Facile Synthesis of Amorphous Ge Supported by Ni Nanopyramid Arrays as an Anode Material for Sodium-Ion Batteries

Hao Wu,[a] Wenjun Liu,[a] Lihua Zheng,[a] Danfeng Zhu,[a] Ning Du,[b] Chengmao Xiao,[c] Liwei Su,[a] and Lianbang Wang*[a]

In this work, we introduce Ni nanopyramid arrays (NPAs) supported amorphous Ge anode architecture and demonstrate its effective improvement in sodium storage properties. The Ni–Ge NPAs are prepared by facile electrodeposition and sputtering method, which eliminates the need for any binder or conductive additive when used as a Na-ion battery anode. The electrodes display stable cycling performance and enhanced rate capabilities in contrast with planar Ge electrodes, which can be owing to the rational design of the architectured electrodes and firm bonding between current collector and active material (i.e. Ni and Ge, respectively). To validate improvement of nanostructures on electrochemical performance, sodium insertion behavior of crystalline Ge derived from Mg,Ge precursor has been investigated, in which limited but effective enhancement of sodium storage properties are realized by introducing porous nanostructure in crystalline Ge. These results show that elaborately designed configuration of Ge electrodes may be a promising anode for Na-ion battery applications.

1. Introduction

Li-ion batteries (LIBs) have been the most widely used energy storage devices to power consumer electronics,[1,2] However, as LIBs are marching into other commercial markets (e.g. electric vehicles and stationary grid storage), some critical issues lie in the path of their large-scale applications, such as limited lithium resources and their increasing price.[3] Therefore, sodium-ion batteries (NiBs) have attracted extensive attention as an alternative for LIBs in the respect of natural abundance and low cost.[4–6] Progress has been made demonstrating that novel sodium storage materials are capable of exhibiting advanced Na-storage performance.[7–9] Due to the close chemical properties of Li and Na, varied materials that have been applied in LIBs are also studied for application in NiBs, revealing an interesting fact that the reactivity of sodium and lithium with anode materials is quite different.[10–12] For instance, graphite, a commercially used anode material in LiBs, fails to intercalate Na effectively,[13] though recent research shows that the barrier can be broken by using cointercalation in a diglyme-based electrolyte with capacities close to 100 mAh g–1.[14] Thus, suitable anode materials with better sodium storage properties are urgently needed.

Germanium has been extensively investigated as a typical alloy-type anode material for LiBs owing to its high lithium storage capacity and high lithium diffusivity.[15–17] Among various types of Na-storage anode materials,[18–20] previous computational studies suggest that germanium is a promising anode material for NiBs due to a strong thermodynamic driving force and moderate volume expansion upon sodiation.[21–23] According to the calculations by Chevrier and Ceder, sodium can alloy with germanium to form NaGe, giving a theoretical capacity of 369 mAh g–1.[24] However, it has been demonstrated by experimental study that sodium insertion into crystalline Ge is negligible.[25] The major obstacle lies with a high diffusion barrier for sodium ions in Ge lattices.[26] The larger ionic radius of Na+ (0.98 Å) as compared to Li+ (0.69 Å) results in a much higher activation energy for migration between interstitial sites in the lattice of the host materials (0.51 eV for lithium vs 1.5 eV for sodium).[27–30] Nonetheless, Baggetto et al. obtained reversible storage of Na in amorphous Ge thin film with a reversible capacity close to 350 mAh g–1.[30] Kohandehghan et al. experimentally demonstrated that the inactive nature of crystalline Ge can be altered by a single lithiation-delithiation cycle, which induces amorphization in crystalline Ge and hence lower barrier for nucleation of the NaGe phase.[31] The expected volume expansion that would occur in going from amorphous Ge to NaGe is about 225%.[34] While in situ TEM experiments of

[a] Dr. H. Wu,[a] W. Liu,[a] L. Zheng, D. Zhu, Dr. L. Su, Prof. L. Wang
State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology
College of Chemical Engineering
Zhejiang University of Technology
Hangzhou 310014, P. R. China
E-mail: wanglb99@zjut.edu.cn

