A Robust Approach for Efficient Sodium Storage of GeS₂ Hybrid Anode by Electrochemically Driven Amorphization

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Sodium ion batteries (NIBs) have become attractive promising alternatives to lithium ion batteries in a broad field of future energy storage applications. The development of high-performance anode materials has become an essential factor and a great challenge toward satisfying the requirements for NIBs, advancement. This work is the first report on GeS₂ nanocomposites uniformly distributed on reduced graphene oxide (rGO) as promising anode materials for NIBs prepared via a facile hydrothermal synthesis and a unique carbon-thermal annealing. The results show that the GeS₂/rGO hybrid anode yields a high reversible specific capacity of 805 mA h g⁻¹ beyond the theoretical capacity, an excellent rate capability of 616 mA h g⁻¹ at 5 A g⁻¹, and a cycle retention of 89.4% after 100 cycles. A combined ex situ characterization study reveals that the electrochemically driven amorphization plays a key role in achieving efficient sodium storage by accommodating excess sodium ions in the electrode materials. Understanding the sequential conversion-alloying reaction mechanism for GeS₂/rGO hybrid anodes provides a new approach for developing high-performance energy storage applications.

Rechargeable lithium-ion batteries (LIBs) have become widely attractive as effective devices for storing electric energy for applications in smart phones, tablet PCs, laptop computers, etc., in recent decades. Currently, rechargeable batteries, which offer high energy densities, occupy a prominent position in the present energy industries and have broadened their scope to include large energy applications such as electric vehicles and energy storage systems, which require a low cost, long-term stability, and high specific energy density.[1] In view of the requirements, sodium-ion batteries (NIBs) hold considerable attraction in the field of large energy storage systems because of the need to go beyond the limits of LIBs. Because the demand for high-energy rechargeable batteries has continuously grown, advanced NIBs have been revisited because of the natural abundance of sodium and price advantages than lithium resources.[2] However, several challenging points still exist to replace current Li systems with Na-based rechargeable batteries. Although both lithium and sodium are alkali metal and have similar physicochemical properties, NIBs are expected to have lower energy densities than LIBs due to the high atomic weight and redox potential (E°(Na/Na⁺) ≈ 2.71 V versus a standard hydrogen electrode; 0.3 V positive of lithium). Additionally, metallic sodium is too dangerous to be utilized as a negative electrode for practical batteries because of its high reactivity with water.[3] Therefore, selecting suitable anode materials for sodium-ion batteries is one of the most important key issues.

There are numerous candidates as anode materials for NIBs to meet the requirements for large-scale energy storage systems. Transition metals that undergo alloying reactions (e.g., Sn, Sb, P, Se, and Ge) have attracted much interest due to their intrinsic high theoretical capacity due to their various oxidation states.[4] Tin (Sn) is one of the most promising anode material for NIBs, delivering the high theoretical capacity of 872 mA h g⁻¹. Wang et al. investigated the phase transformation on sodiated Sn nanoparticles using in situ transmission electron microscopy and proposed a two-step sodiation mechanism.[4b] The microstructural change from the Na,Sn (x =0.5) to its final Na₁₅Sn₄ corresponded to a 60% and 420% volumetric expansion in accordance with the sodiation process. Phosphorus (P) is another attractive anode material, demonstrating a high theoretical specific capacity of 2596 mA h g⁻¹ corresponding to the final phase Na₆P. The operating voltage in NIBs appears in the range of 0.5–0.0 V, which guarantees a high energy density as well as a high reversible capacity. Despite the promising possibility as an anode material for NIBs, there are still problems to be solved such as the sluggish reaction kinetics (p < 1 × 10⁻¹⁴ S cm⁻¹), fatal capacity fading, and large irreversible capacity upon full sodiation to the Na₆P phase.[5] Germanium has been extensively studied as a negative electrode material for LIBs because of its high lithium diffusivity and high lithium storage capacity until the electrode crystallizes into Li₁₅Ge₄ (1384 mA h g⁻¹).[6] Although the dissimilarity between Li/Na ions has led to several orders of magnitude slower sodium diffusion than lithium diffusion in germanium, this value is sufficiently high enough to overcome other transition metal.[7] Recent research on the amorphous phase of germanium provided opportunities in the development of high energy density anode for NIBs. Abel et al. synthesized nanocolumnar germanium thin films by evaporative deposition, delivering a high discharge capacity (403 mA h g⁻¹ = the amorphous Na₃.₅Ge) over the theoretical value (369 mA h g⁻¹ = the fully sodiated NaGe phase).[8] The resultant amorphous
phase Na\textsubscript{1.17}Ge is not present in the phase diagram, but there are the equilibrium phases of Na\textsubscript{3}Ge and NaGe. In the same strategy, Lu allowed the c-Ge nanowires to be amorphized by preliminary lithiation, which would increase sodium storage and reversibility in later sodiation. The observation of the microstructure suggested that the final sodiated phase of crystalline Ge more closely corresponds to Na\textsubscript{1.6}Ge than to the more commonly known NaGe.[9]

