

Carbon-coated Si-Cu/graphite Composite as Anode Material for Lithium-ion Batteries

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The carbon-coated Si-Cu/graphite composite was obtained by mechanical milling of mixture of Si-Cu alloy and graphite followed by pyrolysis reaction of coal-tar pitch. XRD and SEM results showed Cu₅Si alloy was formed after the intensive ball milling and SiC phase appeared after pyrolysis, composite particles were encapsulated by carbon matrix and the surface become smooth and compact. The electrochemical results exhibited the introduction of carbon-coating process decreased reversible capacity but obviously improved cycle performance. The reduced capacity was related to the inactive SiC phase and the improved cycle performance is mainly attributed to the homogeneous distribution of nanosized Si in silicon-copper alloy and elastic carbon matrix.

Keywords: Lithium ion batteries; anode material; ball-milling; carbon-coating

1. INTRODUCTION

It is well known that lithium-ion batteries get wider and wider application in today's information-rich society and have become one of the most potential chemical power sources. Among kinds of anode materials for lithium-ion batteries, graphite has been commercialized owing to its excellent cycling behavior upon repeated charge and discharge cycles, although its theoretical capacity is limited to 372 mAh g⁻¹[1, 2]. On the other hand, the increasing demand for higher energy density battery systems has motivated an ongoing search for new storage electrodes with high gravimetric and volumetric charge capacity and excellent cyclability. Over the last two decades, there has been intensive research on silicon materials. The electrochemical results show that they may be potentially alternative to the carbonaceous materials, since the silicon-lithium alloy systems have a high theoretical energy density and low electrochemical potential versus Li/Li⁺. The major problem associated with the use of silicon appears to be mechanical failure brought about by the repeated large volume changes associated with the alloying/dealloying process [3-5].

Several efforts have been exerted to improve the cyclability of silicon materials. It is believed that decreasing the particle size could improve the performance of silicon electrode, because this can lead to the decrease of macroscopic volume changes of the materials to avoid crack formation and consequent degradation [6-8]. However, the capacity fading upon cycling is still remarkable while merely decreasing the particle size. An effective approach to alleviate the volume change is to disperse the nanosized active silicon homogeneously in an inert matrix, such as Si-TiN, Si-TiC, Si-SiC, Si-C composites produced by mechanical milling [9-14]. Another approach was synthesizing metal silicide alloys using less active or inactive metal elements with active Si, such as Fe-Si, Co-Si, Ni-Si, Cr-Si, Ca-Si, Cu-Si and Mg-Si etc [15-21]. The ductile inactive phase buffers the volume change while lithium insertion and extraction. There are also some researches on carbon-coating by dispersing silicon particles homogeneously in the precursors, such as the solution of PVC, pitch or carbon gel followed by carbonization [22-23]. Those composite materials exhibit improved cycle performances with high capacity, which suggests that the cyclic characteristics of Si-based anode materials could be improved by well dispersing them into buffering matrix.

In this work, Si-Cu/graphite composite was synthesized by high energy mechanical milling. To further improve the electrochemical performance, the carbon-coating process was introduced. The microstructures and the electrochemical characteristics as anode material for lithium ion batteries were investigated. The objective of the investigation is to utilize the high buffering action of active graphite and inert Cu₅Si alloy and low volume effect of C to improve the cycle life of Si active material.

2. EXPERIMENTAL PART

Planetary Mono Mill P-6 (Fritsch, Germany) with an 80ml hardened steel bowl filled with 15 hardened steel balls in the diameter of 10mm was used for milling. The Si-Cu alloy was prepared by mechanical milling the mixture of silicon and copper powders at the speed of 400rpm for 7 hours. The starting materials were Si (<100nm, >99% pure), Cu powder (99.99%), and weighted in molar ratio of Si: Cu = 2:1. The mixture was loaded in the hardened steel bowl and sealed in an argon filled glove box (MBRAUN). The as prepared Si-Cu alloy was annealed at 800 °C for 4 hours under a flow of argon and then ball-milling at 300rpm for 1 hour. The Si-Cu/graphite composite was fabricated by high energy mechanical milling of as formed annealed sample and graphite (1-2 μm, Aldrich) with the weight ratio of 3:2. The resulted product was further disposed by mixing Si-Cu/graphite composite with coal-tar pitch with weight ratio of 1:0.4 using ball-milling at 300rpm for 1 hour then followed by pyrolysis reaction at the temperature of 900 °C in an argon flow for 2 hours. Si/graphite sample was fabricated by milling of graphite and Si with 40:60 wt.% at 450 rpm for 20 min.

