Low-cost carbon-coated Si-Cu₃Si-Al₂O₃ nanocomposite anodes for high-performance lithium-ion batteries

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Abstract

Carbon-coated Si-Cu₃Si-Al₂O₃ nanocomposites have been synthesized *via* a facile mechanochemical reaction and employed as anode materials for lithium-ion batteries. Combined X-ray and microscopic studies show that the nanocomposites are composed of agglomerated nanostructured particles with uniform distribution of crystalline silicon, Cu₃Si, and amorphous Al₂O₃. Electrochemical characterization reveals that the *in situ* incorporation of both the conductive Cu₃Si and electrochemically stable Al₂O₃ phases results in a dramatic improvement of cyclability and rate capability, while the specific capacity decreases with increasing amount of Cu₃Si. By controlling the Cu₃Si content, the composite with a high tap density of $\sim 1.2 \text{ g cm}^{-3}$ delivers a high reversible capacity of 841 mA h g^{-1} , excellent cyclability, and good rate performance up to 3.2 A g^{-1} in half cells. Full-cell test coupled with a commercial spinel cathode also displays a high average operating voltage of $> 3.5 \text{ V}$, a relatively good capacity retention of $\sim 77.2 \%$ after 50 cycles with a high initial efficiency of $\sim 86.3 \%$. The enhanced electrochemical performance is mainly attributed to the presence of the conductive Cu₃Si buffer phase that mitigates structural degradation and offers high conductivity.

Keywords: lithium-ion batteries, anode, silicon, copper silicide, mechanical milling

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1. Introduction

Lithium-ion batteries (LIBs) are being widely used as essential and reliable power sources for many applications including portable electronic devices and electric vehicles [1-3].

Nevertheless, the rapid growth in global energy demand has greatly prompted the search for electrode materials for next generation LIBs with higher energy density and longer cycle lifetime. Silicon has been regarded as the most promising anode candidate due to its highest theoretical capacity ($\text{Li}_{15}\text{Si}_4$, 3579 mA h g^{-1}) among the various alloy anode materials [4, 5]. However, a large volume change ($\sim 300 \%$) upon lithium uptake and removal leads to pulverization of silicon particles and mechanical failure of the electrode [6, 7]. In addition, silicon has low electrical conductivity and suffers from the formation of unstable solid-electrolyte interphase (SEI) during cycling, which consequently results in poor rate capability and severe capacity fade [8, 9].

Several approaches for developing silicon-based anode materials have been proposed and implemented to overcome these shortcomings of silicon anodes. One such technique is the utilization of silicon nanostructures including nanowires [6, 10, 11], nanorods [12], and nanotubes [13], which has led to improved cycling stability by accommodating the volume variation during cycling and enhanced rate performance by shortening the lithium-ion diffusion length. However, the reduction in the size of silicon leads to an increase in the specific surface area and specific volume of the particles, thereby causing a high irreversible capacity loss associated with the unavoidable electrolyte decomposition and a low tap density of active materials. Moreover, the realization of nanostructures generally requires the use of high-cost equipment and complicated synthetic procedures that might hinder its practical applications. Another promising technique is to make the composites with electrochemically inactive volume

buffer phases. The composite systems results in a homogeneous distribution of active/inactive phases in which the inactive phases do not react with lithium and remain unchanged during cycling, thereby reducing the internal stress arising from the drastic volume change of the active particles and providing structural reinforcement for the electrodes. Owing to the above advantages, silicon-based composites composed of active silicon with various inactive metal silicides (FeSi_2 , CoSi_2 , NiSi_2 , TiSi_2 , Cu_3Si , and MnSi) [14-19] or metal oxides (Al_2O_3 , and Li_2O_2) [20, 21] have demonstrated enhanced lithium-storage performance over extended cycling. Furthermore, compared to many nanostructuring strategies, the composite systems could be easily obtained by cost-effective, solvent-free, and scalable milling method.

