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Porous microspherical silicon composite anode material for lithium ion battery

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ABSTRACT

Nano/micro-structured Si/CNT/C and Si-Cu/CNT/C microspheres are prepared by two simple steps of spray drying and carbonization, which are efficient and easy to scale up. In the Si/CNT/C composites, silicon particles (about 50–200 nm) are covered by a layer of carbon formed by pyrolysis of phenol-formaldenhyde resin (PF), which, in turn, connects with the three-dimensional multiwall carbon nanotubes (MWCNTs) conductive network. Numerous open pores, which could buffer volume expansion of silicon and improve the electrode kinetics, are engendered in the microspheres due to the rapid evaporation of solvent and unfoldment of flexible MWCNTs. Moreover, introduction of small amount of copper (5 wt.%) into the microspheres as Cu_3Si phase reinforces the mechanical stability and improves the electronic conductivity. The favorable Si/CNT/C composite structure leads to significantly improved cycling stability and rate performance (ca. 1250 mA h g^{-1} at 5 A g^{-1}) compared to pristine Si particles. Addition of copper further enhances the capacity retention to 91.2% after 80 cycles.

1. Introduction

As the growing demands for the next-generation lithium ion batteries with increased energy and power density used in portable electronic devices and electric vehicles, silicon has attracted extensive attention owning to its high theoretical capacity ($Li_{22}Si_5$, 4200 mAh g^{-1}) and moderate operating voltage (0.4 V vs Li/Li^+) [1–3]. However, silicon based electrodes often show poor cycle performance because of its low conductivity and the dramatic volume change during repeated lithiation/delithiation process, which leads to electrode pulverization and instability of the solid-electrolyte interphase (SEI) [4–7]. Many methods have been developed to overcome these problems, such as porous Si structure, nanosize Si and Si/C composite [8–12]. Ge Mingyuan et al. [8] reported porous silicon nanowires synthesized by direct etching of boron-doped silicon wafers. The large pore size and high porosity of porous silicon contribute to the structural stability during lithium ion intercalation, resulting in high capacity and long cycle retention. Using alginate as binder, the electrode exhibited the reversible capacity of more than 2000 mA h g^{-1} at current rates of 2 A g^{-1} even after 250 cycles. Hysesun Kim et al. [9] prepared mesoporous Si@carbon core-shell nanowires using a SBA-15 template. The composite electrode showed good cycle performance with 87% capacity retention after 80 cycles.

Moreover, studies [13–18] show that a mixed-conduction carbon phase, such as incorporation of graphite, CNT or grahene, can improve the electronic conductivity, thus contributing to better cycle performance and rate performance. In particular, MWCNTs [14,19] are considered to be benefical for stablizing the conducting structure and enhancing mechanical properties. It was reported that the introduction of MWCNT for silicon electrode could increase the cycling performance [20]. Dae Soo Jung [10]. reported a spray drying process to synthesize porous Si/C composite particles. The porous structure arose mainly from HF etching of SiO_2. The composite electrodes exhibit 91% capacity retention after 150 cycles and 1956 mA h g^{-1} at 0.05 C. Our group proposed [18] a hierarchical microstructured pSi/CNT/C composite prepared from nano-SiO_2 as silicon precursor via a combination of spray drying and magnesiothermic reduction, followed by a nano-layer carbon coating by chemical vapor deposition. Carbon coated silicon nano-particles bonded MWCNT uniformly to form the second particles. This composite presented specific capacity of ca. 2100 mA h g^{-1} at 1 A $g^{-1}$and 95.5% capacity retention after 100 cycles.

Although the above Si based materials show excellent electrochemical performance, most of them are difficult for practical application due to the complicated preparation routes,

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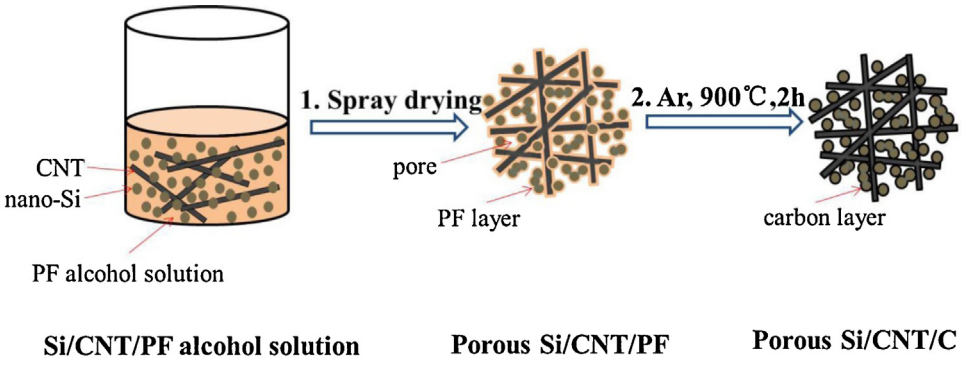

Scheme 1. Schematic for the synthesis route of the spray Si composite.

expensive precursors like SBA-15 template or plagued waste water treatment. Spray drying(SD) method has been widely used for powder preparation and nanoparticle encapsulation in the chemical and food industries owing to its low cost, simple apparatus and easy to scale up [21]. Here, we directly use commercialized nano-Si powder and adopt a two-step procedure consisting of spray drying and carbonization to produce porous Si/CNT/C spheres. Moreover, in view of that Cu and Cu-Si alloy have a low contact resistance and a high mechanical tolerance to volume change [22,23], we add copper into the composite to reinforce the structural stability. The composite electrodes show superior cycle performance and excellent rate capability.