Here, we have introduced a method to solve a fundamental drawback of Ge anodes for NIBs, namely, the low theoretical capacity. Transition metal chalcogenides undergoing sequential conversion and alloying reactions demonstrate a low operating voltage and high theoretical capacity due to their various oxidation states. Multielectron reactions in NIBs provide the opportunity to transfer more than one electron per mole of active materials, improving the high energy density.[10] Germanium sulfide (GeS\textsubscript{2}) as a promising anode material, delivers the high theoretical capacity of 980 mA h g\textsuperscript{-1} when a 1/2 mole of Ge/S can accommodate 1/4 moles of Na\textsuperscript{+} ions (total 5 moles), respectively, have been successfully synthesized via a facile hydrothermal method and subsequent carbo-thermal reduction. Furthermore, the crystallinity of Ge is gradually decreased during the sequential conversion-alloying reactions accompanied by the phase transition and finally it can be expected to change to the amorphous phase. The final sodiated phase of crystalline Ge appears to be amorphous Na\textsubscript{x}Ge (x 1.60), delivering a higher theoretical capacity beyond the previously reported NaGe. To the best of our knowledge, this is the first report on GeS\textsubscript{2} with carbo-thermally reduced graphene oxide (rGO) nanocomposites as anode for NIBs, and it makes the best use of the intrinsic merits for the amorphization to efficiently enhance the high theoretical capacity and fast sodium diffusion kinetics. Newly designed GeS\textsubscript{2}/rGO anode materials for high energy density NIBs will lead to opportunities and pave a new path in the development of large scale stationary energy storage systems.

Germanium sulfide/graphene oxide composites were first prepared by a facile hydrothermal synthesis. The subsequent carbo-thermal annealing ensures sufficient crystallinity and the removal of organic residues in the as-synthesized composites. The sharp diffraction patterns of the germanium sulfide/reduced graphene oxide nanocomposite after post heat treatment for 1 h in the X-ray diffraction (XRD) patterns can be well indexed to the monoclinic GeS\textsubscript{2} with a space group of P2\textsubscript{1}/c (JCPDS#71-0366) and its inset in Figure 1.[11] As the heat treatment progressed, the Ge\textsubscript{S}\textsubscript{2} particles were further reduced to orthorhombic GeS (JCPDS#71-0306) due to the effect of carbo-thermal reduction, and their crystal structures were schematized in the inset. While GeS has a layered structure with weak interlayer interactions similar to black phosphorus and prevents the clustering process of the intercalated alkali metal atoms, the theoretical capacity for sodium storage is only 512 mA h g\textsuperscript{-1} because of the limited intercalation site (Na\textsubscript{x}Ge\textsubscript{2}; 0 x < 2), and it is not suitable for high energy density NIBs.[12] The highly crystalline GeS can be amorphized during sodiation, but we focused on the theoretical capacity of GeS\textsubscript{2}, which has a high theoretical capacity of 1097 mA h g\textsuperscript{-1} (Na\textsubscript{x}Ge\textsubscript{3}; 0 x < 5.6), in order to solve the inferior energy density of the Ge-based anode materials.[13]