Electrochemical performance of the silicon-based composite materials is largely dependent on particle size, morphology, and phase composition. In this regard, designing composite systems with a suitable choice of synthesis route and buffer matrices could emerge as a promising way to achieve low-cost, high-performance silicon-based anode materials for LIBs. Our group recently reported that the incorporation of nano-sized silicon into a multiphase buffer composed of conductive NiSi_2 and electrochemically inert Al_2O_3 by a low-cost high energy mechanical milling (HEMM) could provide enhanced powder conductivity, high electrochemical stability, and strong structure-reinforcing effects, while maintaining a reasonably high tap density ($> 1.2 \text{ mg cm}^{-3}$) [22]. As a result, the silicon-based composite exhibited improvement in the electrochemical reversibility, volumetric and areal capacities, as well as cycling and rate performance, demonstrating the effectiveness of the multifunctional inactive matrices. For practical applications, however, the real electrochemical properties need to be further investigated by fabricating a full lithium-ion cell. In addition, the use of nickel is less favorable in composite strategy because of the high cost of nickel precursor.[23]

Herein, we report a low-cost, facile HEMM approach for synthesizing a carbon-coated silicon-based composite with a combined inactive buffer phase including both crystalline Cu_3Si and amorphous Al_2O_3 and significantly enhanced electrochemical characteristics as an anode material for LIBs. The as-synthesized composite particles have well-intermixed nanostructure with a few microns in size, giving a reasonably high tap density of $> 1.0 \text{ g cm}^{-3}$. The introduction of low-cost copper precursor induces the formation of highly conductive Cu_3Si phase, which has good mechanical flexibility and high electronic conductivity [24], thereby effectively accommodating the large volume change of silicon active particles as well as offering improved conductivity with the composite particles. Moreover, the presence of amorphous Al_2O_3 plays an important role in endowing enhanced interfacial stability during cycling. Furthermore, carbon coating ensures the formation of stable SEI and reduction in interparticle resistance. The synergistic effects derived from the multiphase inactive buffer matrix result in superior electrochemical performance in both half cells and full cells, making it a desirable anode candidate for high-performance LIBs.

2. Experimental

2.1. Sample Preparation

The carbon-coated silicon-based composites with Cu_3Si buffer phase were prepared *via* a two-step HEMM with a SPEX 8000M apparatus. Commercial silicon monoxide (SiO , -325 mesh, Aldrich), aluminum (99%, $17\text{--}30 \text{ }\mu\text{m}$, Alfa Aesar), copper (99%, $45 \text{ }\mu\text{m}$, Acros Organics), and graphite (CGP-G8, Conoco) were used as raw materials without further purification. Stoichiometric amounts of SiO and aluminum (molar ratio of $6 : 4$) were mixed with different amounts of elemental copper powder ($x = 0, 0.33, 0.66$, and 1.0 in reaction (1) below) and sealed

in a hardened stainless steel vial (80 cm³) with hardened steel balls under argon atmosphere. Then, the HEMM was conducted for 8 h at room temperature to obtain the silicon-based composites with Cu₃Si. The mechanochemical reaction occurring during the first HEMM process can be described as shown below in reaction (1):

The composite powders were further mixed with 10 wt. % of graphite and milled for 15 min under argon atmosphere to obtain the carbon-coated silicon-based composites with different Si/Cu₃Si ratios (Si : Cu₃Si = 17 : 1, 16 : 2, and 15 : 3, respectively, for x = 0.33, 0.66, and 1.0 in reaction (1) above). For a comparison, the carbon-coated silicon-based composite without Cu₃Si was also synthesized under the same condition by excluding the addition of elemental copper (Si : Cu₃Si = 18 : 0 for x = 0 in reaction (1) above).

