Short communication

Enhancement of capacity of carbon-coated Si–Cu$_3$Si composite anode using metal–organic compound for lithium-ion batteries

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Abstract

A carbon-coated Si–Cu$_3$Si composite material is prepared using silicon and copper(II) D-gluconate powders by simple mechanical milling and pyrolysis, and is investigated as an anode material for lithium-ion batteries. In this process, the Cu$_3$Si and pyrolyzed carbon uniformly adhere to the surface of the silicon particles. The cycling performance of the composite material exhibits a stable capacity of 850 mAh g^{-1} for 30 cycles. The improved cycling performance is attributed to the fact that the copper silicide and pyrolyzed carbon provide both a better electrical contact with the current–collector and a buffering effect for the volume expansion–contraction during cycling.
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1. Introduction

Carbonaceous materials including graphite, which has a theoretical capacity of 372 mAh g^{-1}, are currently used as anode materials in commercial lithium-ion batteries. The need for smaller and lighter portable electronic devices has, however, led to demands for new anode materials of higher specific energy [1,2]. Among the alternatives to the existing carbonaceous materials, the use of silicon as an anode material in lithium-ion batteries has attracted much attention because of its high theoretical specific capacity of 3580 mAh g^{-1}, but its practical usage has been hindered due to its low electrical conductivity and capacity fading caused by the drastic volume change that occurs during the charge–discharge reaction [3,4].

Many researchers have focused on improving the cycling performance of silicon-based systems. In particular, silicon composite materials composed of active and inactive phases prepared by the ball-milling and pyrolysis of organic compounds have been found [5–15] to exhibit high capacity and improved cyclability. On the other hand, milled composite materials have a large irreversible capacity during the first cycle and also need several pyrolysis steps to obtain a homogeneous silicon distribution and better contact between silicon and the matrix.

In this study, an attempt is made to enhance the reversible lithium-storage capability by both improving the electrically conducting network using a copper silicide material and obtaining a uniform dispersion of the disordered carbon coating. A carbon-coated Si–Cu$_3$Si composite material is prepared by the mechanical mixing of silicon and copper(II) D-gluconate followed by pyrolysis. The electrochemical characteristics of this composite material, when used as an anode material for lithium secondary batteries, are investigated using various analytical techniques.

2. Experimental

A carbon-coated Si–Cu$_3$Si composite material incorporating the metal–organic compound was prepared by the following procedure. Commercial powders of silicon (>99%, 2 μm, Kojundo) and copper(II) D-gluconate (C$_{12}$H$_{22}$CuO$_{14}$, 98%, Aldrich) with a mass ratio of 1.5:8.5 were mixed by mechanical ball-milling for 20 min in a hardened steel vial. The ball-to-powder ratio was 10:1. The vial, which was assembled in an argon-filled glove box, was installed on an SPEX-8000 vibratory mill. The

mixed powders were pyrolyzed at various temperatures for 1 h under an argon atmosphere at a heating rate of $5\,^{\circ}C\,min^{-1}$. After pyrolysis, the furnace was automatically cooled to room temperature. The final product was ground and sieved. Each sample was characterized by X-ray diffraction (MacScience M18XHF-SRA). The thermal decomposition behaviour of the precursor, viz., the copper(II) D-gluconate powder, was studied by thermogravimetric analysis (TGA, Rheometric Scientific). The morphology, microstructure and composition of the synthesized powders were examined by scanning electron microscopy (SEM) in conjunction with electron probe X-ray microanalysis (JEOL JXA-8900R). The hydrogen-to-carbon ratio in each sample was determined by elemental analysis (Flash EA 1112).

