

Synthesis of Fe₂SiO₄@C nanocomposites via a solid state reaction by controlling calcinating temperature

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Abstract. Fe₂SiO₄@C nanocomposites are prepared via a solid state reaction by controlling different calcinating temperature (600 °C 700 °C and 800 °C) under the flow of nitrogen gas. XRD analysis indicates that a typical α -Fe₂SiO₄ phase is detected in the Fe₂SiO₄@C nanocomposites calcinated at 700 °C and 800 °C. SEM results reveals that particle size of the Fe₂SiO₄@C nanocomposites can be controlled by calcinating temperature and the particle size of sample calcinated at 700 °C is in the range of 50~70 nm. These unique properties ensure Fe₂SiO₄@C nanocomposites calcinated at 700 °C possess the best electrochemical performance among the three samples.

Introduction

Lithium ion batteries (LIB) have developed rapidly to the field of hybrid electric vehicles and electric vehicles [1-2]. The development of anode materials with high specific capacity is becoming essential to build advanced LIB for new energy vehicles. Transitional metal oxides (TMO) have been exploited as promising candidates because of their much higher capacity. For example, TMO store lithium based on the conversion reactions [3-6]. Upon lithiation, transition metal nano-domains dispersed in Li₂O matrix are formed by reduction. And then after delithiation, they are reversibly restored to the initial state. TMO deliver high specific capacities up to 600~1000 mA h g⁻¹, but they are usually associated with drastic volume variation (up to 200%) during charge-discharge cycles. As a result, TMO have short-term cycling stability.

As important rock-forming silicates, Fe₂SiO₄ is a kind of low cost and the most abundant mineral in the earth's upper mantle. These compounds are important in geology, geophysics and materials science [7-10]. Employment of Fe₂SiO₄ as anode materials for LIB is rarely investigated. Here, we study the effect of calcinating temperature on the structure and electrochemical performance of Fe₂SiO₄@C.

Experimental

Sample preparation

Traditional solid state reaction was used to prepare Fe₂SiO₄@C nanocomposite from reactants such as FeC₂O₄·2H₂O, nano SiO₂ and ammonium citrate. In a typical synthesis, a mixture of 1.20 g nano SiO₂, 7.20 g FeC₂O₄·2H₂O and 4.533 g ammonium citrate was ball-milled in 20 mL ethanol for 2 h. Then, the resulting mixture was dried at 60 °C in a vacuum drying oven for 4 h. The dried mixture was afterwards transferred to a quartz boat and heated under a flow of N₂ gas. Firstly, the mixture was calcined at 350 °C for 3 h to pre-carbonize the ammonium citrate. Secondly, the mixture was kept at 600 °C for 6 h to obtain the sample FS(600 °C). Similarly, we kept the calcinating temperature at 700 °C and 800 °C to get the sample FS(700 °C) and sample FS(800 °C).

Characterization

Fe₂SiO₄@C nanocomposites were characterized by a powder X-ray diffraction (XRD, Rigaku RINT2000 X-ray Diffractometer, Cu Ka, λ =1.5406 nm). Fe₂SiO₄@C nanocomposites were also determined by a SEM (JSM-6701F, Japan).

Coin type CR2032 cells were used to test the performance of Fe₂SiO₄@C nanocomposite. All cells consists of a Fe₂SiO₄@C anode and a lithium metal counter electrode separated by a microporous polypropylene separator (Celgard 2400). The electrolyte was 1 mol/L LiPF₆ dissolved in a mixture of

ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl-methyl carbonate (EMC). The $\text{Fe}_2\text{SiO}_4\text{@C}$ anode was prepared from the mixture of 85 wt% $\text{Fe}_2\text{SiO}_4\text{@C}$ nanocomposite, 5 wt% carbon black, and 10 wt% aqueous LA132 binder (Chengdu Indigo power sources Co., Ltd.). The assembled CR2032 cells were cycled in the range of 0-3 V using a battery testing system (Wuhan LAND Electronics Co., Ltd.).

