



Metal-organic frameworks derived germanium oxide nanosheets for large reversible Li-ion storage



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ABSTRACT

A Ge-based metal-organic framework (MOF) precursor [C₆H₁₀(NH₂)₂Ge₃O₆] is used to fabricate two-dimensional GeO₂ nanosheets in this work. The obtained micrometer-sized GeO₂ nanosheet delivers superior lithium-storage capability during long cycling (an initial reversible capacity of 1315 mAh g⁻¹ at 100 mA g⁻¹ and the retained capacity of 1393 mAh g⁻¹ after 350 cycles). The observed large capacity and good cyclability have been mainly attributed to its nanosheet structure inherited from the MOF precursor, which can facilitate the electrolyte infusion and the lithium diffusion, maintain the structural stability, and alleviate the large volume change of the electrode during repetitive lithiation/delithiation process.

1. Introduction

Germanium-based electrode materials is a class of promising anodes because of its large theoretical capacity (1600 mAh g⁻¹) based on the maximum storage ability of 4.4 lithium atoms per Ge atom [1,2]. However, the critical challenge for germanium-based anode is that their cyclic stability is not satisfactory because of the large volume expansion accompanied with the lithiation/delithiation process and their poor electrical conductivity [3,4]. To solve these problems, the design of various nanostructures of germanium oxide and the introduction of carbon support/coating to Ge-based electrodes have been explored with enhanced electrochemical properties [5,6]. Metal-organic frameworks (MOFs), consisting of metal ions/clusters and organic ligands, have been extensively investigated for various applications such as catalysis, hydrogen storage, gas adsorption, etc. [7–9]. Recently, MOFs have been explored as the effective template/precursor to prepare porous metal-containing derivatives such as metal oxides, metal sulfides and their carbon composites [10–15]. In particular, their hydrophobic characteristic and the porous structure may be inherited from the MOF precursor, which can facilitate the infusion of organic electrolyte into the electrode and enhance the lithium-ion diffusion and storage. Several types of electrode materials were derived from metal-organic frameworks and exhibited enhanced electrochemical Li-storage properties [10–15]. To the best of our knowledge, there is only a single report about the synthesis of GeO₂ nanosheets [16], and the MOF-derived approach has not been used to fabricate GeO₂. This is also the first-time exploration of GeO₂ nanosheets as electrode materials for lithium-ion batteries.

Herein, this work reports the synthesis of GeO₂ nanosheets derived from the sheet-like Ge-MOF precursor (C₆H₁₀(NH₂)₂Ge₃O₆) by calcination in air. The MOF-derived GeO₂ nanosheet exhibits large reversible capacities as well as excellent cyclability. A larger-than-theoretical reversible specific capacity of 1393 mAh g⁻¹ can be observed after 350 cycles at 100 mA g⁻¹.

2. Experimental section

0.2 g commercial GeO₂ particles (99.99%, Sinopharm Chemical) were suspended in 1 mL deionized water and 7.5 g 1,2-diaminocyclohexane (90%, Sinopharm Chemical) was added dropwise into the GeO₂ suspension under continuous stirring. All reactants were transferred into 50 mL Teflon-lined stainless steel autoclave and were heated at 180 °C for 5 days. After cooling to ambient temperature, white precipitate of Ge-MOF was obtained by centrifugation, washing with acetone and deionized water, and drying under vacuum at 60 °C. The as-prepared Ge-MOF precursor was calcined in air at 600 °C for 2 h with a heating rate of 3 °C min⁻¹. The brown GeO₂ powders were collected and named as the MOF-derived GeO₂.

