Ga$_2$Te$_3$-Based Composite Anodes for High-Performance Sodium-Ion Batteries

Vo Pham Hoang Huy, Il Tae Kim * and Jaehyun Hur *

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Abstract: Recently, metal chalcogenides have received considerable attention as prospective anode materials for sodium-ion batteries (SIBs) because of their high theoretical capacities based on their alloying or conversion reactions. Herein, we demonstrate a gallium(III) telluride (Ga$_2$Te$_3$)-based ternary composite (Ga$_2$Te$_3$–TiO$_2$–C) synthesized via a simple high-energy ball mill as a great candidate SIB anode material for the first time. The electrochemical performance, as well as the phase transition mechanism of Ga$_2$Te$_3$ during sodiation/desodiation, is investigated. Furthermore, the effect of C content on the performance of Ga$_2$Te$_3$–TiO$_2$–C is studied using various electrochemical analyses. As a result, Ga$_2$Te$_3$–TiO$_2$–C with an optimum carbon content of 10% (Ga$_2$Te$_3$–TiO$_2$–C(10%)) exhibited a specific capacity of 437 mAh g$^{-1}$ after 300 cycles at 100 mA g$^{-1}$ and a high-rate capability (capacity retention of 96% at 10 A g$^{-1}$ relative to 0.1 A g$^{-1}$). The good electrochemical properties of Ga$_2$Te$_3$–TiO$_2$–C(10%) benefited from the presence of the TiO$_2$–C hybrid buffering matrix, which improved the mechanical integrity and electrical conductivity of the electrode. This research opens a new direction for the improvement of high-performance advanced SIB anodes with a simple synthesis process.

Keywords: Ga$_2$Te$_3$; Ga$_2$Te$_3$–TiO$_2$–C; anodes; Na ion; sodiation/desodiation

1. Introduction

In the last few decades, lithium-ion batteries (LIBs) have been utilized as an effective alternative to unsustainable fossil fuels in energy storage systems such as portable electronic devices and electric vehicles [1–14]. Nevertheless, by virtue of the limited reserves and the high cost of Li, much attention has been drawn to developing alternative secondary batteries to overcome these issues [15]. Sodium-ion batteries (SIBs) are reputed as one of the most viable secondary batteries among many next-generation batteries because of their many similarities to LIBs and the abundance of Na on earth [16–19]. Because of the chemical similarity between Na and Li, the Na storage mechanism of anode materials is similar to that of LIB systems, including intercalation/deintercalation, conversion, and alloying/dealloying reactions. Therefore, considerable attempts have been dedicated to finding suitable anode materials for SIBs. However, the slow reaction kinetics owing to the large ionic radius (1.03 nm for Na$^+$ relative to 0.75 nm for Li$^+$) causes low cycling stability and rate capability or even complete electrochemical inactivity. Thus, the improvement of desirable anode materials for high-performance SIBs is urgently required for expanding their practical application scope. Recently, alloy-based materials have received considerable attention as SIB anode materials owing to their high theoretical capacities (Na–Si: 955 mAh g$^{-1}$, Na–Ge: 368 mAh g$^{-1}$, Na–Sn: 845 mAh g$^{-1}$, Na–Pb: 486 mAh g$^{-1}$) [20]. However, similar to LIBs, the large volume change of these materials significantly restricts the long-term cycling of SIBs.

At present, there are numerous potential anodes studied for SIBs, which can be classified in accordance with the reaction mechanism: intercalation (carbon-based materials) [21–23], conversion (sulfides and oxides) [24–26], and alloying reaction (Sb, Sn,
and P) [27–29]. Among these, chalcogenide materials (particularly S- and Se-based materials) have received significant attention as they undergo sequential alloying and conversion reactions, resulting in high capacities [30–32]. Te, another chalcogen group element, has recently been recognized as an effective substitute for S and Se by virtue of the high theoretical Na storage capacity (420 mAh g⁻¹) based on alloying with two Na ions (Na₂Te) [33]. Furthermore, the high density of Te (6.23 g cm⁻³) results in a high theoretical volumetric capacity of 2621 mAh cm⁻³, which is comparable to that of S (3468 mAh cm⁻³) and Se (3252 mAh cm⁻³). Furthermore, Te has superior electrical conductivity (ca. 1.9 × 10⁻² S cm⁻¹) when compared to other nonmetallic chalcogenides (S (ca. 5.1 × 10⁻¹⁶ S cm⁻¹) and Se (ca. 1.1 × 10⁻¹⁴ S cm⁻¹) [34]. In line with this, although a Ga₂S₃-based composite anode was previously used as the anode for SIB, the rate performance was not satisfactory due to the low electronic conductivity of S [35]. In contrast, Te-based composite electrodes have achieved good rate performance and high capacity retention thanks to the high electronic conductivity of Te, as shown in Table S1 [36–44]. Despite these great characteristics, the study of the Te-based SIB electrode mechanism has so far been rare [39,45–48].