The test electrodes consisted of the active powder material, Denka black as a conducting agent, and polyvinylidene fluoride (PVdF) dissolved in *N*-methyl pyrrolidinone (NMP) as a binder, with a mass ratio of 7:1.5:1.5, respectively. Each component was well-mixed to form a slurry, which was coated on a copper-foil, followed by pressing and drying at $120\,^{\circ}C$ for 4 h under a vacuum. A laboratory-made, coin-type, electrochemical cell was used with lithium-foil as the counter electrode and 1 M $LiPF_6$ in a mixed solvent of ethylene carbonate and diethylene carbonate (EC + DEC, 1:1, v/v, Cheil Industries Inc.) as the electrolyte. The cell was assembled and all of the electrochemical tests were carried out in an argon-filled glove box. The cells were galvanostatically charged and discharged at $100\,mA\,g^{-1}$ over the voltage range of 0.0–1.5 V (versus Li/Li$^+$).

3. Results and discussion

Thermogravimetric data for the decomposition of copper(II) D-gluconate in an argon atmosphere at a heating rate of $5\,^{\circ}C\,min^{-1}$ is presented in Fig. 1. The weight loss of copper(II) D-gluconate is approximately 84% at $650\,^{\circ}C$ and carbon and copper at present in the product at 78 and 22 wt.%, respectively.

X-ray diffraction patterns of the composite materials synthesized by pyrolysis at various temperatures are shown in Fig. 2.
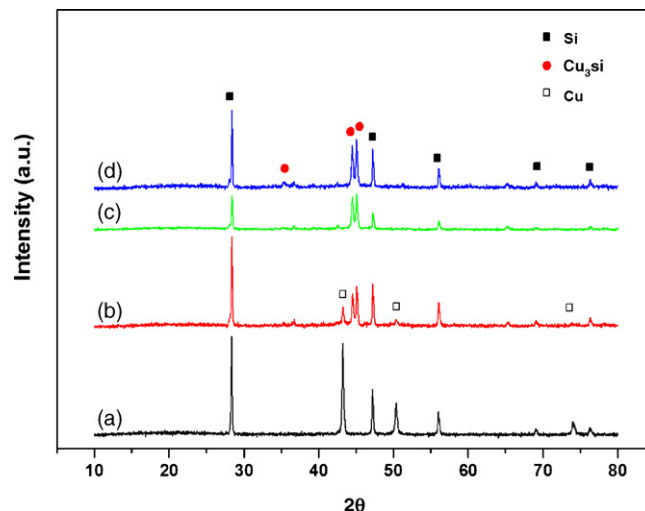

Fig. 2. X-ray diffraction patterns of powders synthesized by pyrolysis at various temperatures (a) $600\,^{\circ}C$; (b) $750\,^{\circ}C$; (c) $900\,^{\circ}C$; (d) $1050\,^{\circ}C$.

All the diffraction peaks are indexed to Si, Cu and Cu_3Si [17,18]. As the pyrolysis temperature increases a Cu_3Si phase starts to form at $750\,^{\circ}C$ and Cu disappears completely at $900\,^{\circ}C$, while the Cu_3Si peaks become sharp at higher temperatures.

Scanning electron micrographs of the agglomerates embedded in an epoxy resin together with electron probe X-ray microanalyses (EPMA) of the corresponding cross-sections of the carbon-coated Si–Cu_3Si composite after heat treatment at 600 and $900\,^{\circ}C$ are shown in Fig. 3. The size of the agglomerates is about 5–30 μm. As observed in the EPMA images (Fig. 3(a)), the size of the Si particles is of the order of a few microns, while the Cu particles are much smaller. Both types of particle were distributed randomly within the composite when the sample is pyrolyzed at $600\,^{\circ}C$. At this temperature, the Cu has not yet reacted with the Si to form Cu_3Si, as confirmed by the X-ray diffraction data in Fig. 2. By contrast, the EPMA image of the composite particles pyrolyzed at $900\,^{\circ}C$ shows that a Cu_3Si layer adheres tightly to the surface of the Si particle which is enclosed by pyrolyzed carbon. This encapsulation may provide a good electrical contact with the current–collector, as well as a buffering effect for volume expansion–contraction during cycling [11–15].

