ZnO Nanomembrane/Expanded Graphite Composite Synthesized by Atomic Layer Deposition as Binder-Free Anode for Lithium Ion Batteries

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ABSTRACT: A zinc oxide (ZnO)/expanded graphite (EG) composite was successfully synthesized by using atomic layer deposition with dimethyl zinc as the zinc source and deionized water as the oxidant source. In the composite structure, EG provides a conductive channel and mechanical support to ZnO nanomembranes, which effectively avoids the electrode pulverization caused by the volume change of ZnO. The anodes made from the flexible composite films without using binder, conductive agent, and current collector show high stable capacities especially for that with a moderate ZnO concentration. The highest capacity stayed at 438 mAh g⁻¹ at a current rate of 200 mA g⁻¹ after 500 cycles. The good performance is considered to be due to the co-effects of the high capacity of ZnO and the support of the EG framework. Such composite structures may have great potential in low-cost and flexible batteries.

KEYWORDS: zinc oxide, expanded graphite, atomic layer deposition, anode, binder-free, lithium ion battery

1. INTRODUCTION

Lithium ion batteries (LIBs) have been widely applied to portable electronic devices since the 1970s owing to their high specific capacity, reversibility, and long cycle life. However, the energy density of current commercialized LIBs can no longer satisfy the demands for growing power-supply requirements, such as electric vehicles and a large-scale stationary grid, due to the low theoretical capacity (372 mAh g⁻¹) of the graphite anode. In the past decade, many transition metal oxides (M₂O₃, M = Fe, Co, Ni, Cu, Zn, etc.) with higher theoretical capacities (>600 mAh g⁻¹) have been studied as anode materials for high-performance LIBs. Among these metal oxides, nontoxic zinc oxide (ZnO) is regarded as an alternative candidate due to its natural abundance, high lithium-ion diffusion coefficient, and much higher theoretical capacity of 978 mAh g⁻¹ which is nearly three times higher than that of graphite. However, the realization of the full capacity of ZnO has been hindered by severe capacity fading caused by the large volume expansion during lithiation. Moreover, the low electrical conductivity of ZnO also needs to be improved. To overcome these problems, materials with high electrical conductivity are incorporated to produce composite structures and nanostructures are introduced to mechanically buffer volume changes. It is noted recently that expanded graphite (EG), as a kind of graphite-based material made from natural graphite, is a three-dimensional (3D) structure with large pores and an ultrahigh specific surface area. The EG normally shows good chemical stability and high electronic conductivity, indicating its potential as an additive in composite anode. In previous literature regarding composite anodes, EG is used as a conductive additive and a flexible support, and the abundant large pores inside the 3D structure provide enough space for lithium-ion storage and volume expansion. For instance, Huang et al. adopted EG as a flexible conductive support to preserve the electrode activity and integrity of the electrode, and the electrochemical performance was improved significantly. Also, Hu et al. embedded carbon-coated Li₃VO₄ nanoparticles in EG as a loading carrier to enable the fast transmission of electrons, which demonstrated that EG can be used as conductive agent with good electrical conductivity. Furthermore, EG can be pressed into a self-standing flexible film easily and has been successfully applied as electrodes or scaffolds to embed electrochemical active materials, such as silicon or sulfur, for binder-free Li-ion batteries. However, in these experiments, EG was combined with the active materials through physical adsorption, which caused the active material to
Atomic layer deposition (ALD) is a thin film deposition technique based on surface chemical reactions. During the reaction, surface-saturating precursor doses are pumped into the reaction chamber alternatively to avoid the occurrence of gas phase reactions. The conformal growth provided by ALD is a direct consequence of the process, which ensures precise film thickness control, good adhesion, and excellent step coverage, even on 3D structures with large aspect ratios.

In this work, a ZnO/EG composite (hereafter: ZG composite) has been successfully fabricated by ALD on EG where dimethyl zinc and deionized water are used as zinc and oxygen sources, respectively. Experimental characterization demonstrates that the ZnO nanomembrane in the composite is tightly coated on the surface of EG, which works as conductive additive and supports the ZnO nanomembrane to avoid the electrode pulverization caused by volume change. Therefore, ZnO nanomembrane deposition on EG by ALD may be a good approach to produce a ZnO/EG composite structure for an anode with better performance.

