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Sn-Co-M-C (M = Zn, Fe) 负极材料的制备及性能研究

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摘要: 以金属氧化物和蔗糖为原料,经混合球磨,高温碳热还原制备 Sn-Co-M-C (M = Zn, Fe) 复合负极材料. 采用 XRD、SEM 测试样品结构,观察样品形貌. 电化学性能测试表明,Sn-Co-Zn-C 电极首次嵌锂比容量 $571 \text{ mAh}\cdot\text{g}^{-1}$,45 次循环后比容量 $369 \text{ mAh}\cdot\text{g}^{-1}$,其比容量和循环寿命好.

关键词: 碳热还原法; 锂离子电池; 负极材料; Sn 基合金

中图分类号: TM912.9

文献标识码: A

商品化锂离子电池主要采用天然石墨或改性石墨为负极材料,其理论比容量($372 \text{ mAh}\cdot\text{g}^{-1}$)难以满足高比能量锂离子电池的发展需求. 金属锡理论储锂容量高($994 \text{ mAh}\cdot\text{g}^{-1}$)、价格低廉,但在锂嵌脱过程,锡发生严重的体积变化而引起粉化、失效^[1-2]. 人们尝试通过掺杂活性、非活性元素与锡构成合金或复合材料,以缓解材料的体积膨胀. 报道的锡基合金主要有 Sn-Co^[3]、Sn-Cu^[4]、Sn-Fe^[5]、Sn-Co-C^[6-12] 等. 其中 Sn-Co-C 电极复合材料已商业化. 然而,该材料体系成本较高,不可逆容量较大. 而碳热还原法制作简便,成本低,污染少,已用于 Sn-Co-C 复合材料的开发^[13].

本文采用蔗糖碳源,通过氧化物碳热还原法制备 Sn-Co-M-C (M = Zn, Fe) 复合材料,并研究了不同碳配比、掺 Zn、Fe 复合材料的结构和电化学性能.

1 实验

1.1 材料制备

1) Sn-Co-C 复合材料

将 Sn、Co 和 C 质量配比分别为 3:2:30,3:2:35 和 3:2:40 的混合物(氧化物和蔗糖)放入玛瑙球磨罐,加少量的去离子水,球磨 2 h 后将物料移入密封管式炉中,通氮气保护,以 $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ 的升温速率调至 $900 \text{ }^\circ\text{C}$,保温 8 h,自然冷却. 将该三种物料分别在玛瑙研钵磨碎即可.

2) Sn-Co-M-C (M = Zn, Fe) 复合材料

将 Sn、Co、Zn (Fe) 和 C 按质量配比 3:1:1:35 混合,依上述步骤,即可得 Sn-Co-M-C (M = Zn, Fe) 复合材料.

1.2 材料表征

采用 X 射线衍射分析仪 (Rigaku Rint 1000, 日本) 测试样品,铜靶, K_α 射线,扫描速率 $6^\circ\cdot\text{min}^{-1}$,扫描范围为 $15^\circ \sim 75^\circ$,电子扫描显微镜 (Hitachi S-4700) 观察样品的微观形貌.

1.3 电池组装与测试

由复合材料、导电剂 (Super-P) 和粘结剂 (PVDF) 按质量配比 8:1:1 压制电极,与金属锂对电极, $1 \text{ mol}\cdot\text{L}^{-1}$ LiPF₆/EC + DMC (体积比 1:1) 电解液, Celgard 2500 隔膜,在氩气气氛的手套箱中组装成 CR2016 型扣式电池. 采用 LAND 测试系统测试电池,充放电曲线的电流密度为 $100 \text{ mA}\cdot\text{g}^{-1}$,充放电电压区间为 0.05 ~ 3 V.

2 结果与讨论

2.1 材料结构与形貌表征

图 1 为 Sn-Co-C 复合材料的 XRD 谱图. 从图 1 可以看出,三种碳配比样品均有 CoSn, CoSn₂ 和 Sn 相组分. 碳含量增加,谱图没有呈现新相,但其三相的主要衍射峰强度有所减弱. 图 2 是 Sn-Co-C (质量配比 3:2:35) 复合材料的 SEM 照片,可以看出,复合材料的颗粒呈不规则形状,其粒径为 $0.1 \sim 0.5 \text{ }\mu\text{m}$.