The microstructure and morphology of the GeS\textsubscript{2}/rGO nanocomposites were observed using typical scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) as shown in Figure 2. The GeS\textsubscript{2} nanoparticles homogeneously spread throughout the graphene oxide sheet as shown in the SEM image (Figure 2a), and they are more distinguishable as dark areas in the transmission electron microscopy (TEM) image (Figure 2b). The right bottom in Figure 2b describes the selected area electron diffraction (SAED) patterns with manifold spots, implying a polycrystalline environment. The frequency of the spots is computed as a function of the radial distance from the center of the diffraction pattern and charted in the right top of Figure 2b as the minor axis and major axis, respectively. In the case of the minor axis, the number of spots ranges from 0 to 160 nm and tends to congregate at ≈70 nm. For the major axis, the frequency mostly appears at ≈150 nm but shows a relatively uniform distribution compared
to the minor axis, ranging from 0 to 320 nm. The lattice fringes of the GeS$_2$ nanoparticles are observed in the HRTEM image with a distance of 0.569 nm, which corresponds to the (002) crystal plane (Figure 2d), and this arrangement of the lattice is converted into the fast Fourier transform (FFT) pattern as demonstrated in the inset. Figure 2e illustrates an STEM image of the GeS$_2$/rGO nanocomposite and the distribution of the Ge, C, and S elements obtained by energy dispersive spectrometer (EDS) mapping. Ge and S exhibit the same distribution designating the GeS$_2$ nanoparticles, and C appears at different sites, which is ascribed to an overlap of the graphene oxide and the lacy carbon grid. To quantify the amounts of rGO in the GeS$_2$/rGO nanocomposites, thermo-gravimetric analysis (TGA) was carried out in air from 25 to 900 °C at the heating rate of 10 °C min$^{-1}$. The weight change of rGO in the GeS$_2$/rGO nanocomposites is estimated to be 30.3% as shown in Figure S1 in the Supporting Information.

The cyclic voltammetry (CV) curves of GeS$_2$/rGO nanocomposites were investigated to confirm the operating potential for the sequential conversion-alloying reactions. The first three CV profiles of the electrode recorded in the potential range of 0.01–2.50 V at the scan rate of 0.02 mV s$^{-1}$ are shown in Figure 3a. The electrochemical reactions of the transition metal sulfide generally have been known in the combination of the conversion reaction and sequential alloying reaction. Similarly, the conversion reaction between GeS$_2$ and Na$^+$ ion is suggested to produce Ge and Na$_2$S, and the subsequent reaction is known as the alloying process transforming metallic Ge to NaGe according to previous literature based on density functional theory simulation.$^{[4a,14]}$ The cathodic peak located at 1.16 V in the 1st sodiation process is generally known to originate from the formation of the solid electrolyte interphase layer, relating with the decomposition of the organic electrolyte and irreversible reactions. The anodic peak of 1.85 V is only shown at the 1st sodiation process.
cycle and broadens in the later cycles. In the subsequent potential sweep, three cathodic peaks are observed at 1.58, 0.52, and 0.05 V, and two anodic peaks are observed at 0.08 and 1.57 V. The GeS$_2$/rGO nanocomposites with different binder systems (carboxymethyl cellulose (CMC) and polyacrylic acid (PAA)) were demonstrated at a constant rate of 100 mA g$^{-1}$ for 100 cycles to examine the long-term cycle stability as shown in Figure 3b. The discharge capacities of both electrodes are 1221 and 1205 mA h g$^{-1}$ with no significant difference. However, in the second and third cycles, the electrode prepared using the CMC binder shows better reversible capacities of 952 and 805 mA h g$^{-1}$ than that of 577 and 520 mA h g$^{-1}$ shown in the PAA binder-based electrode, respectively. The discharge/charge capacity of the CMC binder-based electrode at the 100th cycle is almost 720 mA h g$^{-1}$ with a very high Coulombic efficiency of 99.5% corresponding to a capacity retention of 89.4%. Notably, abundant group-IV transition metals (Si, Ge, and Sn) have been extensively studied with binder systems that exhibit optimal electrochemical performance. Buqa et al. first reported the cycle stability of a nano-Si anode containing a 1% CMC binder as having identical performance to the same anode using 10% of the conventional polyvinylidene fluoride binder.$^{[15]}$ There has been a number of studies on the elastomeric properties of the CMC binder as a way to prevent major problems in Si-based materials due to the large volume expansion of 270%. The formation of a strong covalent bonding (–COOH) and/or the hydrogen bonding (–OH) between germanium sulfides and the carboxyl functional binder (CMC) in water solvent system can be proposed to be the reason for the electrochemical improvement. Interestingly, Komaba et al. examined the redox reaction of Sn-polyacrylate electrodes in an aprotic Na cell with PAA binder and confirmed using ex situ XRD that Sn was transformed into the crystalline Na$_{15}$Sn$_4$ phase after the full discharge process.$^{[16]}$ It is thought that there is a suitable binder system for each transition metal and optimization is needed for sodium full cells in the future.$^{[17]}$ The electrochemical performances of reduced graphene oxide in the GeS$_2$/rGO are presented in Figure S2 in the Supporting Information. The reversible capacity of

