

# Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极电容性能研究

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**摘要:** 低温热分解法制备 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub>. XRD 表征该样品结构特性, 循环伏安和恒流充放电测定电极性能. 结果表明, Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 物相属细小的金红石相, 在 20 mV/s 扫速下该电极比电容达 933 F/g. 1000 次充放电循环后, 比电容衰减 23.6%, 显示良好的循环稳定性和可逆性.

**关键词:** 超级电容器; RuO<sub>2</sub>-TiO<sub>2</sub>-SnO<sub>2</sub>; 热分解法; 比电容

**中图分类号:** TM911; TQ174

**文献标识码:** A

RuO<sub>2</sub> 电极超级电容器比电容可达 185 F/g<sup>[1]</sup>, 但 Ru 价格昂贵, 限制其实际应用. 可替代 RuO<sub>2</sub> 的其它氧化物大多是过渡金属氧化物, 如 MnO<sub>2</sub><sup>[2]</sup>、Co<sub>3</sub>O<sub>4</sub><sup>[3]</sup>、NiO<sup>[4]</sup>、TiO<sub>2</sub><sup>[5]</sup>、SnO<sub>2</sub><sup>[6]</sup> 等. 研究表明, 在 RuO<sub>2</sub> 中掺杂第 2 组分也可提高电极比电容<sup>[7-8]</sup>. 本文应用低温热分解法制备 RuO<sub>2</sub>-TiO<sub>2</sub>-SnO<sub>2</sub> 氧化物涂层, 分析电极的物相结构并测定电极电容性能. 结果显示在扫描速率为 20 mV/s 下, Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极的比电容达到 933 F/g.

## 1 测试与体系

将 RuCl<sub>3</sub> (36.9%)、C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti (98%) 和 SnCl<sub>4</sub> (98%) 按 1: 1: 8 (by mass) 比例分别溶于适量无水乙醇, 超声振荡均匀分散、搁置 12 h, 取适量混合液均匀涂覆于钛板上, 红外干燥, 箱式炉中 300 °C 下氧化 10 min, 出炉、冷却. 如此多次重复涂覆, 最后将钛基涂层烘干、退火 (300 °C、1 h) 空冷.

使用 Philips Xpert-MPD 衍射仪分析涂层结构, CuKα<sub>1</sub> 辐射, 管电压 40 kV, 电流 40 mA. CHI660C 电化学工作站作循环伏安测试和恒流充放电测试, 工作电极 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> (1 cm<sup>2</sup>), 参比电极 232 型饱和甘汞电极, 钛板作辅助电极, 电解液 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>.

## 2 结果与讨论

### 2.1 XRD 图谱

图1是 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极的 XRD 图谱,

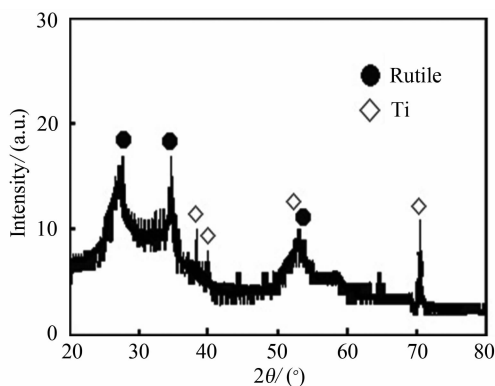


图 1 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极 XRD 图谱

Fig. 1 XRD pattern of Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrode

显示该样品由金红石相和 Ti 组成. 图中, 金红石相的 3 个衍射峰明显宽化且不完全对称, 表明该涂层的晶粒细小并存在相分离. 这与 SnO<sub>2</sub> 易形成较多细小金红石晶粒有关<sup>[9]</sup>. 但如 SnO<sub>2</sub> 含量较多, 则仅部分能与 RuO<sub>2</sub> 形成固溶体<sup>[7,9]</sup>.

### 2.2 循环伏安曲线

图 2 示出 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极在不同扫速下的循环伏安曲线. 如图, 伏安曲线呈现出较好的矩形特征, 即电极可逆性较好. 扫速增大, 氧化还原峰电位差增大, 同时电极比电容逐减 (见表 1).