2.2. Sample Characterization

The microstructure, chemical states, and particle morphology of the carbon-coated silicon-based composites were characterized with a Rigaku X-ray diffractometer (MiniFlex 600) with Cu K α ($\lambda = 1.54059 \text{ \AA}$) radiation, a Kratos X-ray photoelectron spectrometer, scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS, JEOL JSM-5610), high resolution transmission electron microscopy (HRTEM, JEOL 2010F), and scanning transmission electron microscopy (STEM, Hitachi S-5500). A Quantachrome AT-4 Autotap machine was utilized to measure the tap density of the composite samples.

2.3. Electrochemical Measurements

The test electrodes were prepared by the doctor-blade method. Slurries containing active material, Super P conductive carbon, and poly(acrylic) acid (PAA) binder (70 : 15 : 15 wt. %)

were coated onto copper foil current collectors and dried in a vacuum oven at 120 °C for 8 h. The disk electrodes (diameter of 1.2 cm) with a typical active mass loading of 1.5 ~ 2.0 mg cm⁻² were used to assemble the CR2032 type coin cells with a polypropylene (Celgard 2500) separator and a lithium metal reference/counter electrode. The electrolyte used was 1 M LiPF₆ dissolved in ethylene carbonate (EC) / diethyl carbonate (DEC) mixture (1 : 1 by vol.) containing fluoroethylene carbonate (FEC) additive (5 vol. %). The charge-discharge experiments were carried out with an Arbin BT2000 battery tester within the voltage range of 0.0 – 2.0 V (vs. Li / Li⁺) at various current densities for half-cell tests. Commercial spinel manganese oxide cathode was used for full-cell tests, and the cells were cycled within a cut-off voltage of between 2.5 and 4.3 V (vs. Li / Li⁺). An impedance/gain-phase analyzer (Solartron SI 1260) equipped with an electrochemical interface (Solartron SI 1286) was used to perform the electrochemical impedance spectroscopy (EIS) with an ac amplitude of 5 mV over the frequency range of 100 kHz to 0.1 Hz.

3. Results and Discussion

3.1. Structure and Morphology

The X-ray diffraction (XRD) patterns of the carbon-coated silicon-based composites without and with various amounts of the Cu₃Si phase are presented in Fig. 1. The sample without the Cu₃Si phase shows only the characteristic peaks of crystalline silicon (JCPDS No. 77-2110, cubic, S.G. = Fd-3m, a = 5.4298 Å) without any of the diffraction peaks of metallic aluminum, suggesting that SiO is completely reduced to silicon during HEMM for 8 h due to the high reducing power of aluminum. When copper was added during the HEMM process, the composites display three additional peaks at ~ 44.6, ~ 45.1, and ~ 65.4° along with the silicon

peaks, which can be indexed to crystalline copper silicide (Cu_3Si , JCPDS No. 59-0262, hexagonal, space group: $P-3m1$) phase. These newly generated peaks become dominant as the amount of copper increases, while the intensity of the silicon peaks decreases. This may be due to both the decreasing amount of elemental silicon and a reduction in the crystallite size of silicon due to the Cu_3Si inclusion during ball milling. No peaks related to graphite are observed, possibly due to the structural damage imposed by HEMM. In addition, the absence of the Al_2O_3 peaks suggests the presence of amorphous Al_2O_3 in the composites. This is verified by the XPS measurement of the carbon-coated silicon-based composites (Fig. S1). In the Si 2p spectrum (Fig. S1a), the Si 2p peak centered at ~ 99.5 eV can be observed for all the silicon-based composites without and with Cu_3Si , confirming the reduction of SiO to silicon after the HEMM. All the composite samples show the Al 2p peak located at ~ 75.2 eV in the Al 2p spectrum (Fig. S1b), which is obviously at a higher binding energy than that of metallic aluminum (~ 72.7 eV), originating from the Al 2p signal in amorphous Al_2O_3 due to a higher oxidation state of aluminum [25]. Moreover, the O 1s peak at ~ 532.1 eV can be found for all the composite samples (Fig. S1c), further indicating the formation of amorphous Al_2O_3 during ball milling [22]. Therefore, it can be concluded from the combined XRD and XPS analyses that the crystalline silicon, Cu_3Si , and amorphous Al_2O_3 are the major components of the silicon-based composites prepared with copper addition.