Figure 3. Sodium ion storage behaviors of GeS$_2$/rGO nanocomposite electrodes. a) Cyclic voltammetry curves of GeS$_2$/rGO nanocomposite for the initial three cycles between 0.01 and 2.50 V with a scan rate of 0.02 mV s$^{-1}$. b) Cycling performance of GeS$_2$/rGO nanocomposite with different binders at a current density of 100 mA g$^{-1}$. c) Charge/discharge voltage profiles of GeS$_2$/rGO nanocomposite at a rate of 100 mA g$^{-1}$. d) Rate performance of GeS$_2$/rGO nanocomposite with a different binder at different current rates from 50 to 5000 mA g$^{-1}$. 


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rGO, obtained by carbo-thermal annealing at 500 °C for 1 h is 88 mA h g⁻¹ after 200 cycles in the potential range of 0.01–2.5 V at 100 mA g⁻¹. The voltage profiles in Figure 3c demonstrate the excellent electrochemical reversibility with a Coulombic efficiency of 99.5%. Considering the theoretical capacity of GeS₂ (when 1 mole of GeS₂ can accommodate 5 moles of Na⁺) and the mass fraction of graphene oxide, the theoretical capacity of the GeS₂/rGO nanocomposite is expected to be ~700 mA h g⁻¹, but the practical discharge capacity already shows 805 mA h g⁻¹. This is further confirmed to be consistent with the discharge capacity when 1 mole of GeS₂ can accommodate 5.60 moles of Na⁺ and will be discussed in the following paragraph. The reversible capacities are 870, 783, 723, 689, 651, and 616 mA h g⁻¹ at different current densities from 50 to 100, 250, 500, 1000, 2000, and 5000 mA g⁻¹, respectively as shown in Figure 3d. When the current was decreased to 100 mA g⁻¹, it still exhibited a reversible capacity of 722 mA h g⁻¹. This means that the GeS₂/rGO hybrid anode can tolerate high-rate cycling even at 5000 mA g⁻¹ without damaging its structural integrity. The morphology after 100th charge–discharge cycles was observed to confirm the structural stability of the GeS₂/rGO electrodes in Figure S3a,b in the Supporting Information. It is considered that the electrode structure could be homogeneous and rigid owing to the strong bonding of the functional groups by the CMC binder system, and the results are consistent with the electrochemical impedance spectroscopy as shown in Figure 3c.

Figure S4 in the Supporting Information shows the XRD patterns of the GeS₂/rGO electrode discharged at 2.50 V and charged at 0.01 V for the 3rd cycle, respectively. After the 3rd sodiation/desodiation, no obvious peaks except that of Cu foil in both the electrodes were present. This means that the ex situ XRD measurement is limited in its determination of the structural changes in the electrodes.

