Amorphous mesoporous GeO$_x$ anode for Na-ion batteries with high capacity and long lifespan

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It is recently demonstrated that amorphous Ge anode shows higher reversible Na-ion storage capacity (590 mA h g$^{-1}$) than crystallized Ge anode (369 mA h g$^{-1}$). Here, amorphous GeO$_x$ anode is prepared by a simple wet-chemistry reduction route at room temperature. The obtained amorphous GeO$_x$ shows a porous hierarchical architecture, accompanied with a Brunauer–Emmett–Teller surface area of 159 m$^2$ g$^{-1}$ and an average pore diameter of 14 nm. This unique structure enables the GeO$_x$ anode to enhance the Na-ion/electron diffusion rate, and buffer the volume change. As anode for Na-ion battery, high reversible capacity over 400 mA h g$^{-1}$, fine rate capability with a capacity of 200 mA h g$^{-1}$ maintained at 3.0 A g$^{-1}$ and long-term cycling stability with 270 mA h g$^{-1}$ even over 1000 cycles at 1.0 A g$^{-1}$ are obtained.

1. Introduction

Rechargeable sodium-ion batteries (NIBs) are regarded as intriguing energy storage systems, which have attracted increasing attention due to the natural abundance of metal sodium [1–3]. To date, the main research interests concerning NIBs are focused on fabricating various cathode/anode electrode materials which play a decisive role in the electrochemical performance such as specific capacity and cycling stability [4–8]. However, most electrode materials that have been developed for Li-ion batteries (LIBs) are generally unable to work for NIBs, because the size of Na$^+$ ion (1.02 Å in radius) is larger than that of Li$^+$ ion (0.59 Å in radius) [9,10]. With regard to the anode materials, the graphite anode in LIBs shows poor Na-ion storage performance owing to the graphitic lattice mismatching [11]. It is, therefore, highly desirable to explore suitable anode materials for facilitating the development of NIBs [12,13].
In analogy with LIBs, various alloy-type materials such as Si, Ge, Sn, Pb and Sb have been proposed as anodes for NIBs [14–21]. These anode materials can alloy with sodium at room temperature, exhibiting high reversible capacity. As for Ge anode materials, Chevrier & Ceder [1] calculated that germanium (Ge) could alloy with Na at room temperature to form NaGe, and the corresponding theoretical capacity is 369 mAh g\(^{-1}\). Then, several experimental results were reported [22,23]. For example, thin Ge film deposition on roughened Cu foils, prepared by DC magnetron sputtering, exhibited a reversible capacity of 350 mAh g\(^{-1}\) at C/20 (approx. 20 mA g\(^{-1}\)), accompanied with Na alloy/dealloy reaction potentials at around 0.15/0.6 V [22].

Recently, Kohandehghan et al. [24] demonstrated that amorphization of Ge thin film anode by a prior lithiation–delithiation cycle would lead to a dramatic improvement for Na-ion storage performance such as high specific capacity, good rate capability and long-life cycling stability. It is reported that amorphization of Ge anode is able to lower the barrier for nucleation of the Na\(_{x}\) phase(s) and accelerate solid-state ionic diffusion. Accordingly, the activated amorphous Ge thin film delivered a reversible capacity of 418 mAh g\(^{-1}\) at 0.15C (1C = 369 mAh g\(^{-1}\)) after 50 cycles. Subsequently, Korgel et al. reported that amorphous Ge nanowires can provide a reversible capacity as high as 590 mAh g\(^{-1}\) by forming a sodiated phase of Na\(_{1.6}\)Ge rather than NaGe [25]. The related measurements further suggested that the high defect density of amorphous Ge enables more Na ion to alloy with Ge at room temperature. Meanwhile, in situ transmission electron microscopy (TEM) imaging indicated that germanium nanowires exhibit a 300% expansion in volume upon sodiation, which is bad for the electrochemical performance.

Generally, fabricating oxide anodes such as SiO, SnO\(_x\), and GeO\(_x\) is an effective route to address the volume change issues [26–33]. Typically, amorphous GeO\(_x\) was used as anode for high-performance LIBs, and, recently, explored for NIBs. Kajita et al. [30] prepared amorphous GeO\(_x\) (\(x < 1\)) powder by oxidizing Zintl-phase NaGe with isopropyl alcohol at room temperature, showing an initial reversible capacity 342 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\) and with a capacity retention of 216 mAh g\(^{-1}\) after 40 cycles. The generated Na\(_2\)O can act as a buffering phase to accommodate the volume change during cycling [31,32]. Although GeO\(_x\) shows great potential performance for Na-ion storage, related reports are limited.

