催化氧化

图 4 为 β -PbO₂/Ti 和 β -PbO₂/Sb-SnO₂/Ti 电极苯酚电催化氧化的 X%-t 曲线(A) 与 ICE-t 曲线(B). 从图 4 可以看出, 随时间增加, β -PbO₂/Ti 和 β -PbO₂/Sb-SnO₂/Ti 电极苯酚降解过程废水 COD 浓度均有不同程度的降低. 9 mA·cm⁻² 电流密度下经 240 min β -PbO₂/Sb-SnO₂/Ti 电极苯酚 COD 从 832.8 mg·L⁻¹ 下降至 77.2 mg·L⁻¹, 去除率达 90.1%, 而 β -PbO₂/Ti 电极苯酚 COD 的去除率仅 66.9%, 前者电流效率 70.32% 也明显高于后者 49.93%. Sb-SnO₂ 中间层使得电极表面孔隙率变小, 二氧化铅活性层的分布更加紧密、均匀, 提高了其对苯酚电催化氧化的能力. 电极的活性位 M 可与 H₂O 发生电化学反应,

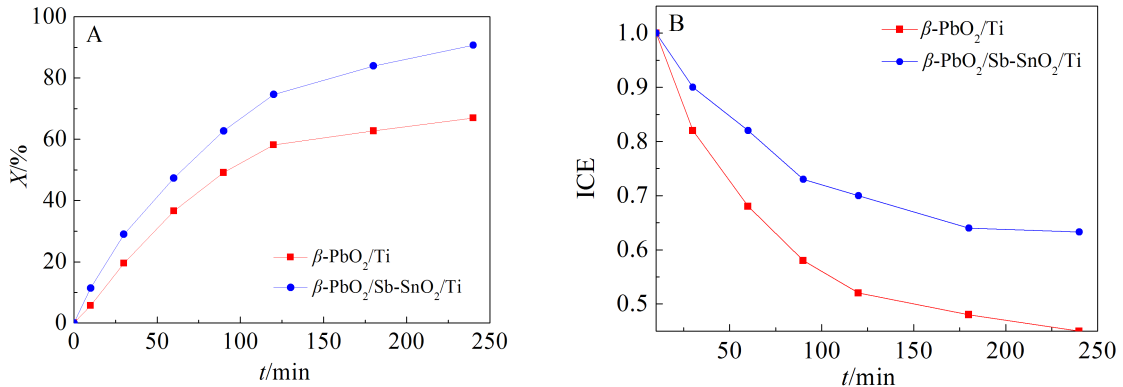


图4 $\beta\text{-PbO}_2/\text{Ti}$ 和 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极苯酚电催化氧化的 $X\%$ - t 曲线(A)及 ICE- t 曲线(B)

Fig. 4 The efficiency of chemical oxygen demand (COD) removal (A) and instant current efficiency (ICE) (B) in relation with time during phenol electro-oxidation using $\beta\text{-PbO}_2/\text{Ti}$ and $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ electrodes

生成 M-OH ^[25], Sb-SnO_2 中间层还可提高电极析氧电位,更利于 M-OH 向 $\cdot\text{OH}$ 生成的方向进行^[26]. 另外,本实验 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极电催化氧化苯酚 COD 去除率及电流效率高于研究中报道^[15-17] 的同类 Sb-SnO_2 复合电极.

2.5 电极寿命

在 60°C 、 $1\text{ mol}\cdot\text{L}^{-1}$ 硫酸溶液中,以 $\beta\text{-PbO}_2/\text{Ti}$ 和 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 为阳极,钛为阴极, $4\text{ A}\cdot\text{cm}^{-2}$ 电流密度,电极间距 20 mm ,测得 E - t 曲线(如图5),依槽电压升至 10 V 作为电极失活的判据,所经历时间即为电极的强化寿命.从图中可以看出, $\beta\text{-PbO}_2/\text{Ti}$ 电极在 4.6 h 时槽压即迅速上升至 10 V 以上, $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极可延至 46 h ,电极寿命提高了约 10 倍.这可能是由于 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 断面内无高阻疏松过渡层及缝隙,电解液、 O_2 或 O^{2-} 向钛基体的扩散受到阻挡而避免 TiO_2 的生成.另外, $\beta\text{-PbO}_2$ 电沉积在 Sb-SnO_2 底层时,第一个单分子层可直接与 SnO_2 键合,进一步提高了 $\beta\text{-PbO}_2$ 与 Ti 的结合力.较低的起始槽压表明 Sb-SnO_2 的添加降低了 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极的背景电势^[28]. 经式(3)转化可知复合电极工业寿命可达 8.6a .