GeO₂ was characterized by various instruments and fabricated as the anode material in the Swagelok-type cells for electrochemical test at 25 °C. The working electrodes were fabricated with 80 wt% active materials (GeO₂), 10 wt% binder (poly (vinylidene difluoride)) and 10 wt% conductive agent (acetylene black). The loading amount of GeO₂ on copper foil was ~2 mg cm⁻². Lithium foil (China Energy Lithium Co., Ltd.) was used as the reference and counter electrode. The electrolyte was 0.15 mL 1 M LiPF₆ in ethylene carbonate (EC) and

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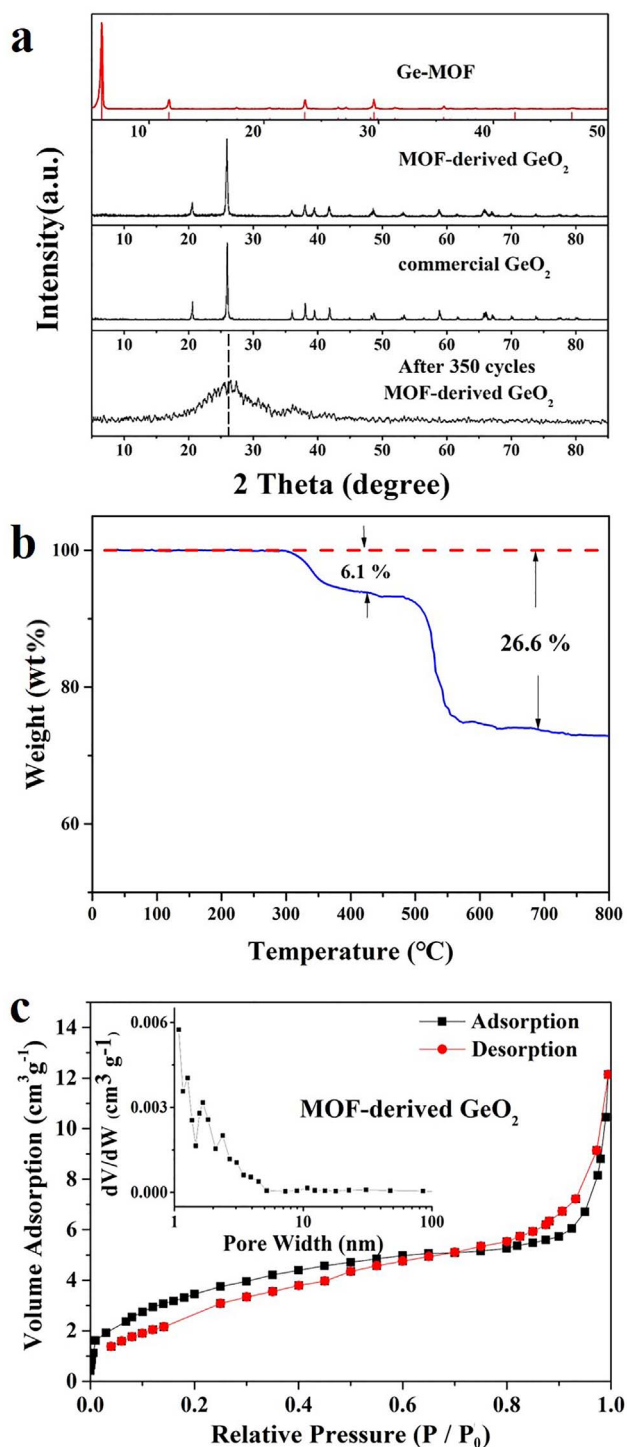


Fig. 1. (a) XRD patterns of Ge-MOF, MOF-derived GeO₂, commercial GeO₂ and the MOF-derived GeO₂ after 350 cycles, (b) TGA curve of Ge-MOF in air, (c) Nitrogen adsorption/desorption isotherm and pore size distribution (the insert) of the MOF-derived GeO₂.

diethyl carbonate (DEC) (1:1, w/w). The galvanostatic discharge and charge were performed at the current of 100 mA g⁻¹ and in the potential window of 5 mV–3.0 V.

