Zn$_2$GeO$_4$ nanorods grown on carbon cloth as high performance flexible lithium-ion battery anodes

T. T. Yu$^{ab}$ H. L. Liu$^{ab}$ M. Huang$^{ab}$ J. H. Zhang$^{\ast ab}$ D. Q. Su$^{ab}$ Z. H. Tang$^{ab}$ J. F. Xie$^{ab}$ Y. J. Liu$^{ab}$ A. H. Yuan$^{ab}$ and Q. H. Kong$^c$

To improve the electrical conductivity and cycling stability of germanium compounds as anode materials for lithium ion batteries (LIBs), Zn$_2$GeO$_4$ nanorods grown on carbon cloth (Zn$_2$GeO$_4$/CC) were designed and fabricated by a simple hydrothermal process combined with a post-annealing treatment. The Zn$_2$GeO$_4$/CC composites possess hierarchical porosity and a network structure. Serving as free-standing and binder-free anodes for LIBs, they exhibit high specific capacity and excellent reversibility. A discharge capacity as high as 1851.9 mA h g$^{-1}$ is attained at a current density of 200 mA g$^{-1}$, and the Zn$_2$GeO$_4$/CC electrode still maintains a high reversible capacity of 1302.3 mA h g$^{-1}$ after 200 cycles. Even at a high specific current of 2000 mA g$^{-1}$, it still retains a capacity of 847.5 mA h g$^{-1}$. The superior electrochemical performance of the Zn$_2$GeO$_4$/CC composites is attributed to the synergistic effects of the hierarchical porosity, Zn$_2$GeO$_4$ nanorods, and 3D carbon cloth network structure, which can effectively accommodate the huge volume change of the Zn$_2$GeO$_4$ nanorods during cycling and maintain perfect electrical conductivity throughout the electrode. Moreover, the excellent mechanical flexibility of the Zn$_2$GeO$_4$/CC composites makes the material a promising candidate for self-supported and flexible electrodes for LIBs.

Introduction

Entering a new era of green energy, several criteria, such as cost, cycle life, safety, efficiency, energy, and power, need to be considered when developing electrical energy-storage systems for transportation and grid storage.\textsuperscript{1–3} Rechargeable lithium ion batteries (LIBs) are one of the prospective candidates because of their inherent advantages including high energy density, long life span, no memory effect, and environmental nontoxicity.\textsuperscript{4,5} However, although graphite used as an anode material in commercial LIBs offers stable cycling performance and low cost, its low theoretical capacity (372 mA h g$^{-1}$) greatly limits its further application in portable electronics and electric vehicles.

To date, many studies have been devoted to the development of high-capacity lithium alloying anodes of silicon (Si) and germanium (Ge) because of their high theoretical capacities of 4200 and 1600 mA h g$^{-1}$, respectively.\textsuperscript{6–9} Between them, Ge has higher lithium-ion diffusivity than Si (400 times faster), higher electrical conductivity (104 times higher than that of Si), and low working potential. Nevertheless, the major drawbacks for the application of the pure Ge anode material are the high price and large volume expansion (370%) during the lithium alloying and dealloying processes, which lead to structural damage and rapid decay in the capacity, limiting the application of Ge anodes.\textsuperscript{10} To reduce the price, germanium compounds, such as GeO$_2$ and Zn$_2$GeO$_4$, have been proposed as intriguing materials for lithium storage applications due to their high theoretical charge–discharge capacity.\textsuperscript{11,12} GeO$_2$ can deliver a specific capacity of up to 2152 mA h g$^{-1}$ and reversibly store 8.4 Li$^+$ ions, and Zn$_2$GeO$_4$ can also exhibit a high theoretical charge–discharge capacity of 1443 mA h g$^{-1}$.\textsuperscript{11,14} Additionally, germanium compounds have several advantages over pure Ge, such as lower cost and better chemical stability and cyclability. Unfortunately, such binary or ternary Ge compounds are not effective for improving the cycling performance during drastic volume change and they have low electrical conductivity.