2. Experimental

2.1. Material preparation

2.1.1. Preparation of spray Si

Firstly, 0.73 g nano-Si (particle size of 50-200 nm, Alfa-Aesar), 0.11 g MWCNT (OD > 50 nm, length of 10–30 μm, purity > 95%, Chengdu Organic Chemicals Co., Ltd., China) and 0.37 g PF (Shandong Shenquan Group, China) were dispersed in 150 mL absolute ethanol. The mixture was stirred for 4 h and sonicated for 1 hour at room temperature. Secondly, the mixture was spray-dried (inlet temperature: 170 °C; outlet temperature: 100 °C) to form PF-wrapped nano-Si and MWCNT composite microparticles (Si/CNT/PF). The obtained precursor was then heated to 900 °C at a speed of 5 °C min^{-1} and this temperature was maintained for 2 h in Ar atmosphere to convert PF to amorphous carbon. The whole preparation route is illustrated in Scheme 1. According to the carbonization rate (57%) of PF, the weight ratio of Si:CNT:C in the composite is 69:10:21. The prepared porous Si/CNT/C particles are designated as spray Si.

2.1.2. Preparation of spray Si-Cu

The given amount of the above-mentioned nano-Si, MWCNT and PF, plus Cu nano-powder (10-30 nm, Aladdin), were dispersed in absolute ethanol. After the same procedure in Scheme 1, the Si-Cu/CNT/C composite with a weight ratio of 65:10:20:5 for Si:CNT:C:Cu was obtained, which is described as spray Si-Cu. The tapping

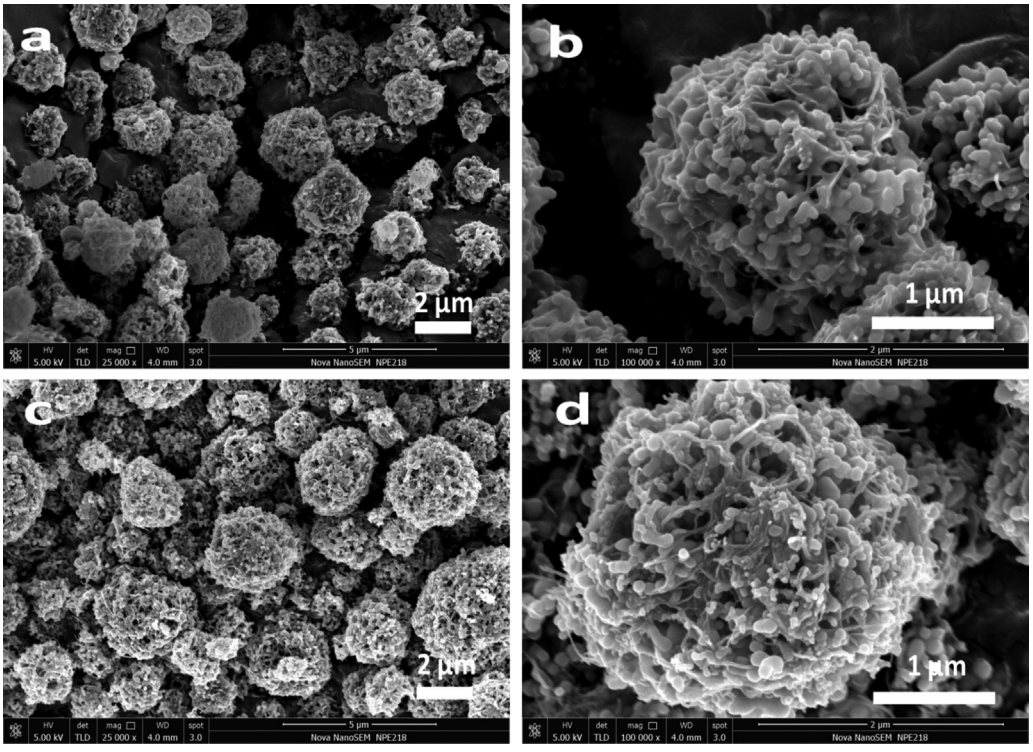

Fig. 1. SEM images of (a, b) Si/CNT/PF after spray drying, (c, d) spray Si after calcination at 900 °C for 2 h in Ar atmosphere.