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Milled flake graphite/plasma nano-silicon@carbon composite with void sandwich structure for high performance as lithium ion battery anode at high temperature

Hedong Chen [a], Xianhua Hou [a, *], Fuming Chen [a], Shaofeng Wang [a], Bo Wu [b], Qiang Ru [a], Haiqing Qin [c], Yingchun Xia [d]

[a] *Guangdong Engineering Technology Research Center of Efficient Green Energy and Environment Protection Materials, Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006, China*

[b] *Multiscale Computational Materials Facility, Key Laboratory of Eco-Materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350100, China*

[c] *Guangxi Key Laboratory of Superhard Material, China Nonferrous Metal (Guilin) Geology and Mining Co., Ltd., Guilin 541004, China*

[d] *Beijing jwgb Sci & Tech Co. Ltd, Beijing 100055, China*

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ABSTRACT

To reduce the influence from volume expansion of silicon during lithium lithiation/delithiation, milled flake graphite/plasma nano-silicon@carbon (MFG/PNSi@C) composite with void sandwich structure is synthesized by assembling thin MFG (thickness of 150 nm) sheets loading with carbon-coated PNSi (plasma nano-silicon) via a facile spray drying method. The MFG/PNSi@C composite, as lithium ion battery anode, exhibits excellent electrochemical performance at room temperature and displays an outstanding cyclic property even at high temperature. The MFG/PNSi@C electrode delivers reversible capacity of 1141 mAh g^{-1}, and high initial Coulombic efficiency of 84.4%, and capacity retention of 84.1% after 200 cycles at a current density of 0.1 A g^{-1}. Even at the current density of 0.2 and 0.4 A g^{-1}, the reversible capacities of 1168 and 1102 mAh g^{-1} can be achieved respectively, with the capacity retention of 68.9% and 63.9% after 200 cycles. Even the work temperature goes up 60 °C, the discharge/charge capacities of 832/808 mAh g^{-1} can be obtained at a current density of 0.1 A g^{-1}. The stable cyclic performance is mainly due to the void sandwich structure of the MFG/PNSi@C composite, which dramatically shortens lithium ion diffusion path and pitch carbon shell can buffer huge volume expansion.

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1. Introduction

Over the past decades, plenty of researches on energy storage have been explored concerning rechargeable lithium ion batteries (LIBs) with stable cyclic performance and high energy density [1–4]. However, traditional commercial LIBs electrodes already can't meet the demands for energy devices (EDs) and energy storage devices (ESDs). Therefore, present cyclic performance and energy density are both necessary to improve. Enhancing the stable cyclic performance for LIBs requires that electrode materials can keep a stable structure during the discharge/charge processes, in addition to solid liquid interface (electrode and electrolyte). Improving the energy density of LIBs needs to develop electrode materials with high specific capacity; and cathode materials have a high discharge/charge platform and anode materials operate at a low working voltage closing to 0 V (vs. Li/Li^{+}) [5]. Lithium ion batteries in the actual application process could be affected by temperature conditions, such as high and low temperature environment, battery over heat, ect. The battery capacity decays fast under high temperature conditions [6–8]. Therefore, we have to investigate the cycling performance of the electrode under various temperatures and ensure batteries can be used in a wide temperature range.

The appropriate electrode materials have to be developed to meet ever-increasing demand of EDs and ESDs and replace graphite anode due to its low theoretical capacity of 372 mAh g^{-1} [9,10]. As for optional anode materials, transition metal oxides and silicon,

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* Corresponding author.
E-mail address: houxianhua@m.scnu.edu.cn (X. Hou).

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which possess high theoretical capacity for storing lithium, are considered as attractive candidates. Compared with transition metal oxides anode materials, Si anode has a higher theoretical specific capacity ($Li_{4.4}Si \approx 4200$ mAh g^{-1}) and lower discharge potential (0.2 V vs. Li/Li^+) which is close to 0 V [10–12]. Despite these fascinating superiorities of silicon anode, other several critical issues also limit the electrochemical performance for the application. For example, owing to serious electrode pulverization and tremendous volume changes (~300%), Si anode can't retain original high capacity and possesses a poor cyclic stability during the discharge/charge processes [13,14]. Huge volume changes cause fracture of Si particles and instability of formed solid-electrolyte interface (SEI) films [15,16]. The repeated formation and rupture of SEI films on the Si anode deplete the electrolyte to form irreversible lithium, which leads to the sustained declines of the capacity. In addition, Si, as semi-conductor of electricity, has a very low electrical conductivity [17,18]. Several effective approaches have been adopted to deal with the above issues, achieving Si-based composite with high Coulombic efficiency and good cyclic stability: a) encapsulating Si particles within carbon matrix material (porous carbon, CNTs, GO, etc.) that can release the structural stress and enhance the electroconductivity of electrodes; [19–21] b) fabricating Si with diverse morphologies (nano-sphere, nano-wire, nano-film, porous structure, etc.) that can accommodate huge volume expansion; [22–24] c) adding a new binder that can fix the active materials better [10], [25–27].

