

沉淀法制备 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 及其 水基超级电容器性能测试

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摘要:以 $\text{Mn}(\text{NO}_3)_2$ 和 NaOH 为原料, 采用沉淀法合成了用作超级电容器电极材料 $\text{Na}_{0.7}\text{MnO}_{2.05}$. 扫描电子显微镜(SEM)观察结果表明所制备样品呈层状板块形貌. 电化学测试结果表明, $\text{Na}_{0.7}\text{MnO}_{2.05}$ 是一种性能比较优良的超级电容器电极材料. 在 $1\text{ mol}\cdot\text{L}^{-1}\text{Na}_2\text{SO}_4$ 电解质溶液中, $0\sim 1\text{ V}$ 的电压范围内, 充放电电流密度为 $200\text{ mA}\cdot\text{g}^{-1}$ 时, 比容量高达 $201\text{ F}\cdot\text{g}^{-1}$, 库伦效率接近 100% .

关键词:超级电容器; $\text{Na}_{0.7}\text{MnO}_{2.05}$; 沉淀法; 水系电解质溶液

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电化学电容器, 也叫超级电容器, 由于其功率密度高、可逆性好、循环寿命长等特点, 有望成为电动汽车的动力源^[1-10]. 目前, 研究人员开发出了混合动力系统, 利用高能量密度的锂离子电池与高功率密度的超级电容器相结合. 其中, 基于水系电解质的钠离子能量储存装置不需要在极度干燥的环境下装配, 安全, 成本低, 符合绿色能源储存要求, 有很好的发展前景^[11-14]. 因为具有资源丰富, 价格低廉, 环境友善, 具备多种氧化价态等特性, 锰氧化物受到研究者的广泛关注^[15-19]. 其中, 具有层状或隧道晶体结构的锂锰氧化物和钠锰氧化物尤其吸引人们的注意^[20-22], 研究结果表明钠锰氧化物在用于超级电容器电极材料方面颇具潜力. 采用沉淀法制备出了层状结构的钠锰氧化物 $\text{Na}_{0.7}\text{MnO}_{2.05}$, 样品成分单一, 结晶度高, 并具有优良的超级电容性能.

1 实验

取 $50\text{ mL H}_2\text{O}_2(5\%)$ 和 200 mL NaOH 溶液(0.6 M)混合均匀, 将制得的混合溶液缓慢滴加至 $100\text{ mL Mn}(\text{NO}_3)_2(0.3\text{ M})$ 溶液中, 常压下匀速搅拌 8 h , 得到共沉淀反应混合物. 将上述沉淀物离心分离, 用去离子水洗涤 $3\sim 4$ 次, $80\text{ }^\circ\text{C}$ 真空干燥 12 h , 得到 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 粉末样品. 材料的表征与电化学性能测试见文献[23].

2 结果和讨论

2.1 结构与形貌分析

图1为样品的XRD图谱. 样品的特征峰与 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 的标准谱图 PDF 27-0751 相符, 未发现原始氧化物及其他杂相, 表明所制备的样品为纯相 $\text{Na}_{0.7}\text{MnO}_{2.05}$, 属于六方晶型. 各特征峰的峰型较为尖锐, 强度大, 表明样品结晶良好. 图2为 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 的微观结构示意图, 由图可知, $\text{Na}_{0.7}\text{MnO}_{2.05}$ 为层状结构, 其片层由锰氧八面体 MnO_6 共边或共角构成, 每个氧原子隶属于3个锰氧八面体, 而层间则由 Na^+ 占据填充.

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若结构中没有空穴,分子式应为 NaMnO_2 , 在结构中 Mn 原子与 Na 原子都有一定的空穴存在,故最后分子式为 $\text{Na}_{0.7}\text{MnO}_{2.05}$. 这种特殊的层状结构其层与层之间容易插入其他离子或分子,因而具有很好的离子交换性能,可制备电化学性能极好的电极材料^[24,25].

图3为样品的SEM图.图3(a)为放大倍数为5000倍样品的SEM图.从中可以看到,沉淀法制得的样品颗粒均匀,表面光滑,分散的比较好,不结块,呈较规则棒状,粒径约为 $10\ \mu\text{m}$ 左右.图3(b)为放大倍数为20000倍样品的SEM图.从中可以看到棒状样品颗粒由多层片状晶粒组装而成.层状结构有利于增大固液接触面积,同时也能缩短离子和电子的扩散路径,有利于降低内阻,有利于改善材料的电化学性能.