X-ray diffraction (XRD) patterns were obtained using automated powder diffractometer with Cu K α radiation (Rigaku D/MAX-2200). Morphologies of the samples were observed with scanning electron microscope (FEI SIRION 200).

The electrodes were prepared by mixing 87 wt. % composite powders as active material, 5 wt. % acetylene black as electronic conductor and 8 wt. % polyvinylidene fluorides (PVDF) dissolved in N-methylpyrrolidinone (NMP) as binder. The as-prepared slurry was coated onto a copper foil followed by drying under vacuum at 120 °C over 3 hours. The electrodes were cut into disks (12.5mm in

diameter). The model cells were assembled in the argon filled glove box using metallic lithium as the counter electrode, 1M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight ratio) as electrolyte solution. The cells were tested at a constant current density of 0.2mA/cm² with voltage cutoff of 1.4V/0.0V versus Li/Li⁺.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of the Si/graphite, Si-Cu/graphite and carbon-coated Si-Cu/graphite composites, respectively. As shown in figure 1(a), the diffraction peaks at $2\theta = 28.4^\circ$, 47.3° , 56.1° , 69.1° can be attributed to reflections of Si (JCPDS file 27-1402), $2\theta = 26.4^\circ$ and 54.5° correspond to those of graphite (JCPDS file 41-1487), and the broad hump at 45° indicates that part of graphite is amorphized. After high energy mechanical milling for 7 hours, a mixture of Si and Cu₅Si located at $2\theta = 44.6^\circ$ (JCPDS file 04-0841) is detected instead of a pure alloy, as shown in Fig. 1(b). New diffraction peaks appear at $2\theta = 35.8^\circ$, 36.9° , 49.6° , 60.3° and 65.4° after pyrolysis carbonization, which can be attributed to the reflection of SiC (JCPDS 73-2082).

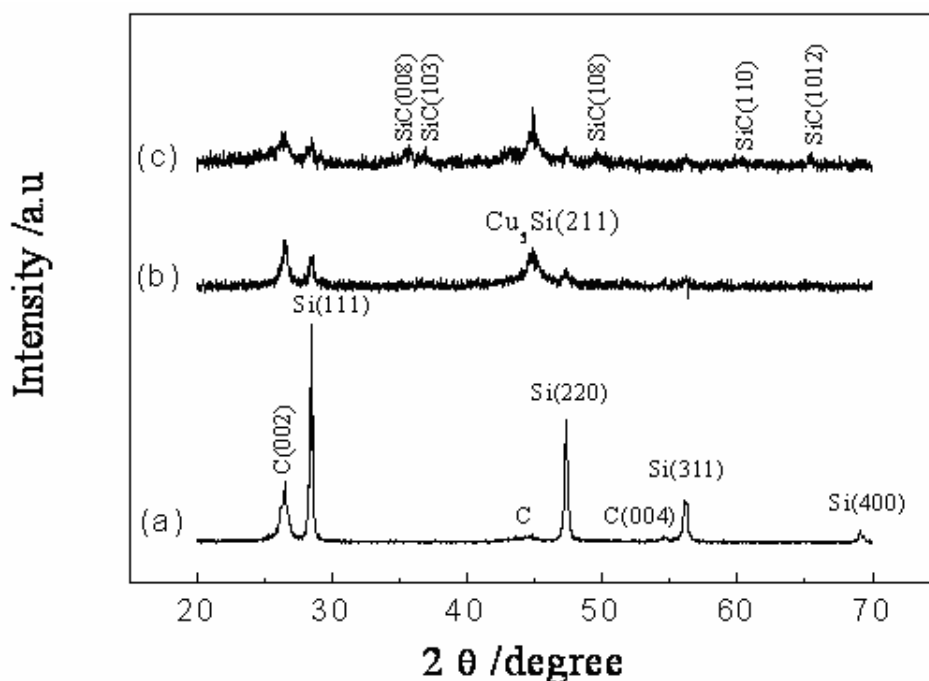


Figure 1. The XRD patterns for (a) Si/graphite, (b) Si-Cu/graphite and (c) carbon-coated Si-Cu/graphite composites.