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2. EXPERIMENTAL SECTION

2.1. Synthesis of EG. The natural graphite flake was dried at 75 °C in a vacuum oven for 5 h to remove the moisture content. It was then mixed and saturated with acid consisting of concentrated sulfuric acid and nitric acid in a ratio of 3:1 for 10–15 h to form the graphite-intercalated compound (GIC). The mixture was stirred from time to time to obtain the uniform intercalation of each flake. The mixture was carefully washed and filtrated with water until the pH of the solution reached 7. After washing, the acid-treated flakes dried at 60 °C in a vacuum oven. GIC was rapidly expanded at 900 °C in a muffle furnace with N₂ as protection gas for 20 s to obtain EG, as schematically shown in Figure 1a.

2.2. Fabrication of ZG. The preparation process of ZG is shown in Figure 1a. The prepared EG was coated with the ZnO nanomembrane in the ALD chamber with dimethyl zinc and deionized water as the zinc and oxidant sources, respectively. The chamber temperature during deposition is 150 °C. The thicknesses of the ZnO nanomembranes were tuned by altering the number of ALD cycles: 50, 100, 200, 300, 400, 600, and 800 cycles, and the samples were named as ZG50, ZG100, ZG200, ZG300, ZG400, ZG600, and ZG800, respectively, for short. Then, the samples were annealed in tube furnace at 600 °C for 120 min with the protection of N₂ gas. For comparison, pure ZnO nanomembranes were also fabricated by ALD on a porous polymer template followed by a high-temperature treatment at 600 °C in oxygen which removed the template.

2.3. Microstructural Characterizations. The morphologies and microstructures of the composites were examined using scanning electron microscopy (SEM, Zeiss Sigma) and transmission electron microscopy (TEM, Nova NanoSem 450). The composition of the sample is characterized by an energy dispersive X-ray (EDX) spectrometer attached to the SEM. The X-ray diffractometer (XRD) patterns were recorded using a Bruker D8 Advance XRD with Cu Kα radiation (λ = 1.5405 Å). Thermogravimetric analyses (TGA) of the ZG composite were performed on SDT Q600 at a heating rate of 10 °C min⁻¹ in a flowing air atmosphere from 30 to 900 °C. Nitrogen sorption isotherms were measured with a QuadraSorb SI MP Station. The samples were degassed in a vacuum at 300 °C for 3 h before measurement.

2.4. Electrochemical Measurements. The prepared composites were pressed into paper-like films and cut into anode strips without binder (Figure 1a). With the lithium metal as the counter electrode, the electrochemical cells were assembled as CR2016-type coin cells at room temperature. The paper-like self-standing films were directly used as the working electrode without any further treatment (Figure 1a). The electrolyte used was a solution of 1 M LiPF₆ dissolved in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 1:1 by volume), and the separator was polyethylene film. The cells were assembled in an argon-filled glovebox (H₂O, O₂ < 1 ppm), and galvanostatic measurements were performed on a battery testing system (LAND CT2001A) in the voltage range of 0–3 V. The current...
rates used were based on the total mass of the electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were recorded using the Zennium/IM6 electrochemical interface.

3. RESULTS AND DISCUSSION

The preparation process of ZnO nanomembranes coated on EG by ALD and battery assembly are schematically depicted in Figure 1a. We noticed that the fabricated ZG composite can be pressed into a self-standing and flexible film like a piece of paper, which can be bent back and forth without being broken. Then, the paper-like ZG film was assembled into a battery directly without any additive binder, conductive agent, and current collector, indicating no dead component was included in current battery device. Figure 1b displays a typical SEM image of GIC, in which the gap between two parallel graphene layers is straight. Figure 1c,d shows the SEM image of pure EG. One can see that EG with a rippled and fluffy nature consists of thermally exfoliated graphene layers. Compared with GIC, EG gets a clearer and larger gap after expansion, in which graphene layers are firmly stacked with gaps (∼100 nm). We consider that the sponge-like structure of EG can provide enough space for the ALD surface reaction and the volume expansion of ZnO during the electrochemical process as well as a conductive network for charge transfer. This will be proven by the following experiments and will be discussed in detail later.