[b] Dr. N. Du
State Key Lab of Silicon Materials
School of Materials Science and Engineering
Zhejiang University
Hangzhou 310027, P. R. China
E-mail: dna1122@zju.edu.cn

[c] Dr. C. Xiao
BTR new energy materials inc.
Shenzhen, P. R. China

[{*}] These authors contributed equally to this work

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amorphous Ge nanowires conducted by Lu et al. confirmed a 300% volume expansion upon sodiation, corresponding approximately to a final sodiated phase of Na$_x$Ge$^{[33]}$. It is well established in the literature that nanostructured electrodes is an effective strategy to avoid mechanical failure and pulverization arising from the swelling.$^{[34–36]}$ Therefore, it is desirable to utilize elaborately designed structure to improve the sodium storage performance of amorphous Ge.

In this work, Ni NPs are introduced to support amorphous Ge that is synthesized by electrodeposition and RF sputtering, respectively. The electrodes exhibit enhanced cycling stability and rate capabilities as anodes for NaIBs, which can be attributed to the rationally designed architecture. The configuration includes pyramid-like Ni arrays on Cu substrate as current collector and structural support, while the amorphous Ge coating layer functions as the active material. The space between each pyramid allows germanium to expand freely upon sodiation without cracking. Moreover, shortened sodium diffusion distance and firm bonding between Ge and Ni are beneficial for the charge transfer in the electrodes. In addition, sodium storage behavior of crystalline Ge with porous structure is investigated.

2. Experimental Section

2.1 Synthesis of Ni Nanopyramid Arrays

The Ni NPs was synthesized by a modified cathodic electrodeposition method as reported elsewhere.$^{[19]}$ In a typical procedure, the electrolytic bath consisted of NiCl$_2$·6H$_2$O 1 mol L$^{-1}$, H$_3$BO$_3$ 0.5 mol L$^{-1}$ and ethylenediamine dihydrochloride 1.8 mol L$^{-1}$. A Ni foil was used as the anodic electrode while a copper foil was employed as the cathodic electrode for Ni NPs deposition. The electrodeposition of Ni was carried out under galvanostatic conditions ($i = -20$ mA cm$^{-2}$) at 60 °C with deposition time of 5 min.

2.2 Synthesis of Ni–Ge Nanopyramid Arrays

Germanium layer was deposited onto the Ni substrate via a radio frequency (RF) sputtering system using a Ge target with high purity of 99.99%. Sputtering was performed at a pressure of 3 Pa with an operating power of 70 W for 20 min.

2.3 Synthesis of Porous Ge Particles

Commercially available Mg$_2$Ge powder was used as Ge precursor, which was heated in a tube furnace at 700 °C for 3 h under air. After cooling down to room temperature, the resulting powder was immersed in 1 M HCl solution for 1 h to remove MgO, followed by washing with deionized water and vacuum-dried at 80 °C for 10 h.

2.4 Characterization

The morphology of the obtained samples was characterized by a field emission scanning electron microscope (FESEM HITACH S4800) equipped with an energy-dispersive X-ray spectrometer (EDX) and a transmission electron microscope (TEM, FEI F20). X-ray diffraction (XRD) patterns were collected using a Rigaku D/max-ga X-ray diffractometer with Cu Kα radiation. Raman spectrum was carried out on an HR800 Raman Spectrometer using an Ar ion laser at 514 nm.