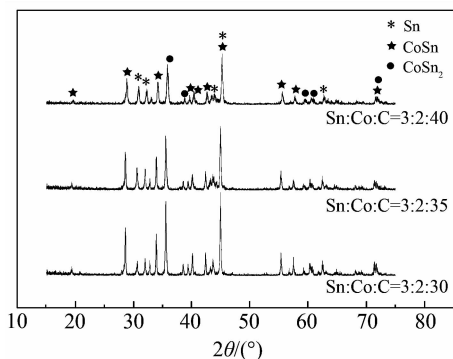


图1 不同碳配比的 Sn-Co-C 复合材料的 XRD 谱图

Fig. 1 XRD patterns of different Sn-Co-C composites

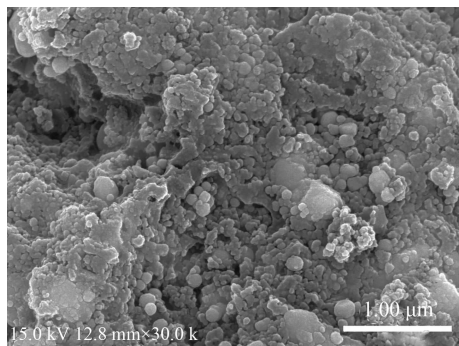


图2 Sn-Co-C(3:2:35)复合材料的 SEM 照片

Fig. 2 SEM image of Sn-Co-C (3:2:35) composite

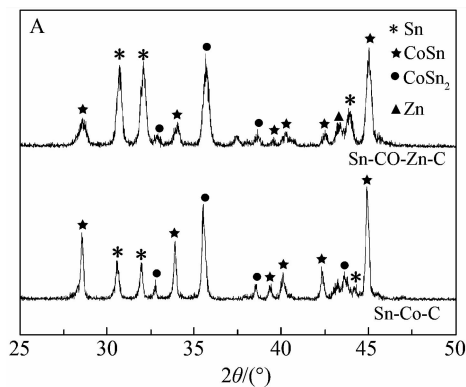


图3 Sn-Co-Zn-C (A) 和 Sn-Co-Fe-C (B) 复合材料的 XRD 谱图

Fig. 3 XRD patterns of Sn-Co-Zn-C (A) and Sn-Co-Fe-C (B) composites

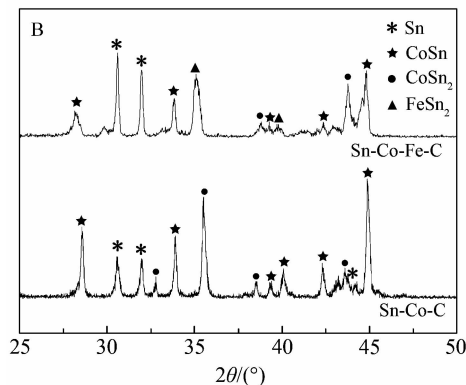


图3所示是掺 Zn 或 Fe 元素的 Sn-Co-M-C (M = Zn, Fe) 复合材料的 XRD 衍射谱图。可以看出,掺 Zn 后,其样品为 CoSn、CoSn₂、Sn、Zn 多相共存,样品 XRD 衍射峰明显增宽,且向高角度方向偏移,这可能与晶粒应力有关。掺 Fe 后,Co 被 Fe 部分取代后,样品主要有 CoSn、CoSn₂、FeSn₂、Sn 四种组分,其衍射峰也增宽,且向低角度方向偏移。因 Zn 原子半径(0.142 nm)小于 Co 的原子半径(0.152 nm),而 Fe 的原子半径(0.156 nm)大于 Co 的原子半径^[14],故样品衍射峰移动可能源于掺杂与被取代元素原子半径的差异。

2.2 电化学性能

图4是不同碳配比的 Sn-Co-C 电极的首次充放电曲线。从图4中可以看出,Sn-Co-C(3:2:30)电极首次嵌锂比容量 389 mAh·g⁻¹,脱锂比容量 243 mAh·g⁻¹,首次库仑效率为 62.5%; Sn-Co-C(3:2:35)电极首次嵌锂比容量 424 mAh·g⁻¹,脱锂比容量 241 mAh·g⁻¹,首次库仑效率为 56.8%; Sn-Co-C(3:2:40)电极首次嵌锂比容量 491 mAh·g⁻¹,脱锂比容量 255 mAh·g⁻¹,首次库仑效率为

