



Article Te-Doped Bi₂Se₃@NC Nanocomposites for High-Performance Li-Ion Battery Anodes

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Abstract: Bismuth-based anodes are promising for lithium-ion batteries owing to their high theoretical capacity, garnering significant attention in recent decades. Despite its intrinsic advantages, this anode material has the shortcoming of excessive volume expansion during the charging and discharging processes, which significantly reduces the cycling stability. In this work, a nitrogen-doped carbon-coated Bi₂Se_{3-x}Te_x composite (Bi₂Se_{3-x}Te_x@NC) with excellent electrochemical properties was synthesized by the solvothermal method followed by heat treatment. Benefiting from its unique structure and Te-doping properties, the nitrogen-doped carbon-coated Bi₂Se_{3-x}Te_x composite maintains a discharge specific capacity of 464.0 mAh g⁻¹ after 60 cycles at a current density of 0.1 A g⁻¹. This research presents an efficient approach for the preparation of nitrogen-doped carbon-coated anode materials and a fresh perspective on battery electrode material design.

Keywords: lithium-ion batteries; anode materials; bismuth base; electrochemical performance

1. Introduction

The lithium-ion battery (LIB) stands out as a groundbreaking discovery that revolutionizes our daily lives. In contrast to traditional energy supply, which was based on fossil fuels, the emergence of lithium-ion batteries has completely changed the previous carbonbased energy supply chain. It creates a new path for sustainable development of reducing global carbon emissions [1]. Notably, the outstanding contributions of John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were recognized with the 2019 Nobel Prize in Chemistry for their pivotal role in the development of LIBs. The tremendous endeavors have been dedicated to improvements to lithium-ion batteries for both electric vehicle applications and stationary energy storage [2]. Multidisciplinary approaches, including electrochemistry, materials engineering, dynamic modeling [3,4], and systems or controls engineering [5,6], have demonstrated their capability to enhance either performance or reliable operation during the battery system's lifetime [7].

Bismuth (Bi) is a highly attractive anode material for LIBs, owing to its high capacity and suitable working potential for application. The theoretical volumetric capacity of metallic bismuth is 3430 mAh cm⁻³, which is much higher than that of graphite. Yang et al. [8] reported the successful synthesis of Bi@C microspheres through aerosol spray pyrolysis technology. By uniformly dispersing Bi nanoparticles into carbon spheres, the Bi@C electrode displayed enhanced conductivity and minimized volume changes during cycling. After cycling for 100 cycles as the negative electrode of LIBs, the reversible capacity of this composite material is approximately 280 mAh g⁻¹. In addition, the work reported by



