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# Nitrogen-doped Carbon Coated Porous Silicon as High Performance Anode Material for Lithium-Ion Batteries

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ABSTRACT

An effective approach to generate nitrogen-doped carbon coating layer on porous silicon (CN@P-Si), one of most promising anode materials for lithium-ion batteries, was addressed in this study to minimize their intrinsic drawbacks of low electrical conductivity and large volume expansion. The resulting enhanced electrochemical performance of the cell using the prepared CN@P-Si materials is attributed to the suppression of volume expansion and formation of the stable solid electrolyte interface by the combination of the porous structure and nitrogen-doped carbon coating layer during the repeated lithiation and delithiation process. After 100 cycles at $0.8 \, A \, g^{-1}$, the capacity retention is 82% in contrast to 69% for the non-coated samples. Even at the increased discharge current of $20 \, A \, g^{-1}$, the cell with CN@P-Si electrode delivers a high specific capacity of $1904 \, mAh \, g^{-1}$. After 100 cycles, the P-Si electrode with pores shows huge pulverization; in contrast the CN@P-Si electrode remains intact with reasonably low volume expansion. Nitrogen-doped carbon coating layer on porous Si surface successfully suppress the pulverization of CN@P-Si electrode owing to its shielding capability. These results suggest that CN@P-Si is an attractive candidate for a high-capacity anode for lithium-ion batteries.

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## 1. Introduction

Over the last few decades, because of significant academic and industrial developments related to rechargeable lithium-ion batteries (LIBs), they have become the representative power sources for various electronics applications. Despite the improved performance of LIBs, major challenges still impede their application in electric vehicles (EVs) and grid-scale energy storage systems: specifically, significantly higher energy and power density, longer cycle life, and reduction in cost need to be realized [1]. In case of EVs, higher-capacity electrode materials are the most important parameter for greater uninterrupted driving distance because the energy density of LIBs (gravimetric and volumetric) is closely related to and determines the EV driving distance.

Currently, in cell technology, investigations on the combinations of a carbon anode and a lithium-metal oxide or -phosphate cathode ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$) are reaching a limited performance. Therefore, the replacement of conventional electrode materials with suitable alternatives has been a major focus of recent research.

Among the developed anode materials, silicon-based materials are a promising alternative to graphite carbon ($370 \, mAh \, g^{-1}$) due to the highest theoretical capacity ($4200 \, mAh \, g^{-1}$, lithiated to $Li_{4.4}Si$) and relatively low discharge potential (the average delithiation potential of Si is 0.4 V). Tremendous efforts have been devoted to their commercialization in the past decade. In spite of their excellent potential, designing silicon-based electrode materials is challenging owing to the detrimental electrode pulverization resulting from huge volume changes and the instability of solid-electrolyte interface (SEI) layers on the electrode surface during lithium insertion (lithiation) and extraction (delithiation) [2]. To overcome these issues, various structural designs of materials such as silicon nanotube [3,4], silicon nanoparticle

[5,6], silicon nanowire [7–9], porous silicon [10–12] were developed. Among these, porous silicon microparticles achieved by a metal-assisted chemical etching method is one of the most efficient approaches for practical industrial applications because of low-cost, facile process. Moreover, the porous microparticles provide significantly high structural stability as anode materials for LIBs because the empty space in the pores can partially accommodate the expanded volume after lithiation, thus resulting in an enhanced cycling performance. In addition, the porous structure of electrode materials affords a larger reaction area between electrodes and the electrolyte, i.e., at the electrode/electrolyte interface; and this improves electrochemical properties of batteries, including specific capacity, cycle life, and rate capability [12–14].

Furthermore, the combination of the porous structure and a coating of a conductive agent can withstand large mechanical strains, suppress the pulverization of silicon, and increase the electronic conductivity, and a resulting increase in the battery performance can be expected [10–12]. The uniform coating layer on the surface would assist in accommodating the volume expansion during lithiation. Recently, a doped carbon with heteroatoms has attracted as promising candidate as conductive coating agent on electrode materials due to its higher power density than that of un-doped carbon coated materials according to previous reports [15], Among heteroatoms for various doping sources, e.g., nitrogen or boron, nitrogen is one of most attractive dopant in carbon network, because the atomic size of nitrogen is comparable to that of carbon and its five valence electrons are available to form strong valence bonds with carbon atoms [16]. Additionally, its higher electronegativity than that of carbon have an effect that carbon atoms neighboring to nitrogen dopants possess a substantially higher positive charge due to the strong electronic affinity of the nitrogen atom [17]. And so, the nitrogen atoms incorporated into carbon networks should lead the formation of stronger interactions between the nitrogen-doped carbon layer and lithium, which might be favorable for lithium insertion [18,19].