Typical ZG samples with different ALD cycles are exhibited in Figure 1e−g, in which the microstructural differences can be observed. All the SEM images show that the ZnO is well deposited on the EG surface by ALD, yet the surface coverage is quite different. The graphene layers in ZG50 (Figure 1e) are not completely coated by ZnO. The oxide deposited with 50 ALD cycles shows a punctate distribution on the EG surface (inset of Figure 1e), due to the lack of reactive surface sites or functional groups on graphene layers. When the number of ALD cycles increase to 300, ZnO covers the surfaces of EG better (Figure 1f), and ZnO nanomembranes start to grow from those active spots. A uniform and smooth ZnO layer can be found on certain parts of the sample surface (see the enlarged SEM image in the inset of Figure 1f). As for ZG800 (Figure 1g), ZnO not only coats the EG surface but also overlaps to form a thick layer in some area (inset of Figure 1g). In addition, the EDX spectrum in the upper-right inset of Figure 1g indicates the deposition of ZnO onto the inner surface of EG. The SEM images of ZG samples with different ALD cycles obviously demonstrate that with the increase of the ALD cycles, the ZnO coverage on the EG surface is enhanced correspondingly, and the thickness of ZnO nanomembrane is also remarkably increased.

To investigate the crystal structure of the composite, XRD characterization were carried out and the patterns of ZG50, ZG300, ZG800, and pristine EG are presented in Figure 2a. A strong diffraction peak (2θ = 26.44°) is observed in the XRD pattern of EG, which should be attributed to the feature peak (002) of graphite. For composite samples ZG300 and ZG800, the characteristic diffraction peaks of ZnO are clearly exhibited (PDF #36–1451). The peaks at 2θ = 31.769, 34.421, 36.252, 47.538, 56.602, and 62.862° are associated with the (100), (002), (101), (102), (110), and (103) lattice planes. However, the diffraction peaks can hardly be distinguished in ZG50, because the amount of ZnO is too small, which is consistent with the above SEM results. With the increase of ALD cycles, the characteristic peak of ZnO is more obvious due to the increased percentage of the ZnO component. The increased ZnO concentrations in the composites are more visualized in the TGA measurements. The results shown in Figure 2b demonstrates that the ZnO concentration increases with the ALD cycles. To estimate the ZnO concentration in the composites quantitatively, we assume that the mass of ZnO deposited in each ALD cycle is n. Thus, the ZnO concentration can be calculated as a function of ALD cycles n

$$\text{ZnO\%} = \frac{\text{mass of ZnO}}{\text{total mass of ZG}} = \frac{m^*n}{M + m^*n} = 1 - \frac{1 + \frac{m^*n}{M}}{M}$$

(1)

where M is the weight of blank EG. To determine the ratio m/M, we have carried out nitrogen adsorption–desorption measurements of the blank EG sample, and the specific surface area is calculated to be 56.668 m² g⁻¹ (see details in Table S1 and Figure S1). For the sake of simplicity, we assume ZnO forms a uniform coating layer on EG surface, and thus, m/M can be determined to be 0.0062 by taking the density of bulk ZnO (5.606 g cm⁻³) in the calculation. The red line in the inset of Figure 2b shows the theoretical value of the ZnO concentration in the ZG composite as a function of the number of ALD cycles. The black squares are experimental results extracted from Figure 2b. It is worth noting that although the ZnO does not actually form a uniform coating layer on the EG surface, especially for fewer ALD cycles, the current simplified consideration still presents quite a good estimation, and good agreement can be observed between theoretical and experimental results as shown in the inset of Figure 2b. The results here indicate that the current ALD-based approach is capable of accurately tuning the composition in the composite materials.
In order to investigate the electrochemical properties of the composites, CV measurements were used to test the anodes made from ZG300 and pure ZnO for the first three cycles at a scan rate of 0.2 mV s\(^{-1}\) between 0 and 3 V, and the results are demonstrated in Figure 3a and the inset, respectively.