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Hong et al. [9] showcased the advantages of a sponge-like porous structure by embedding Bi nanoparticles into a 3D porous carbon skeleton. The Bi/C composite material was synthesized through the one-step carbon thermal reduction (CTR) method. The optimized structure has decreased the diffusion path of Li⁺ and transformed the composite material into a high-performance negative electrode for LIBs. Zhong et al. [10] introduced a novel composite material, Bi@NC, in which the zeolitic imidazolate framework (ZIF-8) was employed as a precursor. In this material, Bi nanoparticles were anchored to an N-doped porous carbon matrix. N-doped porous carbon enhanced the electric conductivity and improved the cycling stability of bismuth anodes. Bi@NC exhibited excellent cyclic stability with a specific capacity of 285 mAh g^{-1} . In spite of the much higher volumetric capacity, the gravimetric capacity of bismuth is about 385 mAh g^{-1} , assuming the alloying process involves three lithium-ions per bismuth forming Li₃Bi. This specific gravimetric capacity is similar to that of a graphite anode. In order to obtain a higher gravimetric capacity, bismuthrelated compounds have been extensively investigated recently. Besides their potential as a thermoelectric material, these compounds are currently viewed as outstanding anode materials for LIBS [10]. Inspired by the successful application of Bi₂Se₃ as a possible anode for Li-ion batteries, there have been an increased number of investigations using Bi₂Se₃ for sodium-ion, zinc ion, potassium-ion, and magnesium-ion battery application [11,12]. Chen et al. [13] proposed a new three-dimensional (3D) composite anode material based on Bi₂Se₃ and Bi₂Se₃ @ NC @ rGO. It has a dual conversion-alloying mechanism, and the three-layer structure was very stable and conducive to K⁺ diffusion and electron transport capabilities. The material maintained a capacity retention of 272.5 mAh-g⁻¹ and good cycling capability after 300 cycles at 100 mA g^{-1} . Sun et al. [14] synthesized a new type of strained Bi₂Se₃, which showed an irregular structure with stacked nanosheets. Due to the increased interlayer spacing and reduced bandgap, this electrode material demonstrated extremely rapid electrochemical kinetics when utilized in sodium-ion batteries. The Bi₂Se₃ electrode material retains a reversible specific capacity of 332.7 mAh g^{-1} after 1000 cycles at 30 A g^{-1} . Dang et al. [15] produced pomegranate-like Bi₂Se₃@C nanocomposite materials through solution heat and selenization reactions. The carbon layer controls the volume expansion during battery charging and discharging while enhancing electronic conductivity, resulting in a high specific capacity of 468 mAh g^{-1} at a low current density of 0.1 A g^{-1} . Tao et al. [16] proposed Bi₂Se₃@C micro/nanostructures and applied them for potassium ion batteries, which showed improved K⁺ storage performance and a significant rate capability of 305 mAh g^{-1} at 1A g^{-1} . Chong et al. [17] employed solvothermal processes, polymerization, and carbonization approaches to fabricate the Bi₂Se₃@rGO@NC composite. Bismuth selenide in the form of nanoflowers was encapsulated in situ using reduced graphene oxide (rGO) and uniformly coated with nitrogen-doped carbon. The Bi₂Se₃ @ rGO @ NC anode material was applied to sodium-ion batteries, showing a reversible initial specific capacity of 288.4 mA h g^{-1} and exceptional cycling stability at 50 mA g^{-1} , and maintaining a considerable capacity of 160.1 mA h g^{-1} over 300 cycles. Zhang et al. [18] synthesized Bi₂Se₃/nitrogen-doped carbon dots (NCDs) using a simple solvent-thermal method, which contains abundant functional groups on the surface. These functional groups facilitate the contact between the aqueous electrolyte and the composites and effectively improve their electrical conductivity. Bi₂Se₃/NCDs, as anode materials for aqueous zinc ion batteries (AZIBs), exhibit outstanding zinc storage performance, with a discharge specific capacity of up to 324 mAh g⁻¹ at 100 mA g⁻¹ and a discharge specific capacity of 162 mAh g^{-1} after 1000 cycles (1000 mA g^{-1}).

Bi-based materials have the advantages of both abundance in nature and suitable lithium deposition potential. Unfortunately, their excessive volume expansion and poor conductivity during charging and discharging processes are significant drawbacks that hinder their practical applications. The strategies of synthesis have been implemented to construct the desired structures. Bi₂Se₃ with various structures, including microrods, nanosheets, layered nanostructures, and microspheres, have been recently synthesized and used as negative electrodes in batteries. Xu et al. [19] reported the method for preparing

Bi₂Se₃ microrods through a microwave-assisted "green" chemical route. The materials synthesized as microrods had a mean diameter of 700 nanometers and a length of around 15 microns, with a uniform size distribution. Chen et al. [20] reported Bi₂Se₃ with the morphology of an assembled flexural nanosheet. The nanosheets are synthesized via the one-step hydrothermal method, and the thickness is estimated to be only around 10 nm. The unique structure may facilitate solid-state Mg²⁺ diffusion. Bi₂Se₃ nanosheets deliver a high reversible capacity of 144 mAh g^{-1} for Mg storage and a remarkable rate capability of 65 mAh g^{-1} at 1A g^{-1} . Han et al. [21] synthesized in-doped Bi₂Se₃-layered nanostructures using the cation exchange technique. The hierarchical nanostructures ensured the composite anode with a high initial capacity. However, the capacity retention is quite poor, and only about 160 mAh g^{-1} remained after 50 cycles. Mao et al. [22] demonstrated that Bi₂Se₃ microspheres doped with S and assembled from stacked nanosheets can be synthesized using the solvothermal method. The size of the microspheres can be adjusted by the synthesis time. The material's electrochemical performance as a Li anode was evaluated. Although the initial discharge capacity was high, the capacity dropped significantly to about 100 mAh g^{-1} after a few cycles. This is probably due to the volume expansion during cycling. Compared with the much larger and irregular-sized Bi₂Se₃ material, these Bi₂Se₃ with specified structures demonstrated better cycling and rate performance. Reducing the size of the bulk Bi₂Se₃ material to the nanoscale and integrating carbon to enable shorter diffusion distances increased the abundance of surface reaction sites and created extra space for expansion. Carbon can stabilize the nano-sized Bi₂Se₃ and facilitate electron transportation due to its unique interconnected network. The voids in the carbon allow the electrolyte to be more permeable for fast Li-ion transportation and to accommodate volume expansion.