Fig. 1. XRD patterns of the carbon-coated silicon-based composites with and without conductive Cu_3Si .

The SEM micrographs of the composite samples ($\text{Si} : \text{Cu}_3\text{Si} = 18 : 0$, $17 : 1$, $16 : 2$, and $15 : 3$) depicted in Fig. 2 indicate that all the powders have a similar particle morphology regardless of the copper content with an average secondary particle size of $< 10 \mu\text{m}$. The formation of micro-sized composite secondary particles could lead to an increase in the tap density of bulk powder, making it possible to achieve high volumetric and areal capacities that are key parameters for commercial implementation [26, 27]. The tap densities of the composite samples were measured to be ~ 0.95 , 1.08 , 1.11 , and 1.18 , respectively, for the $\text{Si} : \text{Cu}_3\text{Si} = 18 : 0$, $17 : 1$, $16 : 2$, and $15 : 3$ samples, which are similar to or even higher than that of graphite ($\sim 1.0 \text{ g cm}^{-3}$) [28, 29]. The approximate amounts of each component in the composite samples were also estimated by the EDS analysis (Fig. S2), and the results show that the amounts of silicon, Cu_3Si , and amorphous Al_2O_3 are almost the same as those calculated based on reaction (1).

Fig. 2. SEM micrographs of the carbon-coated silicon-based composite powders with (a) Si : Cu₃Si = 18 : 0, (b) Si : Cu₃Si = 17 : 1, (c) Si : Cu₃Si = 16 : 2, and (d) Si : Cu₃Si = 15 : 3.

It should be noted that the composite particles synthesized by HEMM, which undergo continuous structural deformation and reconstruction caused by the mechanical stresses induced by the milling process [30], generally exhibit nanostructured morphology consisting of aggregated nanoclusters containing multiple phases, giving rise to enhanced electrochemical performance with the composite materials. In order to observe the microstructure of the composites in more detail, TEM was employed for the silicon-based composites with Si : Cu₃Si = 18 : 0 and 16 : 2. Both samples have the carbon coating layers generated as a result of the second milling step with graphite (Fig. 3a and Fig. S3), which is expected to improve the powder conductivity. However, while the sample without Cu₃Si shows only one interplanar spacing of ~ 0.313 nm (Fig. S3), corresponding to the (111) plane of crystalline silicon, there are lattice fringes with two different interplanar spacings that can be identified to be the (111) plane of

crystalline silicon ($d = \sim 0.313\text{nm}$) as well as the (103) plane of Cu_3Si for the sample with Si : $\text{Cu}_3\text{Si} = 16 : 2$ as shown in Fig. 3b, confirming the presence of both crystalline silicon and Cu_3Si in the composite with the addition of copper. Besides, each phase (silicon, Cu_3Si , and Al_2O_3) is homogeneously incorporated within the composite particle, as evident from the STEM and corresponding EDS mapping images presented in Fig. 3c. It can be also seen that carbon is mainly distributed on the surface of the particle, which is in accordance with the TEM results described above.

Fig. 3. (a) TEM, (b) HR-TEM, and (c) STEM images of the carbon-coated silicon-based composite with Cu_3Si (Si : $\text{Cu}_3\text{Si} = 16 : 2$). In STEM, the EDS mapping images of each element are indicated (silicon: green, copper: blue, aluminum: cyan, and carbon: red).

