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Research paper

High rate capability and long cycling life of graphene-coated silicon composite anodes for lithium ion batteries

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ABSTRACT

With a theoretical specific capacity much higher than that of traditional graphite, silicon (Si) has been considered as a promising anode material for next-generation lithium ion batteries (LIBs). Unfortunately, its practical application has been severely limited by the drawback of drastic volume expansion. In this report, we demonstrate a facile way to prepare binder-free, conductive agent-free silicon/reduced graphene oxide composite (Si/rGO) anode on nickel foam via one-step hydrothermal method followed by a post-annealing process, which delivers extraordinary cyclability and rate performance. The reversible specific capacity of the composite anode retained over 1500 mAh/g at 2 A/g after 2500 cycles and over 600 mAh/g at 4 A/g after 2500 cycles. Especially at a reasonable high current density of 16 A/g, the Si/rGO anode still displayed a specific capacity of 500 mAh/g.

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1. Introduction

The development of rechargeable LIBs with high power density, considerable high energy storage capacity, outstanding cycling and rate capabilities [1], is critically essential to satisfy the ever-growing market of stationary and automotive energy storage applications [2,3], such as power tools and electric vehicles. Accordingly, the research on effective and new electrode materials for LIBs with higher power and energy density has become an urgent need [4,5]. As an cardinal component of LIBs, anode materials would crucially affect the overall electrochemical performances [5]. Moreover, more stable delithiation/lithiation process and higher lithium storage capacity are two primary research directions for LIBs [6,7]. While traditional anode material (graphite) is confronting a great challenge due to its fairly low specific capacity (372 mAh/g) and potential safety concerns in connection with the growth of lithium dendrites [8,9]. Hence new materials with higher lithium storage capacity and better cyclability are of great value for continued exploration. In current research, tin and tin oxide, Si, metal oxides and new alloy materials, etc [10], have attracted considerable attention as promising substitutes for graphite. Among these materials, Si is regarded as a superior candidate in view of its rich reserves and non-toxic characteristic, along with its ultrahigh theoretical lithium storage capacity (3579 mAh/g) [11]. Additionally, the discharge platform is relatively low (0.1 V), contributing to avoiding the formation of lithium dendrites on the surface of the electrode [4,8,12,13]. However, the severe volume expansion of Si particles during the delithiation/lithiation process could give rise to electrode pulverization [14]. It causes a decrease in the intergranular conductivity of the active materials and the increment of electrical contact resistance, ultimately limiting the massive commercial application in LIBs [15,16]. In order to alleviate this problem, multiple methods have been investigated to modify the Si, targeting more stable Si materials with better performance and large-scale commercialization [6,17].

Graphene has been extensively researched as electrode materials due to its ultrahigh specific surface area [18], outstanding electrical conductivity, superb mechanical strength and chemical stability [3,19]. The enormous specific surface area (2630 m2/g) [20] and the loose structure of graphene can promote the infiltration of the electrolyte, thus advancing the electrochemical properties of LIBs [21]. Furthermore, the silicon/graphene composites might substantially ameliorate the performance of electrode in virtue of the potential interaction and synergistic effects of both materials [22]. Although quite a lot researchers have attempted to synthesize silicon/graphene composite materials in

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different ways to ameliorate the electrochemical performances of LIBs, there were still minor successful Si-based anode materials indicating long cyclability and decent capacity at a large current density [23]. Cui et al. synthesized carbon-coated porous micro-sized Si particles, showing an average discharge capacity of about 1490 mAh/g at a current density of 1.05 A/g after 1000 cycles [24]. Chang et al. prepared multilayered Si nanopariticle/reduced graphene oxide on nickel foam, delivering a capacity of about 1500 mAh/g at a current density of 2.4 A/g after 100 cycles [25]. Nevertheless, current preparation approaches and performances of LIBs need to be refined continually, in accordance with previous work.

In this paper, we develop a facile way to manufacture binder-free, conductive agent-free Si/rGO anode on nickel foam through one-step hydrothermal approach followed by a post-annealing process, which exhibits impressive cyclability and rate performance. The reversible specific capacity of the Si/rGO anode maintained over 2400 mAh/g at the current density of 0.2 A/g after 50 cycles, 1500 mAh/g at 2 A/g after 2500 cycles and over 600 mAh/g at 4 A/g after 2500 cycles. Even at a reasonable high current density of 16 A/g, the composite anode still evinced a specific capacity of 500 mAh/g. Combined the merits of submicron Si with rGO, a novel and facile method for the anode materials of the LIBs is designed.