To address some of these issues related to the use of Ge and its compounds as anodes, many researchers have devoted attention to enhancing the electrochemical performances by constructing uniform hybrid structures with carbon, carbon nanotubes, graphene, etc. Paper-like free-standing Ge and single-walled carbon nanotube (SWCNT) composite anodes were prepared by the vacuum filtration of Ge/SWCNT composites. The paper anode with good Ge nanoparticle distribution in the SWCNT network offered better electrical contact, which aided the improvement of the capacity and cycling stability of the superior anodes in LIBs.\textsuperscript{15} Mesoporous Ge/GeO$_2$/carbon...
composites were prepared by block copolymer directed coassembly, and exhibited high coulombic efficiency and reversible capacity (1631 mA h g⁻¹) and excellent cyclability due to the synergistic effects of the mesoporous structure, conductive carbon, and metallic Ge. Co,GeO₄/graphene nanocomposites were synthesized by a hydrothermal method, and exhibited high reversible capacity and good cycling performance and rate capability due to the high electronic conductivity and high specific area of graphene. In general, most carbon based composites employ either graphene or carbon nanotubes as the carbon substrates, and a traditional method needs to be used to further prepare electrodes with conductive carbon and a binder. This may cause some problems, such as the exfoliation of the active materials from the current collector, loss of the entire composite capacity, etc. If the active material can be directly coated onto some special substrate, a free-standing and binder-free electrode can be attained to overcome the disadvantages and achieve high performance. Recently, Yu et al. fabricated a 3D hierarchical MoS₂ nanoflake array/carbon cloth with good rate discharging/charging stability as an anode material for flexible LIBs.

In this work, a novel strategy was proposed for the simultaneous production of a high performance flexible Zn₂GeO₄/CC electrode. GeO₂ acted as a raw material because of the lower cost and an activated carbon fiber cloth was chosen as the conductivity framework for providing fast transport paths for electrons and lithium ions. Most importantly, Zn₂GeO₄/CC composites can be used directly as a free-standing and binder-free electrode. The hierarchical structure remains stable for Li⁺ insertion and extraction and is hence expected to exhibit excellent charge-discharge performance. When evaluated as an anode material for LIBs, the as-formed Zn₂GeO₄/CC composites exhibited high reversible lithium storage capacity, long cyclability, and excellent rate capability. The excellent electrochemical performance was attributed to the Zn₂GeO₄ nanorods, which were uniformly grown on the carbon cloth to form a porous surface structure and can provide a large electrode-electrolyte interfacial area, leading to an improved rate performance, and the porous Zn₂GeO₄/CC composites can buffer the large volume change caused in Zn₂GeO₄ during cycling. The developed strategy, being composed of a simple preparation method, using low-cost raw materials, and forming high-performance electrode products, will effectively promote the commercialization of flexible energy storage devices.

**Experimental section**

**Materials**

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, ≥99.0%), ammonium fluoride (NH₄F, ≥99.0%), urea (CO(NH₂)₂, ≥99.0%), and sodium hydroxide (NaOH, ≥99.0%) were purchased from the Aladdin Chemical Co. Germanium dioxide (GeO₂, ≥99.0%), nitric acid (HNO₃, ≥99.0%), ethanolic, and acetone were obtained from the traditional Chinese Medicine Reagent Co. All the chemicals were used without further purification. Carbon cloth with hydrophilic surfaces (WOS 1002) was purchased from the Tianwan Carbon Technology Co.

**Fabrication of Zn₂GeO₄/CC composites**

The carbon cloth was cleaned by sonication sequentially in acetone, deionized water, and ethanol for 2 h, respectively. Subsequently, nitric acid was used to activate the well-cleaned carbon cloth for 6 h. The Zn₂GeO₄/CC composites were fabricated via a two-step process. In a typical process, 2 mmol Zn(NO₃)₂·6H₂O, 1 mmol GeO₂, 2 mmol NH₄F, 5 mmol CO(NH₂)₂, and 4 mmol HNO₃ were dissolved in 30 mL of distilled water under continuous stirring. The pH value was adjusted to 8 by NaOH solution. Then, the homogeneous solution was transferred into Teflon-lined stainless autoclaves with carbon cloth (diameter of 13 mm) and heated at 200 °C for 24 h. After cooling down to room temperature, the products were collected and washed for at least three cycles using deionized water, and dried at 60 °C in a vacuum box. Afterwards, to improve the acting force between the Zn₂GeO₄ nanorods and carbon cloth, thermal treatment of the as-prepared product was performed at 450 °C for 2 h in N₂ atmosphere to obtain Zn₂GeO₄/CC composites. The mass loading of Zn₂GeO₄ on the carbon cloth was confirmed by weighing, and the results show that the average mass is about 16 mg on the carbon cloth (about 16 mg) with a diameter of 13 mm.