**Figure 4.** Ex situ characterization of the GeS₂/rGO nanocomposite. a) Raman spectroscopy of the GeS₂/rGO electrodes at open circuit voltage, the 3rd charge at 2.50 V, the heat treatment at 300, 400, and 500 °C after the 3rd charge process. SAED images of the GeS₂/rGO electrodes at b) 500 °C, d) 400 °C, and f) no heat treatment after the 3rd charge at 2.50 V. An HRTEM image of the selected area for the GeS₂/rGO electrodes at c) 500 °C, e) 400 °C, and g) no heat treatment after the 3rd charge at 2.50 V.
of the intermediate products with a lower crystallinity, and nanosized particles such as Na$_2$S$_x$ (1 ≤ x ≤ 8), Na–Ge alloys and GeS$_2$ are irreversibly sodiated and do not return to their original phase. An analogy to the electrochemical reaction can be obtained by identifying the crystallinity of germanium in the GeS$_2$/rGO nanocomposites. The ex situ Raman spectroscopy of the GeS$_2$/rGO electrodes at open circuit voltage in the 3rd charge at 2.50 V and heat treated electrodes at 300, 400, and 500 °C after 3rd charge process was investigated to confirm how the GeS$_2$/rGO electrode is able to overcome its intrinsic electrochemical properties as shown in Figure 4a. An intense peak at 355 cm$^{-1}$ is assigned to the GeS$_2$ nanoparticles, corresponding to the symmetrical stretching vibration of the GeS$_4$ tetrahedra.[18] The peak does not appear in the 3rd charged electrode and its annealed samples because the repeated sodiation/desodiation process leads amorphization and may produce GeS$_2$ nanoparticles with low crystallinity during the 3rd charge at 2.50 V, resulting in the reduction of the scattering centers for in-plane scattering. The annealed electrode at 300 °C after the 3rd charge at 2.50 V exhibited a broad peak centered at 279 cm$^{-1}$, which was attributed to the scattering of local transverse optical phonons of amorphous Ge.[19] For the sample annealed at 500 °C, the intensity of the main peak became even greater and shifted to the right at 295 cm$^{-1}$, suggesting an increase in the Ge crystallinity in the electrode. The ex situ XRD and Raman reveal after three repeated charging cycles that the discharge reaction bears an amorphous phase compared to the pristine GeS$_2$ crystalline nanoparticles. This result is further clarified by the alteration of the morphology through the ex situ TEM analysis. In the case of the 3rd charged electrodes without the annealing, an amorphous or very low crystalline region is observed without the SAED rings, as shown in Figure 4f,g. The candidate materials of the clusters homogeneously distributed on graphene oxide are amorphous Ge (a-Ge) and low crystalline S according to the ex situ XRD results. The initial GeS$_2$ crystal structure collapsed then expanded by either the

Figure 5. Ex situ X-ray absorption near edge structure measurements of the GeS$_2$/rGO nanocomposite. a) Discharge process from 1.50 to 0.01 V. b) Charge process at 1.00 and 2.50 V. Charge/discharge voltage profiles of the GeS$_2$/rGO nanocomposite at a rate of 25 mA g$^{-1}$ c) for the 1st cycle and d) 3rd cycle. e) Photon energy of the electrodes with different potential states at a normalized μ (E) of 1.0.
alloying reaction (Na$_x$Ge, $x \leq 1.60$) or conversion reaction (Na$_2$S) with the sodium ion. For the annealed electrodes at 400 °C, the faint diffraction rings in Figure 4d indicate that the nanoparticles after annealing at 400 °C with the average size of the 10 nm are polycrystalline, representing the (002) planes of crystalline Ge (c-Ge). The c-Ge coincides with cubic germanium (JCPDS#79-0001) with the $d$-spacing obtained from the FFT analysis in the inset of Figure 4e. The crystalline nanoclusters of the c-Ge and other crystalline materials are observed when annealed at 500 °C in Figure 4c, and their FFT patterns are shown as the inset. Although a number of impurities with high crystallinity can also be observed due to the high annealing temperature, it reveals that the complete crystallization of a-Ge is achieved through the SAED pattern in Figure 4b. To further verify the sodiation/desodiation mechanisms of the GeS$_2$/rGO electrodes, the oxidation state of a-Ge is more precisely examined by X-ray absorption near-edge structure (XANES) analysis. Figure 5 shows the ex situ XANES analysis of the GeS$_2$/rGO electrodes from the full sodiated electrode at 0.01 V to the desodiated electrode at 2.50 V. The collected points at the 1st and 3rd cycle are indicated from the corresponding charge/discharge voltage profiles as shown in Figure 5c,d, respectively. GeO$_2$ and Ge metal were used as the Ge$^{4+}$ and Ge$^0$ references, respectively. The XANES spectrum clearly shifted to the left during the discharging to 0.50 V versus Na/Na$^+$ for the 1st cycle (the purple line (4) in Figure 5a), and it overlapped with the spectrum of Ge metal, indicating the oxidation of germanium toward Ge$^0$ in Figure 5a. When the GeS$_2$/rGO electrode was fully discharged at 0.01 V in the 1st cycle (the green line (5) in Figure 5a), a left shift of the line (4) indicated the occurrence of an alloying reaction of the Ge metal into the Na–Ge alloy. In the 3rd cycle (the blue line (8) in Figure 5a), the photon energy shifts to lower than that of the 1st cycle, which means that the oxidation state of Ge was further reduced.$^{[20]}$ Considering the aforementioned shift of photon energy and the high performance of the GeS$_2$/rGO electrode, it can be inferred that the discharge capacity beyond the theoretical capacity of GeS$_2$/rGO nanocomposites originate from the amorphization of Ge derived from the sequential conversion-alloying reaction in the electrode materials. In the voltage profile plotting the specific capacity in terms of sodium participation in Figure 5d, light green indicates the capacity resulting from the alloying reaction of NaGe (369 mA h g$^{-1}$), and the dark green indicates the excess capacity due to a-Ge, which corresponds to the ex situ characterizations in Figure 4. The XANES spectrum is also confirmed to shift back to lower valence states after the charging process.$^{[21]}$ The oxidation state of Ge when fully charged to 2.50 V (the blue line in Figure 5b) is located between Ge$^0$ and Ge$^{4+}$, indicating that a-Ge and low crystalline S cannot return to their pristine phase GeS$_2$. High Na$^+$ diffusion and electron diffusion should be satisfied simultaneously in order to achieve complete recovery of GeS$_2$ to its original state in case of NIBs because Na ion has a larger ionic radius than Li ion.$^{[22]}$