The SEM images of Si-Cu/graphite and carbon-coated Si-Cu/graphite composites are given in Figure 2 (a) and (b), respectively. The particles of Si-Cu/graphite composite tend to form large agglomerates, and fine silicon particles are probably pinned in inactive Cu₅Si alloy via good ductibility and affinity to Si of Cu₅Si and the addition of graphite enhances the dispersion uniformity of particles. As expected that carbon-coated particles are encapsulated and the surface become smoother and

more compact, leading to the formation of spherical particle with reduced specific surface area. By this way, Si particle expansion will be locked by elastic carbon and a good contact is ensured.

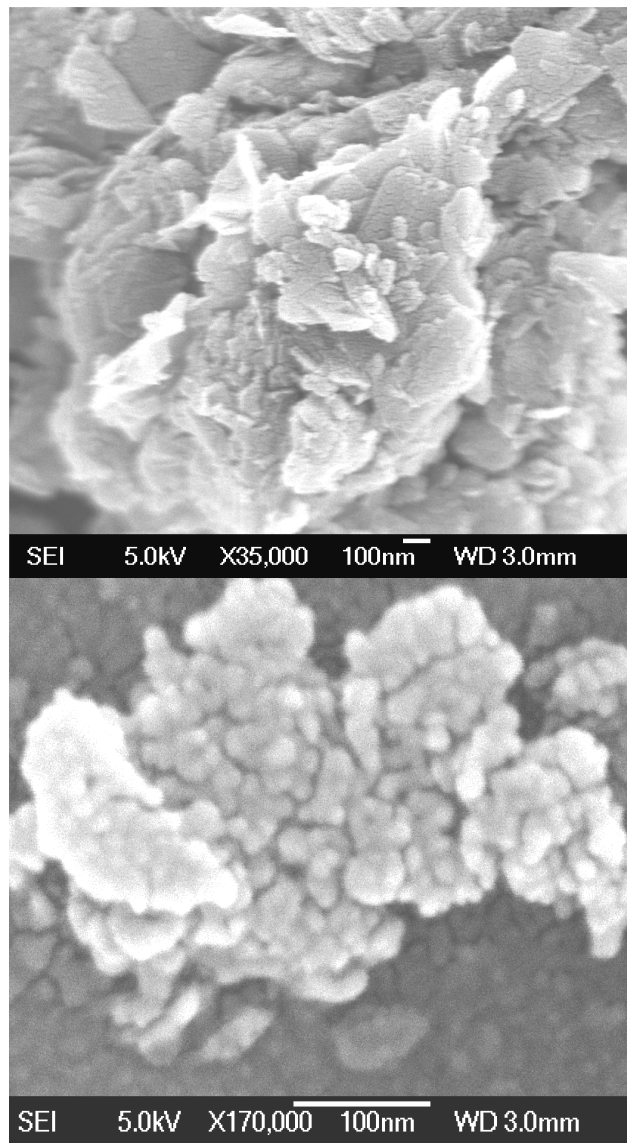


Figure.2. SEM images of (a) Si-Cu/graphite and (b) carbon-coated Si-Cu/graphite composites.

Figure 3 show the discharge and charge profiles of Si-Cu/graphite composite anode. In the first discharge, a sloping voltage plateau appears from 0.7 to 0.6 V, which is mostly attributed to the formation of the solid electrolyte interfaces (SEI) film on the surface of the active particles. The voltage of Li uptake with Si in the first cycle occurs mainly below 0.1V, yielding an extremely flat plateau. The plateau at around 0.45V in the charge curve can be attributed to the Li extraction from the

Li_xSi . It can be noted that the subsequent insertion voltage trends present an obvious shift from the first one and no obvious plateau is evolved, suggesting an irreversible transformation of silicon from a

