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One-pot synthesis of silicon nanoparticles trapped in ordered mesoporous carbon for use as an anode material in lithium-ion batteries

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Abstract

Silicon nanoparticles trapped in an ordered mesoporous carbon composite were prepared by a one-step self-assembly with solvent evaporation using the triblock copolymer Pluronic F127 and a resorcinol–formaldehyde polymer as the templating agent and carbon precursor respectively. Such a one-pot synthesis of Si/ordered mesoporous carbon nanocomposite is suitable for large-scale synthesis. Characterization confirmed that the Si nanoparticles were trapped in the ordered mesoporous carbon, as evidenced by transmission electron microscopy, x-ray diffraction analysis and nitrogen sorption isotherms. The composite showed a high reversible capacity above 700 mA h g$^{-1}$ during 50 cycles at 2 A g$^{-1}$. The improved electrochemical performance of the composite can be ascribed to the buffering effect of spaces formed in the ordered pore channels during the volume expansion of silicon and the rapid movement of lithium ions through the uniform cylindrical pore structure of the mesopores.

Online supplementary data available from stacks.iop.org/Nano/24/025602/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

The development of high-performance Li-ion batteries is urgently needed for various applications, including portable electronics and electric vehicles [1, 2]. However, the low capacity (372 mA h g$^{-1}$) of the currently used graphite anodes is clearly a limiting factor in the development of high-performance Li-ion batteries. One of the most promising candidates for an anode material that could replace graphite is silicon (Si), an element that has a high theoretical capacity (ca. 4200 mA h g$^{-1}$) [3]. However, during the Li alloying and dealloying steps, Si undergoes a significant volume expansion (>300%), which leads to pulverization and loss of electrical contact, resulting in capacity fading [4]. Many methods have been proposed to effectively reduce this volume expansion, in attempts to utilize Si as an anode material.

Among these strategies, Si–carbon composites such as Si@C core–shell nanowires [5], Si/graphene composites [6], Si/graphite composites [7], carbon nanotubes coated with Si [8], and Si/C composite nanofibers [9], prepared using various carbon precursors, have been extensively investigated. There are several reasons for using carbon: first, it can accommodate the volume expansion of Si; second, it has a high electrical conductivity; lastly, it minimizes capacity loss with the formation of stable solid electrolyte interphase (SEI) layers in aprotic organic electrolytes [10]. These methods have shown improved electrochemical stability of Si as a proof-of-concept. However, these techniques are not suitable for large-scale production due to the production of pollutants (e.g. strong acids) associated with their production, and the multiple steps involved in the production processes. Therefore, particulate hierarchical
nanostructure composites such as mesoporous composites are currently of interest as attractive candidates for large-scale applications [10]. Metal or metal oxide/ordered mesoporous carbon (OMC) composites based on CMK-3 have recently been reported as anode materials, due to their uniform pore channels, very high pore volume and interconnected porous structure [11–14]. CMK-3, an ordered mesoporous carbon, is prepared by applying mesoporous silica as a template and sucrose as the carbon source via an impregnation procedure [15]. In this study, we report, for the first time, on the design and preparation of Si nanoparticles (Si NPs) trapped in an OMC (Si/OMC composite). Si nanoparticles captured by F127/phenolic resol by hydrogen bonding were homogeneously dispersed in the ordered mesoporous carbon framework through carbonization. The products display a high capacity and stable cyclic performance. They therefore have potential for use as advanced anode material for lithium-ion batteries. The major advantages of the Si/OMC composite are ease of synthesis using commercial Si NPs, and the potential for large-scale production, as verified by a recent report on the preparation of an OMC on a kilogram scale [16].