Figure 6 shows the schematic illustration for the sequential conversion-alloying reaction mechanisms of GeS$_2$. Crystalline GeS$_2$ transformed into an amorphous Na$_{1.6}$Ge alloy and low crystalline sodium polysulfides after the discharge process. In the subsequent charging process, the amorphous phase remained homogeneously distributed on the surface of rGO rather than converting reversibly back to the original GeS$_2$ after desodiation. The above features indicate that the mobility of the Na atoms increases because of the short diffusion path in the amorphous Na$_{1.6}$Ge and a lower diffusion barrier for Na ions in the a-Ge lattices than in the c-Ge lattices.

In summary, this report is the first to synthesize a GeS$_2$/rGO nanocomposite via a facile hydrothermal method and a carbonothermal annealing, and the first to examine GeS$_2$/rGO nanocomposite as a promising anode material for high-performance NIBs. The nanocomposite exhibits a high reversible specific capacity of 805 mA h g$^{-1}$ beyond the theoretical capacity, an excellent rate capability (562 mA h g$^{-1}$ at 5 A g$^{-1}$), and good cycle stability with a retention of 89.4%. A combined ex situ characterization study reveals that the changes in the oxidation state of the Ge species during the sodiation/desodiation process offer a special strategy to provide reversible sodium storage and a fast electron pathway. Overall, our results represent a

![Figure 6. Schematic illustration of the proposed electrochemical reaction mechanism of the GeS$_2$/rGO nanocomposites. (atom color code: gray, germanium; yellow, sulfur; blue, sodium).](image-url)
promising direction toward electrochemically driven amorphization and toward understanding the sequential conversion-alloying reactions of the GeS2/rGO nanocomposites for high-performance sodium-ion batteries.

**Experimental Section**

**Preparation of Graphene Oxide:** Graphene oxide (GO) was prepared using a method based on modifying the Hummers method.\(^{(23)}\) In a typical preparation, 2.0 g graphite powder (Bay carbon), 1.0 g K\(_2\)S\(_2\)O\(_8\), 1.0 g P\(_2\)O\(_5\), and 20 mL concentrated H\(_2\)SO\(_4\) were stirred together at 80 °C for 4 h and diluted in 500 mL deionized (DI) water. Then, the preoxidized graphite was washed by centrifuging several times until the pH reached the value of 7. The shiny, dark gray graphite was dried at 25 °C in air overnight. The powder was stirred in chilled 75 mL H\(_2\)SO\(_4\), then 10 g K\(_2\)MnO\(_4\) was slowly added into it over 1.5 h in an ice water bath. The solution was stirred in a water bath at 35 °C for 2 h to form a thick paste, followed by the addition of 160 mL water. Finally, 340 mL water containing 8.3 mL 30% H\(_2\)O\(_2\) was added to it until the solution turned from dark brown to yellow. The solution was filtered, and the filter cake was dispersed in water. After that, 10% HCl 500 mL was added to the solution. Then, a brown supernatant was obtained by repeated centrifugation and washing. The final sheets were dried at 60 °C under vacuum.

