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Semimicro-size agglomerate structured silicon-carbon composite as an anode material for high performance lithium-ion batteries

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HIGHLIGHTS

- *m*Si-C: Semimicro-size Si-carbon composite as an anode material for Li-ion battery.
- Facile preparation through an aerosol-assisted process and carbon coating.
- Agglomerate structured Si NPs with conformally formed carbon layer.
- Good cycle stability: 96% capacity retention (1999 mAh/g) after 50 cycles.
- Good rate capability: high capacity (906 mAh/g) at high current density (12 A/g).

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ABSTRACT

A semimicro-size agglomerate structured silicon-carbon (*m*Si-C) composite is constructed by an aggregation of silicon nanoparticles (~100 nm) coated with conductive carbon layer through a facile and scalable aerosol-assisted process to be employed as an anode material for lithium-ion batteries (LIBs). As-formed *m*Si-C composite delivers good electrochemical performances of high reversible capacity (2084 mAh/g) between 0.01 and 1.50 V (*vs.* Li/Li^+) at 0.4 A/g, 96% capacity retention (1999 mAh/g) after 50 cycles and good rate capability (906 mAh/g) at 12 A/g. Such good performances can be attributed to 1) unique composite structure which accommodates the stress induced by volume change of silicon during lithiation/delithiation and facilitates ion transport, and 2) conformally formed carbon layer which enhances conductivity of the composite and helps to form a stable SEI layer. In addition, a high tap density ($0.448\ g/cm^3$) of *m*Si-C composite leads to high volumetric capacity ($933\ mAh/cm^3$), allowing its practical applications as an anode material towards high performance LIBs.

1. Introduction

As of recent introduction of electric vehicles (EV) into automobile market, continuous and massive demands for lithium-ion batteries (LIBs) with high energy/power densities and long life cycle have triggered to develop inexpensive, high energy/power density electrode materials [1–6]. Thus far, graphite based anodes have been used in commercial LIBs but its low theoretical capacity (~372 mAh/g) limits the mileage of EV per charge [1–6]. Hence, it is essential to develop novel LIB anode materials for next generation EV with high energy/power densities and long duration time at economical cost [1–6].

In this context, silicon (Si) has been extensively studied as a suitable anode material for high energy density LIBs owing to its high specific capacity (~3580 mAh/g) and natural abundance [2–5]. However, practical application of Si based anodes is still hindered due to their unsatisfactory performance (fast capacity fading and poor rate performance) mainly caused by huge volumetric change of Si (>400%) during lithiation/delithiation; such a huge change of Si causes several problems including unstable solid electrolyte interphase (SEI) formation, disintegration of electrode structure

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and poor electrical contact among electrode materials [6].

Accordingly, many studies have been devoted to addressing aforementioned issues mainly through 1) reducing the size of Si particle [2,3,7–10], 2) making the composite of Si and carbonaceous agent [7,8,10–20] and 3) formation of the metal oxide layer on Si [20]. First, smaller sized Si based anodes have been demonstrated by constructing various nanostructured silicon (e.g., Si nanospheres [7,8], Si nanowires [2], Si nanotubes [3] and nanoscale ultrathin Si films [9,10]). For instance, based on the work of Liu et al. who theoretically revealed the crucial role of small-sized Si (<150 nm) electrode to sustain the structure of Si particles without cracked nor fractured by first lithiation-induced swelling [11], Kim et al. and many other researchers reported superior performance (specific capacity > *ca.*1000 mAh/g over 50 cycles) of nano-sized Si electrodes to bulk Si electrodes [2–11]. As demonstrated by previous reports, the improved performance of nano-sized Si electrodes is attributable to effective accommodation of large stress or applied strain by small sized Si upon lithiation, which alleviates pulverization of electrode materials as well as keeps electrical contact of Si particles. Additionally, small sized Si enables the short ionic transport distance of lithium ions, allowing their facile mass transport during the process [5]. Second, compositing Si with carbonaceous agent such as carbon, CNT and graphene results in improved electrochemical performance [7,8,10–19]. For instance, there have been many reports on construction of silicon nanocomposites based electrodes (e.g., Si-C [7,8,11–17], Si-graphene [18] and Si-CNT [19]) which exhibit enhanced LIBs performance (long capacity retention and high rate capability). Ng et al. reported around 1857 mAh/g at 0.15 A/g using Si@C nanocomposite [7]. Jung et al. demonstrated high performance anode (1469 mAh/g after 50 cycles at 1 A/g) using nanostructured Si@porous carbon composite [8]. Zhou et al. presented Si/graphene nanocomposite which exhibits much superior cycle performance (1153 mAh/g at 0.2 A/g after 100 cycles) and rate capability (803 mAh/g at 4 A/g) to that of pristine Si nanoparticles (<10 mAh/g at 0.2 A/g after 50 cycles) [18]. Gohier et al. demonstrated Si decorated CNT which shows good cycle performance (57% capacity retention at 35.8 A/g after 100 cycles) and excellent rate capability (760 mAh/g at 53.7 A/g) [19]. Improved performance of Si-carbonaceous agent composite electrodes can be attributed to the role of conductive agents that electronically bridge/connect the Si, making the composite more conductive and thus facilitating electron transport in the electrodes [17–19]. Third, protective coating of thin metal oxide layer (e.g., SiO_x and TiO_2) on the Si nanoparticle leaded to an improved electrochemical performance because of formation of stable SEI layer [20]. There are also many reports on composite of Si and metal oxides (e.g., Si-SiO_x, Si-TiO_2 and Si-SiO_2-C) to improve the electrochemical performance [20]. McCormac et al. reported porous Si-TiO_2 nanofiber composite which delivered high reversible capacity (839 mAh/g) and 50% capacity retention after 180 cycles at 0.135 A/g [20]. Liu et al. reported Si-Si oxycarbide (Si-O-C) nanocomposite exhibiting high reversible capacity (1190 mAh/g) and 76% of capacity retention within 20 cycles [20]. Park et al. reported Si-embedded SiO_x nanocomposite with a high capacity (1914 mAh/g) and improved cycle stability over 100 cycles (capacity >1500 mAh/g) at 0.2 A/g [20]. The improved performance of metal-oxide-Si composite can be attributed to the function of metal oxide as a mechanical buffer layer against the severe volume change of Si [20].

