A NEW APPROACH TO SYNTHESIS OF MICRO/NANOSTRUCTURED SIOX/C COMPOSITE AS HIGH-PERFORMANCE ANODE MATERIAL FOR LITHIUM-ION BATTERIES

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ABSTRACT

Nonstoichiometric silicon oxide (SiO_x) has attracted much attention due to its high theoretical capacity and stable cycling ability. However, the huge volume changes and low electrical conductivity restrict the practical applications of SiO_x anodes [1]. Extensive trials have been devoted to coping with these problems, in a manner most of which involve direct utilization of commercial SiO_x powders, including physical mixing and pyrolysis. Recently, wet chemistry routes [2,3] were actively investigated in SiO_x-based composite preparation with the aim of appropriately reducing the high cost of commercial SiO_x powders, using a simple and low-cost siloxane (e.g., tetraethoxysilane, TEOS) as raw material.

In this work, we employ citrate-nitrate gel combustion method for the first time to synthesize micro/nanostructured SiO_x/C composite. During the combustion process, carbon can be *in situ* introduced and uniformly dispersed in the SiO_x matrix, forming SiO_x/C composite. A simple carbon coating modification was adopted to further enhance the electrochemical performance of the SiO_x/C combustion production by creating a carbon outer layer on secondary particles and simultaneously decreasing the O/Si atomic ratio of the composite.

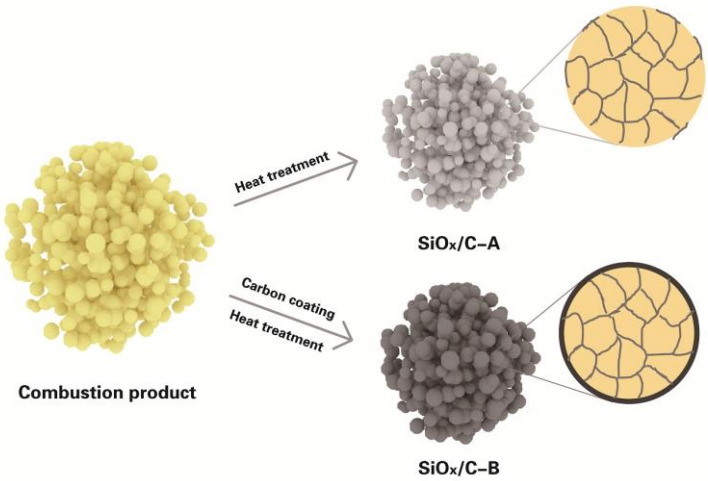

Fig. 1 Schematic representation of SiO_x/C structure of the two kinds of samples.

Schematic representation of SiO_x/C structure of the two kinds of samples is shown in Fig. 1. During the gel combustion process, the fast reaction releases large amount of gas, producing a highly porous intermediate product. A subsequent carbon coating process can not only introduce more carbon, but also recombine the granule structure, and thus leading to a homogeneous and dense contact between carbon and silicon oxide. A consequent extensive carbothermal reduction can bring a lower O/Si ratio and a higher specific reversible capacity.

Table 1 Element composition and atomic ratio of O/Si of the two samples.

Sample	Element content (wt%)			Atomic ratio
	O	C	Si	O/Si
SiO_x/C-A	39.6	22.3	38.1	1.82
SiO_x/C-B	24.1	40.8	35.1	1.21

Table 1 shows the tested elemental composition and the calculated atomic ratio of oxygen to silicon of the two samples. The carbon content in SiO_x/C-A is *ca.* 22.3%, and the x value (O/Si ratio) is calculated to be *ca.* 1.82, which indicates that carbothermal reduction occurred between the as-synthesized silica and the pyrolyzed carbon of citric acid during heating process. After carbon coating modification, a much lower x value is obtained for SiO_x/C-B, which stems from the extensive carbothermal reduction of silicon oxide by the adequate carbon. The lower O/Si ratio corresponds to the high electrochemical activity of the SiO_x phase.

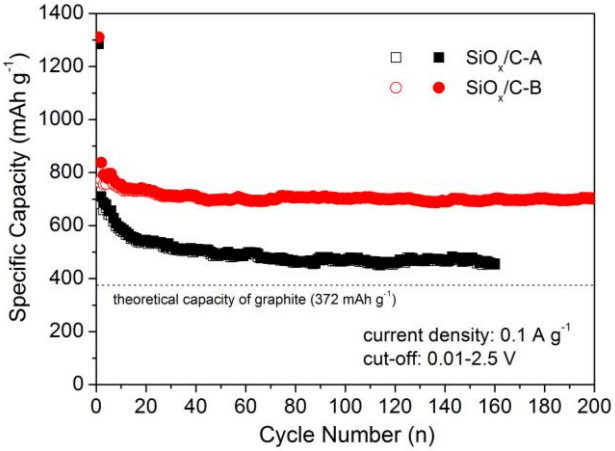

Fig. 2 Cycling performance of the synthesized two SiO_x/C samples.

Fig. 2 displays the cycling performance of the two electrodes at 0.1 A g^{-1} for 200 cycles. As observed, the SiO_x/C-B electrode exhibits a higher specific capacity and better cycling stability than the SiO_x/C-A electrode. After 200 cycles at 0.1 A g^{-1}, the SiO_x/C-B electrode still retains a specific reversible capacity of ca. 700 mAh g^{-1}, which is almost twice higher than the theoretical specific capacity of graphite, whereas the SiO_x/C-A electrode only shows a specific capacity of 450 mAh g^{-1} after 160 cycles.

Considering the facile and mass-productive preparation route and the excellent electrochemical performance, the micro/nanostructured SiO_x/C composite is a promising candidate for anode material of high capacity lithium-ion battery.

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