2.5 Electrochemical Measurements

Electrochemical measurements were carried out using coin type cells (CR2025) which were assembled in an argon-filled glove box (Mbraun, labstar, Germany) by directly using the as-synthesized porous Ni–Ge NPs as the working electrode, a sodium metal foil as the counter electrode and glass fiber (Whatman GF/D) as the separator. The electrolyte was 1 M NaPF$_6$ dissolved in ethylene carbonate/diethyl carbonate (EC:DEC = 1:1, v/v) with a 5% vol. fluoroethylene carbonate (FEC) additive. For the porous Ge particles, electrode slurry was made by mixing 75 wt% active material, 15 wt% acetylene black and 10 wt% polyacrylic acid (PAA) binder in a water/ethanol mixture (1:1 in volume) with magnetic stirring for 2 h, which was subsequently cast onto Ni foam, followed by drying at 100 °C under vacuum overnight. The loading of active materials for Ni–Ge NPs and porous Ge electrodes is typically 0.1 and 1.1 mg cm$^{-2}$, respectively. A galvanostatic cycling test of the assembled cells was performed on a Land CT2001 A system at various discharge/charge current densities. The electrochemical impedance spectroscopy (EIS) measurements were recorded on a CHI760D electrochemical workstation over the frequency range from 0.01 Hz to 1 MHz with the amplitude of 5 mV.

3. Results and Discussion

Figure 1 depicts the schematic illustration of the synthetic process for Ni–Ge NPs. Firstly, the growth of Ni NPs on copper foil was conducted via a template-free electrodeposition method. Secondly, the as-prepared Ni NPs were coated with an amorphous Ge layer by RF magnetron sputtering to obtain Ni–Ge NPs.

Figure 2a displays a representative SEM image of the Ni NPs. After electrodeposition, the copper substrate is covered with nickel nanopyramids with sharp tips, distinct ridges and
polygonal bases. Rough surfaces of the nanopyramids can also be identified from the image despite varying sizes of the pyramids. The inset shows an individual nanopyramid with triangular sloping sides. With the nanostructured substrate established, germanium was sputtered onto the current collector afterwards. Figure 2b and c show SEM images of the Ni–Ge NPAs at high and low magnifications, respectively. The sharp peaks are transformed into round tips while the pyramid-like configuration remains as shown in top and cross-sectional views (Figure 2d), indicating that a conformal germanium layer has been successfully deposited on the Ni scaffold.

To verify the existence of Ni and Ge, EDX was carried out before and after sputtering (Figure 3a and b, respectively). After electrodeposition, the absolutely dominant signals of Ni and Cu confirm composition of the metallic substrate, while the appearance of Ge peaks in Figure 3b implies the germanium coating on the current collector. The insignificant amount of oxygen suggests that slight surface oxidation might occur during sample transportation. Figure 3c shows the XRD pattern...
of the Ni–Ge NPAs, in which only peaks from Cu and Ni can be detected. This implies the amorphous nature of the Ge layer, which is in accordance with the Raman spectrum (Figure 3d). The peak at about 280 cm\(^{-1}\) is associated with amorphous Ge and metallic Ni and Cu have no Raman features.

The sodium storage properties of the Ni–Ge NPAs were investigated in half cells without adding other binders or conductive additives. Figure 4a shows voltage profiles of the nanostructured electrodes, which demonstrate a consecutive slope starting from \(~1.5\) V for the first Na insertion process until a plateau is reached at 0.1 V. The slope along with the small plateau at 0.8 V is mainly contributed by formation of a solid electrolyte interphase (SEI) layer and side reactions with surface oxides, while the other distinct plateau at lower voltage is typical for the NaGe alloying process.\(^{[38,39]}\) During charge, the plateau appeared at around 0.7 V can be ascribed to the phase transition between NaGe and amorphous germanium.\(^{[40]}\) The slight changes in the shape of the sodiation/desodiation curves between the 10th and 20th cycles indicate excellent cycling stability and reversibility of the reaction. Figure 4b shows average reversible capacities of 201 and 103 mA\(\text{h}\)g\(^{-1}\) for every 11 cycles at current densities as high as 0.8 and 1.6 A\(\text{g}\)\(^{-1}\), respectively. When the current density returns back to 0.2 A\(\text{g}\)\(^{-1}\), 92\% of the average capacity for the initial 11 cycles (333 mA\(\text{h}\)g\(^{-1}\)) is restored. By contrast, the planar Ge electrode that is amorphous in nature as well exhibits markedly different rate capabilities. The planar Ge electrode manifests a reversible capacity lower than 60 mA\(\text{h}\)g\(^{-1}\) at 0.2 A\(\text{g}\)\(^{-1}\) and hardly any sodiation under the higher current density of 1.6 A\(\text{g}\)\(^{-1}\).