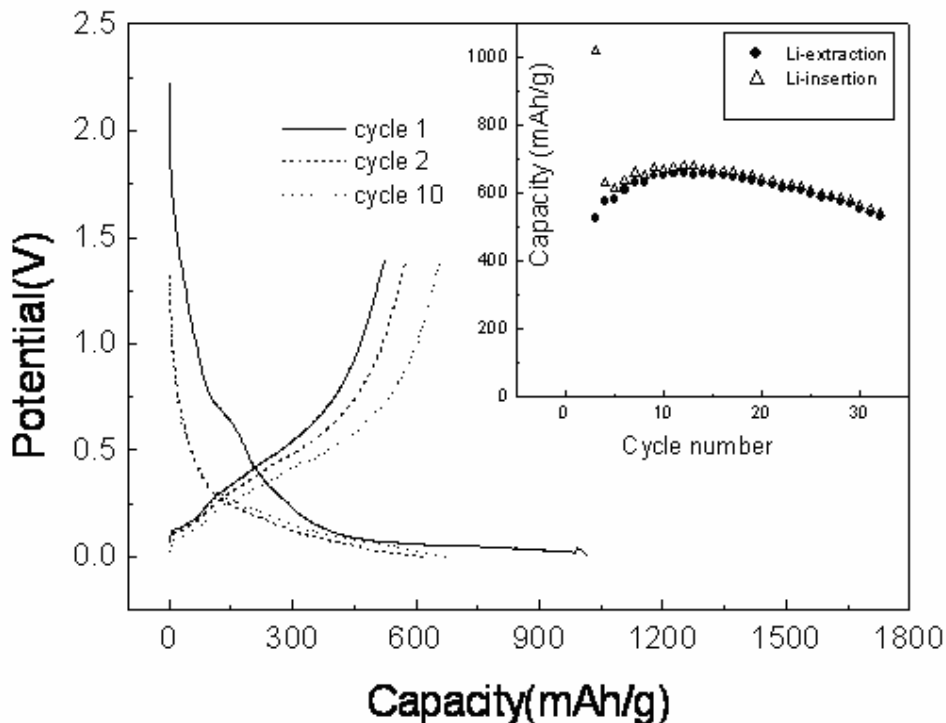


Figure 3. Electrochemical properties of Si-Cu/graphite composite prepared by mechanical milling.

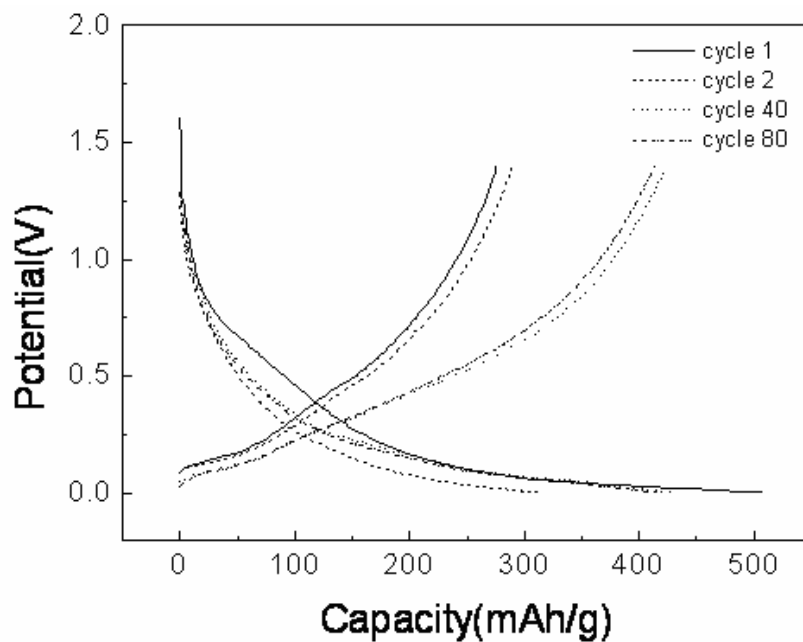


Figure 4. Discharge and charge profiles for carbon-coated Si-Cu/graphite composite.

crystal to amorphous phase. The lithium insertion capacity of the composite electrode is as high as 1021mAh/g with a relative low faradic yield of 51.3%. These irreversible capacities are mainly resulted from the large specific surface area by long-time ball-milling. Although mechanical milling/alloying has been shown to be a powerful technique to produce alloy powders with a homogeneous structure, the high initial irreversible capacity due to large surface area of electrode material is an inevitable limitation. As shown in the figure, the capacity in the tenth cycle is larger than that in first two cycles, which may be due the reason of active material is not completely utilized at the beginning. The discharge capacity decays quickly and remains to be 541 mAh/g at 30th cycle, suggesting Cu_5Si alloy and graphite may be not enough effective to depress the large volume changes of active material.