Compared to selenium, tellurium has similar physical and chemical properties, while tellurium has superior electrical conductivity (2 \times 10² S m⁻¹). This indicates that the substitution of partial selenium for tellurium may help selenium-based materials enhance their rate capability. As one of the defect engineering approaches, the doping method has been extensively investigated to improve conductivity, lessen barriers to Li-ion migration, and regulate the discharge/charge voltage of electrode materials. Heteroatom doping, a form of extrinsic defect, occurs when foreign atoms replace the original atoms at lattice points. Doping a certain number of atoms could lead to the formation of a solid solution. Depending on the nature of the dopant atom or ion, heteroatom doping can be either cationic or anionic. A wide range of cation dopants have been employed for LiFePO₄ to substitute Li and Fe ions and improve their electrical or ionic conductivity. A complete solubility range was found when Fe was partially replaced by M (M = Mn, Mg, Co...). These compounds have shown distinct voltage plateaus and different kinetical behavior [23]. To construct defects in Si, the technique of anion doping has been extensively investigated. The elements of B [24], P [25], N [26], and As [27] are the most common ones to dope Si to decrease the resistance of the cell or to create n-type or p-type semiconductors. The doped Si demonstrates better electrochemical performance than pure Si.

Metal–organic frameworks (MOFs) and their derivatives benefit from ultra-high surface areas, high porosity, and easily modified structures. MOF-derived carbon-encapsulated Bi₂Se₃ composites have demonstrated good electrochemical performance for Li-ion battery anodes [28]. Furthermore, anode materials employing hybrid (alloy and conversion) mechanisms are deemed promising, potentially offering higher theoretical specific capacity or a lower-voltage platform compared to intercalation compounds. The alloying reaction typically ensures a low-voltage platform during charging and discharging. The conversion anode material usually has a higher theoretical specific capacity than the intercalation anode material.

In this work, a new conversion-alloying-type nitrogen-doped carbon-coated $Bi_2Se_{3-x}Te_x$ composite ($Bi_2Se_2Te@NC$) anode for LIBs was prepared using the solvothermal method, followed by a simple tellurization reaction. For the synthesis of composites, Bi-MOFs were used as precursors. Taking advantage of nano-sized particles and nitrogen-doped carbon

coating, the $Bi_2Se_{3-x}Te_x$ composite material displayed excellent electrochemical performance. Compared to undoped $Bi_2Se_3@NC$ electrodes, $Bi_2Se_2Te@NC$ electrodes exhibited higher reversible capacity, improved rate performance, and enhanced cycling stability.

2. Experimental

2.1. Material

Te (99.9%), Se (99.999%), and trimesic acid (H₃BTC 99%) were purchased from Adamasbeta. Bi (NO₃)₃·5H₂O (99.99%), N, N-Dimethylformamide (DMF) (AR, \geq 99.5%(GC)) and MeOH (AR, \geq 99.5%) were bought from Shanghai Titan Scientific, Shanghai, China (GENERAL-REAGENT[®]).

2.2. Material Synthesis

2.2.1. Synthesis of Bi- BTC Precursor

All reagents and chemicals were used directly without further purification. Figure 1 shows the schematic illustration for the preparation of Bi₂Se_{3-x}Te_x@NC nanocomposites. The Bi (BTC) (DMF)·DMF·(CH₃OH)₂ (Bi-BTC) was synthesized through a straightforward and economical solvothermal process as follows: trimesic acid (H₃BTC, 0.7707 g, 3.67 mmol) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 0.9459 g, 1.95 mmol) were dissolved in a solvent mixture of N,N-dimethylformamide/methanol (DMF/MeOH, 30 mL, V/V $\frac{1}{4}$ 1:3). The solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 45 h. After cooling down to room temperature, colorless crystals were obtained. The crystals were washed several times with DMF and MeOH and then vacuum-dried at 60 °C overnight.