![Figure 3](image)

**Figure 3.** (a) CV curves of anode made from ZG300 (first three cycles) at 0.2 mV s\(^{-1}\). The inset shows corresponding CV results from pure ZnO anode for comparison. (b) The 1st, 2nd, 5th, and 10th discharge and charge curves of ZG300 and pure ZnO (inset) at a current rate of 200 mA g\(^{-1}\). The capacity fading is obvious at the first charge process in both ZG and pure ZnO. Such a rapid fading is considered to be due to the change of ZnO morphology, caused by volume expansion.**

According to previous literature,\(^{15,20,51–55}\) the reduction peaks around 0.2 and 0.8 V in the first cathodic scan of the pure ZnO electrode (the inset of Figure 3a) can be ascribed to the reduction of ZnO into Zn, the formation of the lithium–zinc alloy, and/or the growth of the solid electrolyte interface (SEI) layer.\(^{56,57}\) In the subsequent anodic scan, two oxidation peaks appeared at 0.35 and 0.7 V, which correspond to the dealloying process of the lithium–zinc alloy (Li\(_2\)Zn, Li\(_2\)Zn\(_2\), and LiZn\(_2\)) and/or the decomposition of Li\(_2\)O.\(^{58–60}\) In addition, a broad oxidation peak is found at \(\sim 1.5\) V, which may relate to the decomposition of Li\(_2\)O.\(^{56,59}\) In the subsequent second and third cycles, the cathodic peaks shift to the potentials of 0.4 and 1.0 V, which correspond to the reduction of ZnO and the formation of amorphous Li\(_2\)O, respectively.\(^{56,59}\)

During the subsequent anodic scan, a stronger and broader oxidation peak around 1.4 V may be a result of the decomposition of Li\(_2\)O.\(^{56–59}\) Compared with the pure ZnO anode, the CV results of the ZG anode (Figure 3a) have a broader oxidation peak around \(\sim 1.5\) V, similar to that in pure ZnO. In the anodic scan, a stronger and broader peak (0.25 to 1 V) can be observed, which is considered to be due to the overlap of the multistep dealloying reduction peaks.\(^{59}\) The phenomenon indicates that the conductive materials (EG in present case) can serve as a catalyst to alleviate the dealloying process and the decomposition of Li\(_2\)O.\(^{58–60}\) This may finally improve the reversible capacity of the composite anode.\(^{61}\)

Figure 3b shows the 1st, 2nd, 5th, and 10th discharge and charge curves of ZG300 and pure ZnO (inset) at a current rate of 200 mA g\(^{-1}\). The capacity fading is obvious at the first charge process in both ZG and pure ZnO. Such a rapid fading is considered to be due to the change of ZnO morphology, caused by volume expansion.\(^{13,16}\) The inset in Figure 3b illustrates that a continuous capacity fading exists in the pure ZnO anode, and less than 20% charge capacity remains after 10 cycles. As for the ZG anode, the capacity is much more stable, and more than 80% of the charge capacity is retained after 10 cycles. The improved stability of the ZG composite anode is mainly ascribed to the EG framework with large pores and an ultrahigh specific surface area, which can provide enough space for the volume expansion of the ZnO nanomembrane and therefore avoid the electrode pulverization caused by volume change.\(^{17,18}\)