2. Experimental details

2.1. Preparation of the Si/OMC composite

The Si/OMC composite was prepared by the co-assembly of a phenol resol, Pluronic F127 and Si nanoparticles, followed by carbonization. The phenolic resol precursor was prepared by polymerizing phenol (0.46 g, 4.88 mmol) and formaldehyde (37 wt%, 0.79 g) containing formalin (9.75 mmol) by a base-catalyzed method as described previously [17]. The mesostructured polymer–resols were template using the triblock copolymer F127. F127 (0.63 g) was dissolved in 12.6 g of ethanol. An ethanol solution of the resol precursors was added under stirring for 30 min to form a homogeneous solution (phenol/formaldehyde/NaOH/F127 = 1:2:0.1:0.012 in mole ratio). The native oxide layer on the surface of the Si NPs (Alfa Aesar) is helpful, in that it interacts strongly with the resol, which has a large number of hydroxyl groups (–OH), by the formation of hydrogen bonds, thus permitting it to dissolve completely in ethanol [17]. Si NPs were dispersed in ethanol by sonicating the solution for 1 h. A 0.3 g portion of the Si NPs was added to a stirred ethanol solution of resol and F127. The mixture was transferred to a dish and the ethanol was allowed to evaporate at ambient temperature for 8 h. The resulting membrane was heated in an oven at 120 °C for 24 h for thermopolymerization. The products were calcined at 350 °C for 5 h at a heating rate of 1 °C min−1 to remove the triblock copolymer template under a stream of argon. The preparation was finally heated from 350 to 900 °C at a rate of 1 °C min−1 and the final temperature was held for 4 h to allow the preparation to carbonize. Based on thermogravimetric analysis (TGA), the weight percentages of OMC and Si in the Si/OMC composite were estimated to be 50.5 and 49.5%, respectively (figure S1 in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia). In this study, Si/OMC compositions were prepared with different Si contents: 40, 65, and 82 wt%, respectively. The Si contents of the composites were calculated and controlled based on the amount of carbon precursor and Si NPs. After the preparation of the Si/OMC composites, the amount of Si loaded into the samples was determined by TGA (figure S2 in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia). A non-porous carbon/Si composite was prepared to compare its electrochemical properties with the Si/OMC composite. It was synthesized following the same procedure, but without the use of F127 (figure S3 in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia).

2.2. Characterization

The Si/OMC composite was characterized by field-emission scanning electron microscopy (SEM, Carl Zeiss, SUPRA-55VP) and high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-3010). Small-angle and wide-angle x-ray diffraction (XRD) patterns were obtained by small-angle x-ray scattering (SAXS) with a General Area Detector Diffraction System (Bruker, GADDS) and a M18XHF-SRA diffractometer (MAC Science) respectively. N2 adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 instrument. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore volume and pore size distributions were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. TGA was performed using a thermogravimetric analyzer (Versa Therm, Thermo Scientific) with a heating rate of 5 °C min−1. Electrochemical characterizations were performed using coin-type half cells (2032 type) prepared in an argon-filled glove box that contained an electrode, lithium foil (Alfa Aesar) as a counter-electrode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF6 with 1:1 w/w ethylene carbonate:diethyl carbonate (Panax e-tec). The electrode was composed of Si/OMC composite (70 wt%), poly (vinylidene fluoride) binder (20 wt%), and Super P carbon black (10 wt%). The cells were discharged (Li-ion insertion) and charged (Li-ion extraction) in a voltage range from 0.01 to 2.0 V (versus Li/Li+) using a battery tester (WBCS3000, Wonatech). The capacity values were calculated based on the mass of the active materials.

3. Results and discussion

The Si/OMC composite was prepared by a one-pot synthesis via a solvent evaporation induced self-assembly method using phenolic resol as a carbon source, the triblock copolymer Pluronic F127 as a structure-directing agent and Si NPs with a size of approximately 50 nm [18] (scheme 1). F127 was dissolved in ethanol (scheme 1(a)). The phenolic resol and Si NPs were added and the mixture was stirred. The solution was then aged at room temperature to allow the ethanol to evaporate. During the evaporation of the ethanol, the resol–copolymer composite is transformed into an ordered liquid crystalline mesophase. The Si NPs are coated with the
liquid crystalline mesophase because the liquid crystalline mesophase contains a large number of hydroxyl groups (–OH) that can interact with the native oxide layer on the surface of the Si NPs by hydrogen bonding [17] (scheme 1(b)). During the aging at 120°C for thermopolymerization, the integral 3D resin frameworks are finally formed [17] (scheme 1(c)). After calcination, the Si NPs are distributed in the OMC frameworks formed by the decomposition of the template F127 and the carbonization of the crystalline mesophase (scheme 1(d)). This mechanism makes it possible to trap nanoparticles that have a larger diameter than the pore size in the OMC structure, which is difficult in the case of CMK-3. HR-TEM images of the Si/OMC composite show that Si NPs are trapped in the OMC framework after calcination at 900°C. Figures 1(a)–(c) show that the ordered hexagonal mesoporous carbon and Si NPs, which are observed as dark spots, are dispersed in the OMC. The presence of partial mesostructural irregularities around the Si NPs suggests that they are located within the OMC framework. The lattice fringes of the (111) plane, corresponding to a d spacing of 3.0 Å, are observed for the Si NPs across the OMC walls (figure 1(c)). Metal or metal oxide/CMK-3 composites can be synthesized only if the sizes of the metal or metal oxide particles are smaller than the pore size (ca. 5 nm) of the CMK-3, due to the mechanical stability of the pore wall [19]. Therefore, the preparation of metal or metal oxide/CMK-3 composites using commercial nanoparticles with diameters greater than 5 nm is difficult. The Si NPs in the Si/OMC composite do not exist inside the pores of the OMC, unlike metal or metal oxide/CMK-3 composites. The Si NPs are surrounded by an OMC framework because the Si NPs are coated with the liquid crystalline mesophase as a result of the evaporation induced self-assembly. This can be clearly identified from the HR-TEM image of the Si/OMC composite with 82 wt% Si content (figure S4(a) in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia). The presence of partial mesostructural irregularity around the Si NPs suggests that they are located in the OMC framework in the case of the Si/OMC composite with a 50 wt% Si content (figure S4(b) in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia).