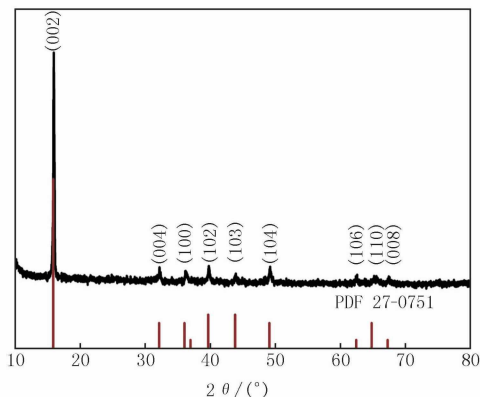


图1 样品的XRD图谱

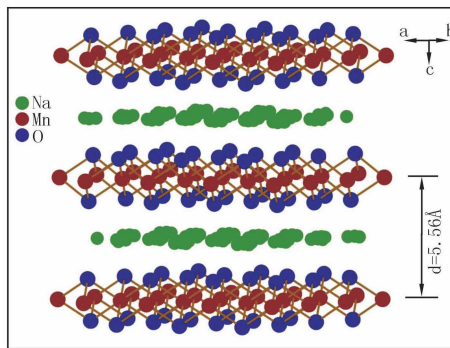
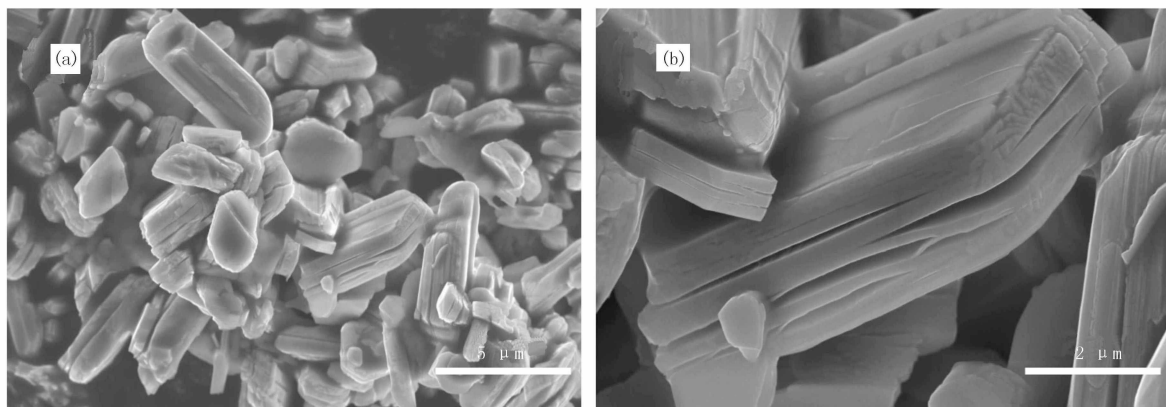
图2 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 微观结构示意图

图3 样品的SEM图

2.2 电化学性能

图4是沉淀法制备的 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 电极在 $1\ \text{mol}\cdot\text{L}^{-1}$ 的 Na_2SO_4 电解质溶液中在不同扫描速率时的循环伏安曲线.由图可知, $\text{Na}_{0.7}\text{MnO}_{2.05}$ 样品的循环曲线在 $-0.2\sim 1\ \text{V}$ 之间正负向扫描(对应于阳极过程与阴极过程)对于电流基线具有明显对称性,从曲线两端可以看出,当扫描方向发生改变时,有快速的电流响应,电流发生快速反向,显示较好的电化学电容特性.在样品的 CV 曲线上,有一对明显的氧化还原峰,峰电位为 $0.41\text{V}(\text{vs SCE})$.可见, $\text{Na}_{0.7}\text{MnO}_{2.05}$ 电极不仅具有双电层电容特性,也有部分赝电容贡献.由于 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 中 Mn 的平均化合价是 3.4,在 Na_2SO_4 电解质溶液中, Na^+ 有可能从 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 晶格中脱出和嵌入,从而伴随可逆的电化学转化^[10].氧化电位和还原电位非常接近,说明其电化学反应可逆程度大,库伦效率高.

图5是样品电极在 $200\ \text{mA}\cdot\text{g}^{-1}$ 电流密度下的充放电曲线.由图可知,电容器的电极电位随时间呈线性变化,具有超级电容器的充放电特征.充电曲线与放电曲线呈三角形对称分布,显示出较好的循环可逆性.材料的首次放电比容量在电流密度为 $200\ \text{mA}\cdot\text{g}^{-1}$ 可达 $201\ \text{F}\cdot\text{g}^{-1}$.该值大于 Xiao Liu 等^[14]人组装的 $\text{Na}_4\text{Mn}_9\text{O}_{18}/\text{Na}_2\text{SO}_4/\text{AC}$ 混电容器,同样电流密度下的比容量($94.5\ \text{F}\cdot\text{g}^{-1}$).