Figure 1. Schematic illustration for the preparation of $Bi_2Se_{3-x}Te_x@NC$ nanocomposites.

2.2.2. Synthesis of Bi₂Se₃ @NC

 Bi_2Se_3 @NC composites were synthesized through a high-temperature solid-phase reaction method. Bi-BTC (100 mg, 0.2 mmol) and Se (15.792 mg, 0.2 mmol) were meticulously ground in an agate mortar for 1h. Subsequently, the mixture was then placed in a quartz tube and vacuum sealed. The quartz tubes containing the raw materials were thermally annealed at 500 °C for 120 min in a muffle furnace to obtain the Bi_2Se_3 @NC composite.

2.2.3. Synthesis of Bi₂Se_{3-x}Te_x@NC

A high-temperature dry media reaction method was adopted to prepare $Bi_2Se_{3-x}Te_x@NC$ composite materials. Bi-BTC (100 mg, 0.2 mmol), Se (15.792 mg, 0.2 mmol), and Te (12.76 mg, 0.1 mmol) were ground in an agate mortar for 60 min. The mixture was then placed in a quartz tube and vacuum-sealed. The material was vacuum-sealed to prevent oxidation in high-temperature environments. $Bi_2Se_{3-x}Te_x@NC$ composite materials were

obtained by thermally annealing the quartz tubes containing the raw material in a muffle furnace at 500 $^{\circ}$ C for 2 h.

2.3. Material Characterization

The crystal structures of the synthesized products were characterized using a Bruker D8-Advance X-ray diffractometer with Cu-K α radiation (λ = 1.5406 Å). Data were measured over the 2 θ range of 10–80° with a step size of 0.02°. The morphology and microstructure were observed by FESEM (JEOL JSM-6700F, Kyoto, Japan) at an accelerating voltage of 5 kv, using a cold field emission electron gun. A LabRAM HR Evolution spectrometer with a 532 nm laser was used to collect Raman spectra. Thermogravimetric analysis (TGA) data were acquired in air using a SDT-Q600 (TA Instruments, New Castle, DE, USA). N₂ adsorption/desorption isotherms were acquired using a Micromeritics ASAP-2020 analyzer (Norcross, GA, USA). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific Escalab 250Xi. (Waltham, MA, USA).

2.4. Electrochemical Characterization

To prepare the working electrodes, the slurry was first prepared by adding 80 wt% active material, 10 wt% sodium carboxymethylcellulose (CMC), and 10 wt% carbon black (Super P) proportionally to distilled water. The slurry was applied to a Cu foil and dried at 110 °C under vacuum for 12 h. Then, active material loading of approximately 1.5–2.0 mg cm⁻² per electrode occurred. CR2016-type coin cells were assembled in a glove box including a counter electrode (Li foil), separator (Celgard 2600 film, Charlotte, NC, USA), and electrolyte (1 M LiPF₆ (ethylene carbonate (EC): dimethyl carbonate (DMC) = 1:1 (v/v))). A Neware battery testing system was used to evaluate galvanostatic charge/discharge and rate performance over the 0.01–3.0 V range. An Autolab PGSTAT302 N (Herisau, Switzerland) or Chi660e (Dalian, China) instrument was used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