3.2. Electrochemical Characterization

Half-cell cycling tests were performed with the carbon-coated silicon-based composites to investigate the anode performance in LIBs. Fig. 4a shows the charge-discharge profiles tested at

a constant current density of 100 mA g^{-1} between 0.0 and 2.0 V (vs. Li / Li⁺). During the first cycle, all the composite electrodes seem to exhibit sloping profiles upon discharge (lithiation) and following charge (delithiation) reactions. The first charge (delithiation) capacities of the samples were $\sim 1180, 1083, 841$, and 615 mA h g^{-1} , respectively, for the Si : Cu₃Si = 18 : 0, 17 : 1, 16 : 2, and 15 : 3 samples. The specific capacity values were estimated from the total mass of the composite materials including carbon. The decrease in the specific capacity values is due to the decreasing amount of electrochemically active silicon phase in the composites as can be seen in the EDS results (Fig. S2). In addition, the initial Coulombic efficiencies (CEs) diminish with the increase in the Cu₃Si content, from $\sim 83 \%$ for the sample without Cu₃Si to $\sim 66 \%$ for the Si : Cu₃Si = 15 : 3 sample. This is believed to be caused by the presence of the electrochemically stable Cu₃Si particles incorporated within the composite that might hinder the delithiation reaction of the active silicon in the first cycle, along with the irreversible SEI formation on the electrode surface [8]. However, from the second cycle, the composite samples with a higher amount of copper addition (Si : Cu₃Si = 16 : 2 and 15 : 3) have much better electrochemical reversibility and cyclability as evident from the well overlapped voltage profiles up to 10 cycles, suggesting that the introduction of Cu₃Si phase provides enhanced ionic or electronic conductivity and mechanical buffering effects against volume change during cycling. Specifically, the sample with Cu₃Si (Si : Cu₃Si = 16 : 2) exhibit more than double the specific capacity of graphite with reasonably high initial CE of $\sim 76 \%$ and improved capacity retention compared to the composite without Cu₃Si.

Fig. 4. (a) Voltage profiles and (b) differential capacity plots of the carbon-coated silicon-based composite at various cycles tested within the voltage window of 0.0 – 2.0 V (vs. Li / Li^+) at a current density of 100 mA g^{-1} . The *ex situ* XRD patterns at various states of charge of the composites with (c) $\text{Si} : \text{Cu}_3\text{Si} = 18 : 0$ and (d) $\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$.

In order to understand the detailed reaction mechanism, the differential capacity plots (DCPs) at initial two cycles for the composite electrodes are presented in Fig. 4b. The sample without Cu_3Si shows a broad peak within the voltage range of 0 – 0.2 V with a sharp peak centered at ~ 0.1 V upon first discharge, which are attributed to the lithiation reactions into silicon, eventually forming a crystalline $\text{Li}_{15}\text{Si}_4$ binary alloy [4, 31]. During the first charge, a broad peak located in the voltage range of 0.3 – 0.8 V is seen along with a sharp peak centered at ~ 0.45 V, arising from the delithiation processes of, respectively, amorphous Li_xSi and crystalline $\text{Li}_{15}\text{Si}_4$. [32, 33] In the subsequent discharge, DCP curve becomes broadened and no sharp peaks can be observed, indicating the formation of amorphous silicon after the initial cycling. In contrast, in the cases of the composites with Cu_3Si , the lithiation and delithiation reaction peaks during the first discharge are much broader compared to the composite without Cu_3Si , possibly due to the reduced crystallite size of silicon. In addition, the sharp peak at ~ 0.45 V occurring upon charge disappears, suggesting that silicon cannot be converted to the fully lithiated phase ($\text{Li}_{15}\text{Si}_4$) even at the end of discharge when Cu_3Si is present in the composites. This is beneficial for improving the electrochemical performance of silicon anode since the formation of crystalline $\text{Li}_{15}\text{Si}_4$ during cycling results in severe volume expansion, consequently leading to the pulverization of the electroactive materials and mechanical degradation of the electrodes.