Voltage profiles of the first charge and the subsequent second and third discharge–charge curves of the carbon-coated Si–Cu_3Si composite material prepared at $900\,^{\circ}C$ and cycled at a rate of $100\,mA\,g^{-1}$ are given in Fig. 4. The first charge and discharge capacities are approximately 1225 and $1019\,mAh\,g^{-1}$, respectively. The initial coulombic efficiency is 83%, which is much larger than that of milled Si composite materials [6,7]. The voltage profile of this material is similar to that of a crystalline Si powder electrode. During the first discharge (Li insertion), the alloying reaction with lithium is observed as a flat plateau region below 0.1 V. The discharge voltage curves of subsequent cycles exhibit different behaviour from that of the first cycle. This is due to a transformation that occurs from the crystalline Si phase to the amorphous Si phase during the first discharge [3,4].
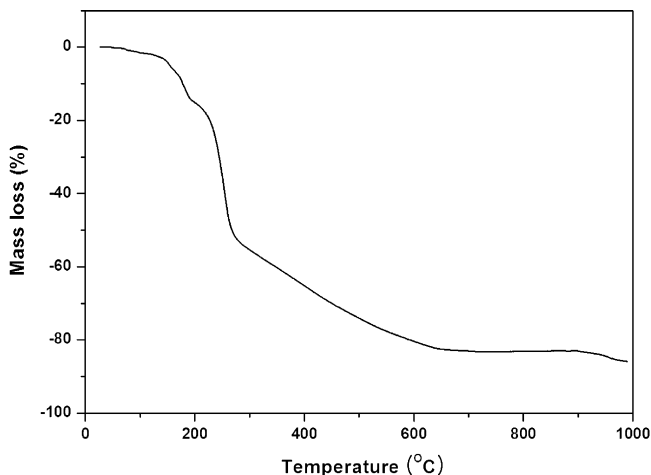

