

Short communication

## Composite anode materials for Li-ion batteries

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### Abstract

The Si ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/Ag composites were synthesized by electroless deposition (ED), and amorphous carbon was incorporated into Si and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  by dehydration reaction using concentrated  $\text{H}_2\text{SO}_4$  as dehydration agent and thermal decomposition of sucrose for the preparation of Si( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/C composites. The Si/Ag(C) composite electrodes demonstrated superior cyclabilities owing to the improvement of electronic conductivity; meanwhile, the high-rate capability of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode was also greatly improved after incorporation of silver and amorphous carbon.

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**Keywords:** Lithium-ion battery; High-rate performance;  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag;  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C; Si/Ag; Si/C

### 1. Introduction

Recently, various anode materials with improved reversible capacity and stability over commercial graphite have been highly proposed for Li-ion batteries. Silicon is an attractive one because of its largest capacity; spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is another candidate owing to its superior structural stability [1,2]. However, the application of silicon is hindered by its poor conductivity and drastic volume changes [3], and low-rate capability resulted from low electronic conductivity also limited the practical use of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [4].

Conductive fillers are routinely added to electrodes to compensate for the low electronic conductivity of electrode active materials and achieve good results. With the presence of conductive additives, the power and cycle life of the battery could be significantly augmented [5,6]. It was found in our previous study that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag [7,8] prepared by solid-state reaction was very useful to improve the high-rate performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

In this study, silver with particle size less than 100 nm was further incorporated into  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and Si by a chemical deposition to study its influence on cycling ability of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and Si. Furthermore, amorphous carbon, as another conductive additive was also incorporated into  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and Si using solid-state reaction and liquid-phase reaction, respectively. Compared with bare silicon and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , Si/Ag (Si/C) composites could exhibit

better cyclability and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C) also showed greatly improved high-rate capability.

### 2. Experiments

#### 2.1. Synthesis of Si ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/Ag composite

The (90 wt% Si)/(10 wt% Ag) and (93.7 wt%  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/(6.3 wt% Ag) composites were synthesized by ED. Dilute  $\text{NH}_3\cdot\text{H}_2\text{O}$  was titrated in 1 M aqueous solution of  $\text{AgNO}_3$  until the deposit disappeared, and a colorless solution was therefore obtained. The above solution obtained and dilute  $\text{CH}_3\text{CHO}$  was dropped simultaneously into the suspension of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  prepared by solid-state reaction method at  $850^\circ\text{C}$  for 12 h or commercial silicon powders with vigorous magnetic stirring at  $80^\circ\text{C}$ . To suppress the sustained growth of silver particles, magnetic stirring was performed throughout the reduction process. The deposited powders were washed with distilled water and dried under vacuum at  $100^\circ\text{C}$  for 12 h [9,10].

#### 2.2. Synthesis of Si( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/C composite

(20 wt% Si)/(80 wt% C) and (95 wt%  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/(5 wt% C) composites were prepared by dehydration reaction using concentrated  $\text{H}_2\text{SO}_4$  as dehydration agent and thermal decomposition of sucrose, respectively. Commercial silicon powders were homogeneously dispersed in a sucrose solution with the help of an ultrasonic bath, and the obtained suspension was further agitated under infrared light until it was converted into

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symp. The concentrated  $\text{H}_2\text{SO}_4$  was slowly added into the as-prepared syrup, mixed homogeneously and dehydrated for 2 h. The resulting product was filtered after dilution by distilled water. Then it was rinsed with distilled water until pH 7 was reached and dried under vacuum for 8 h, ground and sieved [11]. The as-mentioned pristine  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  powders were homogeneously dispersed in the aqueous solution of sucrose with the help of an ultra sonic bath and the obtained suspension was then further agitated with gentle heating until it converted into syrup. Then, the samples were heated in a muffle furnace at  $950^\circ\text{C}$  for 2 h in  $\text{N}_2$  and cooled down to room temperature naturally. The powders obtained were finally ground.

### 2.3. Measurements

X-ray diffraction (XRD) was used to analyze the phases formed. Electron back-scatter diffraction (EBSD) mapping analysis system and transmission electron microscopy (TEM) were, respectively, used to observe silver and silicon distribution.

