Carbon-Coated Zn_2GeO_4 on Ni Foam as Lithium Ion Battery Anodes with Exceptional Long Cycling Stability

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Abstract: In this work we have investigated lithium ion battery anodes based on Zn_2GeO_4 , which were directly synthesized on 3D Ni foam substrates and were in situ coated with a conductive carbon layer. The hybrid electrodes exhibited outstanding electrochemical performance, including an exceptional long-term cycling stability with reversible discharge capacity of over 1100 mAh g^{-1} obtained after being tested for 1000 cycles at 400 mA g^{-1} . This study of hybrid electrodes may present an interesting approach to creating efficient and practical electrodes for energy storage applications.

Keywords: Zn_2GeO_4 , interconnected structure, carbon coating, anode, Lithium ion battery

1. Introduction

High-performance lithium-ion batteries (LIBs) are important power sources for various consumer electronics, such as in cell phones, laptops, and digital cameras. They also hold great promises for applications in future electric vehicles, hybrid electric vehicles, and emerging smart grids [1-3]. However, broader applications of LIBs are still hampered by the limited capacity and insufficient cycling lifetime of traditional graphite-based anodes [4,5]. In the last decade, various materials such as silicon, germanium, and transition-metal oxides have been utilized to fabricate LIB anodes with improved specific capacity, rate capability, and cycling stability. Among them, germanium is being considered as a promising anode material due to its relatively high theoretical capacity (1600 mAh g^{-1}), good Li diffusivity, and high electrical conductivity [6,7]. However, Ge-based LIB anodes currently suffer from high cost as well as poor cycling lifetime that is related to its large volume expansion of $\sim 370\%$ that occurs during the lithiation/delithiation process [8,9]. In order to reduce the fabrication cost, Ge-based oxides have recently been explored for LIB anode applications [10,11]. For example, ternary oxide Zn_2GeO_4 has been proposed as an attractive anode material and it has a theoretical capacity of 1443 mAh g^{-1} that is much higher than those of other metal oxides such as GeO_2 [12-14]. Nonetheless, like other transition-metal oxides, the drastic volumetric change of Zn_2GeO_4 during the lithiation/delithiation process still causes pulverization of the electrode, aggregation of the intermediates, and subsequent

1 detachment of the active materials from the current collector, which result in capacity
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5 decay and poor cycling stability [15]. With a purpose to make improvement on these
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8 aspects, in this work we have investigated Zn_2GeO_4 -based LIB anodes that were directly
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10 synthesized on 3D Ni foam substrates and were *in situ* coated with a conductive carbon
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12 layer. Since 3D materials can act as conductive current collectors, the integrated
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14 electrodes can provide fast electronic transport pathways without the use of any
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16 conductive additives or binders. In addition, the 3D macro porous structures can present
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18 efficient contacts between the electrode and the electrolyte, and thus can benefit lithium
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20 ion diffusion. In this electrode structure that is denoted as $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$, the 3D Ni
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22 foam acted as a highly conductive current collector, and the direct growth avoided the use
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24 of auxiliary additives or binders and thus could increase the electrode's energy density
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26 [16,17]. The *in situ* grown carbon coating on Zn_2GeO_4 surface not only could improve
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28 the electrical conductivity of the electrode, but also could serve as an elastic sheath to
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30 accommodate the volume changes during the lithium ion insertion/extraction process
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32 [18,19]. In addition, the interfacial lithium storage process occurred in the electrode
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34 structure could reduce bulk lithiation and help maintain the integrity of the electrode,
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36 leading to further improved performance. As a result, the binder-free, Zn_2GeO_4 -based
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38 hybrid electrodes synthesized in this work exhibited high reversible capacity, high rate
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40 capability, and exceptional long cycling stability.
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58 2. Experimental methods

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2.1. Material Synthesis.

$\text{Zn}_2\text{GeO}_4@\text{C}$ film was grown on Ni foam using a chemical vapor deposition method. A mixture of ZnO , GeO_2 , and carbon powders with molar ratios of 2:1:3 was placed in a quartz boat and was loaded to the center of a furnace tube, and a Ni foam substrate was placed downstream near the edge of the tube. The furnace was heated up to 1000 °C at a rate of 50 °C min⁻¹ under a constant flow of gas mixture of N_2 (100 sccm) and O_2 (2 sccm). The growth pressure was kept at 2 Torr and the substrate temperature was maintained at 550 °C during the growth process.