Ga-based materials, such as Ga oxide/sulfide anodes, have a large theoretical capacity (682–1591 mAh g⁻¹), innate self-healing capability, and a high tolerance against volume change [49–52]. Ga-based materials have recently emerged as potential electrode materials because of their unique self-healing properties based on the low melting temperature of Ga (29.9 °C). The intermediate liquid Ga formed during sodiation increases the tolerance of volume expansion of active materials, which significantly contributes to the cycling stability [53]. For instance, a composite including reduced graphene oxide and gallium oxide nanosheets (Ga₂O₃ NS/rGO) by Yang et al. provided a steady capacity of 555 mAh g⁻¹ at 0.1 A g⁻¹ [54], whereas a template-derived Ga₂S₃ nanorod anode could obtain a discharge capacity of 476 mAh g⁻¹ at 0.4 A g⁻¹ [55]. Using in situ microscopy, Wu et al. investigated the self-healing properties of a liquid metal Ga-alloy during the charge/discharge process [56]. Considering the aforementioned advantages of Te and Ga, gallium telluride alloys (i.e., Ga₄Te₁) are expected to be great candidate anode materials for SIBs.

In this work, a Ga₂Te₃-based composite electrode (Ga₂Te₃–TiO₂–C) was successfully synthesized utilizing a simple solid-state high-energy ball milling (HEBM) method and studied as a potential SIB anode material. The feasibility of the Ga₂Te₃–TiO₂–C anode for SIBs was investigated through galvanostatic measurements, differential capacity analysis, and electrochemical impedance spectroscopy (EIS). Furthermore, the reaction mechanism of Ga₂Te₃–TiO₂–C anode during sodiation/desodiation was first investigated via ex situ X-ray diffraction (XRD) analysis. In addition, the best C content (10 wt.%) in the Ga₂Te₃–TiO₂–C composite was derived through various electrochemical tests. The high cycling and rate performances of Ga₂Te₃–TiO₂–C(10%) obtained in this study are superior or equivalent to those of the most recent chalcogenide-based electrodes in SIBs.

2. Experiment

2.1. Material Synthesis

The crystalline Ga₂Te₃ alloy was synthesized using a simple solid-state HEBM. First, commercial powder of Ti (325 mesh, 99.99%, Alfa Aesar, Haverhill, MA, USA), Ga₂O₃ (99.99%, Sigma Aldrich, St. Louis, MO, USA), Te (99.9%, Alfa Aesar) (where the ratio is 6:2:3), and ZrO₂ balls were placed in the milling bowl (powder mixture: ball = 1:20, w/w). Under an Ar atmosphere, the powder compound was milled for 10 h at 300 rpm. Subsequently, the obtained powder (Ga₂Te₃–TiO₂) was manually mixed with acetylene carbon black powder (C) (99.9+%, bulk density: 170–230 g L⁻¹, S.A.: 75 m² g⁻¹, Alfa Aesar) in mass ratios of 9:1 (Ga₂Te₃–TiO₂–C(10%)), 8:2 (Ga₂Te₃–TiO₂–C(20%)), and 7:3 (Ga₂Te₃–TiO₂–C(30%)). The mixtures were ball-milled under the same condition as the first
milling. The mechanochemical reaction route for preparing the Ga$_2$Te$_3$–TiO$_2$–C composite is outlined below.

First step: \[2\text{Ga}_2\text{O}_3 + 6\text{Te} + 3\text{Ti} \rightarrow 2\text{Ga}_2\text{Te}_3 + 3\text{TiO}_2 \quad \text{(Ga}_2\text{Te}_3\text{-TiO}_2)\],

Second step: \[\text{Ga}_2\text{Te}_3\text{-TiO}_2 + \text{C} \rightarrow \text{Ga}_2\text{Te}_3\text{-TiO}_2\text{-C.} \quad \text{(2)}\]

2.2. Material Characterization

The morphology and crystallinity of Ga$_2$Te$_3$–TiO$_2$ and Ga$_2$Te$_3$–TiO$_2$–C were characterized by employing XRD (D/Max–2200 Rigaku, Tokyo, Japan) with Cu Ka (\(\lambda = 1.54 \text{ Å}\)) radiation at a scan rate of 2$^\circ$·min$^{-1}$, as well as energy-dispersive X-ray spectroscopy (EDXS), scanning electron microscopy (SEM, Hitachi S4700, Tokyo, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, Tokyo, Japan). The mechanism of phase change state in the electrode during Na ion reaction was performed through ex situ XRD.