Figure 2(a) shows small-angle XRD patterns of the OMC and the Si/OMC composite. The OMC exhibits peaks indexed as (10), (11) and (20) associated with well-ordered hexagonal (p6m) mesostructure [20]. However, the Si/OMC composite displays only a small (10) peak due to the increase in the mesostructural irregularity in the presence of Si NPs. The wide-angle XRD pattern of the Si/OMC composite exhibits sharp peaks corresponding to crystalline Si at around 28°, 47°, 56°, 69°, and 76°, which correspond to the (111), (220), (311), (400), and (330) planes [21], as shown in figure 2(b). The two diffraction peaks at around 21° and 43° are assigned to the (002) and (100) planes for carbon materials [22]. The XRD patterns of the Si/OMC composite confirm the presence of a coexistence of two phases, namely, crystalline Si and carbon. Figure 2(c) provides information on the nitrogen sorption isotherms and the pore size distribution of the OMC and the Si/OMC composite. The XRD patterns of the Si/OMC composite confirm the presence of a coexistence of two phases, namely, crystalline Si and carbon. Figure 2(c) provides information on the nitrogen sorption isotherms and the pore size distribution of the OMC and the Si/OMC composite. While the OMC exhibits a type IV isotherm with an H2 hysteresis loop, indicating the presence of relatively uniform mesopores, the Si/OMC composite shows an H3 hysteresis loop which does not exhibit any limiting adsorption at high p/p0, due to the filling of interparticle textural pores [23]. The pore size distribution and
Figure 2. (a) Small-angle and (b) wide-angle XRD patterns for OMC and Si/OMC composite. (c) N$_2$ adsorption/desorption isotherms and (d) pore size distributions for OMC and Si/OMC composite.

Figure 3. Voltage profiles of (a) commercial Si NPs, (b) OMC, and (c) Si/OMC composite during the first, second, and 50th cycles. (d) Differential capacity plot of the Si/OMC composite during the first, second, fifth, and 20th cycles. (e) Galvanostatic cycling of the Si/OMC composite with different Si contents.
average pore size of the Si/OMC composite are wider and larger than those for OMC, respectively (figure 2(d)). This indicates the degradation of the mesostructural regularity by the Si NPs located in the OMC. The Si/OMC composite has a BET surface area of 371.9 m$^2$ g$^{-1}$ and a pore volume of 0.39 cm$^3$ g$^{-1}$, values that are lower than those of the OMC (602.0 m$^2$ g$^{-1}$ and 0.45 cm$^3$ g$^{-1}$). The decrease in the BET surface area and pore volume demonstrates that the pores of the OMC are partially filled with Si NPs [11].