To confirm the phase changes and structural evolutions of the composites with and without Cu_3Si during the initial cycles, *ex situ* XRD analyses were further carried out on the samples without and with Cu_3Si (Si : Cu_3Si = 16 : 2) at fully discharged (0 V vs. Li / Li^+) and fully charged (2.0 V vs. Li / Li^+) states. Fig. 4c shows that the sample without Cu_3Si has only crystalline silicon peaks before cycling. These peaks are no longer detected and several

diffraction peaks corresponding to $\text{Li}_{15}\text{Si}_4$ appear at the end of discharge (0 V). When charged to 2 V, there are no observable peaks in the XRD pattern, demonstrating that amorphous silicon is formed upon charging. These observations are in good agreement with the aforementioned DCP analysis. In the case of the composite with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) (Fig. 4d), however, the characteristic peaks of $\text{Li}_{15}\text{Si}_4$ are not observed even at full lithiation (0 V) and the Cu_3Si peaks remain unchanged during cycling. This further demonstrates that the presence of Cu_3Si suppresses the formation of $\text{Li}_{15}\text{Si}_4$ due to the buffering effect against volume change, eventually enhancing the cycling stability of silicon anode.

The cyclability of the carbon-coated silicon-based composites tested at a current density of 200 mA g^{-1} is illustrated in Fig. 5a. The composite without Cu_3Si shows poor cycle performance compared to the samples containing Cu_3Si due to the low powder conductivity, large structural changes, and mechanical stress induced by the $\text{Li}_{15}\text{Si}_4$ formation during cycling. The reversible capacity gradually decreases with cycling and the composite retains only $\sim 53\%$ of the initial capacity after 200 cycles. On the other hand, the cyclabilities of the composites with Cu_3Si become improved with the increase in the Cu_3Si content in the composites. The best performance is obtained for the sample with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) in terms of the reversible capacity, initial CE, and capacity retention. It delivers a first reversible capacity of 841 mA h g^{-1} with a reasonably high initial CE of $\sim 76\%$ and maintains the capacity of $\sim 704 \text{ mA h g}^{-1}$ even after 200 cycles, which is 83.7% of its initial capacity. Moreover, the CE of this composite reaches $> 98\%$ after 2 cycles and retains over 99.8% until 200 cycles as can be seen in Fig. 5b, indicating excellent cycling efficiency. The rate performance of the carbon-coated silicon-based composites was also compared at various current densities of 200 mA g^{-1} to 3.2 A g^{-1} (Fig. 5c). While the sample without Cu_3Si shows the highest reversible capacity of $\sim 1176 \text{ mA h g}^{-1}$ at 200 mA g^{-1} , a

severe capacity drop is observed at a current density of as high as 1.6 A g^{-1} and it only delivers a charge capacity of $\sim 320 \text{ mA h g}^{-1}$ at 3.2 A g^{-1} , indicating the low rate capability of the composite without Cu_3Si . However, the charge capacities of the sample with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) are $\sim 840, 820, 810, 800$, and 780 mA h g^{-1} , respectively, at current densities of $200, 400, 800, 1600$, and 3200 mA g^{-1} . When the current density is decreased back to 200 mA g^{-1} , it still exhibits a reversible capacity of $\sim 830 \text{ mA h g}^{-1}$, indicating that nearly 100 % of capacity can be restored. Due to significantly enhanced rate capability, this composite shows good long-term cycle performance at higher current densities (Fig. 5d). The reversible capacity of $\sim 520 \text{ mA h g}^{-1}$ is maintained after 350 cycles at 0.5C (400 mA g^{-1}) rate and the delithiation capacity of $\sim 407 \text{ mA h g}^{-1}$ is still delivered after 500 cycles at 1C (800 mA g^{-1}) rate, demonstrating the superior high-rate cyclability.

Fig. 5. Comparison of the (a) cycle performances and (b) corresponding coulombic efficiencies of the carbon-coated silicon-based composites with and without the conductive Cu_3Si at a current

density of 200 mA g^{-1} within a voltage range of $0.0 - 2.0 \text{ V}$ (vs. Li / Li^+). Comparison of the (c) rate capabilities of the carbon-coated silicon-based composite electrodes and (d) the cycle performances of the composite with $\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$ at various current densities. The specific capacities were calculated based on the total mass of the composite materials.

