



# Porous Zn<sub>2</sub>GeO<sub>4</sub> nanowires with uniform carbon-buffer layer for lithium-ion battery anodes with long cycle life



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## ABSTRACT

Germanium-based multimetallic-oxide materials have attracted significant attention as high-capacity anodes for next generation lithium-ion batteries (LIBs). However, they suffer from poor cyclic stability due to extreme volume expansion and reduced electrical conductivity after repeated cycles. To circumvent these issues, we propose that Ge-based multimetallic-oxide nanowires can be synthesized with electrically conductive carbon to significantly enhance the cyclic stability of the Ge-based anodes. We prepare conformal-carbon-coated Zn<sub>2</sub>GeO<sub>4</sub> nanowires (NWs) using a microwave-induced hydrothermal method with subsequent thermal decomposition. The obtained carbon-coated Zn<sub>2</sub>GeO<sub>4</sub>-NW anode exhibits a discharge capacity of 485 mAh/g and a Coulombic efficiency (CE) of 98.4% after 900 cycles at 0.6C. Furthermore, these anodes exhibit outstanding rate-capability characteristics, even with an increased C-rate of 17.7C. This excellent electrochemical performance can be ascribed to the improved electron and ion transport provided and the structurally reinforced conductive layer comprising a conformal carbon layer. Therefore, it is expected that our approach can also be applied to other multimetallic-oxide materials, resulting in large, reversible capacities; excellent cyclic stabilities; and good rate capabilities for high-performance LIBs.

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## 1. Introduction

Germanium (Ge) is considered one of the most promising potential candidates to replace the conventionally used graphite anodes of lithium-ion batteries (LIBs). Due to the limitations of the specific capacity of graphite (372 mAh/g), it cannot meet the increasing requirements of LIBs for high-energy-density and -power capabilities [1]. Compared to representatively used silicon (Si) with its high energy density, the gravimetric capacity of Ge (1624 mAh/g) is less than that of Si (4200 mAh/g). On the other hand, the volumetric capacity of Ge (7366 Ah/L) is similar to that of Si (8344 Ah/L), due to the greater density of Ge [2–4]. Furthermore, Ge-based anodes, including various oxides, are expected to have the best rate capabilities due to their high conductivities and lithium-ion diffusivities that are several orders of magnitude greater than those of the material characteristics of

Si [5,6]. Moreover, the volume changes in Si-based materials are anisotropic shape changes during cycling. In contrast, Ge-based materials demonstrate isotropic volume changes, meaning that for the applications of LIBs, these Ge-based materials with homogenous volume changes can be designed more easily as compared to Si-based materials with anomalous volume changes [7,8]. Unfortunately, Ge- and Si-based materials cannot endure extreme volume expansions (260% for Ge and 400% for Si) during the lithium-alloying and -de-alloying processes, resulting in severe pulverization of the active materials and rapid degradations in capacity. To resolve this problem, various hybrids and morphologies with heteroatoms and carbonaceous materials have been investigated, including Ge nanowires (NWs) [9], Ge–C NWs [1], Ge–Si heterostructures [10], Si–Ge core-shell nanoarrays [11], Ge–C-graphene [12], Ge–Cu nanoparticles [13], and Si–Ge–Mo ternary composites [14] for LIBs. Among the various strategies, the use of a carbon-buffer layer is the best choice owing to the light weight and relatively low cost of carbon. In several earlier reports, the use of carbon as a buffer layer has shown promising electrochemical performance in terms of

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improved cyclability and specific capacity. However, the synthetic process is rather complicated and costly [15]. Accordingly, large-scale applications based on a Ge-based anode containing a carbon-buffer layer are rare. In order to achieve reasonable battery performance in relatively thick, slurry-based anodes, conductive carbon particles must be added to provide sufficient electrical conductivity through the layer. Passing electricity through the thick layer of an anode decreases the anode capacity, but more importantly, the carbon particles can segregate in the electrode during processing and as a result of mechanical stresses, it can lead to unreliable performance. Better electrical contact can be achieved via conformal carbon coating on an active material. Another issue that must be addressed here is the problem of feasibility as Ge is not an abundant or inexpensive material. Therefore, to discover a stable and high-capacity Ge-based compound, earth-abundant elements would be the best solution to cover all problems mentioned above. Recently, several Ge-containing multimetallic-oxide materials containing cheaper metal elements (Ca, Ba, Pb, and Zn) that effectively reduce the Ge content and the overall cost have been reported [16]. Among these cheaper elements, ZnO is the best choice for a high-performance-anode material since it has demonstrated the most satisfying performance to date. Other materials, such as CaO and BaO, are lithium-inert materials, hindering their satisfactory performances, and Pb also negatively affects the human body and environment [17,18]. Among them, Zn<sub>2</sub>GeO<sub>4</sub> is promising anode material due to its high theoretical specific capacity (1443 mAh/g) [19] and unique catalytic, and electronic properties [20].

Here, we report the electrochemical performances of conformal-carbon-coated Zn<sub>2</sub>GeO<sub>4</sub> NWs for LIBs. The Zn<sub>2</sub>GeO<sub>4</sub> NWs were produced via a microwave-assisted hydrothermal method, using GeO<sub>2</sub> and Zn(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O as reactants. The carbon was coated via thermal decomposition using C<sub>3</sub>H<sub>6</sub> gas in a conventional tube furnace. Battery performance was tested in half-cells and with *in situ* scanning electron microscopy (SEM) of NWs undergoing chemical lithiation. The *in situ* SEM experiments demonstrated that the carbon coating restricted the volume expansion during lithiation, resulting in improved electrochemical performance.