2.3. Electrochemical Measurements

To assess the electrochemical performance of the electrode, the coin-type cells were assembled in an Ar-filled glovebox with Na foil acting as the counter electrode and polyethylene as the separation membrane. The SIB electrolyte was 1 M NaClO$_4$ in propylene carbonate/ethylene carbonate (1:1 by v/v) with 5% fluoroethylene carbonate. An electrode was prepared using a 7.0:1.5:1.5 (w/w) combination of the active material, conductive carbon (Super-P, 99.9%, Alfa Aesar), and poly(acrylic acid) (PAA, Mw 450,000, Sigma Aldrich) binder. Then, electrodes were coated on Cu foil using a doctor blade and dried overnight in a vacuum oven at 70 $^\circ$C (a typical mass loading of 1.0–1.5 mg on a Cu foil diameter of 12.5 mm). Using a battery-testing device (WBCS3000, WonATech, Seoul, Korea), the electrochemical performance of Ga$_2$Te$_3$–TiO$_2$–C was assessed. For a voltage range of 0.01–2.5 V (vs. Na/Na$^+$), the galvanostatic charge–discharge (GCD) profile was investigated. Using cyclic voltammetry (CV) measurements with a scanning rate of 0.1 mV·s$^{-1}$, the electrochemical reactions of the electrodes with Na$^+$ were evaluated. A battery cycler (WBCS3000, WonATech) was used to measure the rate capability at current densities of 0.1, 0.5, 1, 3, 5, and 10 A·g$^{-1}$. The EIS was measured using a ZIVE MP1 (WonaTech) analyzer in the frequency range of 100 kHz–100 mHz at an AC amplitude of 10 mV.

3. Results and Discussion

The XRD results of the as-prepared Ga$_2$Te$_3$–TiO$_2$ following the HEBM process are shown in Figure 1a. The peaks at 26.2$^\circ$, 30.3$^\circ$, 43.4$^\circ$, 51.4$^\circ$, 53.8$^\circ$, 63.0$^\circ$, 69.4$^\circ$, and 79.5$^\circ$ corresponded to the (111), (200), (220), (311), (222), (400), (331), and (422) planes of Ga$_2$Te$_3$, respectively, indicating the formation of monoclinic Ga$_2$Te$_3$. The relatively small peaks observed at 33.3$^\circ$, 48.5$^\circ$, 67.9$^\circ$, and 79.0$^\circ$ matched the (311), (020), (621), and (424) planes of TiO$_2$, respectively. The presence of amorphous C decreased the crystallinity of Ga$_2$Te$_3$ and TiO$_2$ in Ga$_2$Te$_3$–TiO$_2$–C (Figure S1) [57]. The absence of impurity peaks for the precursor components (Ga$_2$O$_3$, Ti, and Te) in Ga$_2$Te$_3$–TiO$_2$ indicated the complete conversion of the raw materials to the target product via a solid-state reaction. Nevertheless, the existence of small diffraction peaks near 2$\theta = 22.9^\circ$, 35.1$^\circ$, and 37.5$^\circ$ were associated with the formation of GaTe (PDF#33-0571) and Ga$_2$Te$_5$ (PDF#45-0954), which are different forms of gallium telluride alloy (as shown in Figure S2). Given the advantages of gallium telluride alloy (i.e., Ga$_2$Te$_5$), they are also expected to be good candidate anode materials for SIBs; thus, the existence of different forms of minor Ga$_x$Te$_y$ (namely, Ga$_2$Te$_5$ and GaTe) did not negatively affect the electrochemical performance of the Ga$_2$Te$_3$–TiO$_2$–C composite (capacity still in the range of 682–1591 mAh·g$^{-1}$). The EDXS showed that the four component elements of the composite in the electrode and the relative content of elements were reasonable with the stoichiometric ratio of Ga$_2$Te$_3$ and TiO$_2$ (Figure 1b), indicating that the Ga$_2$Te$_3$-based composite was synthesized successfully.
Figure 1. (a) XRD pattern of Ga2Te3–TiO2; (b) EDX spectrum of Ga2Te3–TiO2.

Morphological and structural analyses of Ga2Te3–TiO2–C(10%) were conducted, including SEM, HRTEM, and EDXS, as indicated in Figure 2. According to SEM images (Figure 2a,b), the Ga2Te3–TiO2–C(10%) particle size ranged from sub-micrometers to a few micrometers. The HRTEM images (Figures 2c and S3) revealed crystalline lattice spacings of 0.340, 0.294, and 0.208 nm, which corresponded to the (111), (200), and (220) crystal planes of Ga2Te3, respectively, and 0.311 nm, which corresponded to the (002) plane of TiO2. Additionally, amorphous C, which was anticipated to serve as a buffering network for the active material, formed surrounding Ga2Te3 and TiO2. The scanning transmission electron microscopy image with EDXS mapping analysis (Figures 2d and S4) showed a uniform distribution of each element (Ga, Te, Ti, O, and C) in the Ga2Te3–TiO2 particle. Furthermore, the SEM–EDXS analysis results (Figures S5 and S6) of Ga2Te3–TiO2 showed C concentrations almost identical to their theoretical values. Additionally, the stoichiometric ratio of the constituent elements was nearly identical to their theoretical values. According to SEM–EDXS analysis results (Figures S5 and S6) of Ga2Te3–TiO2 with different content of C, the distribution of Te content was relatively less.

