Fabrication and electrochemical properties of Sn/TiO_2 nanowire array composites as Li-ion battery anodes

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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 TiO_2 owns a very small volume expansion ratio (3%) [3] upon Li ion intercalation/ extraction, and exhibits good cyclic stability [4]. Well-ordered TiO_2 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/TiO_2 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/TiO_2 nanowire array composite structure is confirmed by TEM images as shown in Fig. 1. It is clearly seen that Si pariticles distribute uniformly at the lateral surface of nanowires, proving that Si particles have been successfully deposited into the interspace between the TiO_2 nanowires. In Fig. 1(a), the uncrystallized film wrapping TiO_2 is identified as amorphous Si. In Fig. 1(b), crystallized Si is verified beside the TiO_2 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 TiO_2, 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 TiO_2 framework effectively lessen Si volume expansion, preventing formation of the electronic isolation of silicon particles.

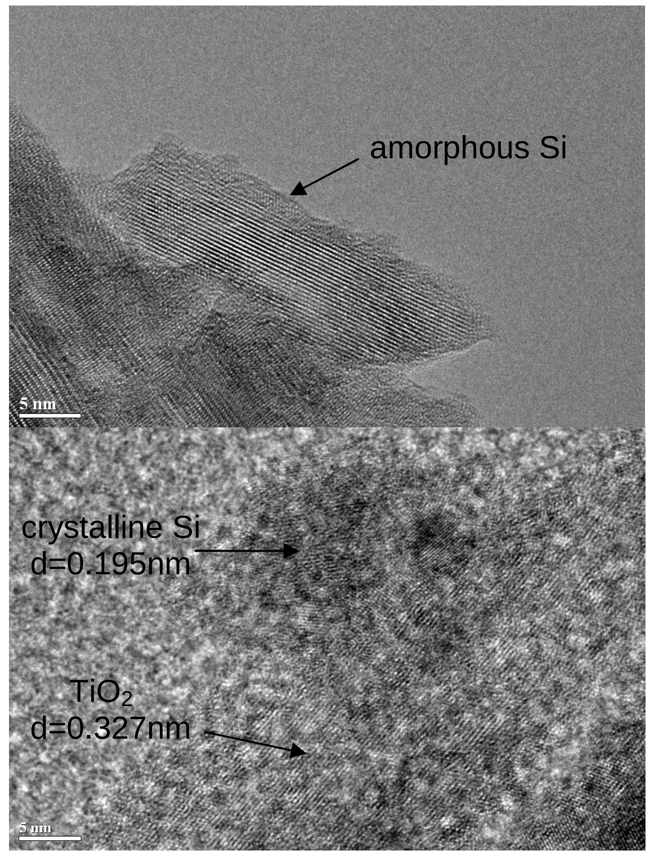

Fig. 1 TEM images of Si/TNA composites

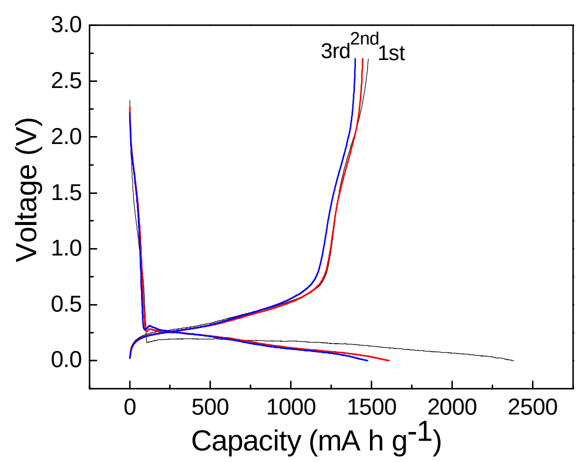

Fig. 2 the initial three cycles' discharge/charge curves of the composites with 75% Si percentages

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References

[1] X.L. Yang, P.C. Zhang, Z.Y.Wen, L.L. Zhang, J. Alloys Compd. 496 (2010) 403.
[2] B. Peng, F.Y. Cheng, Z.L. Tao, J. Chen, J. Chem. Phys. 133 (2010) 034701-1.
[3] M . Wagemaker, G.J. Kearley, A.A. Well, H. Mutka, F. M. Mulder, J. Am. Chem. Soc. 125 (2003) 840.
[4] D.H. Wang, D.W. Choi, Z.G. Yang, V.V. Viswanathan, Z.M. Nie, C.M. Wang, Y.J. Song, J.G. Zhang, J. Liu, Chem. Mater. 20 (2008) 3435.