In this work, amorphous GeO\(_x\) anode for NIBs was synthesized by a modified wet-chemistry reduction route [34–36] at room temperature that is simple and can be easily scaled up. The obtained amorphous GeO\(_x\) shows a hierarchical mesoporous structure. The Brunauer–Emmett–Teller (BET) surface area is about 159 m\(^2\) g\(^{-1}\), the average pore diameter is about 14.0 nm ranging from 5 to 30 nm, with a pore volume of 0.352 m\(^3\) g\(^{-1}\). When the as-prepared GeO\(_x\) material was used as an anode for rechargeable NIBs, high reversible capacity over 400 mAh g\(^{-1}\), fine rate capability of 200 mAh g\(^{-1}\) maintained even at 3.0 A g\(^{-1}\) and long-term cycling stability with 270 mAh g\(^{-1}\) after 1000 cycles at 1.0 A g\(^{-1}\) were obtained. The good Na-ion storage performance may be attributed to the unique amorphous hierarchical porous structure that could facilitate Na ion and electron diffusion, and buffer the volume change.

### 2. Experimental

The synthesis of amorphous GeO\(_x\) sample was carried out by a wet-chemistry reduction route at room temperature, modifying a procedure reported by Han et al. [26]. In a typical experiment, 1.0 g of GeO\(_2\) was stirred in 100 ml of distilled water and dissolved by NaOH solution (0.1 M) added drop by drop under vigorous magnetic stirring at room temperature. After the dispersion became transparent, which is shown in figure 1a, fresh NaBH\(_4\) (98%, Alfa) solution (2 g in 20 ml of distilled water) was injected into the transparent solution, and the mixture was stirred continuously for 5 h. Finally, the obtained yellow powder which is presented in figure 1b was collected by filtration, washed with distilled water, and dried at 40°C under vacuum. Figure 1c shows a sketch of the main process. As a contrast experiment, crystallized GeO\(_2\)/Ge composite was obtained by annealing the as-synthesized amorphous GeO\(_x\) at 700°C under Ar atmosphere. The details of materials characterization and electrochemical measurements are provided in the electronic supplementary material.

### 3. Results and discussion

Figure 2a shows the X-ray diffraction (XRD) pattern of the obtained final product. Clearly, no diffraction peak can be observed, indicating amorphous structure of the synthesized sample. After annealing this sample at 700°C under Ar atmosphere, well crystallized Ge and GeO\(_2\) composites can be detected, as...
**Figure 1.** (a) The transparent solution after NaOH is added and the present main ingredient GeO\(_3^{2-}\) ions are formed from GeO\(_2\), (b) the obtained yellow powder, GeO\(_x\), was collected after washing and drying, (c) the sketch of the main process.

![Image](image-url)
Na/Na\(^+\)) agrees well with the cyclic voltammetry result (electronic supplementary material, figure S1 inset). The initial discharge and charge capacities of the GeO\(_x\) electrode are 834 and 476 mAh g\(^{-1}\), respectively. The corresponding initial coulombic efficiency is as low as 57\%, that is, a large amount of Na\(^+\) is irreversibly consumed. The large capacity loss is generally caused by the irreversible formation of solid–electrolyte interphase (SEI) film/Na\(_2\)O, and the Na\(^+\) alloying reaction. From second cycle forwards, the charge/discharge voltage plateau is replaced by a group of sloping plots. Noteworthy, the irreversible capacity decreased remarkably, suggesting a stable SEI film was generated.

Figure 4\(b\) shows the cycling performance of the GeO\(_x\) electrode at a current density of 0.05 A g\(^{-1}\). The first reversible capacity is 470 mAh g\(^{-1}\). Owing to the large specific surface area, the GeO\(_x\) electrode needs tens of cycles to form a good SEI layer. After 100 cycles, the GeO\(_x\) electrode maintains a specific capacity of 350 mAh g\(^{-1}\) that is 74\% of the first capacity. As a contrast, the crystallized Ge/GeO\(_2\) electrode exhibits low Na-ion storage performance, delivering an initial reversible capacity of 65 mAh g\(^{-1}\) at 0.05A g\(^{-1}\), accompanied with an initial coulombic efficiency of 24\% (electronic supplementary material, figure S4 inset). The Na-storage capacity of Super-P carbon black of about 120 mAh g\(^{-1}\) is noted (electronic supplementary material, figure S6 inset). It is reasonable to conclude that the amorphous phase Ge could enhance the Na-alloying reaction during discharge/charge cycling.