**Structural characterization**

The crystal structure and phase of the Zn₂GeO₄/CC composites were characterized by X-ray diffraction (XRD) measurements using a Shimadzu XRD-6000 diffractometer with Cu-Kα radiation (0.15406 nm). The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab-250Xi) with Al-Kα radiation) with a base pressure of 2 × 10⁻¹⁰ mbar. The surface morphology of the samples was depicted by field emission scanning electron microscopy (FESEM, ZEISS Merlin Compact). In addition, detailed microstructures were investigated using high resolution transmission electron microscopy (HRTEM, JEM-2100F) and energy dispersive X-ray spectroscopy (EDS, Oxford X-Max).

**Electrochemical measurements**

The Zn₂GeO₄/CC composites were used as working electrodes without adding any ancillary materials. Coin-type half cells (CR2032) were laboratory-assembled in an argon-filled glove box with the oxygen and water content below 1 ppm. A piece of the Zn₂GeO₄/CC composites was used directly as the working electrode. The non-aqueous electrolyte used in the cells was 1 mol L⁻¹ LiPF₆ dissolved in ethylene carbonate and diethyl carbonate (EC : DEC, 1 : 1 in vol%). A Celgard 2400 microporous polypropylene membrane and Li foil were used as the separator and counter electrode, respectively. Coin-type half-cell charge and discharge tests were conducted on a LAND (China) battery program-control test system at various current densities between 0.01 and 3.0 V at 25 ± 1 °C. In this work, the capacity values were based on the mass of Zn₂GeO₄ and the carbon cloth acted as a support. The cyclic voltammetry (CV) curves were recorded on a CHI660D workstation (Shanghai, China) between 0.01 and 3 V (vs. Li⁺/Li⁺) at a scanning rate of 0.2 mV s⁻¹. The electrochemical impedance spectra (EIS) of the cells were also
Results and discussion