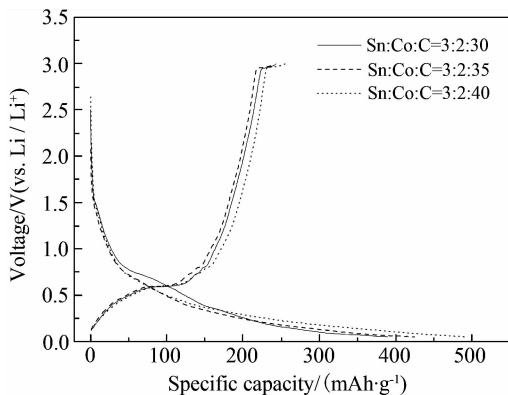


图4 不同碳配比的 Sn-Co-C 电极的首次充放电曲线

Fig. 4 The first charge and discharge curves of different Sn-Co-C composites

51.9%,其嵌锂比容量较高,而库仑效率较低。各电极在 0.4 ~ 0.6 V 均有明显的 Li₃Sn 合金反应平台^[8]。

图5是 Sn-Co-M-C (M = Zn, Fe) 电极的首次充放电曲线。从图中可以看出,Sn-Co-Zn-C 电极首

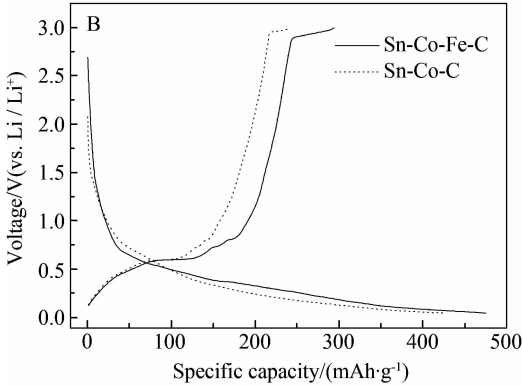
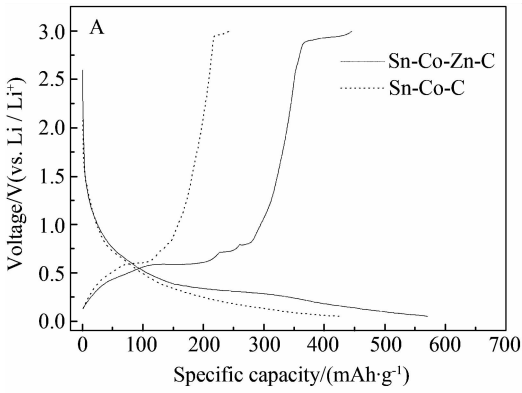


图5 Sn-Co-Zn-C (A)和 Sn-Co-Fe-C (B) 电极的首次充放电曲线

Fig. 5 The first charge and discharge curves of Sn-Co-Zn-C (A) and Sn-Co-Fe-C(B) composites

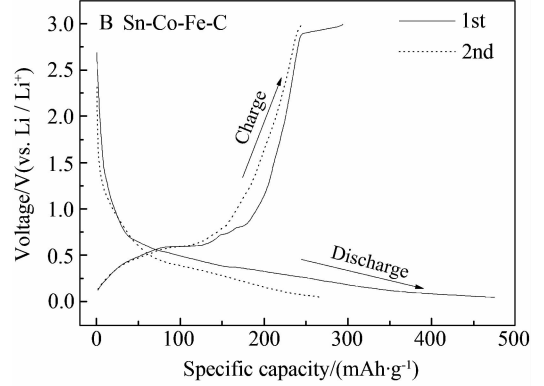
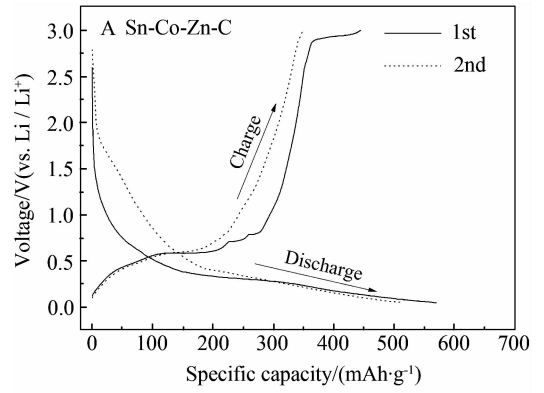


图6 Sn-Co-Zn-C (A)和 Sn-Co-Fe-C (B) 电极的充放电曲线

Fig. 6 The charge and discharge curves of Sn-Co-Zn-C (A) and Sn-Co-Fe-C (B) composites

次嵌锂比容量 $571 \text{ mAh} \cdot \text{g}^{-1}$, 脱锂比容量 $445 \text{ mAh} \cdot \text{g}^{-1}$, 库仑效率为 77.9%; Sn-Co-Fe-C 电极首次嵌锂比容量 $475 \text{ mAh} \cdot \text{g}^{-1}$, 脱锂比容量 $294 \text{ mAh} \cdot \text{g}^{-1}$, 首次库仑效率为 61.9%。掺 Zn 或 Fe 后, 电极比容量分别提高 $147 \text{ mAh} \cdot \text{g}^{-1}$ 和 $51 \text{ mAh} \cdot \text{g}^{-1}$, 库仑效率分别提高了 21.1% 和 5.1%。首次脱锂的过程中, 2.9 V 平台比较长, 在第 2 次充放电, 该平台均消失, 说明该反应不可逆 (见图 6)。