The Na ion storage characteristics of the Ga2Te3–TiO2–C electrode were studied using a half-cell form with Na metal as the counter electrode (Figure 3). The GCD voltage profiles of Ga2Te3–TiO2–C(10%), Ga2Te3–TiO2–C(20%), and Ga2Te3–TiO2–C(30%) for SiBs are shown in Figure 3a and Figures S7. The first discharge/charge capacities of Ga2Te3–TiO2–C(10%), Ga2Te3–TiO2–C(20%), and Ga2Te3–TiO2–C(30%) were 599/414, 550/357, and 462/279 mAh g−1, respectively, which corresponded to initial coulombic efficiencies (ICEs) of 69.1%, 64.9%, and 60.4%, respectively. The poor reversibility between the first and second cycles was because of the SEI layer formation in the first cycle. This poor reversibility was well documented in previous studies [58–60]. The large capacity difference between the first and second cycle indicated the large irreversible capacity contribution from the SEI layer. However, the reversibility of the electrode (Ga2Te3–TiO2–C (10%)) was rapidly enhanced after the second cycle, which could be confirmed by the change in coulombic efficiency (Table S6). According to the EDXS results (Figure S5) and computed theoretical capacities of the separate components (Table S2), the capacity contributions of C and TiO2 to Ga2Te3–TiO2–C(10%) were estimated to be 13% and 22%, respectively. Furthermore, the roles of C and active material were examined (as shown in Figure S8). Ga2Te3–TiO2...
achieved a high initial capacity (606 mAh·g⁻¹), but its capacity gradually decreased due to the instability of the electrode structure without buffering C. Moreover, the electrode with only a buffering matrix (TiO₂–C) showed very low electrochemical efficiency, close to the theoretical capacity (116 mAh·g⁻¹) (Table S2). The low-capacity contribution of the TiO₂–C (~35%) indicated its main role as a buffering matrix. Due to interfacial Na ion storage and electrolyte breakdown, the measured capacities of Ga₂Te₃–TiO₂–C(10%) and Ga₂Te₃–TiO₂ in the SIBs were higher than their theoretical capacities (336 and 333 mAh·g⁻¹, respectively, as computed in Table S3). The change in the reversible capacity of Ga₂Te₃–TiO₂–C for the SIBs was studied using the CE (Table S4) and DCP test of the first 300 cycles (Figure S9). The CE of Ga₂Te₃–TiO₂–C(10%) reached ~99.82% after 150 cycles, slightly decreased, and then stabilized at 98.5% after 300 cycles. The DCP analysis revealed that, for 250 cycles, the main oxidation (at ~0.16, ~1.27, and ~1.42 V) and reduction (at ~0.79 and ~1.58 V) peaks remained stable before becoming wider and shifting. However, this polarization had an almost negligible effect on sodiation/desodiation. The reversible capacity of Ga₂Te₃–TiO₂–C(10%) was 436.6 mAh·g⁻¹ (capacity retention (CR) of 97.7%) after 300 cycles at 100 mA·g⁻¹, which was greater than those of Ga₂Te₃–TiO₂–C(20%) (323.8 mAh·g⁻¹) and Ga₂Te₃–TiO₂–C(30%) (264.9 mAh·g⁻¹) (Figure S1). As shown in Figure S10, although some aggregated particles were observed, the Ga₂Te₃–TiO₂–C(10%) electrode morphology was generally well maintained after 300 cycles. This is because of the presence of TiO₂–C, which efficiently stabilized the electrode structure and mitigated the significant volume variation. In addition, in EDS spectra after 300 cycles, the composition of the Ga₂Te₃ composite electrode was not significantly changed without impurities (Figure S11). This further proved the stability and good retention of the electrode after the electrochemical reaction. At 500 mA·g⁻¹ (Figure 3c), the reversible capacity of Ga₂Te₃–TiO₂–C(10%) slightly increased until 200 cycles, followed by a gradual decrease. The capacity variation depends on the variation of the redox peaks, in which the oxidation and reduction peaks gradually rise with the cycling, leading to a decrease in polarization and an increase in capacity. In contrast, the oxidation and reduction peaks gradually decrease with the increase in cycling, resulting in a reduced capacity due to the increase in polarization [10,61,62]. This trend was also shown in the DCP analysis (Figures S12 and S13) and CE variation (Table S5). The magnitudes of the reduction (at 0.59 and 1.48 V) and oxidation (at 0.16, 1.27, and 1.69 V) peaks gradually raised over 200 cycles, with a