SnO_2/reduced graphene oxide composites prepared by ball-milling method for lithium ion battery

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SnO_2, one of the most promising anode materials for lithium ion batteries (LIBs), has a theoretical specific capacity of 782 mAh/g and much higher energy density compared with traditional graphite anode[1]. However, poor cyclic performance due to low conductivity, volume change and crystallinity deterioration of SnO_2 during the charge and discharge process limits the practical application [2]. Formation of tin dioxide/reduced graphene oxide (SnO_2/rGO) composite was proposed to be an effective way to tackle these problems due to the extraordinary conductivity and mechanical property of the graphene sheets[2]. Numerous methods including microwave assisted thermal reaction method and hydrothermal reaction have been proposed to produce SnO_2/rGO composite[2-4]. However, the performances of the resultant LIBs are still far from satisfaction to meet commercial requirements.

Mechanochemical synthesis via ball-milling is a rapid, facile and economic way for production of high quality nanocomposite, and would be applicable to prepare SnO_2/rGO composite. During the mechanochemical reaction, mechanical energy is converted into chemical energy at a critical point to activate chemical reactions and induce structural change and/or recombination without external heat. Furthermore, ball-milling technology can be extremely suitable for large scale production.

In this work, $SnCl_2 \cdot 2H_2O$ and graphene oxide (GO) were mixed as 75:10 (weight ratio) with water. Then the mixture solution was added into a planetary ball miller in air atmosphere at a speed of 500 rpm for 3 hours. In this process, $SnCl_2$ is used to reduce GO and simultaneously produce SnO_2 through the reaction below:

$$SnCl_2 + GO + H_2O \rightarrow SnO_2/rGO + HCl \qquad (Eqn\ 1)$$

The resulting reaction mixture was washed with water to remove impurities and dried at 60°C for 12 hours.

X-ray diffraction analysis indicates the SnO_2 crystal was formed on the surface of the rGO sheet. This suggests the mechanochemical reaction takes place, i.e., $SnCl_2$ have been converted into SnO_2 and the X-ray photoelectron spectroscopy results show that GO has been reduced to rGO.

Scanning electron microscopy images shown in Fig 1 demonstrate that the composites have a lace-like morphology due to the layer structure of graphene. SnO_2 film is attached tightly onto the rGO sheets due to the chemical reaction (Eqn 1).

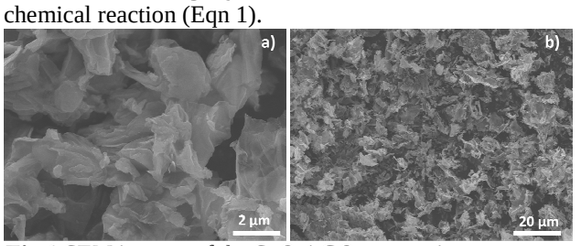

Fig.1 *SEM images of the SnO_2/rGO composite*

Cyclic performance:

To evaluate the charge/discharge performance of as-prepared SnO_2/rGO composites, galvanostatic tests were performed using a current density of 0.5A/g for 50 cycles after 2 cycles at 0.1A/g for activation. Fig.2 gives the charge/discharge profiles of SnO_2/rGO composites at a current density of 0.5A/g in a voltage window of 0.01-2.50V (the curves of the 5th, 25th and 50th cycles). It can be seen from 5th cycle to 50th cycle, the shapes of the charge and discharge curves have barely changed.

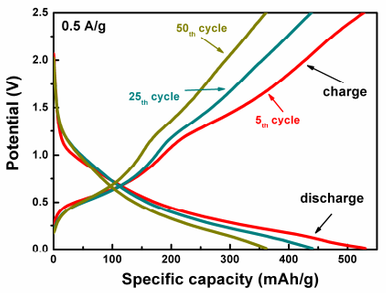

Fig.2 *Charge/discharge profiles of SnO_2/rGO composites at a current density of 0.5A/g in a voltage window of 0.01-2.50 V*

Fig.3 reveals the cycle life of the SnO_2/rGO composite as anode material. The electrode delivers discharge capacity of 796.6 mAh/g at the current density of 0.1A/g for the first discharge (close to theoretical capacity). The capacity is 527.7 mAh/g at 0.5A/g for the 5th cycle. After 50 cycles, the specific capacity still remains at 361.5 mAh/g (averaged 0.7% capacity loss per cycle after the 5th cycle). The coulombic efficiency is almost 100% for every single cycle after the first two cycles, indicating good reversible capacities. The resultant LIBs performance is among the best of SnO_2/rGO composite in the literature [4, 5].

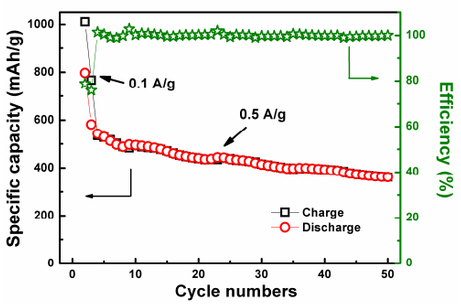

Fig.3 *Reversible charge/discharge capacities and coulombic efficiency against cycle number for SnO_2/rGO composite.*

In summary, SnO_2/rGO composite was successfully synthesized by a simple one-step ball-milling process at room temperature. The composite exhibits high specific capacity and good cyclic performance. It could be a practical way for the mass production of SnO_2/rGO composite for high-performance LIBs.

Reference:

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