Figures 3(a)–(c) show galvanostatic discharge/charge curves for commercial Si NPs, OMC, and Si/OMC composite from 0.01 to 2.0 V (versus Li/Li$^+$) after 1, 2, and 50 cycles. For the first discharge, the Si NPs in the OMC framework form a two-phase structure of partially lithiated Si and unlithiated crystalline Si produced by the diffusion of Li ions [24]. Therefore, the Si NPs and Si/OMC composite display a long voltage plateau at 0.1 V, consistent with the typical characteristics of crystalline Si [24]. However, an obvious voltage plateau was not observed for the OMC (figure 3(b)). The Si/OMC composite (figure 3(c)) exhibits an obvious voltage plateau was not observed for the OMC (figure 3(b)). The Si/OMC composite (figure 3(c)) exhibits an initial discharge capacity of 1275 mA h g$^{-1}$ at 0.1 C. The first discharge capacity of the Si/OMC composite is lower than that of the Si NPs (figure 3(a)). The irreversible capacity in the first cycle induced by SEI formation on the large surface of the Si/OMC composite is at a similar level to other Si/carbon composites [25, 26]. However, during further cycling at 1 C, the Si/OMC composite exhibits more stable cycling properties than the Si NPs after 50 cycles. Figure 3(d) displays differential capacity plots for the Si/OMC composite for 1, 2, 5, and 20 cycles. During the first discharge, the crystalline Si NPs in the OMC form an alloy with the Li ions and the crystalline Si then undergoes solid state amorphization, due to the large atomic displacement of the Si atoms [27]. This reaction occurs at a peak potential of $\sim$0.018 V with an onset potential of 0.10 V. In addition, Li$_{2}$C$_{6}$ is formed by the intercalation of Li ions with the OMC, which occurs at a peak potential of 0.78 V (figure S5 in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia). The first cathodic peak of the Si/OMC composite is shifted from 0.09 to 0.018 V and an additional new peak appears at 0.78 V, in comparison with that of the Si NPs (figure S6 in the supporting information available at stacks.iop.org/Nano/24/025602/mmedia), due to differences in the surface kinetics between the Si/electrolyte and Si/OMC/electrolyte [28]. Upon the second discharge, two peaks at 0.08 and 0.22 V, corresponding to the nucleation and growth of other intermetallics/amorphous Li$_x$Si phase, are observed [27]. In addition, the difference curve for the charge shows two peaks at 0.3 and 0.48 V, corresponding to de-lithiation of the alloy to amorphous Si [29]. These peaks do not change significantly from the fifth to the 20th cycle, unlike those of the Si NPs. The buffer effect of the OMC on the volume expansion of Si was examined through a comparison of its electrochemical stability as a function of various wt% Si contents (figure 3(e)). A rate of 0.1 C calculated by the ratio between the Si and carbon of each sample was used for the first cycle and the first charge capacity was increased with an increase in the wt% Si content. After the first cycle, the charge/discharge rate was increased to 1 C. After the tenth charge, the capacity was decreased dramatically due to the volume expansion of Si. The Si/OMC composite with below 50 wt% Si content exhibited a stable capacity after 30 cycles. These results prove that the carbon content of the Si/OMC composite accommodates the stress with volume expansion and that this improves the electrochemical stability of the composite. The Si/OMC composite with 50 wt% Si content displayed the highest capacity and stability. Figure 4(a) shows the cycling performance of the Si/OMC composite with 50 wt% Si content and the Si NPs coated with non-porous carbon (Si@C) composite. The reversible capacity of the Si/OMC composite increased with cycling and was maintained above 700 mA h g$^{-1}$ for 50 cycles. This capacity of the Si/OMC composite is slightly higher than that of other Si–carbon composites reported recently [30, 31]. The Coulombic efficiency after the first cycle at a rate of 0.1 C becomes stable in the range of 94–100% at a rate of 1 C. The cycling performance of the Si@C composite synthesized without the presence of F127 was tested to identify the effect of mesopore structure on the capacity. The initial discharge capacity of the Si@C composite was approximately 260 mA h g$^{-1}$, followed by a low capacity ($\sim$130 mA h g$^{-1}$) for 50 cycles. A thick non-porous carbon layer of Si@C composite can act as a barrier for Li ion diffusion [32]. Therefore, the higher capacity of the Si/OMC composite can be attributed to the ordered mesopore structures that facilitate uniform penetration of electrolytes into the mesopores and the thin pore walls, which ensure short diffusion paths for Li ions, resulting in a high transfer rate of Li ions into the Si NPs [11]. Figure 4(b) provides information on the rate capability of the Si/OMC composite operating at various rates between 1.5 and 3 C. The reversible capacity of the Si/OMC...
Figure 5. (a) SEM image and (b) HR-TEM image of the Si/OMC composite after the cycling.

4. Conclusions

A Si/OMC composite was prepared for use as an anode material in rechargeable Li batteries. The composite was synthesized by a self-assembly procedure using Pluronic F127, a resorcinol–formaldehyde polymer and Si nanoparticles. The improved cycling performance of the Si/OMC composite can be attributed to the pore structure of the OMC that not only absorbs the stress that arises with volume expansion of the Si but also facilitates the contact of the electrolyte with the Si NPs. This unique pore structure of OMC has promise as a carbon matrix to replace materials such as graphite, graphene and carbon nanotubes for metals and metal oxides to improve their electrochemical performance.

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