The rate capability of the as-prepared amorphous GeO\(_x\) electrode is evaluated with the current density ranging from 0.05 to 3.0 A g\(^{-1}\). Figure 4\(c,d\) exhibits the galvanostatic charge/discharge voltage profiles for the last cycle and cycling properties at different current densities, respectively. The GeO\(_x\) delivered a reversible capacity of 382, 350, 333, 324, 278, 245 and 202 mAh g\(^{-1}\) at a current density of 0.4, 0.6, 0.8, 1.0, 1.5, 2.0 and 3.0 A g\(^{-1}\), respectively. As one can see, the GeO\(_x\) electrode still delivers a reversible capacity of 200 mAh g\(^{-1}\) even at high current density of 3.0 A g\(^{-1}\). After high-rate cycling, a reversible capacity of 380 mAh g\(^{-1}\) is recovered as the current density returned back to 0.05 A g\(^{-1}\). It should be pointed out that the overpotential during discharge/charge becomes more and more apparent as the current densities increased.

Figure 4\(e\) displays the long-term cycling stability at a current density of 1.0 A g\(^{-1}\). Note that the initial two cycles of the coin cell are tested at a low current density of 0.2 A g\(^{-1}\) in order to activate the electrode.
sufficiently. At the current density of $1.0 \, \text{A g}^{-1}$, the GeO$_x$ shows a specific capacity of $300 \, \text{mAh g}^{-1}$. From 100th cycle forward, no remarkable capacity fading is observed. After 1000 cycles, the obtained reversible capacity is maintained as high as $270 \, \text{mAh g}^{-1}$, indicating fine long-term cycling stability.

Electrochemical impedance spectroscopy measurements were conducted to further investigate the electrochemical performance. Figure 5 shows the experimental Nyquist plots of the amorphous GeO$_x$ and GeO$_2$/Ge electrodes before cycling. All of the Nyquist plots consist of a semicircle in the high frequency region, and a straight line in the low frequency region. The diameter of the semicircle is ascribed to the charge transfer resistance on the interface of the electrolyte and active material, while the linear region corresponds to the lithium ion diffusion in the electrodes. As one can see, the amorphous GeO$_x$ electrode exhibits lower charge transfer impedance than the crystalline Ge/GeO$_2$ electrode, because the highly porous surface structure of the amorphous GeO$_x$ facilitates ion/electron diffusion.
Figure 4. The Na-ion storage performance of the GeOₓ electrode. (a) The discharge/charge voltage profiles, and (b) cycling performance at 0.05 A g⁻¹. (c) The discharge/charge voltage profiles, and (d) cycling performance at current density ranging from 0.05 to 3.0 A g⁻¹. (e) The long-term cycling properties at 1.0 A g⁻¹.

Figure 5. The Nyquist plots of amorphous GeOₓ and GeO₂/Ge electrodes.

Above all, the superior electrochemical performance such as high reversible capacity, fine rate capability and long-term cycling life of the as-synthesized GeOₓ is closely related to synergistic effects of the amorphous hierarchical structure. First, the amorphous phase makes the electrochemical sodiation/desodiation of GeOₓ electrode to occur easily, which could store more Na⁺ than that of
crystallized Ge anode, providing high specific capacity [25]. Second, the porous structure and high surface area can provide fast ionic/electronic transport path and enhance the electrochemical reactivity [29]. Third, the hierarchical porous architecture can not only afford high opening void space, but also combine the advantageous properties of microscale and mesoscale structure, which enables the anode to release the strain stress and accommodate the volume change. Therefore, the particle integrity and electrical contact of active materials in the electrode could be well preserved during repeated Na-alloy/dealloy reaction. What is more, the generated inactive Na2O during initial discharge process could also act as a buffering phase to address the volume expansion [32].

4. Conclusion

In summary, amorphous GeOx anode material for NIBs was fabricated by a modified room-temperature wet-chemical approach. The obtained amorphous GeOx exhibits a porous hierarchical structure composed of interconnected nanoparticles. The BET surface area and the average pore diameter were 159 m² g⁻¹ and 14 nm, respectively. The amorphous GeOx shows high electrochemical sodiation reactivity, and the porous hierarchical structure is beneficial for buffering the volume change and the ionic/electronic conductivity during discharge/charge process. As a result, a high reversible capacity over 400 mAh g⁻¹, good rate capability with 200 mAh g⁻¹ at 3.0 A g⁻¹ and long-term cycling life over 1000 cycles are obtained. This work paves a novel route for exploring high-performance anode materials for rechargeable NIBs.

Data accessibility. We include all the experimental data in the electronic supplementary material.

Authors’ contributions. N.L. and Y.Q. conceived the idea and designed the experiments. K.S., N.L., T.X. and Y.H. contributed towards fabrication and characterization of materials. K.S. and N.L. analysed data and wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests. We declare we have no competing interests.

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