The composite electrodes for electrochemical test were made of the Si-based composite (85 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) binder (5 wt%) homogeneously mixed in *N*-methyl pyrrolidone (NMP) solvent by ball milling and then coated uniformly on a copper foil. For the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based composite, the electrode ingredient was 85%:7%:8% in weight ratio and coated on an aluminum foil. Finally, the electrode was dried under vacuum at  $100^\circ\text{C}$  for 10 h.

The charge and discharge capacities were measured with a coin cell (2025 type), in which a lithium metal foil was used as the counter electrode. The electrolyte employed was 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate solution (EC + DMC) (1:1). Cell assembly was carried out in an argon-filled glove box (VAC AM-2). The Si-based composite electrode was cycled in the voltage range from 0.02 to 1.5 V employing a constant current density of  $0.1\text{ mA cm}^{-2}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based composite electrode was cycled between 0.5 and 2.3 V at the rate of 2C.

### 3. Results and discussion

The XRD patterns (Fig. 1) of Si/Ag and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag composites showed that except the characteristic patterns of elemental silver, all diffraction peaks were in accordance with the patterns of silicon and spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and all patterns in Si/C and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C composite samples were attributed to silicon and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  indicating an amorphous feature of incorporated carbon.

The TEM image of Si/Ag and the EBSD image of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag composite obtained by ED method are shown in Fig. 2a and b, respectively. It was clearly observed that nano-sized silver particles with size less than 100 nm were uniformly distributed on the surface of silicon and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles. Compared with the solid-state reaction [7,8] and the direct reduction of  $\text{AgNO}_3$  in other papers [12], the complex reduction, obviously, could produce much smaller conductive particles with narrow size distribution. It was therefore assumed that these highly dispersed nano-sized silver particles could

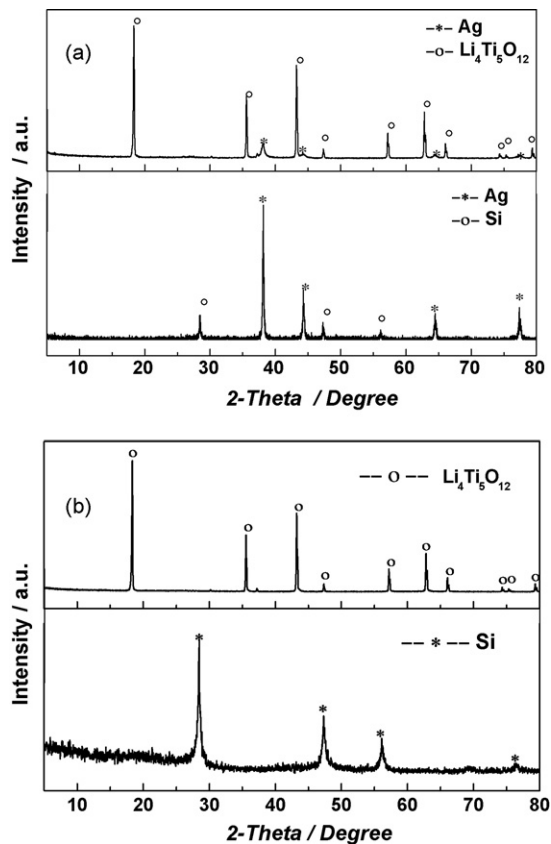


Fig. 1. XRD patterns of (a) the Si ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/Ag composites and (b) the Si ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ )/C composites.

play a positive role in improve electrical contact between silicon ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) particles and current collector. Accordingly, the discharge/charge performance of Si/Ag and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Ag composite electrode would benefit from the good conducting network between active particles.

Fig. 3a shows the TEM image of Si/C prepared by low-temperature carbonization. The silicon particle size was less than 25 nm, with a distinct contrast from the carbon matrix as seen from the image. Therefore, we can conclude that the amorphous carbon with good electronic conductivity formed a conduction pathway for electrochemical reactions. On the other hand, nano-sized silicon particles with small absolute volume changes were embedded in carbon matrix, therefore, there was no direct contact between silicon particles, and the electrochemical sintering process transformed from silicon nanoparticles into dense blocks was suppressed to the utmost of degree. Fig. 3b shows the EBSD image of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C obtained by thermal decomposition of sucrose. Two kinds of particle morphologies existed in the composite, one ascribed to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase, another one, nano-sized and flaky featured, therefore attributed to carbon phase. The average thickness of the flakes was below 50 nm. It was suggested that the nano-sized carbon flakes resided in the void of active powders and formed a conduction pathway which was essential to improve the utilization of the active material  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