Fig. 1. Thermo-gravimetric analysis of copper(II) D-gluconate in argon atmosphere at a heating rate of $5\,^{\circ}C\,min^{-1}$.
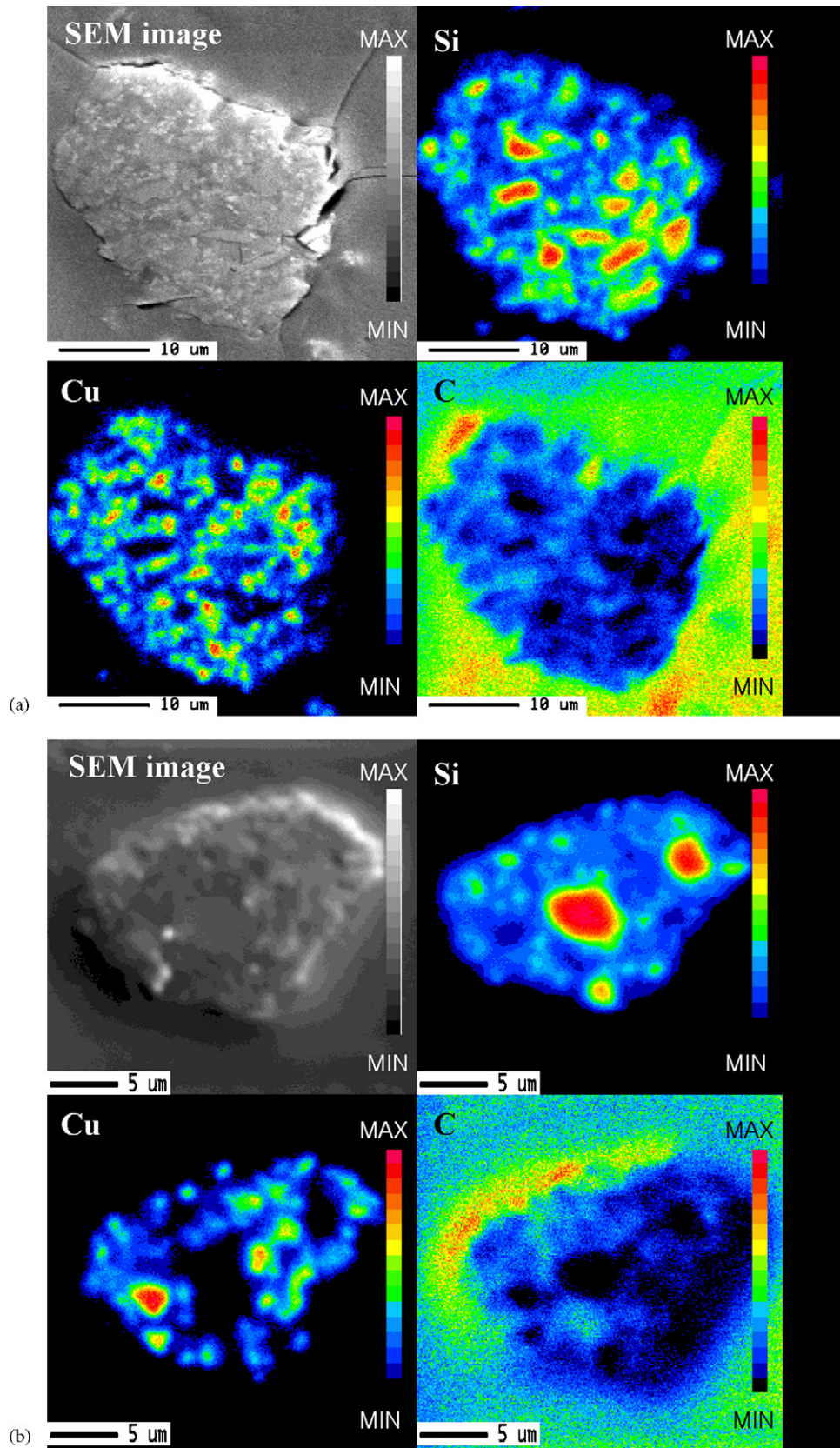
Fig. 3. Scanning electron micrograph and corresponding EPMA mapping of each species of agglomerates after heat treatment at (a) 600 °C and (b) 900 °C.
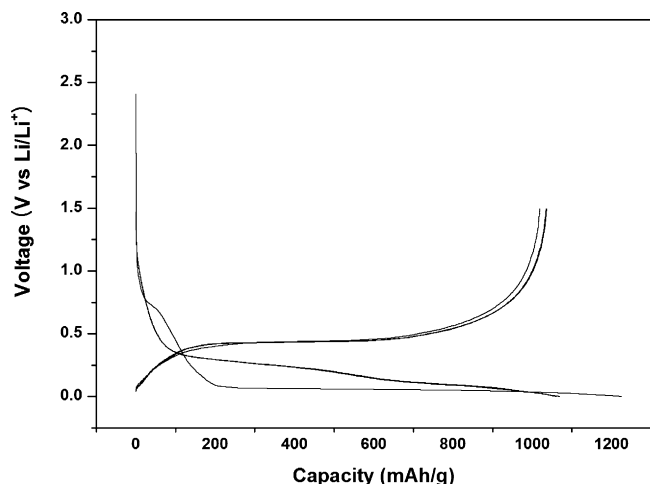
Fig. 4. Voltage profiles of carbon-coated Si–Cu₃Si composite for initial three cycles.

Fig. 6. Cycle-life behaviour of pure Si and Si-based composite electrodes with and without copper silicide.
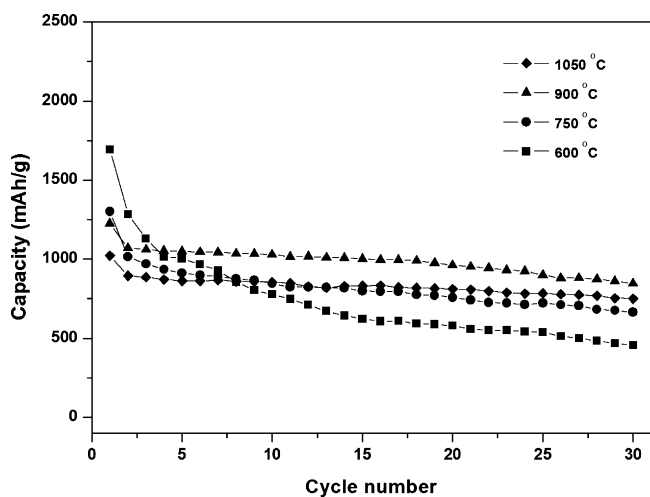

Fig. 5. Cycle-life performance of carbon-coated Si–Cu₃Si composite electrode at different temperatures.