The synthesis strategy of the Zn$_2$GeO$_4$/CC electrode is schematically illustrated in Fig. 1, where Zn$_2$GeO$_4$ nanorods are grown on the surface of a carbon fibre cloth. The surface changes from smooth to porous because of the anisotropic growth of the Zn$_2$GeO$_4$ nanorods. The interlaced network porous structure of the carbon cloth is favorable for the electrochemical reaction of the lithium ions. The formation of Zn$_2$GeO$_4$ nanorods can effectively accommodate the huge volume change. The FESEM images in Fig. 2 show the morphologies of the carbon cloth, commercial GeO$_2$, and Zn$_2$GeO$_4$/CC composites. In the images in Fig. 2a, the carbon cloth shows a microstructure of compact bundle fibers, which is actually an artificial pseudo-two-dimensional network with an ordered texture structure, and each carbon fiber with a smooth surface has a uniform diameter of around 8.5 μm. Fig. 2b shows that the commercial GeO$_2$ samples are bulky grains with diameters of more than 5 μm. It is well known that the large volume expansion of anode materials will lead to a rapid decline in the capacity during the lithiation and delithiation processes. Therefore, to decrease the size, enhance the conductivity, and reduce the cost, Zn$_2$GeO$_4$/CC composites were devised and fabricated using commercial GeO$_2$ grains as raw materials and carbon cloth as a conductivity network structure, respectively. Fig. 2c is a FESEM image of the Zn$_2$GeO$_4$/CC composites. In the images in Fig. 2a, the carbon cloth shows a microstructure of compact bundle fibers, which is actually an artificial pseudo-two-dimensional network with an ordered texture structure, and each carbon fiber with a smooth surface has a uniform diameter of around 8.5 μm. Fig. 2d shows that the Zn$_2$GeO$_4$/CC composites create a hierarchical nanostructure with an interconnected network porous structure of the carbon cloth is favorable for the electrochemical reaction of the lithium ions. The formation of Zn$_2$GeO$_4$ nanorods can effectively accommodate the huge volume change. The FESEM images in Fig. 2 show the morphologies of the carbon cloth, commercial GeO$_2$, and Zn$_2$GeO$_4$/CC composites. In the images in Fig. 2a, the carbon cloth shows a microstructure of compact bundle fibers, which is actually an artificial pseudo-two-dimensional network with an ordered texture structure, and each carbon fiber with a smooth surface has a uniform diameter of around 8.5 μm. Fig. 2b shows that the commercial GeO$_2$ samples are bulky grains with diameters of more than 5 μm. It is well known that the large volume expansion of anode materials will lead to a rapid decline in the capacity during the lithiation and delithiation processes. Therefore, to decrease the size, enhance the conductivity, and reduce the cost, Zn$_2$GeO$_4$/CC composites were devised and fabricated using commercial GeO$_2$ grains as raw materials and carbon cloth as a conductivity network structure, respectively. Fig. 2c is a FESEM image of the Zn$_2$GeO$_4$/CC composites showing that the fiber structure of the carbon cloth still remained. The carbon fiber is covered with numerous Zn$_2$GeO$_4$ nanorods, and the Zn$_2$GeO$_4$/CC composite fibers have a uniform diameter of approximately 10 μm. The high magnification image in Fig. 2d shows that the Zn$_2$GeO$_4$ nanorods have uniform size with a length and diameter of about 80 nm and 30 nm, respectively. The mass ratio of the Zn$_2$GeO$_4$ nanorods to carbon cloth is about 1 : 1, which was confirmed by weighing. The composites create a hierarchical nanostructure with abundant open space and an electroactive surface and buffer the volume change resulting from external bending and repeated Li$^+$ insertion–extraction. Additionally, the carbon cloth is a highly conductive textile with excellent mechanical flexibility and strength.

The crystal structure and composition of the Zn$_2$GeO$_4$ nanorods were further analyzed by TEM, HRTEM and EDS, and the Zn$_2$GeO$_4$ nanorods were obtained by the sonication of the Zn$_2$GeO$_4$/CC composites in an N-methyl pyrrolidone solvent. Fig. 3a is a low magnification TEM image of the Zn$_2$GeO$_4$ nanorods, which shows that the size of the Zn$_2$GeO$_4$ nanorods is relatively uniform. Fig. 3b shows the high magnification TEM image of a single Zn$_2$GeO$_4$ nanorod, revealing that the diameter is about 30 nm. Fig. 3c is the HRTEM image of a Zn$_2$GeO$_4$ nanorod, and the inset is its corresponding selected area electron diffraction (SAED) image, revealing that a Zn$_2$GeO$_4$ nanorod is perfectly monocristalline. The well-defined lattice fringes with lattice spacings of 0.71 nm and 0.30 nm correspond to the (110) and (113) lattice planes of the rhombohedral phase of Zn$_2$GeO$_4$, respectively. This suggests that the growth direction of the Zn$_2$GeO$_4$ nanorods was along the [110] plane. Furthermore, the combination of the EDS spectrum with the element mapping images of Zn$_2$GeO$_4$ provides evidence for the existence of a homogeneous distribution of Zn, Ge and O elements, as shown in Fig. 3d and e. Fig. 3f shows the images of the 3D interconnected Zn$_2$GeO$_4$/CC electrode, which can be easily curved with tweezers. It can be clearly observed that the electrodes exhibited excellent flexibility, which makes them possible for application in flexible devices.

The composition and phase purity of the carbon cloth and Zn$_2$GeO$_4$/CC composites were examined by XRD and are represented in Fig. 4. The sharp and strong diffraction peaks can be indexed to rhombohedral Zn$_2$GeO$_4$ (JCPDS card no. 011-0687) with lattice constants of $a = b = 1.4231$ nm and $c = 0.953$ nm. The observed peaks at 26° and 43° can be ascribed to the (002) and (101) planes of the carbon cloth substrate, which can also be observed in the XRD pattern of the pure carbon cloth. No additional diffraction peaks other than those of Zn$_2$GeO$_4$ and the carbon cloth were observed, implying the high purity of the Zn$_2$GeO$_4$/CC composites. To gain further insight into the chemical composition of the Zn$_2$GeO$_4$ nanorods, XPS measurement was performed. As shown in Fig. 5a, the survey

![Fig. 1](image1.png)  A schematic illustration of the synthesis of flexible 3D Zn$_2$GeO$_4$ nanorods/carbon cloth and the operating principles when used in rechargeable LIBs.

