Enhanced electrochemical performance promoted by monolayer graphene and void space in silicon composite anode materials

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ABSTRACT

The high specific capacity battery electrode materials have stimulated great research interest. Silicon (Si) as a low-cost abundant material with a theoretical specific capacity of 4200 mA h g^{-1}, offers an attractive option for the low-cost next-generation high capacity Li-ion batteries anode. However, successful applications of silicon anode have been impeded by several limitations such as large volume expansion (400%) with lithiation, poor conductivity and unstable solid electrolyte interphase (SEI) with cycles. To address these challenges, we engineered Si nanoparticles by encapsulating them with monolayer graphene (mGra) with empty space generated by melt-self-assembly Cu layer. Here, a new method is introduced to uniform encapsulate the nano-silicon particles. The synthesis process used low-cost Si nanoparticles and Cu foils via chemical vapor deposition methods. The mGra and void space around the Si nanoparticles guaranteed to overcome mentioned problems. The flexibility nature and high conductivity of mGra effectively accommodate the Si volume expansion associated with the lithiation, and function as charges fast channels that allow for ions and electrons transport in fast kinetics. Most important, the crystalized mGra layer served as a flexible protective layer avoiding the SNPs direct exposed to electrolyte, which boosted the formation of stable and thin SEI interface. Our anode demonstrated a high initial coulomb efficiency (CE) 85% with gravimetric capacity ~1450 mA h g^{-1} (based on the total mass) and long cycle life (500 cycles with 89% capacity retention). Such SNP@void@mGra structure orienting excellent cycle life and high charge capacity provide a promising prospect for the next-generation high specific energy battery.

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1. Introduction

Lithium-ion batteries (LIBs) for consumer electronics, electric vehicles and grid-scale energy storage need to meet the simultaneous challenges of safety, energy density, cycle life and cost [1–3]. Electrode materials are key for electrochemical performance. For the anode materials, silicon (Si) is likely used in ever greater proportion for the next-generation batteries because of its high energy density, natural abundance, low cost, and environmental friendliness [4–15]. However, large volume expansion, poor electrical conductivity, low initial and steady-state Coulomb Efficiency (CE) and unstable solid-electrolyte interphase (SEI) are the key problems [16–20]. Significant research efforts have been devoted to overcome these issues [19–29]. Among them, nanosized Si shows a potential opportunity due to fast electrode kinetics and excellent thermal and mechanical characters [20–22,24]. However, for the nanostructured Si particles, large surface area still increase side reactions and overload SEI during repeated cycling, which eventually leads to electrical disconnection, poor cycle life and low CE. In this regard, careful design of nano-Si electrode is required to obtain an optimized balance between the surface protection and

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space availability for the perfect battery performance. To develop desirable nano-Si based anodes, the following strategies should be considered: (1) enough nanoscaled void space created to accommodate the large volume expansion, (2) conductive and flexible matrices provided to improve the conductivity and buffer the volume change, and (3) Si surface protection designed to promote the formation of stable and thin SEI in order to decrease the irreversible capacity loss. For example, hollow core-shell or yolk-shell architectures containing Si core and C shell are effective for high performance [18,24,29]. However, most of the architectures are based on the introduction of conducting amorphous carbon or chemically-derived graphene (Gra) oxide (GO) [28–36]. In general, amorphous carbon or GO often results in brittleness, flaws and poor conductivity, leading to large irreversibility [37,38]. Crystallized monolayer or few-layer graphene (fGra) can offer more flexibility to accommodate the large volume change, and more effective routes for electrons and thermal conduction. Compared with amorphous carbon (∼20 GP) or GO [39], mGra shows superior flexibility and structural stability [40], which can accommodate larger volume change and preserve better structure integration for Si electrode.