The cycling performances of the carbon-coated Si–Cu₃Si composites using copper(II) D-gluconate pyrolyzed at various temperatures are presented in Fig. 5. All the electrodes were tested within a voltage window of 0.0–1.5 V at a constant current of 100 mA g⁻¹. As the pyrolysis temperature increases, the irreversible capacity of the carbon-coated Si–Cu₃Si composite during the first cycle is reduced, as illustrated in Table 1. As shown in the first discharge voltage profile in Fig. 4, the electrolyte decomposes at approximately 0.75 V to form a solid

Table 1
Ratio of hydrogen-to-carbon and corresponding initial irreversible capacity of composites pyrolyzed at various temperatures

Temperature (°C)	H–C ratio (atomic)	Initial irreversible capacity (mA h g⁻¹)
600	0.328	344
750	0.183	287
900	0.097	206
1050	0.048	158

electrolyte interface [19] at the surface of the composite material, and this is the main cause of the irreversible capacity. Table 1 also shows the atomic ratios of hydrogen-to-carbon when copper(II) D-gluconate powders are pyrolyzed at various temperatures. The data demonstrate that a relatively large hydrogen-to-carbon ratio is obtained for compounds pyrolyzed at the lower temperatures. The pyrolyzed compounds with a high ratio possess large initial irreversible capacities due to the reaction with Li near the hydrogen [16]. Although, the irreversible capacity during the first cycle is reduced, as mentioned above, the capacity of the composite pyrolyzed at 900 °C is larger than that of the composite pyrolyzed at 1050 °C, probably due to the fact that a larger amount of inactive copper silicide [5] is formed at the higher temperature.

A comparison of the reversible capacities of pure Si, the carbon-coated Si composite electrode using glucose and the carbon-coated Si–Cu₃Si composite using copper(II) D-gluconate is given in Fig. 6 as a function of the cycle number. The latter two electrodes were pyrolyzed at 900 °C and all three electrodes were tested in the voltage window between 0.0 and 1.5 V at a constant current of 100 mA g⁻¹. Drastic capacity fading is observed for the pure Si electrode. The first discharge capacities of the carbon-coated Si composite electrode using glucose and the carbon-coated Si–Cu₃Si composite electrode are 1310 and 1225 mAh g⁻¹, respectively, while their charge capacities are 1026 and 1019 mAh g⁻¹ with cycling efficiencies of 78 and 83%, respectively. Compared with the carbon-coated Si composite electrode using glucose, the carbon-coated Si–Cu₃Si composite electrode shows better cycling performance with a capacity of more than 850 mAh g⁻¹ for 30 cycles. The capacity retention obtained in this simplified process is also much improved, as compared with that obtained in a previous study involving a similar process [5]. This enhancement of the capacity retention is due to the fact that the Cu₃Si, which uniformly adheres to the surface of the Si particles embedded in the pyrolyzed carbon, improves the electrical conduction path of the composite material with the current–collector and also acts as a buffer to accommodate the volume expansion–contraction of Si during cycling.

4. Conclusions

A carbon-coated Si–Cu$_3$Si composite material was prepared from copper(II) D-gluconate powders by means of mechanical milling and pyrolysis. A copper silicide layer forms and adheres uniformly to the surface of the Si particles. The composite material gives a high reversible capacity of 850 mAh g^{-1} for 30 cycles and a high initial coulombic efficiency of 83%. The superior cycling performance of the composite electrode is attributed to buffering of the mechanical stress that is generated during cycling, and to enhanced electrical connection with the current–collector by the copper silicide and pyrolyzed carbon.

Acknowledgement

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