Results and discussion

XRD analysis

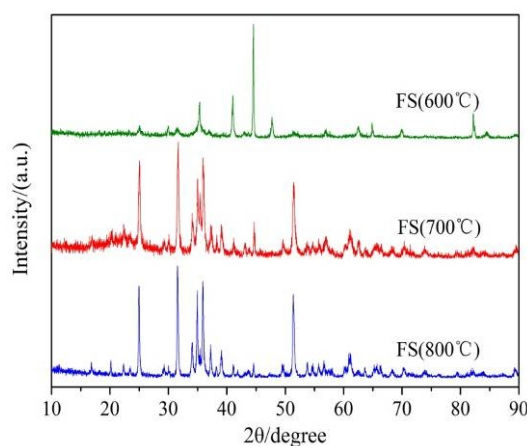


Fig. 1 XRD patterns of $\text{Fe}_2\text{SiO}_4\text{@C}$ nanocomposite

Fig. 1 shows the XRD patterns of FS(600 °C), FS(700 °C) and FS(800 °C). The crystal structure of FS(700 °C) and FS(800 °C) are both belonging to orthorhombic system and Pbnm space group. Its sharp diffraction peak indicates that materials have high degree of crystallinity. Fig. 1 indicates that FS(600 °C) has many iron impurity peak and the peak of Fe_2SiO_4 crystal is very poor. This illustrates calcinating temperature 600 °C is too low to synthesis of Fe_2SiO_4 .

SEM analysis

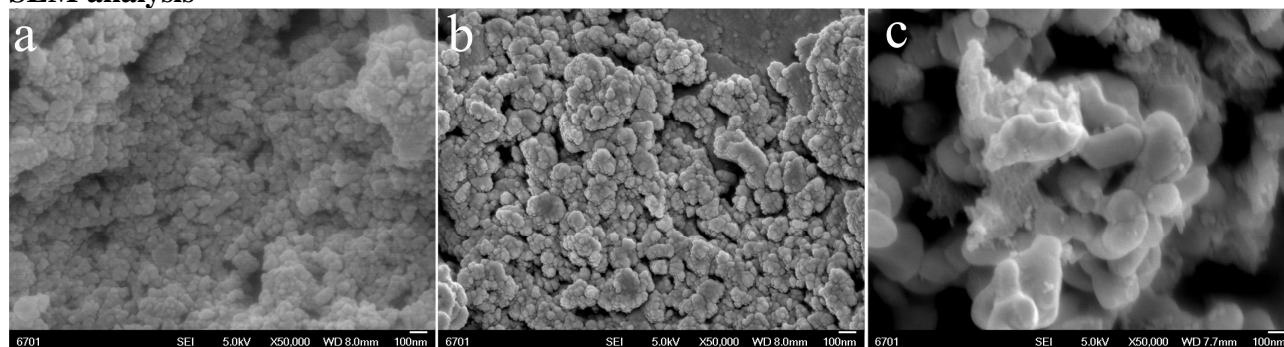


Fig. 2 SEM images of the as prepared $\text{Fe}_2\text{SiO}_4\text{@C}$ nanocomposite: a FS(600 °C), b FS(700 °C), c FS(800 °C)

SEM of FS(600 °C), FS(700 °C) and FS(800 °C) was measured and the results are presented in Fig. 2. FS(800 °C) has a size within the range of 270 nm to 400 nm. FS(600 °C) has a size within the range of 10 nm to 60 nm, mainly between 35 nm to 45 nm. FS(700 °C) has a size within the range of 10 nm to 90 nm, mainly between 40 nm to 55 nm. The particle size of FS(800 °C) is obviously the largest among the three samples. These indicate the particle size of nanocomposite can be controlled by calcinating temperature.

Electrochemical tests

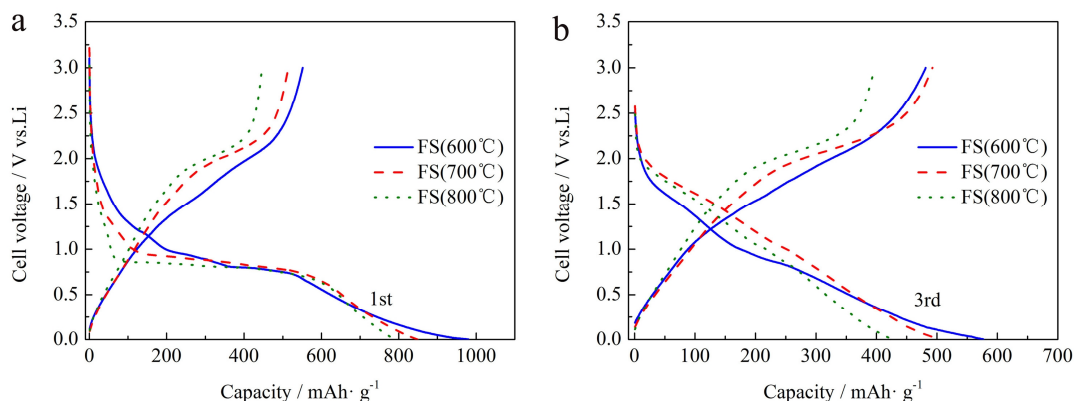


Fig. 3 Initial and third cycles of galvanostatic discharge-charge curves of $\text{Fe}_2\text{SiO}_4@\text{C}$ anode

Fig. 3a and Fig. 3b is initial and the third charge and discharge profiles at the current of 0.1 C for $\text{Fe}_2\text{SiO}_4@\text{C}$ anode materials. Fig. 3a shows that the open-circuit voltage of the assembled cells is found to be higher than 3.0 V. The sample FS(600 °C) have higher initial charge and discharge specific capacity. Initial discharge specific capacities of FS(700 °C) is higher than that of FS(800 °C). In consideration of the FS(600 °C) has much impurity, FS(700 °C) has good charge/discharge performance.