The significant enhancement in cycle and rate performances is primarily achieved by the successful formation of Cu_3Si that could improve the structural stability and provide high ionic/electronic conductivity. Besides, the incorporation of nanosized silicon particles into the amorphous Al_2O_3 buffer matrix, which is electrochemically stable and inactive toward lithium [22, 34], leads to an improved stability of the interfaces between the composite particles and the electrolyte. The carbon coating layers further endows high conductivity and prevents silicon particles from generating unstable SEI on the surface of the composite materials. Therefore, the realization of the nanostructured composite with multifunctional phases leads to an accommodation of the large volume changes of the active materials and prevents mechanical failure of the electrodes by restraining the formation of the $\text{Li}_{15}\text{Si}_4$ phase, enhancing the ionic transport during cycling by providing the short diffusion pathways for lithium ions and imparting high chemical and electrochemical stability during repeated cycling. Furthermore, the enhanced conductivity of the composites with Cu_3Si could be confirmed by the EIS studies (Fig. S4). Although the samples without and with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) exhibit similar charge-transfer resistances ($23.4 \text{ } \Omega$ vs. $18.1 \text{ } \Omega$) after 10 cycles, the composite with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) shows a much lower charge-transfer resistance ($33.3 \text{ } \Omega$) after 200 cycles, compared to the composite without Cu_3Si ($60.3 \text{ } \Omega$). This further supports that the Cu_3Si addition helps maintaining a high conductivity of the composite particles over electrochemical cycling.

Full-cell performance was also assessed by assembling CR2032 coin cells with the carbon-coated silicon-based composite anode ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) and a commercial spinel lithium manganese oxide (LiMn_2O_4) cathode. The spinel cathode shows a reversible capacity of $\sim 100 \text{ mA h g}^{-1}$ with stable cyclability in a half cell test (Fig. S5). For the full-cell test, the ratio of the anode and cathode capacities (N/P ratio) was adjusted at ~ 1.2 and the cells were tested at a current density of 12 mA g^{-1} for initial five formation cycles and then cycled at 60 mA g^{-1} (equivalent to 0.5C rate based on the mass of the cathode material) between the cut-off potentials of 2.5 – 4.3 V (vs. Li/Li^+). Before the full cell operation, the pre-lithiation process was conducted for the composite anode, which is known as a simple and effective method to compensate for the first cycle irreversible capacity loss of the electrode materials [11, 35, 36]. In this study, the composite anode was electrochemically discharged to 0.2 V in a lithium half-cell and reassembled with the spinel cathode. The voltage profiles in Fig. 6a show two sloping regions in the range of 3.7 – 4.2 V upon discharging and 3.3 – 3.9 V during charging, indicating that the average voltage of the spinel lithium manganese oxide / partially-lithiated silicon composite cell is comparable to that of commercial LiCoO_2 / graphite cell ($\sim 3.6 \text{ V}$). The reversible capacity was as high as $\sim 95 \text{ mA h g}^{-1}$ (based on the mass of the cathode material), which is $> 95\%$ of its capacity delivered in a lithium half cell, with a high initial CE of $\sim 86.3\%$. In addition, the full-cell exhibits relatively good capacity retention of $\sim 77.2\%$ as shown in Fig. 6b, delivering a reversible capacity of $\sim 70 \text{ mA h g}^{-1}$ after 50 cycles even at a high current density of 60 mA g^{-1} (0.5 C). These reasonably good electrochemical characteristics in the real full-cell configuration demonstrate that the carbon-coated silicon-based composite can be regarded as a promising anode for high-performance LIBs.