3. Results and discussion

The Ge-MOF structure and its derived GeO₂ were measured by X-ray diffraction (XRD, Rigaku D/max-2550V, Cu K α radiation) (Fig. 1a). All strong diffraction peaks in the XRD pattern for Ge-MOF agree well with previous C₆H₁₀(NH₂)₂Ge₃O₆ [17]. For the MOF-derived GeO₂ and commercial GeO₂, all the diffraction peaks can be assigned to the (100), (101), (110), (102), (111), (200), (112), (211), (203) planes of the hexagonal GeO₂ phase (JCPDS No. 36–1463). As shown in the thermogravimetric analysis (TGA, NETZSCH STA 409PG/PC, a ramp rate of 10 °C min⁻¹) results of Ge-MOF under air atmosphere (Fig. 1b), there is a weight loss of 6.1% from 300 to 460 °C, corresponding to the removal of the absorbed solvent molecules [10,12,17]. Further heating leads to the complete decomposition of MOF skeleton and the volatilization of the organic ligands with a significant weight loss of 26.6% occurred from 490 to 580 °C. Therefore, a calcination temperature of 600 °C in air was adopted in this work to obtain the MOF-derived GeO₂. The Brunauer–Emmett–Teller (BET) measurement was conducted on a nitrogen adsorption apparatus (Micromeritics ASAP 2020), and the specific surface area of MOF-derived GeO₂ was determined to be 12.9 m² g⁻¹ based on the nitrogen adsorption/desorption isotherm (Fig. 1c) and its dominant pore size is in the range of ~1–3 nm.

SEM (JEOL JSM-6700F) images and TEM (JEOL JEM-200CX) image in Fig. 2a–c show the irregular nanosheets of the Ge-MOF precursor with a thickness of ~200 nm. After the calcination, the obtained MOF-derived GeO₂ exhibits the inherited sheet-like morphology (Fig. 2d–e) and its thickness of ~200 nm can be determined by the cross-section SEM image in Fig. 2f. As shown in the elemental mapping images of Fig. 2g, two kinds of elements (Ge and O) are detected with uniform distribution, further confirming the composition of MOF-derived GeO₂ nanosheets.

Electrochemical performances of MOF-derived GeO₂ were investigated as an anode material for lithium ion batteries. As shown in the discharge/charge curves of MOF-derived GeO₂ for the first cycle (Fig. 3a), the voltage plateau at ~0.66 V in the cathodic sweep corresponds to the reduction reaction of germanium oxide [18–22] along with the formation of the solid electrolyte interface (SEI) film. The long voltage slope is observed below 0.40 V, corresponding to the formation of Li-Ge alloys. In the anodic sweep, a clear plateau at ~0.46 V can be assigned to the reversible delithiation of Li-Ge alloys [23,24]. These voltage plateaus are largely in accordance with the corresponding cycle voltammograms (CV) results in Fig. 3b. It is worth noting that there is a small peak located at ~1.1 V, which is possibly due to the oxidation from Ge to GeO₂ [19–21]. This can be also confirmed by the XRD pattern of the electrodes after 350 cycles. A broad peak centered at 25.8° can be observed, which is usually ascribed to the short-range ordered Ge-O crystalline structure [6]. This phenomenon also indicates that reversible decomposition of Li₂O is possible, which may lead to the enhanced Li-storage capacity. The discharge/charge capacities of the MOF-derived GeO₂ for the first cycle are measured to be 2079/1315 mAh g⁻¹, corresponding to a Coulombic efficiency (CE) of 63.2%. The irreversible capacity loss is probably due to the decomposition of the electrolyte and the formation of the SEI film [25].

Fig. 3c shows the cycling performances of MOF-derived GeO₂ nanosheets and commercial GeO₂ nanoparticles. Generally, the MOF-derived GeO₂ electrode exhibits superior cycling performance and higher reversible capacities than commercial GeO₂ electrode. There is an obvious capacity fading in the first 50 cycles for the MOF-derived GeO₂, followed by a gradual capacity increase between the 50th and 150th cycles. The capacity increase can be ascribed to the activation process associated with the improved Li-diffusion kinetics during cycling [12].

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