3. Results and Discussion

Characterization

Figure 2a shows the X-ray diffraction (XRD) patterns of Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC (x = 1) synthesized by heat treatment. All the characteristic peaks correspond to pure Bi₂Se₃ or $Bi_2Se_{3-x}Te_x$. As most of the carbon in the composites is amorphous, there are no obvious crystalline graphite phases in the XRD patterns. The main peaks located at 29.356, 40.265, and 43.693 correspond to (015), (1010), and (110) planes, respectively. All the peaks match well with Joint Committee on Powder Diffraction Standards (JCPDS) card No.33-0214 for Bi_2Se_3 . As shown in Figure 2b, diffraction peaks of $Bi_2Se_{3-x}Te_x@NC$ (x = 1) slightly shifted to lower angles, indicating successful Te incorporation into the crystal lattice. The cell volume expansion of $Bi_2Se_{3-x}Te_x$ can be observed, as Te atoms have a relatively larger atomic size than Se. All diffraction peaks can be well indexed within the space group of R-3m, and the lattice parameters calculated for Bi_2Se_3 are a = 4.1993(6) Å, c = 28.656(7) Å, with the cell volume of 437.62(2) Å³. For Bi₂Se_{3-x}Te_x@NC (x = 1), a = 4.2238(7) Å, c = 29.433(8) Å, with the cell volume = 454.77(2) Å³. The carbon in Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC materials was characterized by Raman spectroscopy. As shown in Figure 2c, defect-induced carbon (band D) and graphitic carbon (band G) correspond to the two peaks at 1334 cm⁻¹ and 1590 cm⁻¹, respectively, which can prove that carbon was successfully introduced into the composite. Furthermore, the specific surface area of $Bi_2Se_{3-x}Te_x@NC$ (x = 1) composites was investigated by N2 adsorption-desorption isotherms. As illustrated in Figure 2d, the isotherm is type IV, indicating that the $Bi_2Se_{3-x}Te_x@NC$ composite is a mesoporous material. In addition, the specific surface area of the $Bi_2Se_{3-x}Te_x@NC$ composite is 41.62 m² g⁻¹. The higher specific surface area facilitates the electrolyte to move around in the active material and provides more active sites for redox reactions, which improves the material's electrochemical performance.



Figure 2. (a) XRD patterns of $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$ nanocomposites. (b) The systematic shift of the 015 peak in expanded view of XRD. (c) Raman spectrum. (d) N_2 absorption–desorption isotherm of $Bi_2Se_{3-x}Te_x@NC$.

To further explore the chemical state of each element in the Bi₂Se_{3-x}Te_x@NC composite, we carried out the XPS test. The presence of the elements Bi, Se, Te, C, N, and O in the Bi₂Se_{3-x}Te_x@NC composite is clearly evident from the measured spectra (Figure 3a). In Figure 3b, Bi $4f_{5/2}$ and Bi $4f_{7/2}$ peaks manifest at approximately ~162.4 and ~157.1 eV, respectively [29]. Furthermore, the peaks at 158.8 and 164.2 eV are attributable to Se $3p_{3/2}$ and Se $3p_{1/2}$, respectively. In the Se 3d spectrum (Figure 3c), two peaks at 52.7 and 53.7 eV are associated with Se $3d_{5/2}$ and Se $3d_{3/2}$ [30]. Meanwhile, two peaks at 585.8 and 575.4 eV should be assigned to Te $3d_{3/2}$ and Te $3d_{5/2}$ for the Te 3d region (Figure 3d). Furthermore, the binding energies at 582.1 and 571.7 eV correspond to metallic Te [28]. The C 1s spectrum found between 281 and 294 eV (Figure 3e) can be divided into peaks at ~287.9 (C=C), ~286.1 (C–N), and ~284.8 eV (C=O), respectively [31].

Figure 4 illustrates the thermogravimetric (TG) curves of the samples heated in air from room temperature to 550 °C at a heating rate of 10 °C min⁻¹. TGA analyses were performed for both commercial Bi₂Se₃ (99.99%) purchased from Adamas-beta and as-synthesized $Bi_2Se_{3-x}Te_x@NC (x = 1)$. Based on the TGA results, the weight loss of commercial Bi_2Se_3 is 14.5 wt%. Between 400 °C and 550 °C, the weight of Bi₂Se_{3-x}Te_x@NC decreases dramatically as a result of the oxidation of the material to Bi_2O_3 , SeO_2 and TeO_2 [32]. The carbon content of $Bi_2Se_{3-x}Te_x@NC$ (x = 1) can be calculated to be 10.1 wt%. The carbon content of this composite is much lower than that in previous reports. Multi-core yolk-shellstructured Bi₂Se₃@C contains about 27.0 wt% carbon [33]. Bismuth nanoparticles, which are embedded in carbon spheres, contain in excess of 56 wt% carbon [8]. Bi dots confined by functional carbon samples contain more than 60% carbon [9]. Although volume expansion can be accommodated by hollow structures or dispersing Bi₂Se₃ nanoparticles within a carbon matrix, these structures may have the disadvantage of reducing the overall volumetric energy density of the anodes. It is well known that the hollow structure has a low pack density, and the significant carbon content of the composite can reduce the effective active materials of Bi₂Se₃. Therefore, in this work, $Bi_2Se_{3-x}Te_x@NC$ with low carbon content is expected to have outstanding electrochemical storage performance without sacrificing volumetric energy density. In addition, the microstructure of the sample was observed by

Scanning Electron Microscope (SEM). As shown in Figure 5a,b, $Bi_2Se_{3-x}Te_x@NC$ exhibits a relatively regular nanosheet structure, with the diameter of the nanosheets ranging from 200 to 500 nm. The elemental mapping results of $Bi_2Se_{3-x}Te_x@NC$ (x = 1) composites (Figure 5c) show that the material contains Bi, Se, Te, C, and N. N doping can both improve migration kinetics and enhance lithium storage performance [34,35].