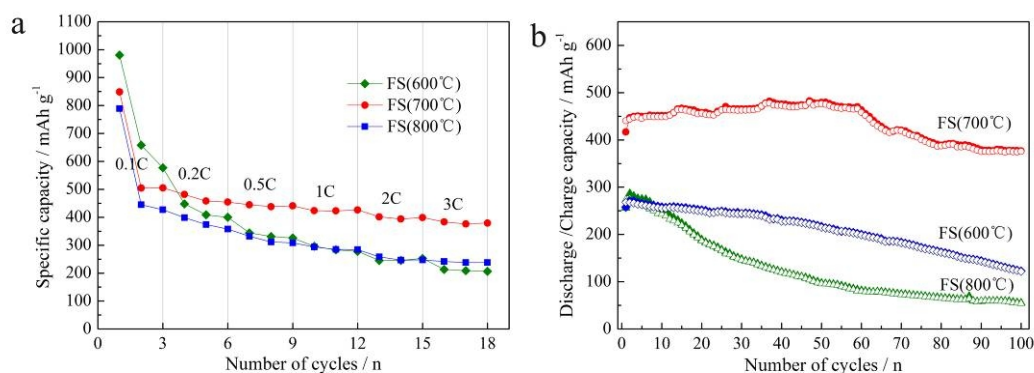


Fig. 4 (a) Rate performance of the $\text{Fe}_2\text{SiO}_4@\text{C}$ anode synthesized under different temperatures. (b) Cycling performance of the $\text{Fe}_2\text{SiO}_4@\text{C}$ anode at a charge-discharge rate of 1 C for 100 cycles.

The rate performance of $\text{Fe}_2\text{SiO}_4@\text{C}$ anodes are shown in Fig. 4a. The first discharge capacity of FS(600 °C) is the highest, while capacity attenuation is the largest at enhanced discharge current rates. FS(800 °C) exhibits the lowest discharge specific capacity and poor rate performance. The first discharge specific capacity of FS(700 °C) is less than that of FS(600 °C), while the specific capacity is stable at enhanced discharge current rates. Therefore, FS(700 °C) anode exhibits good rate performance. The reversible capacities of 514.5 mAh g^{-1} , 465.3 mAh g^{-1} , 428.7 mAh g^{-1} , 412.6 mAh g^{-1} , 384.5 mAh g^{-1} and 372.4 mAh g^{-1} were obtained at the current rates of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 3 C. The capacity ratio of 3 C/0.1 C is 72% indicating the excellent rate performance of the FS(700 °C) anode. These indicate suitable temperature is beneficial to fabricate $\text{Fe}_2\text{SiO}_4@\text{C}$ materials with improved electrochemical properties.

After the rate performance tests, the $\text{Fe}_2\text{SiO}_4@\text{C}$ anode was further discharge-charged at the current rate of 1 C for 100 cycles and the results are presented in Fig. 4b. With the increase of cycles, the specific capacities of all the samples are gradually decline. The first and 100th discharge capacities of FS(600 °C) at 1 C are measured to be 286.8 mAh g^{-1} and 55.2 mAh g^{-1} , respectively. The capacity retention ratio of FS(600 °C) is 19.3% (The 100th discharge capacity divide the first discharge capacity), which indicates poor cycling performance of FS(600 °C). The first and 100th discharge

capacities of FS(800 °C) at 1 C are measured to be 271.2 mAh g⁻¹ and 122.5 mAh g⁻¹. The capacity retention ratio of FS(800 °C) is 45.2%. The first discharge capacities of FS(700 °C) at 1 C are measured to be 446.9 mAh g⁻¹ and the 100th discharge capacities of FS(700 °C) at 1 C are 376.7 mAh g⁻¹. The capacity retention ratio of FS(700 °C) is 84.3%. Obviously, the capacity and capacity retention ratio of FS(700 °C) are the highest among the three samples, indicating the best cycling stability of FS(700 °C).

Conclusions

In summary, we have prepared Fe₂SiO₄@C nanocomposites and the particle size of nanocomposites can be controlled by calcinating temperature. FS(700 °C) possess a particle size in the range of 50~70 nm and shows h excellent rate performance and cycling performance, which is quite different.

Acknowledgments

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