![Fig. 2](image2.png)  (a) The FESEM image of pure carbon cloth, and the inset is the FESEM image of a single carbon fiber; (b) the commercial GeO$_2$ powder; (c and d) the Zn$_2$GeO$_4$/CC composites with different magnifications, and the inset in (c) is the FESEM image of a single Zn$_2$GeO$_4$/CC fiber.
XPS spectrum revealed that the sample was composed of Zn, Ge and O species. Fig. 2b shows a high-resolution Zn 2p XPS spectrum, which shows two typical characteristic peaks of the oxidation state of Zn$^{2+}$, corresponding to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ at 1022.18 eV and 1045.4 eV. The high-resolution Ge 3d XPS spectrum (Fig. 2c) presents a sharp peak at 31.2 eV, which could be attributed to the Ge–O bond. Finally, the observed peak at 530.81 eV is assigned to O 1s, as shown in Fig. 2d.

To evaluate the electrochemical lithium storage of the unique microstructure, the 3D porous Zn$_2$GeO$_4$/CC composites were directly applied as anodes for LIBs. Fig. 3a shows the first three CV curves of the Zn$_2$GeO$_4$/CC electrode in the voltage range of 0–3 V at a scan rate of 0.1 mV s$^{-1}$. During the initial cathodic sweep, a strong reduction peak at around 0.28 V was observed, which was assigned to the decomposition of Zn$_2$GeO$_4$ as well as irreversible reactions that are related to the formation of SEI films and the decomposition of the electrolyte. This peak
shifts to 0.58 V in the second cycle and 0.43 V in the third cycle. The irreversible phenomenon in the first several cycles was partially attributed to the multistep reaction of Zn$_2$GeO$_4$. In the anodic scan process, a broad oxidation peak at 1.1 V was observed, which was associated with the delithiation of the Li-metal alloys. Remarkably, the CV curves did not change significantly after the first cycle, revealing good stability and reversibility for the insertion and exaction of lithium ions. Fig. 6b presents the voltage–capacity profiles of the Zn$_2$GeO$_4$/CC anode for the 1$^{st}$, 2$^{nd}$, 10$^{th}$, and 200$^{th}$ cycles at a current rate of 200 mA g$^{-1}$ between 0.01 and 3.0 V. During the first discharge process, the main potential plateau is located at around 0.1 V (vs. Li$^+$/Li), which agrees well with the lithiation process of Zn$_2$GeO$_4$, and the initial discharge/charge capacity is found to be 1851.9/1716.2 mA h g$^{-1}$, corresponding to the initial coulombic efficiency (CE) of 92.7%. In general, the irreversible capacity loss is mainly attributed to the formation of a solid electrolyte interface (SEI) membrane from the decomposition of the electrolyte, which is commonly observed for most anode materials. 24,25 The Zn$_2$GeO$_4$/CC composites exhibited sloping voltage profiles, and the long plateaus at about 0.74 V shown in the first discharge disappeared during the 2$^{nd}$, 10$^{th}$, and 200$^{th}$ discharges, suggesting that the reductive decomposition of the electrolyte was effectively prevented due to the formation of a SEI film in the first discharge, which greatly relieved the irreversible capacity loss of the following cycles. 26,27 Therefore, the second discharge/charge capacity is found to be 1699.5/1595.8 mA h g$^{-1}$, and the CE increases to 96.1%. After the 200$^{th}$ cycle, the reversible capacity maintained a nearly constant value of approximately 1302.3 mA h g$^{-1}$ and the CE steadily reached about 99.9%.