**Material Synthesis:** GeCl\(_4\) (2.33 mmol, Aldrich) was vigorously stirred in high purity ethanol (>99.9%, 80 mL) containing as-prepared GO (50 mg) for 30 min. Then, thiocetamide (9.32 mmol, Aldrich) was added into the solution and stirred for 30 min to induce full sulfurization during the hydrothermal synthesis. After that, the mixture was transferred into a Teflon-lined stainless-steel autoclave (100 mL). All mixing processes were conducted in an Ar-gas filled glove box with H\(_2\)O content < 0.3 ppm and O\(_2\) content < 0.1 ppm. The autoclave was maintained at 160 °C for 15 h and subsequently cooled at room temperature. The final product was rinsed by ethanol and DI water three times, respectively, and loaded into a commercial freeze dryer (FreeZone 2.5; Labconco). The sample was maintained in a vacuum of 0.055 mbar for 48 h. Finally, the as-synthesized GeS\(_2\)/rGO nanocomposite was thermally reduced after heat treatment at 500 °C with a flow mixture of C\(_2\)H\(_2\) and N\(_2\) (90:6 sccm) for 1 and 2 h and naturally cooled under only N\(_2\). To prepare the reduced graphene oxide (rGO) without the germanium sulfide nanoparticles, GO was first freeze-dried in the same condition, and then heated at 500 °C for only 1 h under the same process as above.

**Material Characterization:** The X-ray diffraction pattern of the GeS\(_2\)/rGO nanocomposite was confirmed by XRD (D/MAX-RR 12KW, RIGAKU, TOKYO, JAPAN) with a wavelength of \(\lambda = 0.15418\) nm over an angular range of 10° ≤ 2θ ≤ 70° at a step width of 0.01°. The microstructure and morphology of the GeS\(_2\)/rGO nanocomposites were analyzed by SEM (XL30, Philips) at an acceleration voltage of 10 kV and TEM (Tecnai G\(_2\) F30 S-Twin, FEI) operated at 300 kV. The amount of GO was confirmed by using a TGA (TG 209 F3, NETZSCH) in an air atmosphere at a heating rate of 10°C min\(^{-1}\) from 25 to 900 °C. Raman spectroscopy was conducted with an ARAMIS from Horiba Jobin Yvon with an argon ion laser excited at 514 nm. The XANES spectra of Ge were characterized at the 8C (Nano XAFS, 3.0 GeV) beamline at the Pohang Light Source in South Korea. For the ex situ Raman, TEM, and XANES characterizations, the coin cells were disassembled at a designated charge (2.50 V vs Na/Na\(^+\)) and discharge voltages (0.01 V vs Na/Na\(^+\)). The anode electrodes were carefully collected, washed with propylene carbonate (PC) to remove the electrolyte and dried inside an Ar-filled glove box overnight to remove excess solvents.

**Electrochemical Measurements:** Electrochemical tests were carried out using a 2032 coin-type half-cell with Na metal as both the counter and reference electrodes. The electrode slurry was prepared by mixing GeS\(_2\)/rGO nanocomposites:Super P (Timcal):a suitable binder in a weight ratio of 75:17:8 by hand mixing and sonication for 20 min to disperse all the components homogeneously. CMC (Aldrich)/deionized water and PAA (Aldrich)/N-methylpyrrolidone (Aldrich) were used as a binder/solvent pair, respectively. The slurry was pasted on a copper foil by a doctor blade followed by drying in an oven overnight at 80 °C. The batteries were assembled in an Ar-gas filled glove box with H\(_2\)O content < 0.3 ppm and O\(_2\) content < 0.1 ppm. The electrolyte was prepared by dissolving 1 M NaClO\(_4\) (98%, Aldrich) in PC/fluoroethylene carbonate (98.2 wt%) (Panaxetec, South Korea). The glass fiber membranes (GF/D, Whatman) were used as separators. Cyclic voltammetry was performed by a multichannel battery tester (BioLogic VMP3, France) with a cut-off voltage ranging from 0.01 to 2.5 V (vs Na/Na\(^+\)) at a sweep rate of 0.1 mV s\(^{-1}\). The galvanostatic measurements were carried out in the potential range of 0.01 and 2.5 V (vs Na/Na\(^+\)) using a battery cycler (WBCS3000, WonAtech). For the rate capability tests, the charge-discharge rate was varied from 25 to 5000 mA g\(^{-1}\) at 25 °C in a constant-temperature convection oven.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (Grant No. 2017R1A2B2010148). It was also supported by the Climate Change Research Hub of KAIST (Grant No. N11170059). The authors acknowledge technical support from staffs of the 7D-XAFS at PAL in the experiments.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

alloying reaction, amorphization, conversion reaction, germanium sulfides, sodium-ion batteries

Received: December 13, 2017
Revised: January 11, 2018
Published online:


