Preparation of Si/TiO$_2$ Composite by the Sol-Gel Method Using As the Lithium-Ion Battery Anode

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Abstract. Si was a promising anode material for next-generation LIBs due to its extremely large capacity of 4200mAh/g (Li$_{4.4}$Si phase). However, during repeated lithium insertion/extraction processes, the accompanied huge volume change (400%) induced the structural failure of the active material and resulted in rapid capacity fading. To overcome this problem, Si/TiO$_2$ composite with different mole ratio were prepared by the sol-gel method. The inclusion of TiO$_2$ not only worked as a stable electric conductive pathway but also buffered the volume expansion of the Si during the process of charging and discharging. The Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 electrode reaches 480mAh/g, 2590mAh/g and 980mAh/g, and it delivered a charge capacity of 461mAh/g, 2510mAh/g and 891mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 96%, 96% and 91%. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 48 and 33mAh/g, respectively, which was much lower than the Si/TiO$_2$ composite electrode.

1. Introduction

LIBs have been widely used in many types of portable devices due to their high specific energy, high battery voltage, and long cycle life. However, commercially-used graphite anode material has a low specific capacity of 372mAh/g [1]. Currently, to find new anode materials with high specific capacity is an interest research direction. Therefore, alternative high capacity anode materials are strongly required. Silicon has high theoretical specific capacity (4200mAh/g) [2] and low working potential, which can be used as the lithium-ion battery anode materials in the future. However, in the process of charging and discharging, Si has large volume changes (400%) [3]. This huge volume change gives rise to the collapse of electrodes and insulation of active material, eventually resulting in rapid capacity fading and poor cycle performance.

There are little volume change of the TiO$_2$ in the process of charging and discharging, so it can buffer volume expansion problem of the Si. In this paper, the Si/TiO$_2$ composite with different mole ratio were prepared by the sol-gel method [4]. It was found that the composite prepared by the different mole ratio of 1:3 has a higher energy densities and good cycle performance.
2. Material and Methods

Si powder (0.07g, 0.28g, 0.56g, 30nm in diameter, Nanostructured & Amorphous Materials, Inc) was added into the ethanol (10ml) and was mixed with the ultrasonic bath for 10min. Solution A contained the HNO3 (2ml) and the de-ionized water (5ml). Solution B prepared with the tetrabutyltitanate and the ethanol (25ml) using the magnetic stirring for 30min. The solution A and B were mixed slowly. The mixture was aged at room temperature for 24h, dried at 70℃ for 24h. After that, the mixture was grinded fully and was calcined at 500℃ for 3h. The composite of Si and TiO2 with different mole ratio was prepared. For comparison, the pure Si was also prepared.

The electrode was prepared by mixing the active material, the acetylene black and polyvinylidene difluoride (PVDF) with the weight ratios of 80:10:10. The mixture was coated on the copper foil and was vacuum dried at 120℃ for 12h. The copper foil coated with the anode materials was cutted into electrode tabs. The CR2032 coin cell was assembled in an Ar-filled Mikrouna glove box by using the prepared electrode as anode, lithium film as the counter electrode, Celgard 2400 as separator and 1MLiPF6 in EC:DMC (1:2 in volume) as electrolyte. The electrochemical performance was investigated by carrying out galvanostatic charge–discharge experiments between cut-off potentials of 0.02 and 2.0 V at constant current densities of 42mA/g using Land cell test system (Land CT2001A, China).

3. Results and Discussion

Figure 1: X-ray diffraction patterns of (a) TiO2, (b) Si nanoparticles, the Si/TiO2 composite with the different mole ratio of 1:2(c), 1:3(d), 1:4(e).

Figure 1 showed the XRD patterns of the sample TiO2, pure Si and Si/TiO2 composite with different mole ratio of 1:2, 1:3, 1:4. The TiO2 (Fig.a) pure Si (Fig.b) presented well-defined peaks, respectively. After sintering at 500℃ in the air, the structure of the Si/TiO2 composite with the different mole ratio of 1:2,1:3,1:4 did not changed since no apparent changes could be observed for all XRD diffraction peaks[5] (Fig. c d and e). It show that the samples of different molar ratio of composite with the increment of TiO2, Si and TiO2 relative strength of peak also has the rule change. The carbon was not detected because of its amorphous structure.
Figure 2: Images of the Pure Si(a) and the Si/TiO$_2$ composite with different mole ratio of 1:2(b), 1:3(c), 1:4(d).