图 7 是不同碳配比的 Sn-Co-C 电极的循环寿命曲线, Sn-Co-C (3:2:35) 电极 45 周循环后比容量为 $287 \text{ mAh} \cdot \text{g}^{-1}$, 其循环寿命较好, 而可逆容量较低。

图 8 示出 Sn-Co-M-C (M = Zn, Fe) 电极的循环寿命曲线。从图 8 中可以看出, Sn-Co-Fe-C (31:1:35) 电极首次放电比容量 $475 \text{ mAh} \cdot \text{g}^{-1}$, 循环 45 周后其比容量仅 $240 \text{ mAh} \cdot \text{g}^{-1}$, 而 Sn-Co-Zn-C (3:1:1:35) 电极首次放电比容量为 $571 \text{ mAh} \cdot \text{g}^{-1}$, 循环 45 周后其比容量为 $369 \text{ mAh} \cdot \text{g}^{-1}$ 。可推测掺 Fe 或 Zn 后, 样品晶粒产生较大的应力, 故在一定

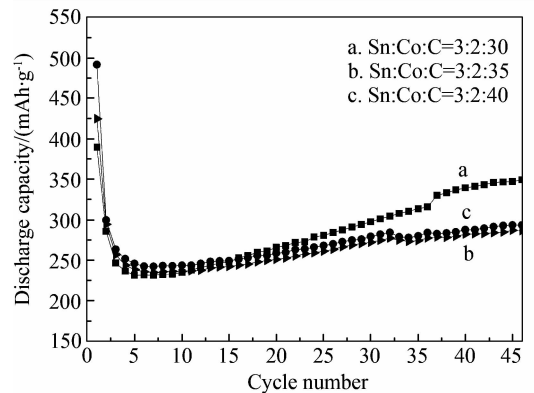


图7 不同碳配比 Sn-Co-C 电极的循环寿命曲线

Fig. 7 Cycling performances of Sn-Co-C composites

程度上抑制了锂脱嵌过程晶粒的应力变化。

3 结 论

金属氧化物和蔗糖, 按不同质量配比高温碳热还原制备 Sn-Co-M-C (M = Zn, Fe) 复合负极材料。Sn-Co-Zn-C (3:1:1:35) 电极首次比容量为 571

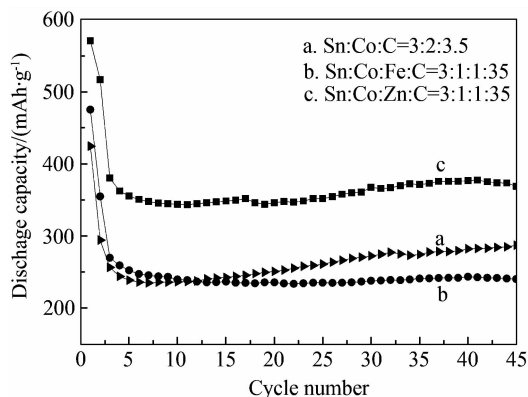


图8 Sn-Co-M-C (M = Zn, Fe)电极的循环寿命曲线

Fig. 8 Cycling performances of Sn-Co-M-C (M = Zn, Fe) composites

$\text{mAh} \cdot \text{g}^{-1}$, 45周循环后其比容量为 $369 \text{ mAh} \cdot \text{g}^{-1}$, 掺Zn有助于提高电极比容量并改善其循环寿命。

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Preparation and Performance of Sn-Co-M-C (M = Zn, Fe) Composites as an Anode Material

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Abstract: The anode materials of Sn-Co-M-C (M = Zn, Fe) composites were prepared by carbothermal reduction method from metal oxides and sucrose in N_2 atmosphere. Their structural and electrochemical properties were studied by XRD, SEM and charge-discharge test. Among them, the Sn-Co-Zn-C composite showed higher specific capacity and good cycle performance. The initial special discharge capacity of $571 \text{ mAh} \cdot \text{g}^{-1}$ could be obtained, while $369 \text{ mAh} \cdot \text{g}^{-1}$ was still kept after 45 cycles.

Key words: carbothermal reduction method; lithium-ion battery; cathode material; Sn-based alloy