High-Rate and Long-Cycle Silicon/Porous Nitrogen-Doped Carbon Anode via a Low-Cost Facile Pre-Template-Coating Approach for Li-ion Batteries

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Exploring low-cost, facile, and scalable fabrication procedure for silicon/carbon composite with excellent electrochemical performance is urgently required to promote the practical application of high-capacity silicon material for Li-ion battery anodes. Using commercial cost-effective AlSi alloy nanopowder as the silicon source, here we present a facile approach via pre-template-coating and chemical acid etching methods for synthesizing silicon/porous nitrogen-doped carbon composite with a unique core-porous shell structure. At the pre-template-coating stage, the AlSi alloy nanopowder is initially coated by carbon via the solution deposition and carbonization of PVP. The Al template is subsequently removed by acid etching, affording silicon nanoparticles wrapped by the highly conductive nitrogen-doped carbon. The escape of hydrogen gas during acid etching leads to the nitrogen-doped carbon shell with a microporous structure. The silicon/porous nitrogen-doped carbon composite with 88% Si delivers a high reversible capacity of 1730 mAh g^{-1} (based on the total mass of the composite) after 100 cycles at a current density of 1000 mA g^{-1} with a coulombic efficiency of approximately 100%. Moreover, the rate capability is significantly improved. With the increase in the current density from 200 to 500, 1000, 2000 and 3000 mA g^{-1}, high capacity retention values of 99.7, 97.5, 93.7 and 91.5%, respectively, are obtained. A long cycle life at a high rate is also achieved, with a notable capacity of 665 mAh g^{-1} after 600 cycles at a high current density of 5000 mA g^{-1}. The low-cost, facile, and scalable synthesis of the approach silicon/ porous nitrogen-doped carbon composite with exceptional electrochemical performance from a commercial AlSi alloy powder makes it extremely promising as a practical anode material for high-energy Li-ion batteries.

1. Introduction

In the past decades, extensive efforts have been focused on the fabrication of Li-ion batteries with a high energy density and long cycle life by the exploration of new electrode materials and design of various nanostructured composite materials [1–4]. Among these materials, the earth-abundant silicon (Si) is considered as a promising next-generation anode material because of its considerably higher theoretical specific capacity (4200 mAh g^{-1})

compared with that of the commercial graphite anode (372 mAh g^{-1}) [5–7]. In addition, the low discharge potential (0–0.4 V vs. Li$^+$/Li) and environmental benignity of Si make it highly desirable as an anode material [8–10]. However, the practical utilization of Si anode has been significantly hindered by the poor electrochemical performance, which is related to its low intrinsic electrical conductivity and drastic volume change (∼300%) during Li alloying/de-alloying process. These factors in turn lead to the pulverization of the Si electrode and instability of the solid electrolyte interface (SEI) film [11–15].

To overcome these drawbacks, considerable progress has been made by utilizing nanoscale structures, such as Si nanoparticles [16–20], Si nanotubes [21–24], nanowires [25–27], nano-porous Si

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[28–30], and Si/C nanocomposites [31,32]. Fracture and fragmentation during lithiation and delithiation can be suppressed or even prevented by reducing the particle size of Si to the nanometer regime [33–36]. Moreover, coating the Si surface with carbon leads to a marked improvement in the electrochemical performance because of the enhancement in electronic conductivity, ease of particle expansion, and suppression of the SEI side reactions [37]. Therefore, Si/C nanocomposites are considered to be among the most viable candidates for practical application as high-capacity Si based anodes in high-energy Li-ion batteries. However, the fabrication of low-cost, scalable materials for Si nanoparticles and Si/C nanocomposites is still challenging. A majority of the current reported Si nanoparticles have been produced by the pyrolysis of silane or by the magnesiothermic reduction of silica at high temperatures exceeding 1000 °C, which results in ineffective energy consumption and high manufacturing costs. For Si/C nanocomposites, post-coating approach, which involves the formation of a composite with carbon on the already obtained Si nanoparticles, is the typical approach applied. To generate a porous structure in the Si/C nanocomposites, additional additives as templates are typically required for post-coating approach, thereby complicating the procedure. It is believed that the synthesis of specific materials and the manufacturing costs are predominantly dependent on the choice of the precursors used.

As opposed to silane or silica precursors, commercially economical AlSi alloy powder, which has been widely used in the powder metallurgy industry, can afford Si nanoparticles by the simple chemical acid etching of Al at room temperature. More importantly, Al in the alloy precursor can serve as a template to generate a porous structure. Previously, our group has reported a Si/graphene paper anode by the acid etching of micro-AlSi alloy powder for Li-ion batteries [38]. However, the rate performance of the anode was still poor because of the agglomeration of Si nanoparticles between the graphene layers. Among numerous carbon precursors, polyvinylpyrrolidone (PVP) has been widely used as a dispersing and capping agent. The polymer is easily soluble in water with a hydrophilic head and long hydrophobic tail, which allow for efficient dispersion of the material it attaches to, resulting in a uniform coating on the particle surface [39,40]. Besides, because of the presence of nitrogen, PVP can be easily carbonized to produce nitrogen-doped carbon materials, which could enhance the electronic conductivity and mechanical stability of the carbon structure [41].