2.2. Structural Characterizations.

The $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrodes were characterized by X-ray diffraction (XRD, Xpert, Philips) using a Cu $K\alpha$ radiation source and by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD instrument) with a monochromatic Al $K\alpha$ source (1486 eV). The morphology and structure of the electrodes were analyzed by SEM (FEI Quanta 450FEG) and TEM (JEOL 2100). Thermogravimetric analysis (TGA, Mettler-Toledo TGA/DSC apparatus) was conducted using a 10 °C min⁻¹ heating rate under an ambient air flow.

2.3. Electrochemical Tests.

Ni foam with the $\text{Zn}_2\text{GeO}_4@\text{C}$ film was directly used as binder-free LIB anode and Li metal was used as the counter electrode. CR2032-type coin cells were assembled in a glove box filled with Ar and were used to evaluate the electrochemical performance of

the electrodes. 1 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume ratio) was used as the electrolyte, and Celgard 2500 membrane was used as the separator. All charge/discharge tests were carried out by an Arbin BT2043 system in the voltage range of 0.01 - 3.0 V. The specific capacities were calculated based on the total mass of Zn₂GeO₄ and carbon, which was determined after carefully measuring the weights of the Ni foam before and after the growth of the Zn₂GeO₄@C film. EIS measurements were conducted using an electrochemical analyzer (Ivium Compact State10800) in the frequency range of 100 kHz to 10 mHz.

3. Results and discussion

The Zn₂GeO₄@C/Ni electrodes were synthesized using a single-step chemical vapor deposition method, and ZnO, GeO₂, and carbon source powders with molar ratios of 2:1:3 were placed at the center of a tube furnace. The Ni foam was placed downstream near the edge of the tube and the local temperature was kept at 550 °C, while the source materials at the center of the tube were heated up to 1000 °C under a gas mixture of N₂ and O₂. In the high temperature region, the ZnO and GeO₂ source powders reacted with carbon to generate Zn and Ge vapors as well as CO or CO/CO₂ vapor mixture. When the mixed vapors diffused to the low temperature region, the Zn and Ge vapors were oxidized by the CO or the CO/CO₂ vapor mixture to form Zn₂GeO₄ on the Ni foam substrate. Meanwhile, the CO or the CO/CO₂ vapor mixture was simultaneously reduced to create a carbon film coating on the surface of Zn₂GeO₄, forming the Zn₂GeO₄@C/Ni hybrid

electrode structure [20,21]. The overall redox reactions could be described by the following equations:

Fig. 1a shows a typical scanning electron microscope (SEM) image of the 3D Ni foam substrate covered with the $\text{Zn}_2\text{GeO}_4@\text{C}$ film, which shows that the coverage was uniform across the Ni foam surface. The high-magnification SEM images (Fig. 1b & 1c) show the morphology of the polycrystalline $\text{Zn}_2\text{GeO}_4@\text{C}$ film, which exhibits interconnected structures with many pores and interfaces. This interconnected architecture could reduce the aggregation of electrochemically active materials during the charge/discharge process, and thus could improve the mechanical stability of the electrode [22,23]. The porous structure could increase the contact area between the $\text{Zn}_2\text{GeO}_4@\text{C}$ electrode and the electrolyte, which could allow a better access of the liquid electrolyte and improve lithium ion diffusion [24]. The structure of the $\text{Zn}_2\text{GeO}_4@\text{C}$ film was further studied by energy dispersive X-ray (EDX) element mapping (Fig. 1d - 1g), and the elemental maps of Zn, Ge, O, and C show uniform and continuous distribution throughout the Ni foam network. The carbon weight ratio in the $\text{Zn}_2\text{GeO}_4@\text{C}$ electrodes was estimated to be $\sim 9\%$ based on EDX analysis results (Fig. S1 and Table S1,

Supporting Information). The X-ray photoelectron spectroscopy (XPS) measurement result (Fig. S2, Supporting Information) also revealed the elemental composition and electronic structure of the $\text{Zn}_2\text{GeO}_4@\text{C}$ electrodes.

