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# Electrosprayed silicon-embedded porous carbon microspheres as lithium-ion battery anodes with exceptional rate capacities

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## ABSTRACT

Silicon-embedded porous carbon microspheres with an exceptional conductive framework for ions and electrons were obtained by electrospraying a mixed polymer solution of polystyrene and polyvinylpyrrolidone, containing silicon nanoparticles, carbon nanotubes and carbon blacks, and subsequent heat treatment. In the composite microspheres, silicon particles were embedded in the porous carbon framework composed of interwoven carbon nanotubes, filled carbon blacks and interconnected amorphous carbon derived from polymers. The cage-like porous carbon microspheres could not only accommodate the volume expansion of silicon but also ensure a robust electrical contact, fast transport for electrons and ions. Therefore, the silicon/carbon anode exhibits a high capacity of 1325 mAh $g^{-1}$ at 0.2 A $g^{-1}$ after 60 cycles and superior rate capability with a capacity of 925 mAh $g^{-1}$ at a large current density of 5 A $g^{-1}$.

## 1. Introduction

Lithium ion batteries (LIBs) have been widely used in the energy storage field for their high energy density, long service life and environmental benignity [1–3]. However, the graphite anodes of commercial LIBs fail to meet the increasing needs and demands of energy storage markets due to its limited theoretical capacity of 372 mAh $g^{-1}$. Silicon (Si) is considered as one of the most promising anode candidates for its highest capacity of 4200 mAh $g^{-1}$ and relatively low and flat operating potential [4–7]. Nevertheless, there are several fatal drawbacks with regard to the silicon anodes, which hamper their further application and commercialization. Firstly, silicon is known as one kind of semi-conductor materials for its inferior electronic conductivity, which usually means low active material utilization, poor rate performance and rapid capacity fade in the battery [1]. Worse still, silicon anodes usually suffer large volume change (>300%) during the charge/discharge process [6], inevitably causing the collapse of electrode structure, pulverization of active material and continual formation of the unstable solid-electrolyte-interphase (SEI), which results in a rapid capacity decay of batteries [8,9].

To overcome these problems, effective strategies of minimizing Si particles to nanoscale and coupling them with carbonaceous material are usually carried out at the same time [6,10]. The nano structure of silicon can shorten the diffusion pathway of $Li^+$ ions and alleviate the strain caused by volume expansion. Meanwhile, the addition of carbon into the composite could enhance the integrated conductivity notably, contributing to higher utilization of active material and better rate capability. Although the nanotechnologies enhances the battery performance to a considerable extent, nano structure design also has its disadvantages [11–13]. On one hand, nano materials usually result in low tap density and poor volumetric energy density, hindering its wide application in

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practical production. On the other hand, the complicated fabrication of nano structure usually boosts the manufacture cost and prolongs the production period. Therefore, to develop silicon/carbon (Si/C) composite with micron scale and porous structure by assembling nano Si with conductive carbon nanomaterials could effectively suppress the intrinsic defects of Si anode and avoid the flaws of nano design for electrode, as well as further promote commercial production and application [13]. Generally, there are several easy and efficient ways to obtain the micro-scale materials, such as microemulsion approach [8,10], electrospray technique [14–16], spray drying method [4,17,18], and so on. Zhang et al. successfully fabricated the Si/C microspheres with electrospray process and subsequent heat treatment [14]. Hou et al. produced the plum-pudding-like Si/C microspheres through spray drying [17]. Xu et al. successfully designed and synthesized watermelon-inspired Si/C microspheres to improve the electrochemical performance of densely compacted Si/C anodes [18]. Li et al. developed core-shell structured Si/C microspheres with spray drying and subsequent surface coating [4]. The electrochemical performance improvements for the Si/C composites mentioned above are quite notable and encouraging. However, as the size of Si/C composite and thickness of carbon matrix increases, the diffusion way of Li ions and transfer distance of electrons become lengthened, which would result in a poor rate capability for Si/C anode. Accordingly, the conductivity of the composite needs to be improved to accelerate the electron transfer. Meanwhile, interconnected porous structure should be also developed in order to make an intimate contact between anode materials and electrolyte and leave Li ions a shorter distance to diffuse.