Fig. 4a compares the first discharge/charge voltage curves of pure silicon, Si/Ag composite and Si/C composite elec-

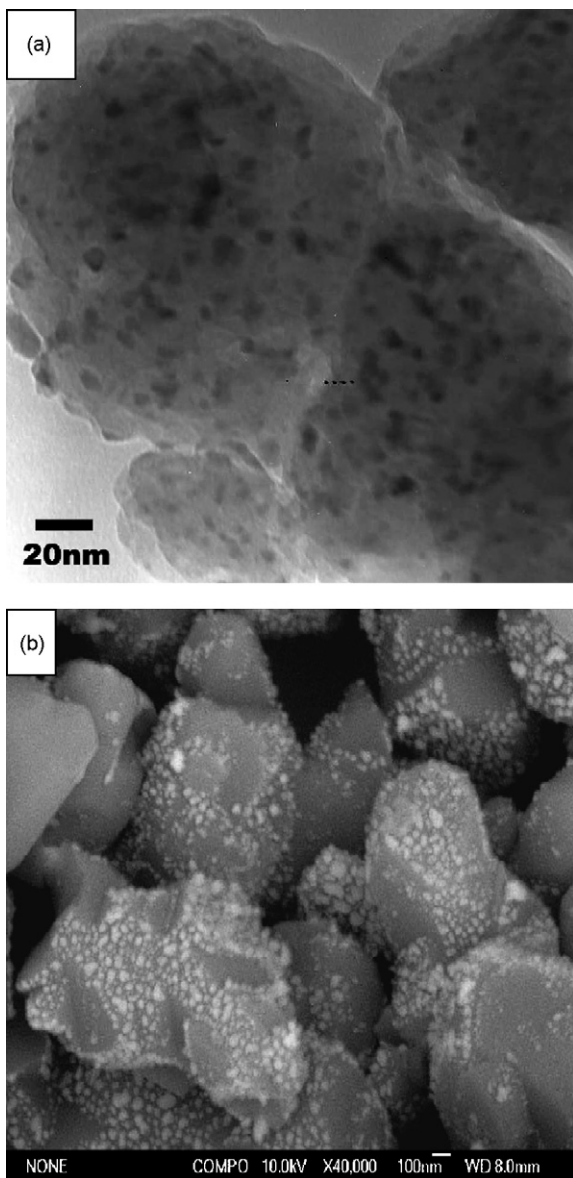


Fig. 2. (a) TEM images of the Si/Ag composite and (b) SEM images of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$  composite.

trodes cycled at a constant current density of  $0.1 \text{ mA cm}^{-2}$ . The pure silicon electrode delivered a large specific capacity of  $3973 \text{ mAh g}^{-1}$ , which was much close to its theoretical value, but only 73% of it could be reversibly extracted. After the addition of silver, the first discharge capacity dropped to  $2729 \text{ mAh g}^{-1}$  with an improved coulombic efficiency of 86%, that is to say, extraction depth of  $\text{Li}^+$  from silicon could be furthered with the help of silver. The release of polarization between discharge and charge process benefited from the Ag-improved conducting network. In the case of Si/C composite, 80 wt% of carbon was added into silicon powders, but the composite electrode still demonstrated a large discharge capacity of  $1209 \text{ mAh g}^{-1}$  because of relative light mass of carbon compared with silver. The decreased coulombic efficiency may be related to the absorbed  $-\text{OH}$  group which would irreversibly trap  $\text{Li}^+$  in the first cycle. The initial capacity drop was an expected