Figure 3. XPS (a) survey spectrum, (b) Bi 4f, (c) Se 3d, (d) Te 3d, and (e) C 1s spectra of $Bi_2Se_{3-x}Te_x@NC$ nanocomposite.



Figure 4. TG curves of the commercial Bi_2Se_3 and as-prepared $Bi_2Se_{3-x}Te_x@NC$.



Figure 5. (a,b) SEM images and (c) elemental mappings (Bi, Se, Te, C, and N) of Bi₂Se_{3-x}Te_x@NC.

The electrochemical performance of Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC was evaluated using CR2016 coin cells. The amount of active materials loaded onto each electrode was around 1.5–2.0 mg cm⁻². The cycling was tested at the current density of 0.1 A g⁻¹, and the rate performance was studied under the current density of $0.1/0.2/0.5/1.0/2.0 \text{ Ag}^{-1}$. Figure 6a displays the CV curves of the samples tested at a scan rate of 0.1 mV s^{-1} , within the voltage range of 0.01–3.0 V (vs. Li⁺/Li). During the first cathodic scan, the cathodic peak at 1.39 V indicates the conversion of Bi₂Se₃ to Li₂Se, Li₂Te, and metallic Bi. The subsequent peak at 0.69 V may be attributed to the formation of a Li₃Bi alloy and a solid electrolyte interface. On the initial anodic scan, a distinct anodic peak appears at 0.93 V. This could lead to the conversion of Li3Bi to metallic Bi through oxidation. The peaks at 1.89 and 2.14 V reflect the formation of Bi_2Se_2Te . The CV curves of the second and subsequent cycles are in good agreement with the curve of the first cycle, suggesting the excellent cycle stability of the $Bi_2Se_{3-x}Te_x@NC$ composite. Figure 6b shows the galvanostatic discharge-charge curves of $Bi_2Se_{3-x}Te_x@NC$ composites at 0.1 A g⁻¹. There is a clear difference in the galvanostatic charge/discharge (GCD) curves between the first cycle and the following cycles. This could be attributed to the irreversible reactions such as solid electrolyte interface (SEI) formation. The $Bi_2Se_{3-x}Te_x@NC$ charging and discharging curves show multiple distinctive voltage plateaus, which indicates a significant phase transformation. For the discharging curve, plateaus with a voltage of around 1.4 V and 0.7 V are observed. For the charging curve, plateaus with voltage of around 0.85 V and 2.1 V can be easily identified. All peaks on the CV curves (Figure 6a) are well matched with charge–discharge plateaus on the GCD plot. During the first cycle, the $Bi_2Se_{3-x}Te_x@NC$ composite demonstrated charge and discharge specific capacities of 558.4 and 696.6mAh g^{-1} , respectively, and the Coulombic efficiency of the initial cycle was relatively low at 80.2%, which was mainly due to the SEI formation during the first cycle.

Figure 6c shows the Coulombic efficiency of $Bi_2Se_{3-x}Te_x@NC$ at 0.1 A g^{-1} and the cycling stability of $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$. The first-cycle specific capacities of $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$ are 654.9 and 696.6 mAh g^{-1} , respectively. In the 60th cycle, the reversible specific capacity of $Bi_2Se_{3-x}Te_x@NC$ dropped to 464.0 mAh g^{-1} , and the Coulombic efficiency increased to around 96.9%. However, the specific capacity of $Bi_2Se_3@NC$ material dropped to 401.9 mAh g^{-1} after 60 cycles. This shows that the $Bi_2Se_{3-x}Te_x@NC$ composite has better electrochemical performance than $Bi_2Se_3@NC$. This provides new ideas for improvements to bismuth-based anode materials.



Figure 6. (a) Cyclic voltammetry curves and (b) discharge/charge curves of $Bi_2Se_{3-x}Te_x@NC$ nanocomposites. (c) Cycle performance and (d) rate capabilities of $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$.