In this work, we developed a novel strategy to fabricate Si/C microspheres with a porous and conductive framework structure by electrostatic spray technique and subsequent heat treatment. For the Si/C composite, the porous structure which accommodates volume expansion of Si and facilitate ion transport was directly achieved via polymer pyrolysis instead of the additional template etching method, and the conductive framework was constructed by the interwoven carbon nanotubes (CNTs) and branch-like carbon blacks (CBs). Meanwhile, the amorphous carbon layer originating from polymers can both encapsulate Si nanoparticles (NPs) and further anchor them to the conductive carbon skeleton of CNTs and CBs, forming an integrative structure of Si/C microspheres. As a result, the Si/C microsphere anode exhibits a stable cycle stability at high capacity (maintaining a capacity of 1325 mAh $g^{-1}$ after 60 cycles with a retention rate of 86.94%) and superior rate capability (delivering a capacity of 925 mAh $g^{-1}$ even at the current density of 5 A $g^{-1}$). This facile-manufactured Si/C microsphere composite displays huge application potential in the field of the high-energy-density anode materials and it also brings a new perspective on designing a porous and conductive structure.

## 2. Experimental

### 2.1. Materials and experimental procedures

A specific amount of polystyrene (PS, $M_w = 250{,}000$, J&K Scientific LTD) and polyvinylpyrrolidone (PVP, K30, Aladdin) were dissolved in the DMF solution by continual stirring at 80 °C for 3 h. Subsequently Si NPs (<100 nm, Hongwu Nanometer LTD), CNTs and CBs (Ketjenblack EC-600JD) were together added into the homogeneous mixture and treated with ultrasonic treatment for 2 h, where the weight ratio of PS:PVP:Si:CB:CNT is 6:6:5:2:1. Then a synringe pump was used to keep the feed rate at 1.5 mL $h^{-1}$ and a high voltage of 19 kV was applied between the nozzle and the substrate, which is 18 cm away from the nozzle. After the electrostatic spray process, the sample was carefully scraped from the collector. In order to obtain more carbon in the subsequent heat treatment, the composite needed to be pre-oxidated at 150 °C for 10 h and 350 °C for 1 h. Then the material was heated in argon at 700 °C for 3 h with a heating rate of 10 °C $min^{-1}$. The obtained Si/C composite undergoing pre-oxidation process was defined as P—Si/C. For comparison, the Si/C composite obtained from direct carbonization, without undergoing pre-oxidation process, was defined as N—Si/C, where N stands for none.

### 2.2. Characterization

The morphology details of the obtained sample were investigated by field emission scanning electron microscopy (FE-SEM, ZEISS Supra 55) and high-resolution transmission electron microscope (HR-TEM, FEI TECNAIG2 F30). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA instrument at a heating rate of 10 °C $min^{-1}$ from 30 °C to 850 °C in air. X-ray diffraction test was carried on a Rigaku D/MAX 2500/PC diffractometer using Cu K$\alpha$ radiation ($\lambda = 0.154$ nm). The BET data of the samples was collected on a Micromeritics ASAP 2020 adsorption machine.

### 2.3. Electrochemical test

In a typical procedure, the slurry was composed of 80 wt% Si/C composite, 10 wt% acetylene black and 10 wt% sodium alginate binder in the deionized water. After continuous stirring for 8 h, the homogeneous mixture was then applied onto a copper foil by a doctor blade and dried at 110 °C under vacuum overnight. Subsequently, the anode electrode was cut into discs with a diameter of 12 mm, where the mass loading of active material is about 0.9 mg $cm^{-2}$. Before electrochemical tests, the CR 2032 coin-type cells were assembled in an Ar-filled glove box using the Li foil as the counter electrode and the Celgard 2400 film as the separator. The electrolyte used in the battery was composed of 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC) (volume ratio: 1:1:1) with 2 vol % vinylene carbonate (VC) as the additive. Galvanostatic charge and discharge tests were performed on a Land 2001A cell test system (Wuhan,China) with a potential window of 0.01–1.5 V (vs Li/$Li^+$) at room temperature. The specific capacity of the anode was calculated by the total weight of the Si/C composite. CV experiments were carried out on a VMP3 electrochemical workstation (Bio Logic Science Instruments) at a scan rate of 0.1 mV $s^{-1}$ with a voltage range of 0.1 V—1.5 V. EIS testing was carried on a CHI660C electrochemical workstation with a perturbation voltage of 5 mV in the frequency range of 100 kHz to 10 mHz.

## 3. Results and discussion

### 3.1. Structure and morphology of silicon/carbon microspheres

Fig. 1 shows the fabrication process and schematic structure of the porous Si/C microspheres. The precursor microspheres were firstly prepared from the Si/CNT/KB-containing PS/PVP solution under typical electrospray conditions, as described in experimental section. PS and PVP were selected to form spherical precursors during electrospray and make space for the volume expansion by means of their low carbon yields during subsequent heat treatment. Based on the different heat treatment routes, two kinds of Si/C composite microspheres of N—Si/C and P—Si/C were obtained after final carbonization. N—Si/C was formed via direct carbonization in argon, while P—Si/C was formed via anterior pre-oxidation in air and posterior carbonization in argon. As shown in the typical structure, Si NPs embedded in porous carbon matrix serve