reduction in polarization (Figure S12), and then reduced after 200 cycles, with a rise in polarization (Figure S13). At 100 and 500 mA·g⁻¹, the fluctuation of the DCP profile was examined as a function of the cycle number (Figure S14). The DCP curves of the Ga₂Te₃–TiO₂–C(10%) electrode showed that the overall intensity of the redox peaks was generally stable as the cycle number increased to 300 at 100 mA·g⁻¹. At 500 mA·g⁻¹, the overall magnitudes of the redox peaks increased up to 250 cycles and then decreased with an increase in polarization. Despite the decrease in capacity after 250 cycles, the overall capacity of Ga₂Te₃–TiO₂–C(10%) was still the highest over 500 cycles, reaching 204 mAh·g⁻¹ after 500 cycles with a CR of 76.4%. Figure S15 shows a comparison of the CE variations in Ga₂Te₃–TiO₂–C with varying C contents at 100 and 500 mA·g⁻¹. Table S6 (at 100 mA·g⁻¹) and Table S7 (at 500 mA·g⁻¹) provide summaries of the detailed CE values for the electrodes throughout the first 10 cycles. As shown in Table S6, the ICE of the Ga₂Te₃–TiO₂–C(10%) electrode was slightly higher (69.2%) than that of the Ga₂Te₃–TiO₂–C(20%) (ICE = 64.8%) and Ga₂Te₃–TiO₂–C(30%) electrodes (ICE = 60.5%). Then, after 10 cycles, the CE of the Ga₂Te₃–TiO₂–C(10%) electrode marginally increased and reached the highest among the three various electrodes. This tendency was also discovered at 500 mA·g⁻¹ (Table S7). After the first cycle, the high CE of the Ga₂Te₃–TiO₂–C(10%) electrode showed a high degree of sodiation/desodiation reversibility. The CV curves of the Ga₂Te₃–TiO₂–C(10%) electrode for the first five cycles in the voltage range of 0.005–2.5 V vs. Na/Na⁺ are shown in Figure 3d. A large reduction peak was observed at 1.37 V during the first discharge process, which denoted the intercalation of Na into Ga₂Te₃ to form Na₂Te and Ga. The reaction between Ga and Na to generate NaGa₄ was attributed to being responsible for the peak at 0.52 V. Thus, Na₂Te and NaGa₄ were the
final products after the discharge step was complete. In the charge step, two oxidation peaks were noticed at 0.92 and 1.72 V. The first peak was the result of Na being completely excluded, turning NaGa$_4$ into Ga. Then, Ga intruded into Na$_2$Te to form Ga$_2$Te$_3$ when the anode was charged to 1.72 V. The ex situ investigations concern a thorough analysis of this phase transition. After the second cycle, the curves nearly overlapped, indicating the excellent stability and reversibility of Ga$_2$Te$_3$–TiO$_2$–C(10%). The CV curves of Ga$_2$Te$_3$–TiO$_2$–C(20%) and Ga$_2$Te$_3$–TiO$_2$–C(30%) were almost identical to that of Ga$_2$Te$_3$–TiO$_2$–C(10%), with a similar level of cyclic stability after the second cycle (Figure S16). In addition, the electrochemical performance of Ga$_2$Te$_3$–TiO$_2$ was examined (Figure S17). The GCD profiles of Ga$_2$Te$_3$–TiO$_2$ presented initial charge/discharge capacities of 606/426 mAh g$^{-1}$, corresponding to an ICE of 70.2%, which is higher than that of the Ga$_2$Te$_3$-based composite with different C contents. Despite this high ICE of Ga$_2$Te$_3$–TiO$_2$, the capacity gradually decreased with the increase in cycle number, and reached 309 mAh g$^{-1}$ after 30 cycles, with a capacity retention of 67%. This is much lower than the Ga$_2$Te$_3$–TiO$_2$ electrode with various carbon contents. In addition, the CV curves did not overlap in the first five cycles. Therefore, the presence of C clearly stabilized the electrode structure, leading to the enhanced electrochemical performance. The rate performances (Figure 3e) and normalized capacity retentions (Figure 3f) of the electrodes were determined. At 0.1, 0.5, 1.0, 3.0, 5.0, and 10.0 A g$^{-1}$, the average specific capacities of Ga$_2$Te$_3$–TiO$_2$–C(10%) were 455, 408, 374, 348, 321, and 318 mAh g$^{-1}$, respectively (Figure 3e), which were considerably greater than those of Ga$_2$Te$_3$–TiO$_2$–C(20%) and Ga$_2$Te$_3$–TiO$_2$–C(30%). Surprisingly, even at 10 A g$^{-1}$, Ga$_2$Te$_3$–TiO$_2$–C(10%) had a CR of up to 96% (Figure 3f). Additionally, Ga$_2$Te$_3$–TiO$_2$–C(10%) demonstrated a high rate performance when the discharge rate was reduced from 10 A g$^{-1}$ to 0.1 A g$^{-1}$, resulting in high CR (99.3%).

