Fabrication and electrochemical properties of Sn/TiO₂ nanowire array composites as Li-ion battery anodes

Zhen Wei, Tao Huang, Aishui Yu *

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, Fudan University, Shanghai 200438, China

Introduction

Among various anode materials, simple substance Si have emerged as potential anode materials for LIBs due to its high theoretical specific capacity, abundant amount on earth and low cost [1, 2]. Its theoretical specific capacity (4200 mA h g⁻¹) is much larger than that of the already-commercialized graphite (372 mA h g⁻¹). However, substantial volume changes are associated with the Li alloying and de-alloying process, which causes fast crack and pulverization of Si and results in rapid capacity fade. On the other hand, nanostructured TiO₂ owns a very small volume expansion ratio (3%) [3] upon Li ion intercalation/ extraction, and exhibits good cyclic stability [4]. Well-ordered TiO₂ nanowire arrays offer a large internal surface area and excellent pathways for Li-ion to transfer between interfaces. So it is an excellent material employed as a stable anode for lithium ion batteries.

Herein, we design and fabricate a novel material of Si/TiO₂ nanowire array (TNA) composite, which combines the advantages of high specific capacity of Si with the structural stability of TNA. The specific capacity of TNA is greatly improved by introducing Si component. The as-prepared Si/TNA composite is already connected to titanium current collector, needless of binder and conductive agent for Li ion battery application.

Results and discussion

The Si/TiO₂ nanowire array composite structure is confirmed by TEM images as shown in Fig. 1. It is clearly seen that Si particles distribute uniformly at the lateral surface of nanowires, proving that Si particles have been successfully deposited into the interspace between the TiO₂ nanowires. In Fig. 1(a), the uncrystallized film wrapping TiO₂ is identified as amorphous Si. In Fig. 1(b), crystallized Si is verified beside the TiO₂ nanowire. The distance between the adjacent lattice fringes can be assigned to the interplaner distance of Si (220), which is d_{220}=0.195 nm. Two kinds of Si phase are identified.

Fig. 2 depicts the initial three cycles’ specific capacities of TNA/Si composites with 75% Si percentages. The composite shows initial discharge capacities of 2384 mA h g⁻¹, and the corresponding charge capacities is 1480 mA h g⁻¹. The corresponding Coulombic efficiencies is 62.1%. Comparing with pure TiO₂, the capacities of TNA/Si composites are improved greatly. Typically the composite with 75% silicon owns the highest reversible capacity and superior Coulombic efficiency. The large amount of silicon component afford huge capacity and the steady TiO₂ framework effectively lessen Si volume expansion, preventing formation of the electronic isolation of silicon particles.

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References