Transmission electron microscopy (TEM) examinations show more details of the $\text{Zn}_2\text{GeO}_4@\text{C}$ structure. As part of the preparation of the TEM grids, the $\text{Zn}_2\text{GeO}_4@\text{C}$ film was exfoliated from the Ni foam through a sonication process. This process often lasted 30 minutes or more, suggesting that the $\text{Zn}_2\text{GeO}_4@\text{C}$ film was robust and strongly adhered to the Ni foam. A typical TEM image of the exfoliated $\text{Zn}_2\text{GeO}_4@\text{C}$ film is shown in Fig. 2a. The high-resolution TEM (HRTEM) image in Fig. 2b shows a clear crystal lattice with an inter-planar spacing of 0.29 nm, which was indexed to the (113) lattice fringes of the rhombohedral Zn_2GeO_4 structure. The ordered dot patterns in the fast Fourier transform (FFT) image shown in the inset of Fig. 3b also confirmed the formation of single crystalline Zn_2GeO_4 . The HRTEM image in Fig. 2c shows that an amorphous carbon layer with a thickness of ~ 5 nm was coated on the surface of Zn_2GeO_4 . Fig. 2d is a dark-field TEM image of the exfoliated $\text{Zn}_2\text{GeO}_4@\text{C}$ film, in which the red arrow line indicates the EDX line-scan measurement position and direction. The EDX line-scan profiles are presented in Fig. 2e, which further confirmed the carbon coating on the surface of Zn_2GeO_4 . The crystal phase of Zn_2GeO_4 was also characterized by X-ray diffraction (XRD), and the spectra are shown in Fig. 2f, in which the peaks were indexed to the rhombohedral phase of Zn_2GeO_4 , JCPDS card No. 11-0687.

Electrochemical measurements were carried out after directly applying the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrodes as anodes in coin-type LIB cells. Fig. 3a shows the cycling performance of a typical $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ anode at a current density of 0.2 A g^{-1} . During the first cycle, the discharge and charge capacities were approximately 1414 and 1066 mAh g^{-1} , respectively. The irreversible capacity loss could be attributed to the formation of a solid electrolyte interface (SEI) layer. The Columbic efficiency was calculated to be 75.4%, which was much higher than previously reported values of Zn_2GeO_4 -based anodes [11,15]. It can be seen that after the initial activation cycles, the discharge and charge capacities became stable and increased to 933 and 925 mAh g^{-1} , respectively, during the 50th cycle, and the discharge capacity retention was as high as 90.8% when compared to the second cycle. The Columbic efficiency increased rapidly to 98.2% after 5 cycles and remained at over 99% in the subsequent cycles. The rate capability of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ anode was characterized to examine the fast charge storage process, and typical galvanostatic charge/discharge curves are shown in Fig. S3 (Supporting Information). As can be seen in Fig. 3b, the reversible capacities were 898, 832, 745, 631, and 503 mAh g^{-1} at rates of 0.4, 0.8, 1.6, 3.2, and 6.4 A g^{-1} , respectively. Even at a high rate of 9.6 A g^{-1} , the anode still delivered a high capacity of 396 mAh g^{-1} . In addition, the capacity at each rate was stable without noticeable fading (Fig. 3b), demonstrating the excellent rate capability of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ anode.

Fig. 3c shows the galvanostatic charge/discharge curves of the anode at a current