![Figure 2](image-url)

Figure 2. (a) SEM image; (b) size distribution; (c) HRTEM image; (d) EDXS elemental mappings of Ga, Te, Ti, O, and C in Ga$_2$Te$_3$–TiO$_2$–C(10%).
The reaction mechanism during the first sodiation/desodiation process of the Ga2Te3–TiO2–C(10%) electrode was investigated using ex situ XRD (Figure 4a,b). Peaks corresponding to Na2Te and Ga were observed at a discharge voltage of 1.37 V (D: 1.37 V). When the electrode was fully discharged (D: 5 mV), NaGa4 peaks were observed and Na2Te peaks remained. The NaGa4 phase partly disappeared when the electrode was charged to 0.92 V (C: 0.92 V). In a charging state of 1.72 V, the Na2Te phase partly disappeared, Ga was observed, and NaGa4 completely disappeared. Only the peaks corresponding to Ga2Te3 were observed again when the electrode was fully charged to 2.5 V (C: 2.5 V). Ga2Te3 undergoes the following structural changes during sodiation/desodiation:

1st discharge

- Intercalation stage
  \[ \text{Ga}_2\text{Te}_3 + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{Ga}_2\text{Te}_3 \] (2.5–1.37 V). (i)

- Conversion stage
  \[ \text{Na}_x\text{Ga}_2\text{Te}_3 + (6^-)\text{Na}^+ + (6^-xe^-) \rightarrow 3\text{Na}_2\text{Te} + 2\text{Ga} \] (1.37–0.52 V). (ii)

- Alloy stage
  \[ 4\text{Ga} + \text{Na}^+ + e^- \rightarrow \text{NaGa}_4 \] (0.52–0.005 V). (iii)

1st charge

- De-alloy stage
  \[ \text{NaGa}_4 \rightarrow 4\text{Ga} + \text{Na}^+ + e^- \] (0.005–0.92 V). (iv)

- De-conversion stage
  \[ 3\text{Na}_2\text{Te} + 2\text{Ga} \rightarrow \text{Li}_x\text{Ga}_2\text{Te}_3 + (6^-x)\text{Na}^+ + (6^-xe^-) \] (0.92–1.72 V). (v)

- De-intercalation stage
  \[ \text{Na}_x\text{Ga}_2\text{Te}_3 \rightarrow \text{Ga}_2\text{Te}_3 + x\text{Na}^+ + xe^- \] (1.72–2.5 V). (vi)

It is noteworthy that, after the first cycle, the Ga2Te3 phase (major peaks at 53.8°, 69.4°, and 71.5°) was completely recovered without any impurity peaks, showing a highly reversible interaction of Ga2Te3 with Na ions. The alloying/dealloying and conversion mechanism of the Ga2Te3 electrode during charge/discharge is shown by the ex situ XRD results, as schematically depicted in Figure 4c.

For the first, fifth, and 20th cycles, the EIS profiles of the Ga2Te3–TiO2–C(10%), Ga2Te3–TiO2–C(20%), and Ga2Te3–TiO2–C(30%) electrodes were obtained (Figure 5). The simplified equivalent circuit shown in Figure 5d includes the electrolyte resistance (R\text{ct}), charge-transfer resistance (R\text{ct}), SEI layer resistance (RSEI), interfacial double-layer capacitance (C\text{dl}), Warburg impedance (Z\text{w}), and constant phase element (CPE). The R\text{ct} at the electrode–electrolyte interface is denoted by compressed semicircles in the mid-frequency region of the Nyquist plot. For all the electrodes, R\text{ct} gradually decreased as the cycle number increased from 1 to 20. Ga2Te3–TiO2–C(10%) exhibited the lowest value of R\text{ct} after 20 cycles (Table S8), demonstrating the most facile Na ion transportation, which led to the highest Na storage performance.
408, 374, 348, 321, and 318 mAh·g⁻¹, respectively (Figure 3e), which were considerably greater than those of Ga₂Te₃–TiO₂–C(20%) and Ga₂Te₃–TiO₂–C(30%). Surprisingly, even at 10 A·g⁻¹, Ga₂Te₃–TiO₂–C(10%) had a CR of up to 96% (Figure 3f). Additionally, Ga₂Te₃–TiO₂–C(10%) demonstrated a high rate performance when the discharge rate was reduced from 10 A·g⁻¹ to 0.1 A·g⁻¹, resulting in high CR (99.3%).

