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A long-life nano-silicon anode for lithium ion batteries: supporting of graphene nanosheets exfoliated from expanded graphite by plasma-assisted milling

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ABSTRACT

In order to enhance the cycleability and electronic conductivity of Si-based anodes, we fabricated a hierarchical micro-nano structured silicon/graphene nanosheets (Si/GNs) hybrid by discharge plasma-assisted milling (P-milling) using Si nanoparticles and expanded graphite (EG) as starting materials. Owing to the synergistic effect of rapid plasma heating and ball mill grinding with Si nanoparticles as nanomiller, the graphene nanosheets was exfoliated efficiently from the loose structured EG, which tightly wrapped and connected the Si nanoparticles to form microsized composite agglomerates. This high powder tap density Si/GNs hybrid exhibited a high reversible capacity of 942 mAh g^{-1} (857 mAh cm^{-3}) at the current density of 0.2 Ag^{-1}, with 88% capacity retention after 100 cycles. The charge capacity remained super stable more than 350 times when the electrode was cycled with a fixed lithiation capacity of 1000 mAh g^{-1} at a current density of 0.2 Ag^{-1} between 0.01 and 1.5 V (vs. Li/Li^+). This superior cycle performance was attributed to the microsized GNs matrix which facilitated the electronic conductivity and the Li^+ diffusion in the hybrid, and effectively accommodated the volume change of Si nanoparticles during Li^+ alloying and dealloying processes.

1. Introduction

The silicon (Si) has been investigated as a promising high capacity anode material for lithium ion batteries (LIBs) to replace the commercially graphite anodes [1,2]. Unfortunately, the practical use of pure Si in LIBs is still hindered by the fast capacity fading due mainly to the large volume change and structural cracking upon repeated Li^+ insertion/extraction in Si [3,4]. Another problem is that structural cracking of electrode exposes the new surface of Si to deposit solid electrolyte interphase (SEI), which resulted in large irreversible capacity [5,6]. In addition, the low intrinsic electronic conductivity of Si usually leads to large potential polarization and inferior rate-capability and thus lower reversible capacity [7]. Many researchers have demonstrated that creating a hierarchical structure with nano-architectural Si uniform dispersed in micrometer-sized carbon matrix is the most appealing strategy to overcome these issues and to improve the overall electrochemical performance of Si-based anodes in LIBs [8,9]. In these hierarchical Si-C hybrids, the nanosized Si can endure much higher strain and effectively mitigate the pulverization of the active materials, while the carbon matrix could supply superior electronic conductivity and volume buffering effect for the active Si [10]. However, nanosized Si particles tend to aggregate during repeatedly alloying–dealloying if the carbon matrix do not well hold the Si particles, resulting in the inevitable capacity decay. In addition, generally the use of nanomaterials could lead to a decrease in volumetric density and thus relatively low volumetric capacity in the Si-based nanocomposite anodes [8].

In terms of the conductive carbonaceous matrix, graphene and graphene nanosheets (GNs), with unique physical and chemical properties such as high electronic conductivity, excellent mechanical flexibility and superior chemical stability, have been a hotspot as a suitable additive in the Si-based composite anode by various strategies for recent years [11–13]. Usually, the GNs was produced by the mechanical peeling of graphite [14,15], chemical vapor deposition (CVD) [16,17] and chemical or thermal reduction of graphene oxide [18–20]. However, the reported methods of mechanical peeling graphite and chemical synthesized graphene were low cost-effective and would be not suit for mass production. The widely reported preparation routes for Si/GNs nanocomposites based on graphite oxide often required harsh conditions such as strong oxidizing and reducing reagents, high temperature and

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time-consuming preparation process [14,21,22]. And the GNs prepared from the graphene oxide always remained plenty of residual oxygen functional groups and structural defects which lowered the electrical conductivity of GNs [23]. Furthermore, how to distribute uniformly the Si nanoparticles in the as-prepared GNs matrix remains a problem.

As demonstrated in our previous work, a P-milled Si/graphite composite with a structure of Si nanoparticles embedded homogeneously in GNs could be produced by directly milling method using nano-Si and flake-graphite by a simple discharge plasma assisted milling (P-milling) [24]. A large amount of GNs could be peeled from the microsized graphite under the synergistic effect of rapid heating of the plasma and the mechanical grinding of mill balls together with Si nanoparticles as nanomiller. Although the cycling stability of this P-milled Si/graphite composite was much enhanced in comparison with pristine-Si, it was found that part of the Si nanoparticles lose contact with the GNs during long-term cycling, leading to gradually capacity fading. In addition, because of the strong van de Waals force between the graphene layers in the flake-graphite, long P-milling time of 20 h was served to exfoliate the GNs from the graphite. And thus, replacing the flake-graphite to expandable graphite was expected to produce a new Si-graphene hybrid structure by using P-milling. It is well known that expandable graphite has an increased interlayer spacing among graphene layers in compared with flake-graphite, which would weaken the van der Waals interactions and facilitated the exfoliation of graphene layers [25–27].