The anode materials $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$ (x = 1) underwent rate performance testing at the current densities of 100, 200, 500, 1000, and 2000 mA g⁻¹, which are shown in Figure 6d. In comparison to $Bi_2Se_3@NC$, the discharge specific capacities of $Bi_2Se_{3-x}Te_x@NC$ composites at 100, 200, 500, 1000, and 2000 mA g⁻¹ are 571.7, 522.8, 465.9, 418.6, and 382.2 mAh g⁻¹, respectively. Furthermore, when the current density returns to 100 mA g⁻¹, the discharge specific capacity can be restored to 481.2 mAh g⁻¹. Under the same current density, the discharge specific capacities of $Bi_2Se_3@NC$ materials are 555.6, 470.3, 387.3, 351.5, and 317.5 mAh g⁻¹, respectively.

The specific capacity of the previously reported commercial Bi₂Se₃ anode was 66.2 mAh g⁻¹ at a current density of 0.2 A g⁻¹ and 43.0 mAh g⁻¹ at 2 A g⁻¹, respectively. The commercial Bi₂Se₃ without carbon coating shows drastic capacity fading even after a few cycles. It almost lost 50 percent of its initial capacity over five cycles [33]. However, Bi₂Se_{3-x}Te_x@NC exhibits quite stable cycling performance during 60 cycles and well-maintained capacity. Coulombic efficiency of Bi₂Se_{3-x}Te_x@NC is more than 97%, indicating that side reactions between electrolyte and electrode are minimized compared with bare Bi₂Se₃. Thus, Bi₂Se_{3-x}Te_x@NC exhibits much higher discharge capacity and superior cycling stability than both commercial Bi₂Se₃ and Bi₂Se₃@NC. The superior electrochemical performance can be credited to the synergetic effect of nitrogen-doped carbon coating and Te doping.

In order to further explore the electrochemical performance of the Bi₂Se_{3-x}Te_x@NC composite, we conducted an EIS study of the Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC cells before cycling and after 60 cycles (Figure 7). The curves in Nyquist plots exhibit compressed semicircles in the high-frequency region and an inclined line in the low-frequency region. In the equivalent circuit diagram, R_s, R_f, and R_{ct} represent the solution resistance, the resistance of SEI film formation, and the charge transfer resistance, respectively. W₀ and CPE are denoted as Warburg impedance and constant phase elements, respectively. For the fresh cell, the R_{ct} of Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC is 616.5 and 162.3 Ω , respectively. After 60 cycles, the R_{ct} of Bi₂Se₃@NC and Bi₂Se_{3-x}Te_x@NC is reduced to 187.3 and 54.6 Ω , respectively. The smaller R_{ct} of the Bi₂Se_{3-x}Te_x@NC than that of the Bi₂Se₃@NC suggests that the Te-doped anode possesses better charge transfer kinetics and higher electronic conductivity.



Figure 7. Nyquist plots of $Bi_2Se_3@NC$ and $Bi_2Se_{3-x}Te_x@NC$ (**a**) fresh cells before cycling; (**b**) after 60 cycles, and the equivalent circuit model is plotted as the inset.

4. Conclusions

In conclusion, Te-doped Bi₂Se₃@NC composites were synthesized successfully as a novel anode material for LIBs. Te was successfully incorporated into the crystal lattice, which was confirmed by the XRD technique. The impact of Te on the electrochemical performance of the half-cell was evaluated. The Bi₂Se_{3-x}Te_x@NC composites demonstrated better electrochemical performance than that of Bi₂Se₃@NC.The specific gravimetric capacities of the Bi₂Se_{3-x}Te_x@NC composites for initial discharge and charge were 696.6 and 558.4 mAh g⁻¹, respectively. Bi₂Se_{3-x}Te_x@NC composites delivered a specific discharge capacity of 500 mAh g⁻¹ at 0.1 A g⁻¹ for 60 cycles. This study introduces a straightforward doping engineering strategy for improving Bi₂Se₃ conversion-alloying-type anode material. However, the strategy of doping to alter the properties and electrochemical performance of alloyed anode materials is not always effective, as it may be more susceptible to degradation from a thermodynamic perspective. It is worth investigating and designing an optimized strategy for other advanced electrode materials in the near future.

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