Figure 2a showed the plane-view SEM images of the pure Si. From the images, the Si particles with the size of 30nm. Fig.2b shows that the Si/TiO$_2$ composite with the mole ratio of 1:2, a layer of the TiO$_2$ particles formed on the surface of the Si nanoparticles coated layer, but there is still a Si particles exposed and not fully covered live. Fig.2c shows that the Si/TiO$_2$ composite with the mole ratio of 1:3, there are no Si particles in the surface, the Si surface is coated the TiO$_2$, completely, and the TiO$_2$ layer is uniform. Fig.2d shows that the Si/TiO$_2$ composite with the mole ratio of 1:4, the Si though covered by the TiO$_2$ but the TiO$_2$ on the surface of the Si has reunion seriously [6]. The results show that the mole ratio of 1:3 is better.

Figure 3: Voltage profiles (a) and Cycling performance (b) for the pristine Si and Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 at 42 mA /g
Figure 3a showed the typical voltage profiles of the pure Si and the Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 electrode cycled between 0.02 and 2.0 V at 42 mA/g, respectively. The first discharge capacity of the composite (1:2, 1:3, 1:4) electrode reaches 480mAh/g, 2590mAh/g and 980mAh/g and it delivered a charge capacity of 461mAh/g, 2510mAh/g and 891mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 96%, 96% and 91%. The lower efficiency for the first charge/discharge could be mainly due to the larger surface area of the carbon-coated Si nanoparticles with porous nanofiber structure and formation of irreversible solid electrolyte interphase (SEI) layer[7,8] in the first discharge process. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 48 and 33mAh/g, respectively, which was much lower than the composite electrode. The results provided clear evidence that the Si/TiO$_2$ composite with different mole ratio of 1:3 can enhance Li storage properties.

Figure 3b displayed the cycling performances of the Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 electrodes and Si nanoparticle electrode. It could be seen that the capacity of the pure Si electrode decreased to about 30mAh/g after 30 cycles. As shown in Fig. 3b, the Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 anode retained the reversible discharge capacity of 198mAh/g, 350mAh/g and 780mAh/g at the 30th cycle, respectively. In all 30 cycles, Si/TiO$_2$ composite with different mole ratio of 1:3 had higher capacities and better capacity retentions [9] than the other mole ratio and the pure Si due to the protection of Si with TiO$_2$.

Fig. 4 showed the impedance spectra of the pure Si and the Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 electrode with the first cycle. The electrochemical impedance spectra consist of one depressed semicircle and a line. The semicircle at high frequency can be ascribed to the charge transfer resistance, which is related to the electrochemical reaction between the particles or between the electrode and the electrolyte. The sloping line is related to lithium-ion diffusion in the active material [10, 11]. As shown in Fig. 4, the charge transfer resistance of the Si/TiO$_2$ composite with different mole ratio of 1:2, 1:3, 1:4 were 1200Ω, 250Ω and 1100Ω at the first cycle, whereas it increased greatly to 2070 Ω for the pure Si. The improvement [12] in the electrochemical performance for Si/TiO$_2$ composite with different mole ratio of 1:3 could be attributed to good electrical contact between the active materials and carbon during the lithium insertion and extraction cycles.
Figure 4: The impedance spectra of the pristine Si(a) and the Si/TiO2 composite with different mole ratio of 1:2(b), 1:3(c), 1:4(d)

4. Conclusions
The Si/TiO2 composite with different mole ratio of 1:2, 1:3, 1:4 electrode reaches 480mAh/g, 2590mAh/g and 980mAh/g, and it delivered a charge capacity of 461mAh/g, 2510mAh/g and 891mAh/g at the first cycle, corresponding to an initial coulombic efficiency of 96%, 96% and 91%. In contrast, the cell with the pure Si nanoparticle exhibited an initial discharge/charge capacity of 48 and 33mAh/g, respectively, which was much lower than the Si/TiO2 composite electrode.

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