The rate performance of the Zn$_2$GeO$_4$/CC electrode was further studied by cycling at different current densities ranging from 100 to 2000 mA g$^{-1}$. As shown in Fig. 6c, the capacity decreased from 1615.9 to 1496, 1265.8, 1222.2, 1032.1 and 847.5 mA h g$^{-1}$ when the current density was increased from 100 to 200, 500, 800, 1000, and 2000 mA g$^{-1}$, respectively. Notably, a capacity of 847.5 mA h g$^{-1}$ was retained at the relatively high current density of 2000 mA g$^{-1}$, illustrating the high rate capability of the Zn$_2$GeO$_4$/CC electrode. After cycling at the highest current density of 2000 mA g$^{-1}$, the capacity recovered to about 1573.4 mA h g$^{-1}$ as the current density was switched back to 100 mA g$^{-1}$, corresponding to a capacity retention of ~97.4%, which indicates high stability as well as excellent reversibility of the electrode. Fig. 6d displays the cycling performance and coulombic efficiency of the Zn$_2$GeO$_4$/CC electrode at 200 mA g$^{-1}$ for 200 cycles in a voltage range of 0.01 to 3 V. After 200 cycles, the anode still had a reversible discharge capacity of 1302.3 mA h g$^{-1}$, reaching 50.6% of the first discharge capacity. Meanwhile, the CE quickly increased to 92.7% for the second cycle from 68.6% for the first cycle, and furthermore, it approached 99.9% after 200 cycles, showing excellent reversibility of the electrode. For comparison, the Zn$_2$GeO$_4$ nanorods were also selected to do comparative experiments by the same assembly process, and the capacity profile for 100 charge–discharge cycles is shown in Fig. 6d. The reversible capacities of the Zn$_2$GeO$_4$ nanorods can be retained at 398 mA h g$^{-1}$ at the end of 100 charge–discharge cycles, and they also present decent cyclic stability. Nevertheless, the reversible capacity of the Zn$_2$GeO$_4$ nanorods is lower than that of the Zn$_2$GeO$_4$/CC composites. The improved rate performance was attributed to the Zn$_2$GeO$_4$/CC electrode buffering the large volume change, and the hierarchical structure remained stable for Li-ion insertion and extraction. To further understand the lithium-storage properties, an AC impedance measurement was employed. The electrochemical impedance spectra (EIS) of the Zn$_2$GeO$_4$/CC composites were investigated with a fresh cell and after 200 cycles at 200 mA g$^{-1}$, as shown in Fig. 7. The Nyquist plots consist of one semicircle in the high frequency region and a straight line in the low frequency region. The semicircle portion is related to the reactions occurring on the electrode–electrolyte interface, which reflects the charge transfer impedance and SEI impedance. The results show that the Zn$_2$GeO$_4$/CC composite electrode after 200 cycles exhibited lower charge transfer resistance than the fresh cell, which indicates that the fresh cell had the highest charge transfer resistance. Compared with the inset, the semi-circle of the Zn$_2$GeO$_4$/CC electrode at high frequency is much smaller than that of the carbon cloth, indicating that the Zn$_2$GeO$_4$/CC electrode also had lower charge transfer resistance than the carbon cloth. This decreased charge transfer resistance was attributed to the improved electrical contact between the Zn$_2$GeO$_4$ nanorods and carbon cloth substrate. 28,29 The whole impedance value of the Zn$_2$GeO$_4$/CC electrode decreased when undergoing cycling, implying a better electrochemical performance based on the knowledge of traditional planar electrodes. 30 However, the Zn$_2$GeO$_4$/CC electrode suffered an obvious capacity decay, which can be interpreted as a small part of the Zn$_2$GeO$_4$ nanorods detaching from the carbon cloth after 200 cycles, resulting in the decreased capacity. 31 Additionally, the results suggest that the higher diffusivity of the lithium ions with the increasing charge–discharge cycles reduced the charge transfer resistance. To confirm the 3D porous Zn$_2$GeO$_4$/CC network structure can relieve the volume expansion, the morphology and structure of the Zn$_2$GeO$_4$/CC electrode after 20 cycles at 200 mA g$^{-1}$ were characterized by FESEM observations.
performance, and highly valuable porous carbon based composites are expected to promote the practical application of wearable and portable energy storage devices.

**Conflicts of interest**

There are no conflicts to declare.

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