density of 0.2 A g^{-1} . Interestingly, the discharge curves after the first cycle only showed sloped curves in the region of 1.5 - 0.01 V, and no plateau was observed in the voltage range of 0.7 - 0.8 V, where a common plateau usually shows up during the discharge process of Zn_2GeO_4 -based anodes after the first cycle [13,18]. Such sloped discharge curves have been observed in nanostructure-based LIB anodes and have been related to the interfacial lithium storage process [25-28]. Based on this observation and previously published reports, we suggest that the interfacial lithium storage mechanism played an important role in the charge/discharge cycling process of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ anode. As proposed by Maier and co-workers, lithium storage capabilities of nanomaterials could be significantly improved through a synergistic interfacial storage process, in which the Li^+ ions are stored at the interstitial sites in Li_2O at the solid/solid interfaces, while the electrons are stored on the surfaces of the metals, such as Zn and Ge in the Zn_2GeO_4 electrode (Fig. 3d) [29,30]. The reaction kinetics of this interfacial lithium storage process is much faster than that of bulk intercalation and phase transformation, and this process has also been proposed to be very reversible due to reduced bulk lithiation depth and alleviated volume variation, which can lead to improved cycling performance. To further inspect the cycling stability, the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ anode was tested using a long-term galvanostatic charge/discharge process at 0.4 A g^{-1} for 1000 cycles, which lasted about 8 months, and the measurement results are shown in Fig. 3e as well as Fig. S4 & S5 (Supporting Information). It can be seen from Fig. 3e that the anode capacities increased gradually and the discharge capacity reached 1029 mAh g^{-1} during the 160th

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5 cycle and 1220 mAh g⁻¹ during the 800th cycle, which was very close to the theoretical
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7 capacity of Zn₂GeO₄ (1443 mAh g⁻¹). Even during the 1000th cycle, the anode still
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9 showed a capacity of 1128 mAh g⁻¹, which was more than three times higher than the
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11 theoretical capacity of graphite (372 mAh g⁻¹). To the best of our knowledge, such an
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13 exceptional long-term cycling stability has never been reported for Zn₂GeO₄-based LIB
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15 anode materials, and this improved performance could be partly attributed to the
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17 interfacial storage mechanism that reduced bulk lithiation depth, suppressed bulk
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19 degradation, and maintained the integrity of the electrode.
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28 The Zn₂GeO₄@C/Ni electrode was also examined after the long-term cycling test to
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30 investigate possible morphology and structure changes. The SEM images in Fig. 4a & 4b
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32 show that the interconnected and porous morphology of the Zn₂GeO₄@C film was still
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34 retained after being tested for 1000 cycles. The Zn₂GeO₄@C film also remained attached
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36 to the Ni foam substrate, suggesting that this interconnected architecture and the *in situ*
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38 carbon coating could effectively prevent the aggregation and abscission of
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40 electrochemically active materials during the cycling processes. From the elemental
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42 mapping images (Fig. S6, Supporting Information) it can be seen that the homogeneous
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44 distributions of Zn, Ge, O, and C were also preserved, proving that the anode structure
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46 was very stable and the active materials remained anchored firmly to the Ni substrate
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48 surface. Fig. 4c shows the EDX spectrum of the tested anode. It can be seen from this
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50 figure that, besides Zn, Ge, O, and C, P and F also appeared in the anode, confirming the
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formation of a SEI layer on the anode surface due to the decomposition of LiPF₆. The XRD data shown in Fig. 4d and the TEM images shown in Fig. 4e & 4f reveal more information regarding the electrochemical reactions of the Zn₂GeO₄@C electrode during the charge/discharge process. The peaks in the XRD spectrum could be indexed to ZnO, GeO₂, Li₂O, and Ni, as labeled in Fig. 4d. The TEM image shown in Fig. 4e indicates that nanoclusters were formed in the Li₂O matrix, and the HRTEM and FFT images shown in Fig. 4f suggest that these nanoclusters could be associated with ZnO and GeO₂ nanoparticles. In fact, the obtained inter-planar spacings of 0.192, 0.214, and 0.224 nm of the nanoclusters matched well with the (102) facet of ZnO, (200) and (111) facets of GeO₂, respectively. Based on these results and previously published studies, the following electrochemical reactions were proposed for the Zn₂GeO₄@C electrodes during the charge/discharge process [11,21]:

Specifically, during the initial discharge process, Zn₂GeO₄ was reduced irreversibly