Fig. 6. (a) Voltage profiles at the initial two cycles and (b) cycle performance of the full cell with a spinel lithium manganese oxide cathode and a partially-lithiated silicon composite with Cu₃Si (Si : Cu₃Si = 16 : 2) anode within the voltage window of 2.5 – 4.3 V (vs. Li / Li⁺). The specific capacity was calculated based on the mass of the cathode material.

4. Conclusions

Carbon-coated silicon-based composites with a conductive Cu₃Si phase have been prepared by a facile, low-cost, environmentally benign HEMM process and demonstrated as a potential

anode for LIBs. The realization of the unique carbon-coated composite nanostructure composed of multifunctional phases including active silicon, conductive Cu_3Si , and highly stable Al_2O_3 leads to high tap density ($> 1.0 \text{ g cm}^{-3}$) comparable to that of graphite and a remarkable electrochemical properties in terms of a high reversible capacity of $\sim 841 \text{ mA h g}^{-1}$ (based on the total weight of the composite), superior cycling stability over 200 cycles, and an excellent rate capability. In this composite structure, the conductive Cu_3Si phase contributes to high conductivity and structural stability by suppressing the formation of $\text{Li}_{15}\text{Si}_4$ that could cause a large volume change. Simultaneously, the well-intermixed $\text{Cu}_3\text{Si}/\text{Al}_2\text{O}_3$ phase acts as a robust inactive conducting matrix that keeps particle connectivity and provides enhanced electrochemical stability during cycling. Furthermore, the successful formation of nanosized silicon embedded in the carbon-coated composite allows fast electronic transport and facile ionic diffusion, resulting in rapid charge-discharge capability. The simple and low-cost synthesis method combined with good electrochemical performance achieved in full-cell configuration demonstrates the significant advantages of the carbon-coated silicon-based composites with conductive Cu_3Si as an anode material for high-performance LIBs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Figure captions

Figure 1. (a) XRD patterns of the carbon-coated silicon-based composites with and without conductive Cu_3Si .

Figure 2. SEM micrographs of the carbon-coated silicon-based composite powders with (a) $\text{Si} : \text{Cu}_3\text{Si} = 18 : 0$, (b) $\text{Si} : \text{Cu}_3\text{Si} = 17 : 1$, (c) $\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$, and (d) $\text{Si} : \text{Cu}_3\text{Si} = 15 : 3$.

Figure 3. (a) TEM, (b) HR-TEM, and (c) STEM images of the carbon-coated silicon-based composite with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$). In STEM, the EDS mapping images of each element are indicated (silicon: green, copper: blue, aluminum: cyan, and carbon: red).

Figure 4. (a) Voltage profiles and (b) differential capacity plots of the carbon-coated silicon-based composite at various cycles tested within the voltage window of 0.0 – 2.0 V (vs. Li / Li^+) at a current density of 100 mA g^{-1} . The *ex-situ* XRD patterns at various states of charge of the composites with (c) $\text{Si} : \text{Cu}_3\text{Si} = 18 : 0$ and (d) $\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$.

Figure 5. Comparison of the (a) cycle performances and (b) corresponding coulombic efficiencies of the carbon-coated silicon-based composites with and without the conductive Cu_3Si at a current density of 200 mA g^{-1} within a voltage range of 0.0 – 2.0V (vs. Li / Li^+). Comparison of the (c) rate capabilities of the carbon-coated silicon-based composite electrodes and (d) the cycle performances of the composite with $\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$ at various current densities. The specific capacities were calculated based on the total mass of the composite materials.

Figure 6. (a) Voltage profiles at the initial two cycles and (b) cycle performance of the full cell with a spinel lithium manganese oxide cathode and a partially-lithiated silicon composite with Cu_3Si ($\text{Si} : \text{Cu}_3\text{Si} = 16 : 2$) anode within the voltage window of 2.5 – 4.3 V (vs. Li / Li^+). The specific capacity was calculated based on the mass of the cathode material.

Graphical Abstract