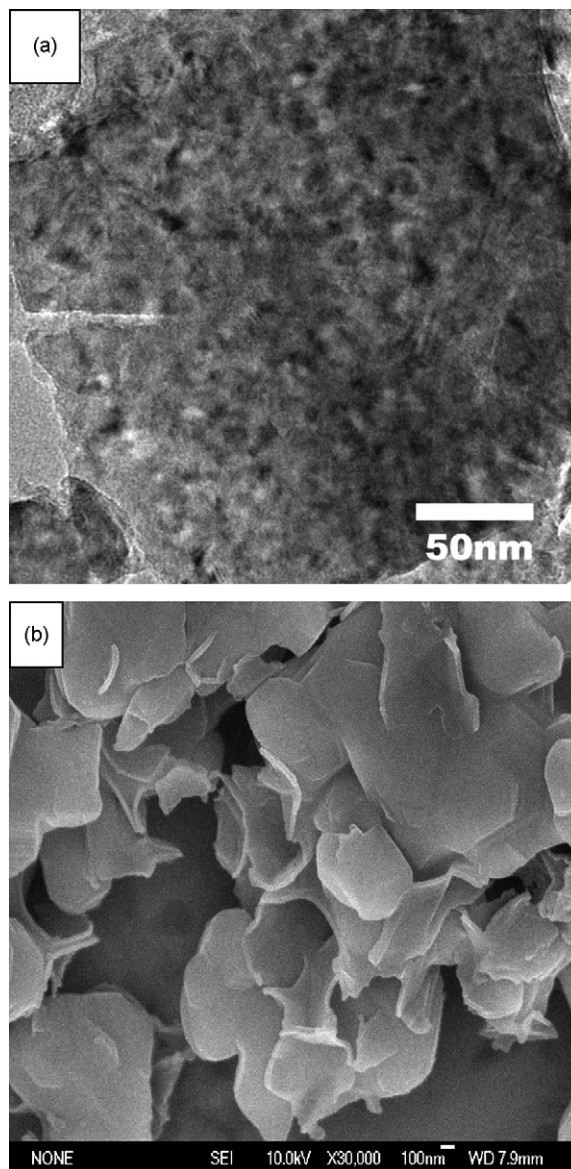


Fig. 3. (a) TEM images of the Si/C composite and (b) SEM images of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  composite.

phenomenon in common disordered carbon, but it could be avoided with increase of cycling.

As shown in Fig. 4b, the first discharge capacity of pristine  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$  composite and  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  composite electrodes cycled at the rate of 2C was 162.2, 244.2 and  $219.1 \text{ mAh g}^{-1}$ . There were two platforms for every sample, the main discharge platform of pristine  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  composite at the first cycle was 1.53 V, but the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$  composite was 1.45 V. The Ag and C additives greatly improved the first discharge capacity. Metal silver mainly increased the capacity at about 1.5 V platform, while amorphous carbon increased the capacity at both 1.5 and 0.5 V platforms.

Fig. 5a shows the charge capacity and coulombic efficiency versus cycle number for pure silicon, Si/Ag composite and Si/C composite electrodes cycled at a constant current density ( $0.1 \text{ mA cm}^{-2}$ ). As shown in Fig. 5a, the pure silicon electrode

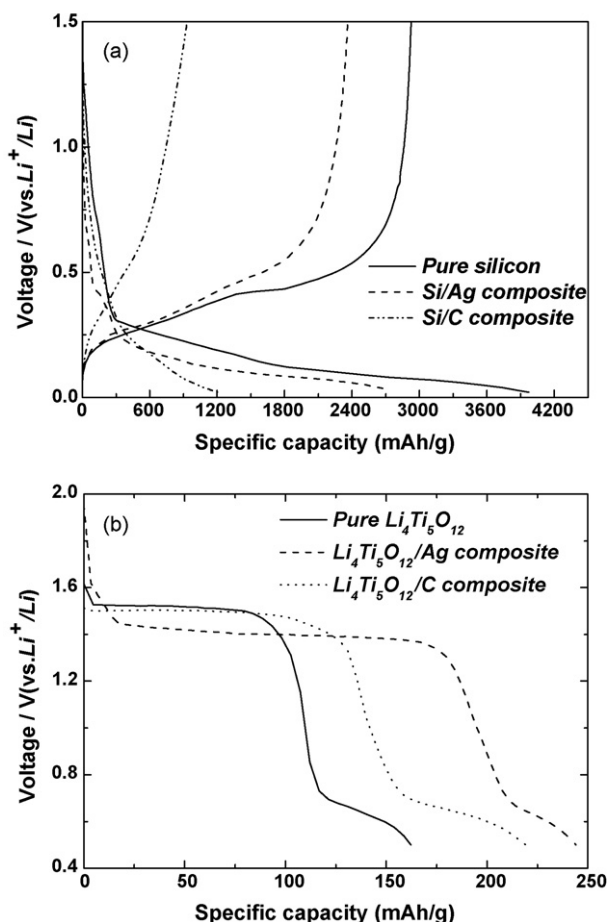


Fig. 4. (a) The first charge–discharge curves of the pure Si and the Si/Ag(C) composite. (b) The first discharge curves of the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag(C) composite.