Herein, to develop a low-cost, facile, and scalable fabrication procedure for Si/C nanocomposites with high electrochemical performance, a commercial cost-effective AlSi alloy nanopowder and PVP were used as the silicon and carbon sources, respectively. Si/porous nitrogen-doped carbon (Si/p-NC) with a unique core–porous shell structure was synthesized by pre-template-coating and chemical acid etching methods. At the pre-template-coating stage, the AlSi alloy nanopowder was initially coated by carbon via the solution deposition and carbonization of PVP. The Al template was subsequently removed by acid etching, affording silicon nanoparticles wrapped by the highly conductive NC. The removal of the Al template and escape of hydrogen gas (product from the reaction between Al and HCl) during acid etching are hypothesized to afford a Si particle core and a nitrogen-doped carbon shell with a porous structure. The porous structures in the Si core and carbon shell were demonstrated to be beneficial for volume accommodation and rapid ion transport, affording excellent cycling stability and rate capability. The Si/p-NC composite with 88% Si delivered a high reversible capacity of 1730 mAh g^{-1} (based on the total mass of the composite) after 100 cycles at a current density of 1000 mA g^{-1} with a coulombic efficiency (CE) of approximately 100%. Moreover, the rate capability was significantly improved. With the increase in the current density from 200 to 500, 1000, 2000, and 3000 mA g^{-1}, high capacity retention values of 99.7%, 97.5%, 93.7%, and 91.5%, respectively, were observed. A long cycle life at a high rate was also achieved, with a notable capacity of 665 mAh g^{-1} after 600 cycles at a high current density of 5000 mA g^{-1}. The low-cost, facile, and scalable synthesis of the Si/p-NC composite with exceptional electrochemical performance from a commercial AlSi alloy powder makes it extremely promising as a practical anode material for high-energy Li-ion batteries. The pre-template-coating approach is also expected to expand the synthetic methods for Si-based functional materials.

2. Experimental section

Nano-AlSi alloy powder with 10 wt% Si and an average particle size of 80 nm was purchased from Shanghai Chaowei Nano-technology Co., Ltd. (Shanghai City, China) and used without any further treatment. Pre-template-coating and chemical acid etching methods were utilized to synthesize the Si/p-NC composite. First, 2 g of the nano-AlSi powder was added to 30 mL of anhydrous ethanol and subjected to sonication for 5 min at room temperature,
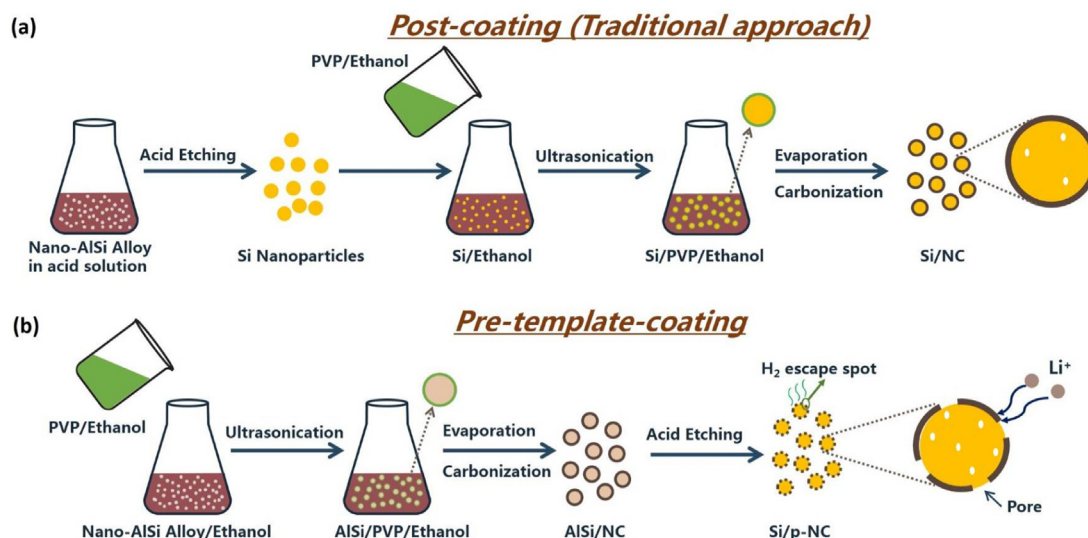

Fig. 1. Schematic illustration of (a) the post-coating approach for Si/NC and (b) the pre-template-coating approach for Si/p-NC from a low-cost AlSi alloy powder.