In this work, we designed and produced a Si/GNs hybrid with hierarchical micro-nano structure by a high cost-effective method combined with rapid thermal treatment and then P-milling, using commercial available expandable graphite as the resource of GNs because of the following reasons. Firstly, after a rapid heat treatment, the expandable graphite was turn into expanded graphite (EG) with a porous and loose structure, and then could be efficiently exfoliated by the subsequent P-milling to form the GNs with a uniform layer of graphene. Secondly, the in-situ formed flexible GNs could wrap the Si nanoparticles during P-milling to form the secondary Si/GNs hybrid granules in few micrometers. Thirdly, the GNs prepared from thermal expansion of expandable graphite could have less structure defects and exhibit superior buffering effect on the volume change of Si than the counterpart prepared from the graphene oxide. In the light of this hierarchical structure with nanoscale active material Si and microscale matrix material GNs, the Si/GNs hybrid yielded a large reversible capacity and a relatively high volumetric capacity, excellent cycle stability, and enhanced rate performance.

2. Experimental

2.1. Material preparation

The expandable graphite (99.9% purity, 100 mesh, Qingdao Xinghua Graphite Products Co., Ltd.) was quickly inserted into a tube furnace preheated to desired temperature and held in the furnace for desired time duration under Ar atmosphere to obtain the worm-like expanded graphite (EG). The preheated temperature and duration time was settled at: (i) 400 °C–60 s, (ii) 600 °C–60 s, (iii) 1000 °C–10 s, (iv) 1000 °C–60 s, (v) 1000 °C–120 s. Si nanoparticles (99.9% purity, 50–100 nm in size, Xuzhou Jiechuang New Material Technology Co., Ltd.) and the as-obtained EG (1000 °C–60 s) were used as raw materials. An optimized mass ratio (30:70) of Si to EG powder was mixed and placed in a stainless steel vial with stainless steel balls. The mass ratio of balls to mixed powder was 50:1. P-milling was conducted under pure Ar with a vibration type ball mill (milling cylinder vibration with double amplitude of 7 mm and frequency of 24 Hz). The plasma was build up inside the mill vial by using the vial as one electrode and fixing another electrode inside the vial. A dielectric barrier discharge

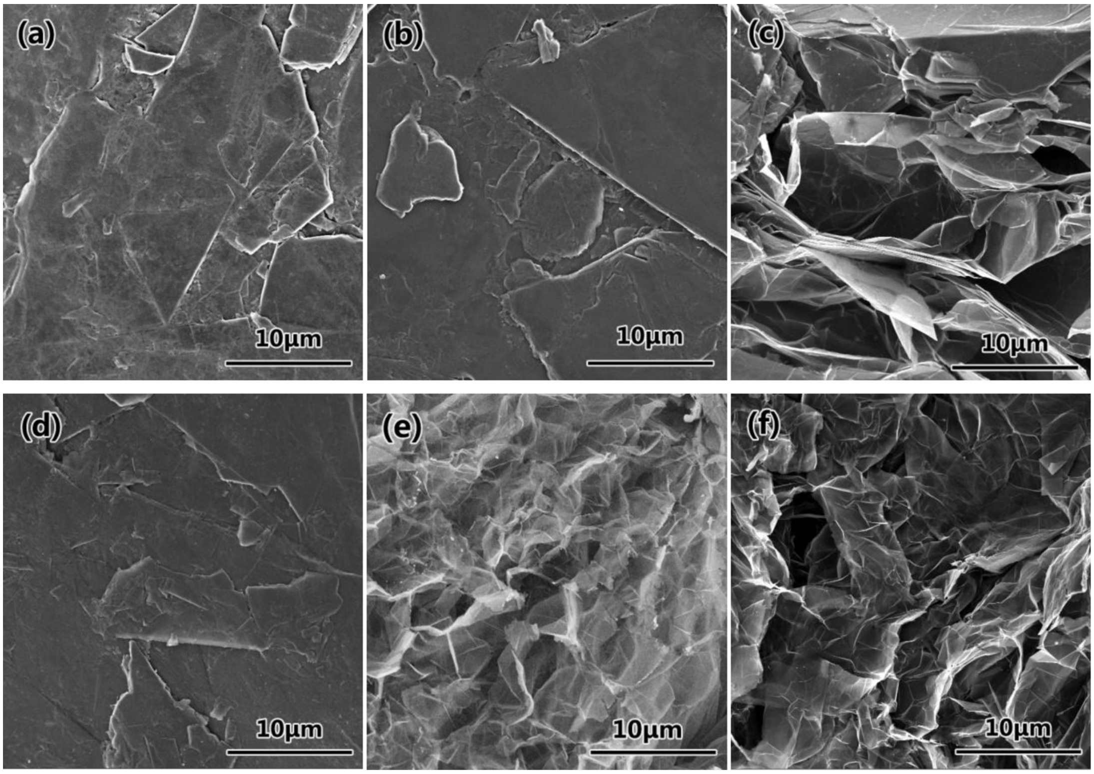

Fig. 1. SEM images of (a) pristine expandable graphite and expanded graphite obtained by rapid thermal treatment with different preheated temperature and duration time: (b) 400 °C–60 s, (c) 600 °C–60 s, (d) 1000 °C–10 s, (e) 1000 °C–60 s, (f) 1000 °C–120 s.