However, there are still several technical barriers which hamper practical application of Si materials [14,21]. First, low tap density of Si nanoparticles (Si NPs) leads to far lower volumetric energy density compared with commercial graphite [14,21]. Second, Si NPs can generate several health and safety issues including inhalation and explosion risks during dealing with them in the work place [22]. Although it is logical to develop bigger-sized (micro-sized) Si materials to enhance volumetric energy density [14,21,23], current micro-sized Si electrode suffer from many obvious disadvantages including 1) more liable to pulverization by volume change of Si during lithiation/delithiation and 2) long ion/electron transport paths, which result in capacity fading and poor rate capability [14,21]. Thus, pros and cons of conventional Si materials above have required the development of secondary agglomerate of micro-size Si superstructure built on nano-sized particles as primary building blocks to utilize advantages of both micro-sized and nano-sized Si materials [14,17,21].

There have been several reports on the secondary agglomerate structure of micro-sized Si materials constructed with nanoscale building blocks which show impressive performances [12–14,17,21,23]. Construction of agglomerate structured micro-sized Si was demonstrated mainly through aggregation of nanoparticles, compositing Si with preformed conductive carbon by chemical vapor deposition (CVD) process and thermal disproportionation of Si precursors [12–14,17,21,23]. For instance, Cho and Park et al. produced agglomerate structured micro-sized porous Si-C composites by catalytic etching of micro-sized Si followed by conductive carbon coating, which showed stable capacity retention within 70 cycles [12]. Yushin et al. reported a agglomerate structured micro-sized porous carbon-silicon composite with a high tap density (0.49 g/cm^3) by Si deposition onto porous carbon via a chemical vapor deposition (CVD) process, which exhibited a high volumetric capacity (1270 mAh/cm^3) at a high current density (149 mA/g) and good capacity retention within 100 cycles [17]. Wang et al. and Park et al. reported agglomerate structured micro-sized porous Si-C composites through thermal disproportionation of SiO followed by conductive carbon coating using acetylene gas as a carbon source, exhibiting good electrochemical performance (1459 mAh/g at 1 A/g after 200 cycles) [14,21]. Recently, Liu et al. prepared pomegranate structured micro-sized Si through aggregation and polymerized encapsulation of Si NPs using Si NP, resorcinol and CNT as conductive percolating matrix for active material, showing excellent cycling stability (1160 mAh/g after 1000 cycles at 2.1 A/g) and high coulombic efficiency (99.87%) [23]. Nonetheless, to date, synthesis of such superstructured micro-size Si and its composite materials still remains as a challenge because rather complicated current synthetic processes are not adequate for commercial scale as well as require expensive chemical/physical facility using toxic precursors (e.g., SiH_4) [2–5,10–15,18–21,23].

Aware of these backgrounds, herein, we report a semimicro-size agglomerate structured Si-C (*m*Si-C) composite by interconnection of Si NPs covered with carbon layer. The synthetic process for semimicro-size composite of carbon coated Si NPs involves 1) an aerosol process to form a agglomerate structure of Si NPs and polymer (polyacrylic acid) through evaporation induced assembly and 2) conductive carbon layer deposition as inspired by our previous work [14,24]. Different from previously reported agglomerate structured Si-C composites by complicated syntheses, our synthesis and *m*Si-C composite have several advantageous features of 1) facile and scalable fabrication of composites by commercially available aerosol process, 2) tunable precursor composition (e.g., Si NP or carbon source), 3) formation of aggregated aerosol product constructed from homogeneously mixed precursor, and 4) well-defined agglomerate superstructure at the secondary particle level. The as-formed *m*Si-C composite shows excellent capacity retention of 96% after 50 cycles (1999 mAh/g) due to unique structure of *m*Si-C composite; where the interparticle space in the composite can accommodate the volume expansion of Si and the homogeneously formed carbon layer ensures electrical conduction pathways. We believe that such advantages of our *m*Si-C composite (excellent performance, economical cost and facile/scalable