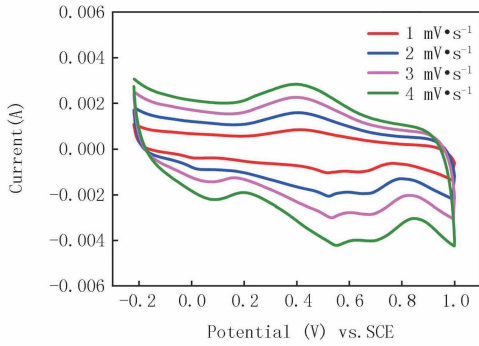
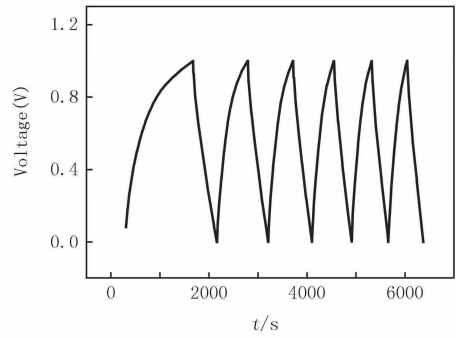
图4 $\text{Na}_{0.7}\text{MnO}_{2.05}$ 样品在不同扫描速率下的循环伏安曲线图5 样品电极在 $200 \text{ mA}\cdot\text{g}^{-1}$ 电流密度下的充放电曲线

图6为样品的循环性能示意图.由图6可知,对称型 $\text{Na}_{0.7}\text{MnO}_{2.05} // \text{Na}_{0.7}\text{MnO}_{2.05}$ 超级电容器在 $200 \text{ mA}\cdot\text{g}^{-1}$ 的电流密度, $0\sim 1 \text{ V}$ 的电位范围内,在约250次循环后,比容量达到稳定.其比容量由 $201 \text{ F}\cdot\text{g}^{-1}$ 经2000次循环衰减到 $137 \text{ F}\cdot\text{g}^{-1}$,容量保持率接近68%.电容器的库伦效率在约50次循环后稳定,基本保持在100%.

图7是样品电极的交流阻抗图谱.频率范围是 $0.1\sim 100 \text{ kHz}$.可以看出,该图谱在低频区为一条斜线,在中频区是一个半圆.该阻抗谱可以用图中所示的等效电路拟合.其中, R_{ct} 代表法拉第电荷转移电阻,为 1.80Ω , C_{dl} 代表双电层电容, C_F 代表法拉第赝电容.

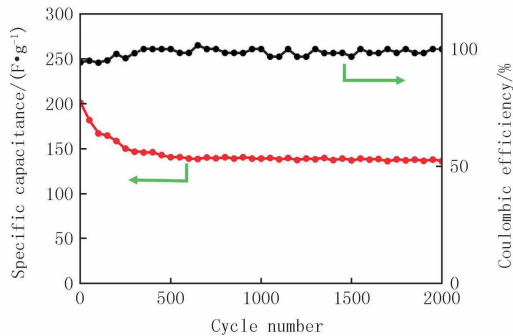


图6 样品的循环性能和库伦效率曲线

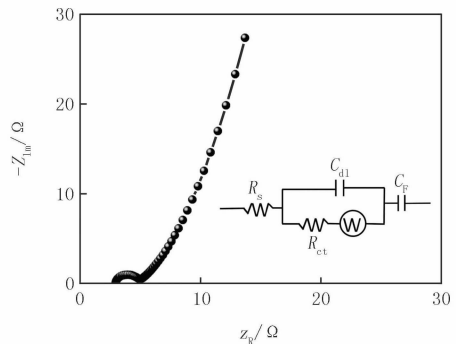


图7 样品电极的交流阻抗图谱

3 结论

以 $\text{Mn}(\text{NO}_3)_2$ 和 NaOH 为原料,采用沉淀法合成了用作超级电容器电极材料 $\text{Na}_{0.7}\text{MnO}_{2.05}$,所制备样品为层状结构.在 Na_2SO_4 水系电解液中, $0\sim 1 \text{ V}$ 的电压范围内,电流密度为 $200 \text{ mA}\cdot\text{g}^{-1}$ 时,样品首次放电比容达 $201 \text{ F}\cdot\text{g}^{-1}$,其比容量经2000次循环衰减到 $137 \text{ F}\cdot\text{g}^{-1}$,容量保持率接近68%.电容器的库伦效率在约50次循环后稳定,基本保持在100%.

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$\text{Na}_{0.7}\text{MnO}_{2.05}$ via Chemical Precipitation Synthesis as an Electrode Material for Aqueous Na-ion Supercapacitors

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Abstract: Sodium manganese oxides $\text{Na}_{0.7}\text{MnO}_{2.05}$ for supercapacitor electrode material was synthesized using $\text{Mn}(\text{NO}_3)_2$ and NaOH via chemical precipitation method. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) shows that the obtained $\text{Na}_{0.7}\text{MnO}_{2.05}$ is single-phased with layered structure. The electrochemical performance was characterized by cyclic voltammetry (CV), impedance measurements and galvanostatic charge-discharge tests in symmetric Na-ion supercapacitors with $1 \text{ mol} \cdot \text{L}^{-1}$ Na_2SO_4 solution as electrolyte. The $\text{Na}_{0.7}\text{MnO}_{2.05}$ material shows a high specific capacity of about $201 \text{ F} \cdot \text{g}^{-1}$ at a current density of $200 \text{ mA} \cdot \text{g}^{-1}$ and a high coulombic efficiency approaching 100%, except the initial 50 cycles.

Keywords: supercapacitor; $\text{Na}_{0.7}\text{MnO}_{2.05}$; precipitation method; aqueous electrolyte

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