Figure 3. Electrochemical performances of Ga₂Te₃–TiO₂–C composites for SIBs: (a) GCD profiles of Ga₂Te₃–TiO₂–C(10%) at 100 mA·g⁻¹; (b) cycling performances of composite at 100 mA·g⁻¹ and (c) 500 mA·g⁻¹; (d) CV curves of Ga₂Te₃–TiO₂–C(10%); (e) rate capabilities of Ga₂Te₃–TiO₂–C composites; (f) capacity retention of Ga₂Te₃–TiO₂–C composites from 0.1 to 10 A·g⁻¹.
Figure 4. (a,b) Ex situ XRD patterns obtained at selected cutoff potentials in initial sodiation/desodiation process; (c) schematic of electrochemical reaction mechanism of Ga$_2$Te$_3$–TiO$_2$–C(10%) electrode during cycling.
trode–electrolyte interface is denoted by compressed semicircles in the mid-frequency region of the Nyquist plot. For all the electrodes, $R_{ct}$ gradually decreased as the cycle number increased from 1 to 20. Ga$_2$Te$_3$–TiO$_2$–C(10%) exhibited the lowest value of $R_{ct}$ after 20 cycles (Table S8), demonstrating the most facile Na-ion transportation, which led to the highest Na-storage performance.

Currently, there are only a few reports on Ga-based or Te-based anodes for SIBs. However, chalcogenide materials (In$_2$S$_3$, Sb$_2$Se$_3$, etc.) have high specific capacities when they undergo sequential conversion and alloying reactions owing to their unique properties. A comparison of the performances of Ga$_2$Te$_3$–TiO$_2$–C(10%) and other chalcogenide materials demonstrated the high potential of the Ga$_2$Te$_3$-based composite electrodes for future applications (Table 1).

![Figure 5. EIS-based Nyquist plots for (a) Ga$_2$Te$_3$–TiO$_2$–C(10%), (b) Ga$_2$Te$_3$–TiO$_2$–C(20%), and (c) Ga$_2$Te$_3$–TiO$_2$–C(30%) after one, five, and 20 cycles; (d) equivalent circuit.](image-url)
Table 1. Comparison of performances of chalcogenide-based anodes for SIBs.

| Anode                  | Cycling Performance | Rate Capability | Synthesis Method       | Ref.       |
|------------------------|---------------------|-----------------|------------------------|------------|
| Ga2S3                  | 476 mAh·g⁻¹ after 100 cycles at 0.4 A·g⁻¹ | 283 mAh·g⁻¹ at 2 A·g⁻¹ | Vapor thermal annealing | [55]       |
| Ga2S3–C                | 385 mAh·g⁻¹ after 200 cycles at 0.1 A·g⁻¹ | 94 mAh·g⁻¹ at 2.0 A·g⁻¹ | Sulfuration process    | [35]       |
| Sb2Se3/C               | 485.2 mAh·g⁻¹ after 100 cycles at 0.2 A·g⁻¹ | 237.9 mAh·g⁻¹ at 2.0 A·g⁻¹ | Hydrothermal process   | [31]       |
| Sb2S3–rGO              | 537 mAh·g⁻¹ after 70 cycles at 0.1 A·g⁻¹ | 290 mAh·g⁻¹ at 3.2 A·g⁻¹ | Ultrasonication method | [63]       |
| Sb2S3–C                | 455.8 mAh·g⁻¹ after 10 cycles at 0.1 A·g⁻¹ | 263 mAh·g⁻¹ at 1.0 A·g⁻¹ | Modified natural slurry nore | [64]       |
| Sb2S3@SnS@C            | 437 mAh·g⁻¹ after 100 cycles at 1 A·g⁻¹ | 448 mAh·g⁻¹ at 5.0 A·g⁻¹ | Hydrothermal method    | [65]       |
| Sb2S3                  | 384 mAh·g⁻¹ after 50 cycles at 0.2 A·g⁻¹ | 239 mAh·g⁻¹ at 5.0 A·g⁻¹ | Hydrothermal method    | [66]       |
| In2S3/C                | 372 mAh·g⁻¹ after 200 cycles at 0.5 A·g⁻¹ | 236 mAh·g⁻¹ at 2.0 A·g⁻¹ | Electrosprning process | [67,68]   |
| Co3Se4@C               | 449 mAh·g⁻¹ after 20 cycles at 0.1 A·g⁻¹ | 328 mAh·g⁻¹ at 5.0 A·g⁻¹ | Annealing process     | [69]       |
| Fe3Se4@C               | 439 mAh·g⁻¹ after 25 cycles at 0.05 A·g⁻¹ | -                | Electrosprning process | [70]       |
| Bi2Te3                 | 364 mAh·g⁻¹ after 1200 cycles at 5 A·g⁻¹ | 339 mAh·g⁻¹ at 10 A·g⁻¹ | Chemical reduction method | [36]       |
| SbTe–C                 | 421 mAh·g⁻¹ after 200 cycles at 0.1 A·g⁻¹ | 413 mAh·g⁻¹ at 1 A·g⁻¹ | Ball milling           | [71]       |
| Ga2Te3–TiO2–C         | 437 mAh·g⁻¹ after 300 cycles at 0.1 A·g⁻¹ | 318 mAh·g⁻¹ at 10 A·g⁻¹ | This work              |            |