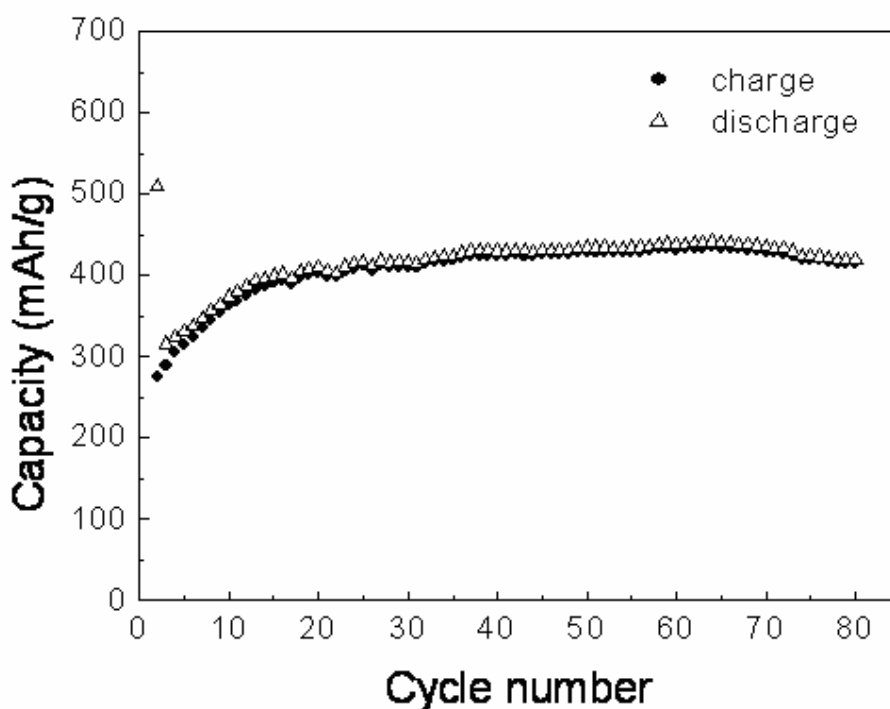


Figure 5. Capacity vs. cycle number performance for carbon-coated Si-Cu/graphite composite.

In order to decrease the initial irreversible capacity and further improve the cycling stability, carbon-coating process was introduced. Despite some reversible capacity, pyrolyzed carbon acts mainly as matrix and binder for graphite and high capacity silicon active species. Fig. 4 presents the discharge and charge profiles of the carbon-coated sample. Compared with the sample before coating, the lithium insertion capacity reduces greatly and delivers an initial discharge capacity of about 510 mAh/g, which may due to deactivation of some active silicon particles. There are many reasons responsible for the deactivation of Si, such as formation of inactive SiC as confirmed in Fig. 1 (d), coating with inert phases etc. Although the first columbic efficiency is only increased to 54% and the reason is still not sure, the voltage plateau related to SEI decreases and shortens. It is suggested that

carbon-coating process reduce the surface area of particle therefore depress the irreversible side reaction. The ideal situation is that active Si particles are completely and compactly enclosed by the carbon matrix. The capacity of the composite increases continually before 40th cycle, suggesting some Si in the matrix of Si-Cu alloy and graphite is slowly utilized as the contact of active materials and electrolyte increased. Moreover, the composite shows a reversible capacity of over 410 mAh/g up to the 80th cycle, which indicates a good cyclability. As a dramatic volume variation of 300% accompanies to the lithium alloying process with Si to form $\text{Li}_{4.4}\text{Si}$, it could pulverize the electrode, inducing poor cyclability. The problem is improved by dispersing nanosized Si homogeneously in the matrix of Si-Cu alloy and graphite, especially, carbon-coating process using pyrolysis reaction of coal-tar pitch. Both of the factors achieve the reasonably improved interface affinity, buffer the significant volume expansion during discharge and charge and enhance connection for electronic and ionic conduction, thus improve the cyclability of composite electrode.

4. CONCLUSIONS

The Si-Cu/graphite composite was synthesized by mechanical milling of a mixture of silicon-copper alloy and graphite powders then a carbon-coating process was accomplished by adding coal-tar pitch to the composite and pyrolysis. The Si-Cu alloy particles comprised of an electrochemically active Si and inactive Cu_5Si phases distributed uniformly in the matrix of graphite. The inactive phase improves electronic conductivity and accommodates the large volume changes of Si during cycling. Graphite provides not only mechanical and conductivity support for the dispersed phase, but also possesses electrochemical reactivity towards lithium. By carbon-coating, particles were encapsulated by pyrolytic carbon, which enhance connection for electronic and ionic conduction and effectively suppressed the adverse volume effect of silicon upon cycling. As a result, the carbon-coated Si-Cu/graphite composite shows stable capacity retention during cycling. A further improvement is to increase the initial reversibility and restrain the formation of SiC.

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