Recently two research work just reported the Si-Gra composite anodes for LIBs [17,41], the direct anchor graphene onto Si surface can accommodate some volume expansion of silicon, but the bearing strength is limited via the sliding process [17], while the electroless deposition Ni layer can serve as dual effect: catalyst and sacrificial layer for generating void space [41], but using Ni as catalyst, the Gra layer number is difficult to control due to the dissolution and precipitation mechanism for Gra growth [42], which is completely different from the Cu catalyst with surface adsorption function and the monolayer Gra is easy to be controllably synthesized on Cu surface. In this work, we encapsulate Si nanoparticles (SNPs) by monolayer graphene (mGra) with designed void space between SNPs and mGra created by molten Cu template chemical vapor deposition. Such synthesis method shows several advantages: (1) mGra can accommodate large strain and stress, which is different from the previously-reported multilayer Gra, GO and amorphous carbon; (2) the molten Cu route facilitates uniform and fully encapsulated Cu layer outside the nanostructure Si, which is difficult achieved for the other methods such as magnetron sputtering, etc.; (3) the void space is created by nitric acid etching and its size can be easily adjusted; (4) our simple and facile synthesis has potential for mass production. SNPs can dwell in the built-in void space of mGra shell with face-to-face rather than point-by-point contact mode [43], which can greatly extend the Si-C contact interfacial area and then create more efficient channels for fast transport of both electrons and ions. The mGra's flexibility and the void space between each SNP and mGra, accommodate the SNP expansion without rupturing the protective layer, which ensures the formation of a stable and thin SEI layer on the outer surface. Moreover, mGra and the void space work synergistically as following: although the void space was left to accommodate the volume change, yet the void size cannot be too large in order to maintain the volumetric capacity, for example, for a 50 nm silicon nanoparticles, considering the 400% volume expansion, a 15 nm void space should be set aside for accommodating the volume expansion, but due to the anisotropy [44–46] of the expanding silicon, one direction volume expansion may exceed 15 nm for lithiation, while the another direction cannot reach this far, and then the flexible mGra can help to accommodate the volume and shape change.

2. Experiment section

2.1. Materials synthesis

Synthesis mGra on nano-Si: SNPs used in this work were purchased from Shanghai Haotian Nano Company. A facile melting-self-assembly method was employed to fabricate the SNP/Gra composites. The commercial SNPs were first coated with Cu layer (Cu foil, 99.5%, Alfa Aesar) in an atmospheric CVD furnace at 1100 °C for 1 h under Ar and H_2. Then, the furnace was quickly cooled down to 950 °C to make the melted Cu self-assembly onto SNP surface. At the same time, graphene was in situ grown on to Cu layer by flowing 10 standard cubic centimeters (sccm) of CH_4, 20 sccm H_2 and 200 sccm Ar under atmospheric pressure at 950 °C for 40 min to form monolayer Gra and for 60 min to form few-layers Gra. Thus SNP@Cu@Gra architecture was achieved. The Cu layer was then sacrificed by diluted nitric acid aqueous solution (1:1 with de-ionized water) to finally form SNP@void@Gra composite.

2.2. Materials characterization

The morphologies and elements mapping of SNPs and the SNPs-based composites were observed by field-emission SEM (FEI Nova NanoSEM 45). TEM and HRTEM images were attained on a JEOL JEM-2100 instrument equipped with a CCD camera by operating at an acceleration voltage of 200 kV. Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS) attached in TEM. Raman spectroscopy was detected at an operating power level of 2 mW on a confocal Raman spectrometer (Thermfisher, US) using 532 nm excitation laser with spot size of 0.7 μm. The phase was checked by X-ray diffraction (XRD) on an X′Pert PRO diffractometer (PANalytical B.V., Holland) with high-intensity Cu K_{a1} irradiation ($\lambda = 1.5406$ Å). The TG analysis was performed by the vertical zero friction dilatometer L75VS Linseis (Germany) from room temperature to 900 °C in air.

2.3. Electrochemical measurements

Electrochemical performances of the composites were investigated on typical coin cells (CR2032) assembled in an Ar-filled glove box. Metal Li foil was used as the counter electrode and Celgard 2300 membrane as the separator. The electrolyte was 1 mol L^{-1} $LiPF_6$ in a mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC: DMC=1:1). CV curves were measured on a PARSTA 2273 electrochemical workstation at a scanning rate of 0.1 mV s^{-1} from 0 to 2 V. Electrochemical impedance spectrum (EIS) measurement was performed within a frequency range between 0.1 Hz and 1 MHz. Galvanostatic charge-discharge tests were carried out on battery measurement system (Land, China) at various current densities within a voltage range of 1.5–0.005 V vs. Li/Li$^+$ at a constant temperature (25 °C). The electrode was prepared by slurry coating and then dried in oven for 12 h. The ratio of active material: binder (alginate): super P was 8:1:1. The mass loading of the active material on the current collector was ∼0.3 mg, and the mass loading density per unit area was ∼0.6 mg cm^{-2}. The graphene content in the Si@void@mGra composite was estimated by TGA, which was ∼5 wt%, as shown in the supporting Fig. S9.

3. Results and discussion

Fig. 1(a and b) shows the schematic illustration of the design and synthesis of the SNP@void@mGra composite. SNPs are first wrapped by Cu layer via melt-self-assembly (Fig. 1b), and mGra or