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5 to form metallic Zn and Ge, as well as a Li_2O matrix (Equation 4). When the discharge
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7 voltage became close to 0 V, the as-formed Zn and Ge reacted with Li and produced
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9 Li_xGe and Li_yZn alloys separately (the forward processes in Equations 5 and 6). During
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11 the charge process, the Li_xGe and Li_yZn alloys were delithiated to yield Zn and Ge (the
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13 backward processes in Equations 5 and 6), which were subsequently oxidized by Li_2O to
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15 form ZnO and GeO_2 (the forward processes in Equations 7 and 8). Starting from the
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17 second cycle, the redox reactions described by Equations 7 and 8 as well as the
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19 alloying/dealloying reactions described by Equations 5 and 6 would take place repeatedly.
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21 The XRD and TEM examination results and the observed high Columbic efficiency of
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23 nearly 100% (Fig. S5, Supporting Information) suggested that the lithiation/delithiation
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25 reactions described by Equations 5 - 8 were highly reversible in the $\text{Zn}_2\text{GeO}_4@\text{C}$ anode.
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27 The structural stability of the anode was also examined by electrochemical impedance
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29 spectroscopy (EIS) measurement. The Nyquist plots of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrode
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31 before the electrochemical test and after being tested for 1000 cycles are shown in Fig. S7
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33 (Supporting Information). It can be seen from this figure that the diameter of the
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35 semicircle in the high-frequency region only slightly increased after the electrode was
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37 tested for 1000 cycles, corresponding to a slight increase in the electrode's resistance,
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39 which suggested that the formed SEI film was very stable. This could be attributed to the
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41 beneficial effects of the carbon coating on Zn_2GeO_4 surface, which acted as a nearly
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43 sealed sheath to prevent a direct exposure of Zn_2GeO_4 to the electrolyte, leading to a
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45 stable SEI film on the electrode's surface and reduced decomposition of the electrolyte
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5 during the cycling test [31,32].
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8 9 **4. Conclusion**

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12 In summary, the above results clearly demonstrated that the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$
13 electrodes studied in this work exhibited high reversible capacity, high rate capability,
14 and exceptional long-term stability for lithium storage applications. There were several
15 factors that could contribute to the good performance of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrodes:
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17 Firstly, the direct growth of the $\text{Zn}_2\text{GeO}_4@\text{C}$ film on Ni foam ensured good mechanical
18 adhesion between the electrochemically active materials and the current collector, and at
19 the same time avoided the use of additive agents or polymer binders that were commonly
20 found in LIB anodes. Secondly, the carbon coating helped the formation of a stable SEI
21 layer on the electrode surface, improved electron transport, and also functioned as a
22 buffer to accommodate the volume changes of the electrode [9,33]. Thirdly, the
23 interfacial lithium storage mechanism facilitated lithium ion transport, reduced the depth
24 of bulk lithiation, and suppressed bulk degradation, leading to good rate capability and
25 excellent long-term cycling stability. This study of LIB anodes based on hybrid ternary
26 metal oxide structures may present an interesting approach to realizing efficient and
27 practical electrodes for energy storage applications.
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Figure Captions

Fig. 1. (a-c) Typical SEM images of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrode at different magnifications. (d-g) EDX elemental mapping images of Zn, Ge, O, and C.

Fig. 2. (a) TEM and (b, c) HRTEM images of the $\text{Zn}_2\text{GeO}_4@\text{C}$ film exfoliated from Ni foam substrate. The inset in (b) is the FFT image. (d) Dark-field TEM image of the $\text{Zn}_2\text{GeO}_4@\text{C}$ film, in which the red arrow line indicates the EDX line-scan measurement position and direction. (e) EDX line-scan profiles of Zn, Ge, O, and C. (f) XRD spectra of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrode and the pristine Ni foam substrate.

Fig. 3. Electrochemical performance of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrode. (a) Cyclic performance at 0.2 A g^{-1} . (b) Charge/discharge capacities at various current rates. (c) Typical galvanostatic charge/discharge curves at 0.2 A g^{-1} . (d) Schematic illustration of the interfacial lithium storage mechanism. (e) Long-term cycling performance of the electrode at 0.4 A g^{-1} for 1000 cycles.

Fig. 4. (a, b) SEM images, (c) EDX spectrum, (d) XRD spectrum, (e) TEM image, and (f) HRTEM image of the $\text{Zn}_2\text{GeO}_4@\text{C}/\text{Ni}$ electrode after being tested at 0.4 A g^{-1} for 1000 cycles. The inset in (f) is the FFT image of the GeO_2 nanoparticle.

Figures

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