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Capacitance Behaviors of Ti/Ru0.1Ti0.1Sn0.8O2 Electrodes

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$Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极电容性能研究

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摘要： 低温热分解法制备 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$. 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, $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 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_2-TiO_2-SnO_2；热分解法；比电容

中图分类号： TM911；TQ174　　**文献标识码：** A

RuO_2 电极超级电容器比电容可达 185 F/g[1],但 Ru 价格昂贵,限制其实际应用. 可替代 RuO_2 的其它氧化物大多是过渡金属氧化物,如 MnO_2[2]、Co_3O_4[3]、NiO[4]、TiO_2[5]、SnO_2[6]等. 研究表明,在 RuO_2 中掺杂第 2 组分也可提高电极比电容[7-8]. 本文应用低温热分解法制备 RuO_2-TiO_2-SnO_2 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, $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极的比电容达到 933 F/g.

1　测试与体系

将 $RuCl_3$(36.9%)、$C_{16}H_{36}O_4Ti$(98%)和 $SnCl_4$(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 ℃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 ℃、1 h)空冷.

使用 Philips Xpert-MPD 衍射仪分析涂层结构, $CuK\alpha_1$ 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 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$($1cm^2$),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_2SO_4.

2　结果与讨论

2.1　XRD 谱图

图1是 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极的XRD图谱,

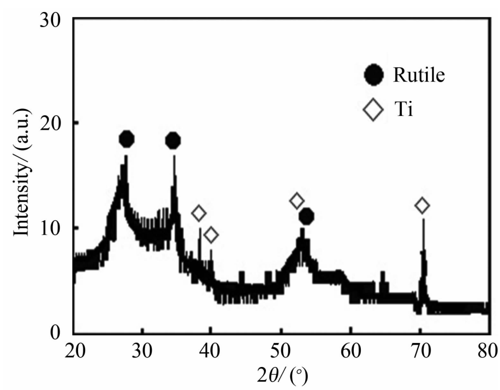

图 1　$Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极 XRD 图谱
Fig. 1　XRD pattern of $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ electrode

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_2 易形成较多细小金红石晶粒有关[9]. 但如 SnO_2 含量较多,则仅部分能与 RuO_2 形成固溶体[7,9].

2.2　循环伏安曲线

图 2 示出 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 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 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极在5 mA/

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表 1 不同扫速下 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极的比电容

Tab. 1 Specific capacitance of the $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ electrode at different scan rates

Scan rate/$mV \cdot s^{-1}$	5	10	15	20	25	35
C_s, RuO_2/$F \cdot g^{-1} \cdot cm^{-2}$	1022	979	960	933	883	830

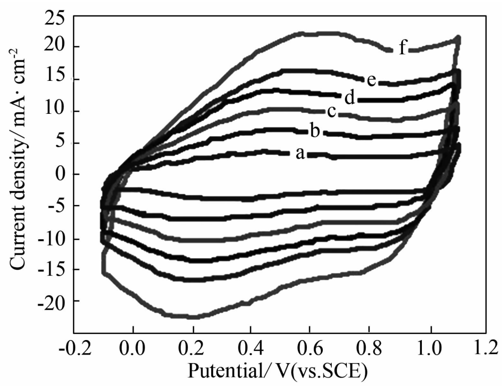

图 2 不同扫速 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极的循环伏安曲线

Fig. 2 Cyclic voltammograms of $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ electrode at different scan rates

a ~ f/$mV \cdot s^{-1}$: 5; 10; 15; 20; 25; 35

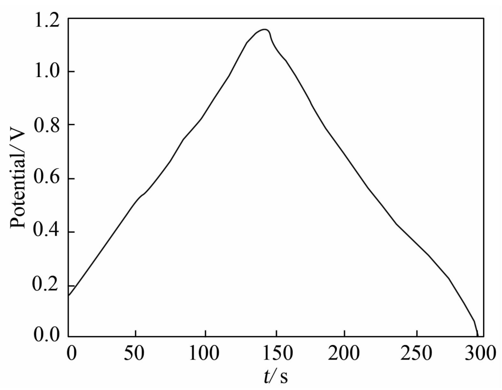

图 3 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极于 5 mA/cm^2 的恒电流充放电曲线

Fig. 3 Charge/discharge curves of $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ electrode at current density of 5 mA/cm^2

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 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极在扫速 20 mV/s、电位窗口为 $-0.1 \sim 1.1$ V 下的比电容循环寿命曲线. 由图可见,电极比容量达 933 $F \cdot g^{-1} \cdot cm^{-2}$.

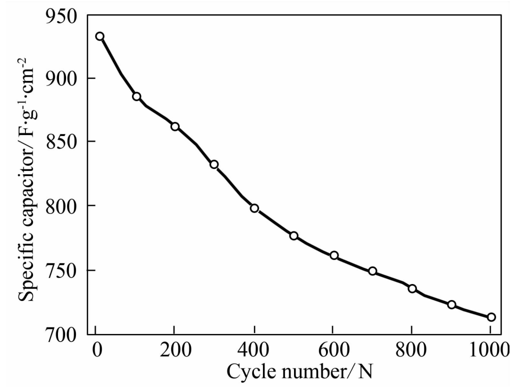

图 4 扫速 20mV/s 电位窗口 $-0.1 \sim 1.1$V 时 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 电极比电容循环寿命

Fig. 4 Cycle life of $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ electrode at potential window of $-0.1 \sim 1.1$V and scan rate 20 $mV \cdot s^{-1}$

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_2 的 $Ti/Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 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 mV/s 扫描速率下,该电极比电容达 933 F/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/$Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ Electrodes

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Abstract: The Ti/$Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 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/$Ru_{0.1}Ti_{0.1}Sn_{0.8}O_2$ 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_2-TiO_2-SnO_2; thermal decomposition; specific capacitance