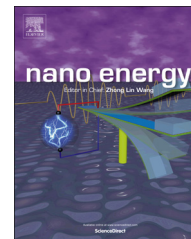




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RAPID COMMUNICATION

Dual conductive network-enabled graphene/Si-C composite anode with high areal capacity for lithium-ion batteries



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Abstract

Silicon has been regarded as one of the most promising alternatives to the current commercial graphite anode for Li-ion batteries due to its high theoretical capacity and abundance. Although high gravimetric capacity (mAh/g) of Si-based materials can be achieved, areal capacity (mAh/cm²), an indication of the energy stored at the electrode level, has rarely been discussed. Herein, a novel micro-sized graphene/Si-C composite (G/Si-C) is reported, in which micro-sized Si-C particles are wrapped by graphene sheets. Owing to dual conductive networks both within single particles formed by carbon and between different particles formed by graphene, low electrical resistance can be maintained at high mass loading, which enables a high degree of material utilization. Areal capacity thus increases almost linearly with mass loading. As a result, G/Si-C exhibits a high areal capacity of 3.2 mAh/cm² after 100 cycles with high coulombic efficiency (average 99.51% from 2nd to 100th cycle), comparable to that of commercial anodes. The current findings demonstrate the importance of building a conductive network at the electrode level to ensure high material utilization at high mass loading and may shed light on future designs of Si-based anodes with high areal capacity.

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Introduction

Lithium-ion batteries (LIBs) have been intensively studied because of their relatively high energy density, which makes them attractive for use in many electronic devices [1]. Recently, the emerging market for electric vehicles requires

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LIBs with higher energy density [2,3]. Developing new anode materials with high specific capacity is an effective way to increase the energy density of LIBs. Due to its high theoretical capacity (3579 mAh/g) and abundance, silicon has been regarded as one of the most promising alternatives to the currently-used graphite anode, which has a low theoretical capacity of 372 mAh/g [4,5]. However, there is a major barrier to the practical application Si: its large volume change during charge/discharge causes to severe pulverization of Si particles and degradation of Si electrodes, leading to poor cycling stability [6]. Extensive efforts have been devoted to improving the cyclability of Si-based anodes with encouraging results, including development of various Si nanostructures/nanocomposites, novel binders and electrolyte additives [7-16].

However, most of the advances in Si-based materials to date were reported in the form of gravimetric capacity (mAh/g), while areal capacity (mAh/cm²) has rarely been discussed. Gravimetric capacity describes the capacity that a *material* can deliver. However, in practical applications the performance of anodes is evaluated at the *electrode* level, and areal capacity is an indication of the energy that an *electrode* can store. Although high gravimetric capacity of Si-based materials can be achieved, it usually comes with very low mass loading, which in turn leads to electrodes with limited areal capacity [11,13]. In the few reports involving high mass loading, higher areal capacity was demonstrated with: (1) limited cycle numbers; (2) fixed gravimetric capacity/reduced voltage range; (3) low coulombic efficiency; or (4) electrodes fabricated by special techniques which are not compatible with industrial slurry coating approaches, such as binder-free electrodes [17-21].

We previously demonstrated a micro-sized Si-C composite composed of interconnected Si nanoscale building blocks and carbon conductive network [22-24]. However, the conductive network is only within the micro-sized particles and no such a network exists between particles, potentially leading to large interparticle contact resistance. Due to its extraordinary electronic conductivity and two-dimensional morphology [25,26], graphene has been identified as an excellent conductive additive in various composites to enhance the electrochemical performance of electrode materials by improving electron transport and maintaining electrical contact in electrodes [27-31]. However, graphene has majorly been incorporated with nanomaterials to form nanocomposites and graphene-containing micro-sized composites have been less reported.

Herein, we report a novel micro-sized graphene/Si-C composite (G/Si-C), in which micro-sized Si-C particles are wrapped by graphene sheets. The two-dimensional conductive graphene sheets act as a conductive network between particles and thus decrease the contact resistance of the whole electrode. Thanks to it having conductive networks both within single particles and between different particles, G/Si-C shows a higher degree of material utilization at high mass loading compared to the raw micro-sized Si-C composite (Si-C). An areal capacity of 3.2 mAh/cm² after 100 cycles and high coulombic efficiency (average 99.51% from 2nd to 100th cycle) are achieved by G/Si-C, comparable to that of commercial LIBs [32], making it a promising anode material for practical applications in LIBs.

Material and methods

Synthesis of G/Si-C

Graphite oxide (GO) was firstly prepared from natural graphite powder (300 mesh, Alfa Aesar) by a modified Hummers method [33,34]. In a typical process, 1 g of SiO (2 μm) was dispersed in 150 mL water under stirring for 30 min. Then 3 g of PDDA (Sigma-Aldrich) was added and the mixture was stirred for another 30 min. Afterwards, as-prepared GO solution was added dropwise to the PDDA-SiO suspension with a mass ratio of 28:1 between SiO and GO. After 2 h stirring, the GO/PDDA-SiO was obtained by vacuum filtration followed by washing sequentially with water and ethanol, and finally drying in vacuum oven at 80 °C overnight. The GO/PDDA-SiO was then transferred to a horizontal quartz tube. Ar/H₂ (95:5 v/v) was introduced at a flow rate of 1500 sccm for 20 min to purge the system. Afterwards the flow rate was reduced to 100 sccm and the tube was heated to 950 °C with a ramping rate of 10 °C/min and kept for 5 h. The samples were taken out of the tube at temperatures below 40 °C and immersed in 20 wt% HF solution (H₂O:ethanol=5:1 by volume) at room temperature for 3 h to remove SiO₂. The obtained porous Si was collected by filtration and washed with distilled water and ethanol in sequence several times. The final product was dried in a vacuum oven at 60 °C for 4 h. Carbon coating of G/Si was done by thermal decomposition of acetylene gas at 800 °C for 10 min in a quartz furnace. The mixture of acetylene and high-purity argon (argon:acetylene=9:1 by volume) is introduced at a flow rate of 100 sccm. Si-C was prepared similarly without the addition of GO.

Characterization

The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu K α radiation ($\lambda=1.5418$ Å). The operating voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM). Raman spectroscopy was conducted with a WITec CMR200 confocal Raman instrument.

Electrochemical measurements

Electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.) with the G/Si-C and Si-C electrodes as the working electrode and the Li metal as the counter electrode. The working electrodes were prepared by casting the slurry consisting of 80 wt% of active material and 20 wt% of poly(acrylic acid) (PAA) binder. Six different electrode types with different mass loadings of active materials (around 1.2, 2.0 and 3.2 mg/cm²; see Table S1 in Supporting Information for details) were fabricated using G/Si-C and Si-C. 1 mol/L LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC:DEC:DMC, 2:1:2 by vol %) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The

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