Figure 3c shows the Nyquist plots of the electrodes operated at room temperature before galvanostatic discharging/charging cycles, in which all EIS spectra are similar and composed of a semicircle in the high-to-medium frequency region and a slope line in the low frequency region.\(^{62}\) The numerical value of the diameter of the semicircle on the Z\(_s\) axis gives an approximate indication of the charge transfer resistance (R\(_{ct}\)).\(^{63–65}\) An equivalent circuit for this ZG/Li battery is used to fit the Nyquist plots, as depicted in the upper panel of inset of Figure 4c. Here R\(_s\) and R\(_a\) are resistances from electrolyte (s) and charge transfer (ct). W\(_c\) is the Warburg impedance. CPE is the respective constant-phase element accounting for the depressed semicircle in the experimental spectra. The fitted R\(_s\) are 151.6, 105.5, 82.7, and 120 \(\Omega\) for EG, ZG50, ZG300, and ZG800, respectively. An apparent decrease of R\(_s\) for ZG300 was observed. Charge transfer resistance, occurring at the interface between the electrode-active component and the liquid electrolyte, would be affected by the surface area of the electrodes.\(^{62,66,67}\) From the SEM images, the surface of the ZG composite with fewer ALD cycles was partially covered by ZnO, rather than coated with a uniform layer. It would ineluctably cause a decrease of the reaction surface area. When the number of ALD cycles increases to 300, ZnO covers the surfaces of EG better and a uniform and smooth ZnO layer can be found on the sample surface (Figure 1f). An enhanced reaction surface was obtained. With further increase of the ALD cycles, ZnO not only coated the EG surface but also overlapped to form a thick layer (Figure 1g). For a specific mass of electrode, the thick layer of ZnO would reduce the exposed surface area. Thus, the ZG300 electrode with greatest reaction surface was tested.\(^{66}\) An enhanced reaction surface manifested the lowest R\(_s\).\(^{68}\) It is worth noting that the reduction of the resistance can furnish the composite with enhanced electron and ion transportation during the electrochemical reactions and, thus, improve the Li\(^+\) storage performance of the composite anodes.\(^{53}\)

Figure 4a presents the rate performance of the ZG anodes. Both the current density and capacity were calculated based on
total mass of the electrode, rather than the weight of ZnO. the ZG300 composite anode shows a much higher specific capacity compared with those of the ZG50 and ZG800 anodes. As the current rates increase from 50 to 100, 200, 500, and 800 mA g\(^{-1}\), the ZG300 electrode exhibits the best capacity retention, varying from 510 to 490, 462, 435, and 417 mAh g\(^{-1}\), respectively. In addition, the capacities of the ZG300 and ZG50 electrodes are stable, while the ZG800 is relatively unstable with fast capacity decay. To detect the stability and specific capacity in more detail, we take a long-cycle test about ZG composite anodes at a current rate of 200 mAh g\(^{-1}\) for 500 cycles (Figure 4b). The cycling performance was tested sequentially after rate cycling using the same battery. The result shows that the specific capacities of all the ZG composites turn out to be quite stable. ZG300 has the highest capacity of 436.4 mAh g\(^{-1}\), and the Coulombic efficiency (Figure S3) is over 98% during the whole charge and discharge process with a slight fluctuation. The specific capacity of composite anodes as a function of the number of ZnO ALD cycles is shown in the inset of Figure 4b. The nanomembrane consists of closely stacked ZnO nanocrystals formed during high-temperature annealing. After 500 cycles at 200 mA g\(^{-1}\) (Figure 5b), the dense nanomembrane with uniformly dispersed ZnO nanocrystals is still there. The corresponding insets show high-resolution TEM images of the samples. The distances of lattice planes (0.19, 0.28, and 0.26 nm) corresponds to the (102), (100), and (002) planes of ZnO (PDF \#36–1451), respectively. The TEM results shown in Figure 5 indicate that the ZnO nanocrystals did not crack or aggregate, and they maintained uniform dispersion in the ZnO nanomembrane after 500 cycles. The successful inhibition of ZnO pulverization in the ZG composite due to the EG support should be the key for the observed excellent performance.

4. CONCLUSION

ZnO nanomembranes were successfully deposited on the EG framework with a large surface area by ALD. The composite was pressed into a self-standing paper-like film, which shows good flexibility and can be used as an anode directly. In the composite, EG provides conductive channels and mechanical support to the ZnO nanomembrane, and therefore, the composite shows a high stable capacity in the battery device without using any conductive agent, binder, and current collector. Detailed electrochemical analyses of the composite with different ZnO concentrations show that the specific capacity increased with ZnO concentration at first and then decreased, with a maximum stable capacity in the composite with 300 ZnO ALD cycles. With the current rate of 200 mAh g\(^{-1}\), the specific capacity remains at 438 mAh g\(^{-1}\) after charging.
and discharging for 500 cycles. The results presented in this work may pave the way for production of low-cost and green LIBs or even flexible devices in the future.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b11735.

Supporting figures and tables including nitrogen sorption isotherms results, additional SEM images, and Coulombic efficiency of the composite anode (PDF)

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**Notes**

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