### 2.3 恒电流充放电曲线

图3绘出 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极在 5 mA/

表1 不同扫速下 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极的比电容  
Tab.1 Specific capacitance of the Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrode at different scan rates

Scan rate/ $\text{mV} \cdot \text{s}^{-1}$	5	10	15	20	25	35
$C_s, \text{RuO}_2/\text{F} \cdot \text{g}^{-1} \cdot \text{cm}^{-2}$	1022	979	960	933	883	830

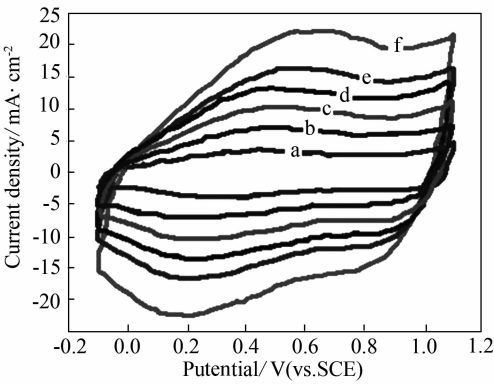


图2 不同扫速 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极的循环伏安曲线

Fig.2 Cyclic voltammograms of Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrode at different scan rates  
 $a \sim f/\text{mV} \cdot \text{s}^{-1}$ : 5; 10; 15; 20; 25; 35

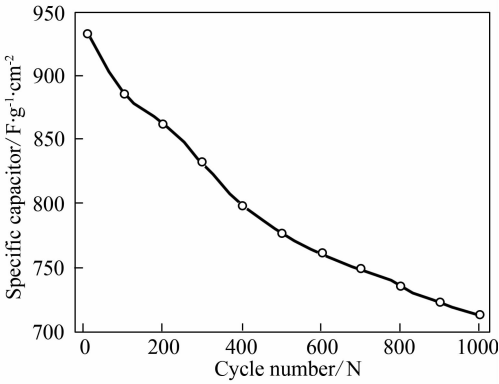


图4 扫速 20mV/s 电位窗口  $-0.1 \sim 1.1 \text{ V}$  时 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极比电容循环寿命

Fig.4 Cycle life of Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrode at potential window of  $-0.1 \sim 1.1 \text{ V}$  and scan rate  $20 \text{ mV} \cdot \text{s}^{-1}$

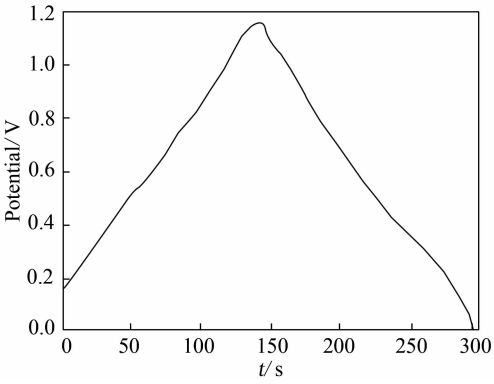


图3 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极于  $5 \text{ mA}/\text{cm}^2$  的恒电流充放电曲线

Fig.3 Charge/discharge curves of Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrode at current density of  $5 \text{ mA}/\text{cm}^2$

$\text{cm}^2$  恒电流下充放电曲线. 由图看出, 电极充放电电压随时间大体呈线性变化, 且接近对称, 显示出较好的电极可逆性和较好的电容特性.

2.4 电极稳定性

图4 是 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 电极在扫速  $20 \text{ mV}/\text{s}$ 、电位窗口为  $-0.1 \sim 1.1 \text{ V}$  下的比电容循环寿命曲线. 由图可见, 电极比容量达  $933 \text{ F} \cdot \text{g}^{-1} \cdot \text{cm}^{-2}$ .

1000 次循环后, 比电容衰减 23.6%.

3 结 论

由低温热分解法制备的仅含 10% RuO<sub>2</sub> 的 Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> 涂层, 添加 Sn 组元可使晶粒细化, 导致该样品特征衍射峰宽化. 在  $20 \text{ mV}/\text{s}$  扫描速率下, 该电极比电容达  $933 \text{ F}/\text{g}$ , 1000 次充放电循环后, 电极比电容衰减 23.6%.

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## Capacitance Behaviors of Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> Electrodes

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**Abstract:** The Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> electrodes were prepared by low temperature thermal decomposition. The structural characteristics were analyzed by X-ray diffraction(XRD). The performances were tested by cyclic voltammetry and constant current charge-discharge measurements. The results show that,the Ti/Ru<sub>0.1</sub>Ti<sub>0.1</sub>Sn<sub>0.8</sub>O<sub>2</sub> belongs to small rutile phase. A high specific capacitance of 933 F/g is obtained at scan rate of 20 mV/s. The cycle life test shows a 23.6% specific capacitance lost after 1000 cycles. The electrode has a good cycle stability and reversibility.

**Key words:** supercapacitor; RuO<sub>2</sub>-TiO<sub>2</sub>-SnO<sub>2</sub>; thermal decomposition; specific capacitance