2. Experimental

2.1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was synthesized using flaky graphite powder by a modified Hummers method [3,4,17]. 1 g $NaNO_3$ and 2 g flaky graphite powder were added to a solution of 60 ml concentrated H_2SO_4, under constant agitation in an ice bath for 30 min. Under vigorous stirring, 6 g $KMnO_4$ powder was added slowly to keep the temperature of the suspension lower than 5 °C for 2 h. The resulting solution was then heated at 35 °C for 30 min, followed by slow addition of 100 ml de-ionized water and another heating treatment at 95 °C for 20 min. Subsequently, 30 ml H_2O_2 (30%) was added to the system, resulting in bubbling and a color change of the solution from brown to bright yellow. After continuous ultrasonication until bubbles disappeared, the resulted GO was collected and then washed with 200 ml aqueous HCl solution (3%) [26]. After centrifugation at 8000 rpm for 5 min to remove metal ions, and followed by being washed many times with de-ionized water until the pH value of the solution was around 7 [27], GO powder was finally obtained by re-dispersing in de-ionized water for 1 h, and freeze-dried in vacuum.

2.2. Preparation the electrode material of Si/rGO

The binder-free, conductive agent-free Si/rGO materials were prepared on nickel foam via a hydrothermal process. Submicron Si powder was purchased and washed by ethonal/HF mixture solution to remove the oxide layer on the surface before using. Typically, 50 mg GO was added to 50 ml deionized water under ultrasonic stirring for 1.5 h, obtaining a uniformly dispersed GO solution [24]. 100 mg Si powder was added to the solution above with continuous ultrasonic agitation for 30 min. Afterwards the nickel foam with a diameter of 15 mm and a thickness of 1.6 mm was immersed into the solution and stirred for another 5 min. The mixed Si/GO solution with the nickel foam above was then transferred into a 100 ml Teflon-lined stainless-steel autoclave and heated at 180 °C for 14 h. After cooling down to the room temperature, the nickel foam was collected and freeze-dried in vacuum, then pressed using a hydraulic crimping machine, and calcined at 600 °C for 2 h in a nitrogen environment in a tubular furnace [8,9]. The as-obtained nickel foam-supported Si/rGO materials were directly applied as the working electrode and were assembled into the half coin cell.

2.3. Material characterization

X-ray diffraction (XRD) patterns were examined on a Bruker-D8 Advanced X-ray Diffractometer (Cu Kα radiation: λ=1.5406 Å) with a scanning speed of 2 deg/min. The morphology of the Si/rGO materials was observed by a field-emission scanning microscope (FE-SEM, JSM-5900LV, JEOL). TEM/HR-TEM images were taken on a JEOL JEM-2100F microscope. XPS measurements were performed on a KRATOS XSAM800 X-ray photoelectron spectrometer with Mg Kαexcitation source (1253.6 eV).

2.4. Electrochemical measurements

The prepared Si/rGO materials, free of binder and conductive agent, were directly employed as the working electrode. $LiPF_6$ (1 M) in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) with a volume ratio of 1: 1 was adopted as electrolyte, and lithium metal was used as both counter electrode and reference electrode. Half coin-cells were assembled in an Ar-filled glovebox with the moisture and oxygen level below 1 ppm. The galvanostatic charge-discharge tests were measured on a LAND battery channel

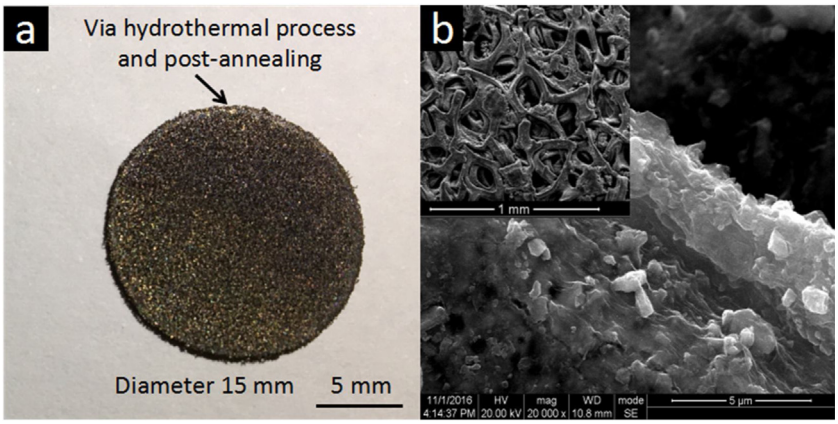

Fig. 1. (a) Photograph of the electrode prepared by hydrothermal process followed by post-annealing. (b) SEM image of Si/rGO materials on nickel foam.

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