3 结论

1) 采用刷涂热解-电镀工艺制得 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极,适宜的 NaF 浓度能够促使电极表面活性二氧化铅层晶格的成型和分散. Sb 的掺杂改善晶格结构, $\text{Cu}(\text{NO}_3)_2$ 的加入抑制 Pb^{2+} 生成 $\text{Pb}(\text{II})$ 、 $\text{Pb}(\text{III})$,提高活性层纯度.

2) Sb-SnO_2 中间层可消除 PbO_2 的聚团,改善其微观形貌,降低表面界面电阻,提高复合电极析

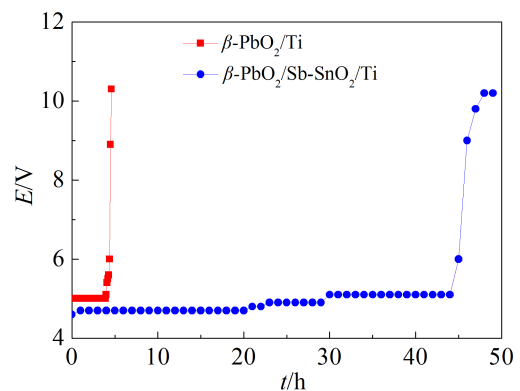


图5 $\beta\text{-PbO}_2/\text{Ti}$ 和 $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极的寿命曲线

Fig. 5 Service time curves of the $\beta\text{-PbO}_2/\text{Ti}$ and $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ electrodes

氧电位.

3) $\beta\text{-PbO}_2/\text{Sb-SnO}_2/\text{Ti}$ 电极电催化氧化苯酚废水有较高的 COD 去除率与电流效率,电极寿命提高了 10 倍,工业寿命估计可达 8.6a .

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Electro-Catalytic Properties of β -PbO₂/Sb-SnO₂/Ti Electrode on Phenol Oxidation

LI Peng¹, ZHAO Yue-min², WANG Li-zhang^{1*}, ZHANG Yan-le³, LU Zhao-qing¹

(1. School of Environment and Spatial Informatics, China University of Mining and Technology,

Xuzhou 22116, Jiangsu, China; 2. School of Chemical Engineering and Technology,

China University of Mining and Technology, Xuzhou 22116, Jiangsu, China;

3. Xuzhou engineering consulting center, Xuzhou 22116, Jiangsu, China)

Abstract: The combination technology of brush pyrolysis and electroplating was employed in the preparation of β -PbO₂/Sb-SnO₂/Ti electrode. X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) results showed that the Sb-SnO₂ as an interlayer would restrain the formation of lead fluoride and the crystallization degree on the electrode surface could be as high as 100%. The grain size was calculated by Scherrer formula to be 25.2 nm and the agglomeration of lead dioxide was effectively eliminated. The potential span of diffusion control phase, oxygen evolution potential, Tafel slope for the β -PbO₂/Sb-SnO₂/Ti electrode during the polarization were 1.85 ~ 2.15 V, 2.08 V and 0.84, respectively, which exhibited much better electrochemical properties as compared with those of the β -PbO₂/Ti electrode with the values of 1.40 ~ 1.80 V, 1.75 V and 0.36, respectively. Furthermore, the β -PbO₂/Sb-SnO₂/Ti and β -PbO₂/Ti electrodes were taken as anodes participating in the electrocatalysis degradation of phenol simulated wastewater under current density 9 mA·cm⁻² within 240 min. Experimental results revealed that the efficiencies of chemical oxygen demand (COD) removal and instant current efficiency (ICE) during phenol degradation were 90.1% and 63.28% for the β -PbO₂/Sb-SnO₂/Ti electrode, while 66.9% and 44.96% for the β -PbO₂/Ti electrode. Ultimately, the accelerated life test was performed to evaluate the service time of β -PbO₂/Sb-SnO₂/Ti. The results presented that the industrial life of β -PbO₂/Sb-SnO₂/Ti was 8.6a, which is 10 times longer than that of β -PbO₂/Ti, suggesting that β -PbO₂/Sb-SnO₂/Ti would have a relatively high engineering application value.

Key words: stannic and antimony oxides interlayer; β -PbO₂/Ti; polarization curve; instant current efficiency; accelerated life test