Solvothermal Synthesis and Electrochemical Performance of Nano-Ni_3Sn_2 Used as Anodes for Lithium-ion Batteries

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Abstract: A nano-Ni_3Sn_2 intermetallic compound was prepared by solvothermal method for an anode material of lithium-ion batteries. The samples were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The electrochemical performances of the materials were evaluated by galvanostatic charge and discharge cycling in a lithium-ion model cell: Li/$LiPF_6$ (EC+DMC)/Ni_3Sn_2. It was found that the first delithiation capacity of nano-Ni_3Sn_2 was 136 mAh·g^{-1}. The annealed Ni_3Sn_2 electrodes exhibited a better capacity retention compared to the unannealed Ni_3Sn_2 electrodes.

Key words: lithium-ion batteries; anodes; Ni_3Sn_2; solvothermal synthesis; electrochemical performances
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A new generation of lithium-ion batteries, which was composed of tin-based oxides anode, was developed by Fuji Photo Film Company in early 1997[1]. The Sn-based oxides or Sn-based alloys are attractive due to their extremely large theoretical capacities and energy densities than that of carbon-based materials.

Ni-Sn intermetallic compounds were widely studied due to their high theoretical capacities and excellent cycling properties. Many preparation methods of Ni-Sn intermetallic compounds have been developed, such as ball milling[2], and electroplating[3]. Solvothermal method was considered as a promising way for the synthesis of nanosized materials due to its low synthesis temperature and simple synthesis route[4]. In this paper, nano-Ni_3Sn_2 was synthesized by solvothermal method and the electrochemical performances of the powders were investigated.

1 Experimental

Nano-Ni_3Sn_2 was synthesized by solvothermal method at 150 ℃, 170 ℃, 190 ℃ and 240 ℃ for 24 h. The sample prepared at 240℃ was annealed at 900 ℃ for 1 h with argon protection.

The structure of the samples was identified by powder XRD and the morphology of the samples was observed in a Philips-FEI Sirion 200 field emission scanning electron microscopy (FESEM).

Electrochemical reactions of Ni_3Sn_2 with lithium were investigated using a two-electrode cell: Li/$LiPF_6$ (EC+DMC)/Ni_3Sn_2. Cells were galvanostatically cycled at a constant current density of 20 mA·g^{-1} between 0.05 and 2 V vs. lithium.

2 Results and discussion

The XRD pattern strongly proved that the Ni_3Sn_2 compound could be synthesized by solvothermal method at 240 ℃ as shown in Fig.1. From the Debye-Sherrer Equation of peak width vs. grain size, the average

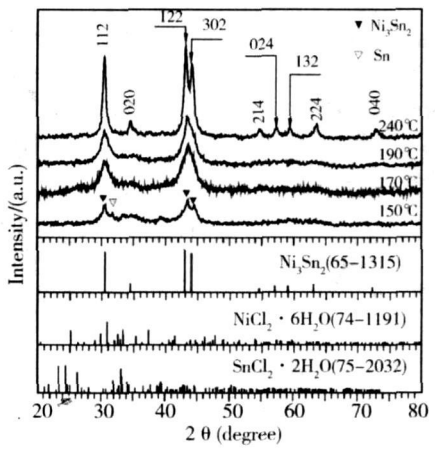

Fig.1 XRD patterns for Ni_3Sn_2 samples prepared by solvothermal method at different temperatures, and the idealized calculated pattern of Ni_3Sn_2, $NiCl_2 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$

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grain size was estimated to be around 25.3 nm. As shown in Fig. 2, the synthesis temperatures play an important role in influencing the morphology of the samples. granules grew and crystallized when synthesis temperature increased.

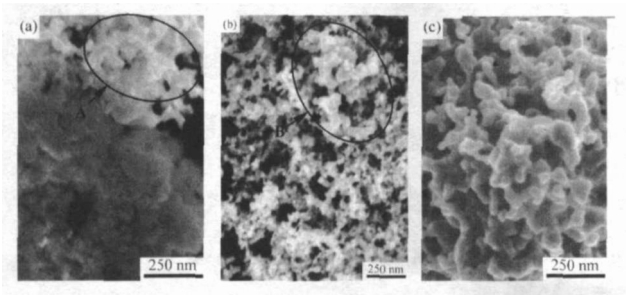

Fig. 2　FESEM images for Ni_3Sn_2 samples prepared by solvothermal method at different temperatures: (a) 150 ℃, (b) 170 ℃ and (c) 240 ℃.

The first charge (lithiation) capacity of nano-Ni_3Sn_2 electrodes reached up to 380 mAh·g^{-1} while the discharge (de-lithiation) capacity fell down to 136 mAh·g^{-1} as shown in Fig. 3.