4. Conclusions

We demonstrated a Ga2Te3-based composite as a prospective anode material for SIBs. The Ga2Te3–TiO2–C(10%) anode achieved a high reversible capacity of 437 mAh·g⁻¹ after 300 cycles at 0.1 A·g⁻¹, as well as a high rate capability (CR of 96% at 10 A·g⁻¹ relative to 0.1 A·g⁻¹). The nanoconfined Ga2Te3 crystallites embedded within an electrically conductive TiO2–C hybrid matrix effectively accommodated the Ga2Te3 particle volume variation and avoided the agglomeration of Ga during electrochemical reactions. In addition, Na ion diffusion kinetics and mechanical stability were enhanced by this beneficial morphology, thereby achieving high capacity and long-term cycling performance. These findings offer a new direction toward the development of high-performance SIBs with long cycle lifetimes and expansion of the Ga- and Te-based materials in other electrochemical energy storage systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15186231/s1, Figure S1: XRD pattern of Ga2Te3–TiO2–C with different concentration of C. Figure S2: The existence of different forms of Ga2Te9 (namely, Ga2Te3 and GaTe). Figure S3: HRTEM image of Ga2Te3–TiO2–C(10%). Figure S4: SEM image of distribution of the elements in Ga2Te3–TiO2–C(10%). Figure S5: EDX spectrum of as-synthesized Ga2Te3–TiO2–C(10%). Figure S6: EDX analysis of (a) Ga2Te3–TiO2–C(20%), and (b) Ga2Te3–TiO2–C(30%). Figure S7: Galvanostatic discharge-charge profiles of (a) Ga2Te3–TiO2–C(20%) and (b) Ga2Te3–TiO2–C(30%) for SIBs. Figure S8: Cyclic performance of various electrodes at 100 mA g⁻¹. Figure S9: DCP profiles of Ga2Te3–TiO2–C(10%) during 300 cycles measured at 100 mA g⁻¹: (a) 1–150 cycles, (b) 150–300 cycle. Enlarged view of (c) reduction and (d) oxidation peaks. Figure S10: SEM image of Ga2Te3–TiO2–C(10%) after 300 cycles. Figure S11: EDX analysis of Ga2Te3–TiO2–C(10%) after 300 cycles. Figure S12: (a) DCP profiles of Ga2Te3–TiO2–C(10%) during initial 200 cycles measured at 500 mA g⁻¹. Enlarged view of (b) oxidation and (c) reduction peaks. Figure S13: (a) DCP of Ga2Te3–TiO2–C(10%) from 300 cycle to 500 cycles measured at 500 mA g⁻¹. Enlarged view of (b) oxidation and (c) reduction peaks. Figure S14: DCP profiles of Ga2Te3–TiO2–C(10%) (a) at 100 mA g⁻¹ during 300 cycles and (b) at 500 mA g⁻¹ during 500 cycles. Figure S15: Coulombic efficiency of Ga2Te3–TiO2 with different C content at current densities of (a) 100 and (b) 500 mA g⁻¹. Figure S16: (a) CV curves of Ga2Te3–TiO2–C...
(20%) and (b) Ga$_2$Te$_3$–TiO$_2$–C (30%) for SIBs. Figure S17: (a) Galvanostatic discharge-charge profiles of Ga$_2$Te$_3$–TiO$_2$ at a current density of 100 mA g$^{-1}$, (b) CV curves of Ga$_2$Te$_3$–TiO$_2$. Table S1: Rate performance of Te-based composite anode for SIB. Table S2: Calculation of capacity contribution of Ga$_2$Te$_3$, TiO$_2$ and C in the Ga$_2$Te$_3$–TiO$_2$–C composite for SIB. Table S3: Calculation of theoretical capacity of Ga$_2$Te$_3$–TiO$_2$–C (10%) and Ga$_2$Te$_3$–TiO$_2$ for SIB. Table S4: Coulombic efficiency variation of Ga$_2$Te$_3$–TiO$_2$–C (10%) at various cycle numbers measured at 100 mA g$^{-1}$ for SIB. Table S5: Coulombic efficiency variation of Ga$_2$Te$_3$–TiO$_2$–C (10%) at various cycle numbers measured at 500 mA g$^{-1}$ for SIB. Table S6: Coulombic efficiency of Ga$_2$Te$_3$–TiO$_2$–C at current density of 100 mA g$^{-1}$ during initial 10 cycles for SIB. Table S7: Coulombic efficiency of Ga$_2$Te$_3$–TiO$_2$–C at current density of 500 mA g$^{-1}$ during initial 10 cycles for SIB. Table S8: Charge-transfer resistance (Rct) of Ga$_2$Te$_3$–TiO$_2$–C for SIB.

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