faded almost all of its first capacity within only five cycles. After the addition of silver and carbon additives, the Si/Ag composite electrode remained a capacity above 500 mAh g<sup>-1</sup> and the Si/C composite electrode delivered a stable reversible capacity near to 1000 mAh g<sup>-1</sup> without obvious capacity fading after 30 cycles, which was expected as a result of the increase of electronic contact, meanwhile, possible volume changes of silicon particles during repeated cycling were also effectively absorbed by amorphous carbon matrix. These results were in good consistency with other reports [11,13,14]. The cycling behaviors of the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag composite and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/C composite are shown in Fig. 5b. The 50th discharge capacities were 153, 196.2 and 178.9 mAh g<sup>-1</sup> with the capacity degradations of 2.67, 3.59 and 3.19% compared to the second cycle for the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag composite and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/C composite, respectively. The Ag and C additive greatly improved the reversible capacity of the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, although the capacity degradation of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag(C) composite was bigger than the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> at the rate of 2C, its absolute value of discharge capacity after 50 cycles was much higher than the precursor.

The greatly increased reversible capacity of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag(C) composite could be attributed to the improvement of cathode

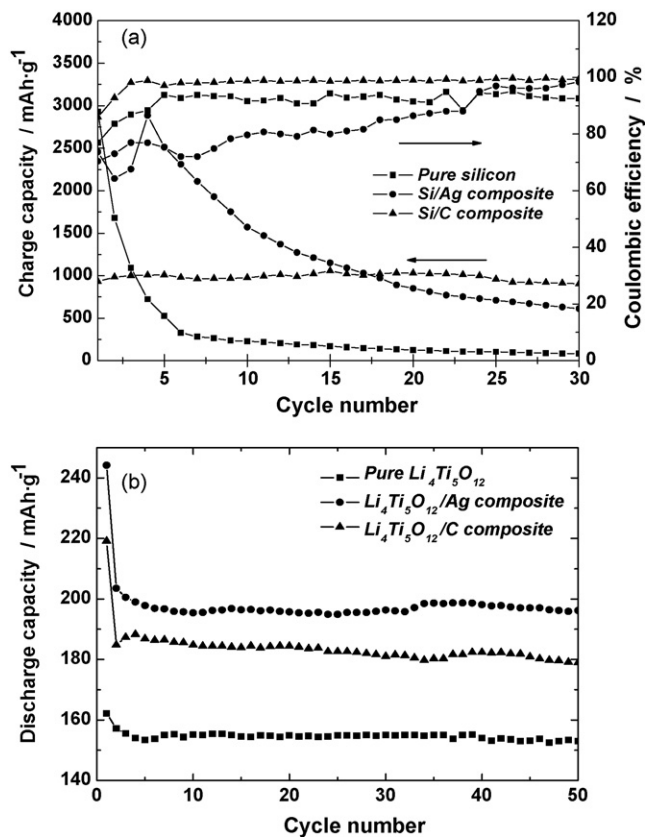


Fig. 5. Variation of the charge capacities for (a) the pure Si and the Si/Ag(C) composite and discharge capacities for (b) the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/Ag(C) composite.

utilization. The Ag and C additive resided in the surface of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> matrix and formed a conduction pathway which was essential to improve the electronic conductivity of the electrode and the utilization of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> material, leading to improvement in charge and discharge performance and furthermore the cycle life of the battery.

#### 4. Conclusions

The Ag and C additives were useful to improve the electrochemical performance of silicon and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. The Si/Ag and Si/C composite electrodes demonstrated superior cyclabilities owing to the improvement of electronic conductivity and effective buffering of volume changes, meanwhile, the high-rate capability of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrode was greatly improved after incorporation of silver and carbon.

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