The improved electrochemical performance can be attributed to the rationally designed Ni–Ge configuration where the nickel matrix serves as both structural support and electron collection/transport medium. The space between each pyramid effectively accommodates the enormous volume swelling and alleviates the concomitant stresses resulted from repeated Na alloying/dealloying with Ge. Furthermore, the rough surfaces of the Ni NPAs provide better interface adhesion between the coating layer and the substrate so that they maintain contact during volume changes thereby increasing the cycling stability. To gain insight into the reaction kinetics in the electrodes, EIS tests were performed on the Ni–Ge NPAs and planar Ge electrodes. As shown in Figure 4d, the Nyquist plots show two distinct
associated with the Warburg impedance ($Z_w$) for the Ni NPAs electrodes. The inclined line in the low frequency region is responsible for the enhanced rate capabilities as summarized above.

Inspired by the idea that nanoscaling is of advantage for the kinetics of Na$^+$ insertion and extraction, the sodium storage properties of crystalline germanium with nanostructure is investigated. Figure 5a shows the solid structure of the pristine Mg$_2$Ge particles. After annealing in air and subsequent acid pickling process, the bulk Mg$_2$Ge precursor transforms into porous Ge particles, which are shown in Figure 5b. The presence of numerous pores is due to selective removal of MgO that is generated during the oxidation of Mg$_2$Ge. Although the size of porous Ge particles is around several micrometers, the wall thickness of the porous structure is approximately 100–250 nm. Furthermore, the substantial amount of interconnected void (Figure 5c) enables electrolyte to permeate through the particles, hence a decreased sodium diffusion distance. The crystalline characteristic of the porous Ge particles is verified by XRD pattern as shown in Figure 5d. The sodiation behavior of crystalline Ge is investigated using coin-type half-cells. The typical electrochemical response of porous crystalline Ge electrodes is presented in Figure 5e. During the first cycle, the discharge curve comprises a plateau at 1.0 V and a following slope. The initial discharge capacity of 252 mAh g$^{-1}$ is mainly contributed by formation of an SEI layer, reduction of native surface oxides and partial sodiation of germanium. During the first charge process, the potential increases almost linearly from 0.2 V to reach a reversible capacity of 97 mAh g$^{-1}$. Unlike amorphous Ge, crystalline Ge electrodes exhibit no distinct plateaus at 0.1 and 0.7 V during discharge and charge processes, rendering limited sodiation and desodiation capacities of ~100 mAh g$^{-1}$ for the 2nd and 5th cycles. Nonetheless, the value is still higher than those of crystalline bulk germanium and silicon electrodes (ca. 20 mAh g$^{-1}$), which are unable to sodiate at ambient temperature.$^{[19,25]}$ This implies that nanostructure of electrodes can boost its sodium storage properties, despite the incompetence of altering the inactive nature of the anode materials. Extended cycling performance of the porous Ge electrodes is shown in Figure 5f. The reversible capacity maintains at ~80 mAh g$^{-1}$ after 20 extended cycles. Reasonable cycling stability probably benefits from the interconnected porous structure that averts pulverization at early cycling stage.

4. Conclusion

In summary, amorphous Ge anode material coated on the Ni NPAs for rechargeable sodium-ion batteries embraces an improved electrochemical performance compared with the planar Ge electrodes. In this configuration, the nickel matrix serves as both structural support and electron collection/transport medium, while the space between each pyramid effectively accommodates the stresses induced by Na alloying/dealloying with Ge. The rough surfaces of the Ni NPAs and shortened sodium diffusion distance are believed to be responsible for the enhanced rate capabilities. Furthermore, limited improvements in sodium storage properties of crystal-
line Ge electrodes have been achieved by using porous Ge particles, despite the inability of nanostructure to alter the inactive nature of the anode materials. Nevertheless, the architecture of the Ni–Ge NPs provides a promising way to fabricate the optimized anodes, which can be potentially used in high-performance NiBs.

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**Conflict of Interest**

The authors declare no conflict of interest.

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