## 2. Experimental

### 2.1. Preparation of mesoporous Zn<sub>2</sub>GeO<sub>4</sub> NWs

The Zn<sub>2</sub>GeO<sub>4</sub> NWs were synthesized via a straightforward microwave-assisted hydrothermal method without any surfactant assistance. In a typical synthetic procedure, GeO<sub>2</sub> (0.209 g) and Zn(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (1.19 g) were added to 40 mL of deionized water. The mixture was stirred for 30 min. Then, NaOH solution was introduced dropwise to the vigorously stirred solution to adjust the pH. After additional agitation for 20 min, the obtained white, colloidal precipitate was transferred into a microwave vessel, sealed, and maintained at 150 °C for 10 min using a microwave synthesizer. Then, the precipitate was cooled naturally under ambient conditions.

### 2.2. Carbon-coating process

The ultrathin, carbon-coated, mesoporous Zn<sub>2</sub>GeO<sub>4</sub> NWs were prepared by loading the Zn<sub>2</sub>GeO<sub>4</sub> NWs (10 g) on a ceramic boat in a conventional tube furnace, and then they were thermally decomposed in an atmosphere of 10% C<sub>3</sub>H<sub>6</sub> and 90% Ar gases at a flow rate of 100 cc/min at 700 °C. The heating rate and holding time were 3 °C/min and 5 h, respectively. After the carbon coating, the tube was cooled to room temperature.

### 2.3. Characterizations of the Zn<sub>2</sub>GeO<sub>4</sub> NWs before and after carbon coating

The Zn<sub>2</sub>GeO<sub>4</sub> NWs and ultrathin, carbon-coated-Zn<sub>2</sub>GeO<sub>4</sub> powders were investigated via SEM (NOVA NanoSEM200, FEI Corp.) and transmission electron microscopy (TEM, Tecnai, FEI Corp.) with energy-dispersive X-ray spectroscopy (EDX). Furthermore, the crystal structure was determined by X-ray diffraction (XRD, Rigaku) analysis, equipped with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in the  $2\theta$  range of 20–80°. The quality of the carbon coating was investigated with Raman spectroscopy (wavelength of 632 nm, Nicolet Omega XR Dispersive Raman, Thermo Electron Corp.) at a low laser-power density and an exposure time of 4 s to avoid laser-induced thermal impacts during the measurements. The spectra were recorded at a resolution of 4 cm<sup>-1</sup> between 3000 and 90 cm<sup>-1</sup>. The carbon contents were measured with elemental analysis (EA). The samples were thermally decomposed in an excess of oxygen, and the combustion products, such as carbon dioxide, water, and nitric oxide, were collected. (The elemental composition of an unknown sample can be calculated via the measurement of the masses of these combustion products.) The specific surface area was determined via N<sub>2</sub> adsorption at 196 °C using an adsorption apparatus (Micromeritics ASAP 2010, USA) while the adsorption data was fitted to the Brunauer–Emmett–Teller (BET) equation. The specific pore volume was obtained from the total amount adsorbed at relative pressures near unity. The pore-size distribution was analyzed using the Barrett–Joyner–Halenda (BJH) method. For post-mortem analyses, the cycled 2032-coin-type cells were disassembled in an Ar-filled glove box, and a specially designed hermetic vessel was used to transfer the obtained anodes for analysis. For the X-ray photoelectron spectroscopy (XPS, Ulvac-PHI, PHI 85000 Versa Probe) analysis, photoelectron excitation was performed using Al K $\alpha$  (117.4 eV) radiation at a constant power of 100 W and pass energy of 15 kV. The diameter of the X-ray spot was 100  $\mu\text{m}$ . To observe the structural evolution, a direct solid-state lithiation test without an external electrical potential was performed using a nanomanipulator (MM3A, Kleindiek). To avoid oxidation, the entire process was carried out inside the dual-beam focused-ion-beam (FIB) chamber (Quanta 3D, FEI Corp.). The Zn<sub>2</sub>GeO<sub>4</sub> NWs were transferred from the substrate to the nanomanipulator's tungsten tip via Pt deposition in the FIB chamber. The bulk Li was cut inside the chamber to create a pristine surface. Subsequently, the harvested Zn<sub>2</sub>GeO<sub>4</sub> NWs was translated to the bulk Li where the fractured ends of the Zn<sub>2</sub>GeO<sub>4</sub> NWs made direct contact with the surface of the bulk Li. The entire lithiation process was exposed to the electron beam during the SEM measurements. Therefore, it might be possible to accumulate charges for different materials.

### 2.4. Cell fabrication and tests

A working electrode was manufactured by applying coating slurries consisting of Zn<sub>2</sub>GeO<sub>4</sub> NWs, and carbon-coated Zn<sub>2</sub>GeO<sub>4</sub> NWs as the active materials (60 wt%), Denka black (DB) as the conducting agent (20 wt%), and polyacrylic acid (PAA) as the binder (20 wt%) dissolved in ethanol on a copper-foil current collector. To evaporate the solvent in electrode, the slurry on Cu foil was dried in the oven at 60 °C for overnight and then the pre-dried electrode was then rolled and dried in a vacuum oven at 80 °C for 6 h. The loads of the active material of each electrode had thicknesses of 30  $\mu\text{m}$  and were in the range of 0.15 mg/cm<sup>2</sup>. All the specific capacities of the Zn<sub>2</sub>GeO<sub>4</sub> and carbon-coated-Zn<sub>2</sub>GeO<sub>4</sub> electrodes were calculated based on the total masses of the active materials, including each carbon layer. The test cells were comprised of a working electrode, lithium foil as the counter and reference electrodes, and a polypropylene (PP) membrane

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