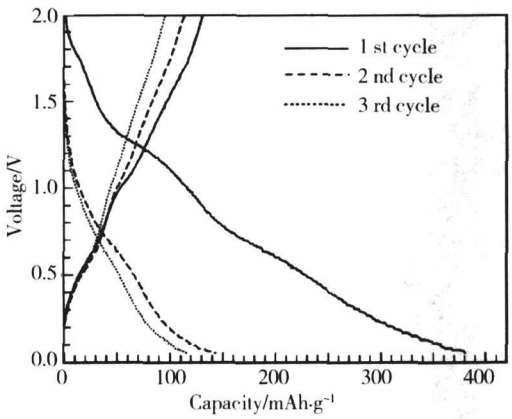

Fig. 3　The charge – discharge curves for nano – Ni_3Sn_2 electrode with a current density of 20 mA · g^{-1}

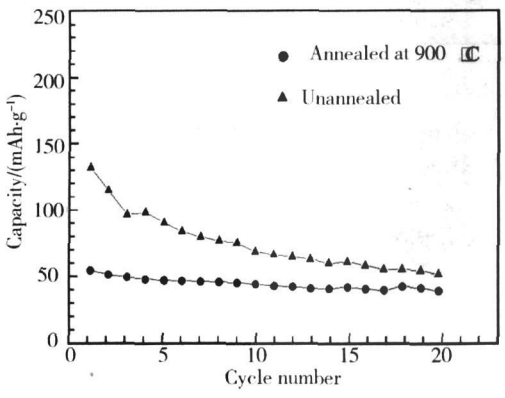

Fig. 4　Discharge capacity vs. cycle number for samples unannealed and annealed at 900 ℃ for 1 h in Ar

As shown in Fig. 4, the annealed Ni_3Sn_2 electrodes exhibited a low capacity degradation than original sample. However, its initial discharge (de-lithiation) capacity was lower than original Ni_3Sn_2.

Fig. 5 shows the EIS plots of original Ni_3Sn_2 and its annealed electrodes. From Fig. 5, it was known that the resistances of Li^+ ions migrate and charge transfer increased quickly when the original Ni_3Sn_2 electrode cycling, while annealed Ni_3Sn_2 electrode demonstrated a stable reaction resistance. It is reasonable to suppose that the solid electrolyte interphase (SEI) film would be quickly formed on surfaces of original Ni_3Sn_2 particles with small size, whereas the formation and growth of SEI film have been considered as a key factor on the resistance increase and the capacity degradation[5]. Therefore, the stable cycling property of annealed Ni_3Sn_2 can be attributed to the stable SEI film formed on surfaces of annealed Ni_3Sn_2 particles.

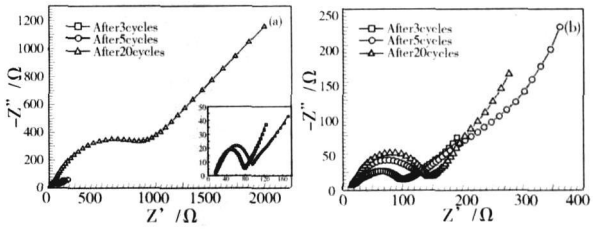

Fig. 5　EIS plots of Ni_3Sn_2 electrode after different cycles at delithiated state: (a) unannealed; (b) annealed at 900 ℃ for 1 h in argon environment.

3　Conclusions

Nano-Ni_3Sn_2 was successfully synthesized by solvothermal method in ethanol solution at 240 ℃ for the first time. The first delithiation capacity of nano-Ni_3Sn_2 was 136 mAh·g^{-1}, which was lower than its theoretical capacity. The annealed Ni_3Sn_2 electrodes exhibited a stable cyclic capacity compared to the unannealed Ni_3Sn_2 electrodes.

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Bronsted酸性离子液体催化的 Aldol反应

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摘 要: 通过酮和醛的 Aldol反应在 Bronsted酸离子液体 BMImHSO$_4$ 中制备了一系列 α, β—不饱和酮。所建立方法的主要优势有: 高转化率和选择性、温和的反应条件、产物容易分离、离子液体可循环使用。

关键词: Bronsted酸离子液体; 催化剂; Aldol反应; α, β—不饱和酮
中图分类号: TQ 622.6

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锂离子电池负极材料纳米 Ni$_3$Sn$_2$ 的溶剂热合成与电化学性能

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摘 要: 采用溶剂热法合成锂离子电池负极材料纳米 Ni$_3$Sn$_2$ 合金粉末并研究了该合金粉末作为新型锂离子二次电池负极材料的电化学性能。合成的合金粉末经过了 XRD和 FESEM的表征, 采用 Li/LiPF6 (EC+DMC) / Ni$_3$Sn$_2$ 模拟电池测定合成的合金粉末的电化学性能。研究表明, 该合金粉末的首次可逆容量为 136 mAh·g^{-1}, 退火后的合金粉末表现出更好的循环稳定性。

关键词: 锂离子电池; 负极; Ni$_3$Sn$_2$; 溶剂热合成; 电化学性能
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