The graphitic nitrogen in the carbon matrix which was seen as nitrogen-carbon species obtained regarding to the site location in carbon framework after doping process of nitrogen, has higher enhancement of the electronic conductivity through electron donation and the generation of the numerous extrinsic defects and active sites [20]. Therefore, the nitrogen-doped carbon is considered with promise as a coating agent for silicon materials to realize an excellent battery performance [21]. Due to this advantage, nitrogen-doped carbon coating method to modify the SiO, Si, $Li_4Ti_5O_{12}$, $LiFePO_4$ and $TiO_2$ electrode materials, has already been reported to improve their electrochemical properties [21–25]. Nevertheless, in these reports, a nitrogen-doped carbon layer was generated by employing either reaction with expensive ionic liquid or ammonia ($NH_3$) gas treatment with a rigorous reaction condition as nitrogen sources. Note that, these methods not only require special equipments and expensive source materials, but also ammonia gas is a corrosive gas and may be fatal if inhaled as it is a severe respiratory tract irritant. Additionally, multistep reaction for separated coating carbon and nitrogen causing increased fabrication cost. Thus, we developed a simple coating technique by using ethylenediamine (EDA) as a carbon and nitrogen source with single step to form a thin layer of nitrogen-doped carbon on the surface of porous silicon, which was regarded as by various characterization tools. In our previous study [26], we confirmed that the uniform nitrogen-doped carbon layer improves electrochemical performance via the improvement of the electrical conductivity and the maintenance of the electrical contact between the electrode component materials. Therefore, similar enhanced properties could be expected in case of silicon materials.

In this study, we have designed porous silicon (denoted as P-Si) coated with the nitrogen-doped carbon coating (denoted as CN@P-Si) by a facile chemical reflux method to realize a long cycle life and high rate capability of the battery. Porous Si from bulk which was synthesized by the metal-assisted chemical etching process has been reported by S. Park et al. group [12]. However, to further improvement of electrochemical performance, the approach was modified and employed for the nitrogen-doped carbon coating process of this research. The CN@P-Si electrode showed reduced volume expansion around 56% after the 1st lithiation process in contrast to the 153% volume expansion of pristine silicon. Thus, the synthesized CN@P-Si anode materials achieved an excellent cycling performance and a high specific capacity in high-current applications because of the effects of the porous structure and the conductive coating layer.

## 2. Experimental Section

The P-Si particles were prepared from bulk silicon particles (~5 μm Kojundo Co.) by using the metal-assisted chemical etching process as described in our previous report [27] or elsewhere [12]. To prepare the etching solution, 0.04 mol of silver nitrate and 4.6 mol of hydrofluoric acid were dispersed in DI water. Then, 3 g of bulk silicon was added, and the homogeneous mixture was stirred continuously for 1 h. After the etching process, the precipitate was dissolved in a 900 ml solution of 50 wt.% nitric acid to remove the residual silver nanoparticles, and thoroughly washed 3 times with DI water and then filtered. The resulting porous silicon powder was dried in vacuum at 60 °C for 1 h. For coating with the nitrogen-doped carbon, the P-Si powder was dispersed in 100 ml of ethylenediamine (EDA) as a coating agent (i.e., carbon and nitrogen source) using the reflux method and the solution was stirred at 120 °C for 24 h. The amount of coated EDA on the P-Si was about 17.5%, which was estimated by the amount of coated carbon and nitrogen by an elemental analyzer and the decreased weight during heat treatment in Ar atmosphere by thermal gravimetric analyzer. The homogeneous solution was centrifuged, and the sediment was collected. More details of the coating process can be found elsewhere [26]. Subsequently, the product was carbonized at 800 °C for 4 h in an Ar atmosphere.

The morphologies of the commercial bulk silicon and synthesized porous silicon and the coated sample were investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4200) and high-resolution transmission electron microscopy (HR-TEM, Titan, FEI Corp.). Energy filtered TEM (EF-TEM, Titan, FEI Corp.) was employed for the analysis of the elemental composition of the nitrogen-doped carbon coating sample. The crystalline structures of the synthesized porous silicon and the coated sample were characterized using X-ray diffraction measurement (XRD, Rigaku X-ray diffractometer) equipped with Cu-Kα (λ = 1.5418 Å) radiation in the 2θ range from 10° to 90°. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe Ulvac-PHI) was used to detect the surface chemical composition of the nitrogen-doped carbon layer. In addition, the amounts of carbon and nitrogen in the synthesized materials were determined by using an elemental analyzer (EA1108/CHNS-0, Carlo Erba/Fisons/CE Instrument) and thermal gravimetric analyzer (SDT Q600 V20.9 Build 20).

For the investigation of electrochemical performances, the electrodes were prepared as follows. The slurry composed of CN@P-Si or P-Si as active materials, acetylene black, and polyacrylic acid binder (PAA) (6:2:2 weight ratio) were cast onto copper foil current collector to obtain a thickness of approximately 15–20 μm with a loading amount of approximately 1.2 mg cm$^{-2}$ after a roll-pressing. The prepared electrodes were dried overnight at 120 °C in vacuum before use. Then, the coin-type half cells (CR2032) were assembled with a Li counter electrode, the prepared