In this work, milled flake graphite/plasma nano-silicon@carbon (MFG/PNSi@C) composite with void sandwich structure, as an anode for LIBs, was assembled by thin MFG sheets (thickness of 150 nm) loaded with PNSi@carbon particles by spray drying method. The void space of sandwich structure can buffer the severe volume expansion and contraction of Si during the lithiation and delithiation processes, and can provide migration channel for lithium ion. In addition, the thin MFG sheets and carbon layer can enhance the conductivity of the MFG/PNSi@C electrode. After 200 cycles, the MFG/PNSi@C electrode can maintain a stable capacity of 984 mAh g^{-1} at the current density of 0.1 A g^{-1}, exhibiting a high initial Coulombic efficiency of 84.4%. Moreover, the capacity of the MFG/PNSi@C electrode can retain 690 mAh g^{-1} at the current density of 0.4 A g^{-1}. More importantly, the MFG/PNSi@C electrode demonstrates a good cyclic property at a current density of 0.4 A g^{-1} at the temperature range between 10 °C and 60 °C. Even the work temperature goes up 60 °C, the capacities of 832/808 mAh g^{-1} can be achieved during of discharge/charge process. The results indicate that the MFG/PNSi@C composite exhibits an outstanding electrochemical performance.

2. Experimental section

2.1. Preparation of the MFG/PNSi@C composite

The plasma nano-silicon (PNSi) powders (size: ~100 nm) were prepared from commercial crystalline silicon (CCSi) using radio frequency induction plasma system (TEKNANO-15; TDU15 Kw, Canada) with the high temperatures processing capability and high quench rates, as shown in Fig. 1a [28]. The milled flake graphite (MFG) was obtained by milling flake graphite with the zirconia ball (size: 0.1 mm) at the high rotational speed of 3000 rpm for 25 h, as shown in Fig. 1b. The Schematic procedure for the fabrication of MFG/PNSi@C composite was displayed in Fig. 1c. 20 g of the MFG sheets and 1 g of citric acid were dispersed in 600 ml of deionized water and stirred for half an hour; 3 g of pitch was dissolved in 100 ml tetrahydrofuran (THF) and stirred for half an hour, forming the uniform pitch/THF solution; 10 g of nano-silicon was well dispersed in 400 ml deionized water by Ultrasonic Cell Crusher. Then, above of three miscible liquids were mixed and stirred at the speed of 1000 rpm for 1 h. Obtained homogeneous suspension was spray dried to form the MFG/PNSi@pitch precursor under the centrifugal rotational speed of 35000 rpm; the inlet temperature was 220 °C and the outlet temperature was 120 °C. The MFG/PNSi@pitch precursor of spherical secondary particles was calcined at 500 °C for 3 h and followed by 900 °C for 3 h in a high temperature quartz tube furnace under a Nitrogen atmosphere, forming the MFG/PNSi@C composite.

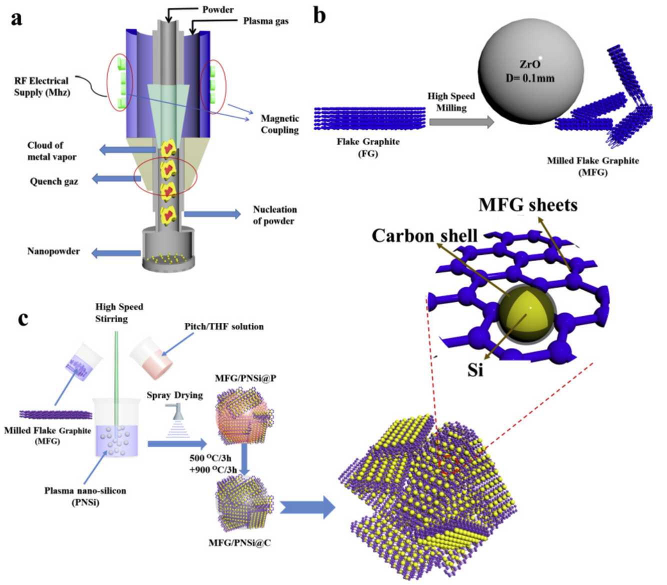

Fig. 1. Schematic drawing (a) of radio frequency induction plasma technology; Schematic illustration (b) of the preparation of MFG sheets via high-energy ball milling of flake graphite; Schematic procedure (c) for the fabrication of MFG/PNSi@C composite. (A colour version of this figure can be viewed online.)

2.2. Materials characterization

The phases and crystal structures of the MFG/PNSi@C composite were characterized by powder X-ray diffractometry (XRD; PANalytical X'Pert PRO) at a scan rate of 10 °C min^{-1} at home temperature and transmission electron microscopy (TEM; JEM-2100HR). The cross-sectional and surface morphology of the MFG/PNSi@C composite were investigated by field emission electron microscopy (FE-SEM; ZEISS ULTRA 55). The carbon phases of the MFG/PNSi@C composite were determined from micro-Raman spectroscopy (Jobin Yvon LabRam HR800). The silicon content of the MFG/PNSi@C composite were tested from thermogravimetric analysis/differential scanning calorimetry (TGA/DSC, Nezsch Sta 409) performed up to a temperature range of 25 °C–900 °C at a heating rate of 10 °C min^{-1} under air flow. The Brunauer-Emmett-Teller (BET) test of samples was determined via Micromeritics ASAP-2020M nitrogen adsorption apparatus.

2.3. Electrode fabrication and synthesis

The electrode materials were assembled in CR2430 button cells inside an argon-filled glove box. The working electrode was obtained by coating the slurries on a copper foil with 10 μm thickness. The coated copper foil was then dried at 80 °C for 12 h. The slurries were composed of 80 wt% active materials, 10 wt% Super P and 10 wt% carboxymethyl cellulose (CMC; Aladdin). The electrolyte compounds were formed by dissolving 1 M $LiPF_6$ in ethylene carbonate (EC), diethyl carbonate (DC) and ethyl methylcarbonate

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