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Introduction

The ever-increasing demand for advanced energy storage techniques in various applications has driven the energy storage market to strive for higher energy density and longer cycling life.1,2 Accordingly, the development of new anode materials for lithium-ion batteries with high specific capacity is an urgent priority to increase the energy density.³ Due to its high theoretical capacity of 978 mA h g⁻¹, higher lithium-ion diffusion coefficient, and natural abundance, ZnO is considered as a promising alternative anode to the currently-used graphite.4-7 However, similar to the case of all other high-capacity anodes, the application of the ZnO anode is hindered by its poor cyclability arising from the pulverization of the electrode due to large volume changes (221%);^{8,9} thus, to use ZnO as a negative electrode against volume changes, an advanced nanostructure design and composites with carbon materials have been demonstrated.7,10,11 Among them, two-dimensional NMs show an exclusive advantage because they can be deformed to form a wrinkled structure, with apparent strain accommodation

Three-dimensional carbon/ZnO nanomembrane foam as an anode for lithium-ion battery with longlife and high areal capacity[†]

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Herein, an electrode architecture design using three-dimensional carbon/ZnO nanomembrane composite foam (C/ZnO NM foam) was proposed to achieve highly stable areal capacity at a practical mass loading. The composite, consisting of three-dimensional interconnected carbon foam anchored with two-dimensional ZnO NMs, was directly used as an anode of a lithium-ion battery without additional additives. The large surface area and high porosity of the carbon foam lead to a high ZnO loading of $3-4 \text{ mg cm}^{-2}$. The flexibility of the ZnO NMs, effective electronic and ionic transport throughout the three-dimensional composite structure, and capacity from the carbon foam enhance the areal capacity and stability of the composite. Thus, the synthesized anode retains 92% capacity after 700 cycles at 2 A g⁻¹ and after 500 cycles at 5 A g⁻¹ and manifests a remarkable areal capacity of 4.3 mA h cm⁻². The proposed approach and the composite structure produced in this study may have important potential applications in many fields requiring high energy storage capacity.

upon lithiation without cracking.^{12–14} Furthermore, coating with carbon layers or fabricating uniformly dispersed nanoparticles in a carbon matrix are effective ways to improve the cycling life by constraining the volume change and controlling the formation of a solid electrolyte interphase (SEI).^{1,7} For example, Wi *et al.*⁴ reported the synthesis of graphene oxide/carbon doublecoated 3D porous ZnO aggregates *via* a solvothermal method. The conformal carbon layer on each nanoparticle buffered the volume change, thus prolonging the cycling life.

However, the highly stable gravimetric capacity of ZnO-based materials usually suffers from low ZnO mass loadings (<1 mg cm⁻²).¹⁵ For example, Yu et al.¹⁶ fabricated an aluminastabilized ZnO-graphene anode with a highly stable capacity of 600 mA h g^{-1} at 100 mA g^{-1} , but its areal capacity was only 0.9 mA h cm⁻². This is much lower than the typical areal capacity of 2 mA h cm^{-2} of the commercial graphite electrode and too low for application in electric transportation (4 mA h cm^{-2}) ;¹⁷⁻²⁰ this demonstrates that highly stable specific capacity alone does not guarantee practical applications for electrodes.17 A high mass loading is desirable for high energy density. However, a high electrode mass always results in a thick electrode via traditional slurry-based processing, and electrochemical processes are inevitably limited by charge transport resistance and easy detachment of the thick electrode from the current collector.²¹⁻²³ Furthermore, the use of inactive materials, including conductive agents, binders, and metallic current collectors, further offsets the energy density.24 Thus, new electrode architectures endowing a high mass loading and avoiding

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the use of inactive additives without scarifying the electrochemical performance should be prepared.

Consequently, the construction of hybrid materials with freestanding porous carbon current collectors has been investigated as a feasible technique.15,25,26 The interconnected structure design provides enough space for high mass loading, avoids the thick active material from peeling off, and does not require organic binders.^{25,27} Fan et al.²⁸ fabricated a mulberrylike ZnO anchored in a 3D graphene aerogel anode with a highly stable capacity of 445 mA h g^{-1} up to 500 cycles. In their study, the ZnO mass loading was about 0.9 mg, corresponding to an areal capacity of 0.54 mA h cm⁻². Zhang et al.²⁹ developed a route to grow ZnO@ZnO QD/C core-shell nanorod arrays on a flexible conductive carbon cloth substrate. Owing to the shortened Li diffusion distance, sufficient conductivity, and good structure stability of the nanorod arrays, the selfsupported nanorod arrays manifested high stability even with a mass loading of $1.7-2 \text{ mg cm}^{-2}$. The areal capacity is up to 1.5 mA h cm $^{-2}$, which, to date, is the largest area capacity reported for a Zn-based anode. However, it is not comparable to that of the current lithium-ion batteries,15 and the mass loading should be further improved. Moreover, the gravimetric capacity was calculated using the mass of the active material instead of the entire electrode. The porous carbon material as a current collector contributed little to the capacity while accounted for more than 50% of the total weight of the electrode. This significantly lowered the total energy density and thus made porous carbon materials less attractive for practical applications in batteries.

Herein, we report an electrode architecture design using 3D carbon foam as a conductive scaffold and flexible ZnO NMs as a high energy active material. This architecture was proposed to eliminate the limitation of charge transport resistance and detachment of thick electrodes in the case of high mass loading. Its vast void space enables a high mass loading of the active material, and the porous structure facilitates rapid ion migration throughout the electrode. Thus, when ZnO NMs with an areal mass of 3-4 mg are added, as a model system, the composite C/ZnO NM foam exhibits excellent performance. The anode retains 92% capacity after 700 cycles at 2 A g^{-1} and 500 cycles at 5 A g^{-1} . It should be emphasized that the carbon foam used herein not only works as a current collector, but also contributes to the total capacity (200 mA h g^{-1} at 320 mA g^{-1}). The absence of inactive components in the electrode and high mass loading lead to a high areal capacity (4.3 mA h cm⁻²). As abovementioned, our ingenious C/ZnO composite possesses the merits of an ideal electrode material: super-long lifespan and high areal capacity.

Experimental

Material synthesis

Preparation of ZnO NMs. ZnO NMs were synthesized using the atomic layer deposition (ALD)-based technology reported in our previous study,³⁰ and the corresponding schematic is shown in Fig. S1.[†] Porous polyurethane was used as a template. The deposition of ZnO NMs on the template was conducted at 150 °C in a homemade reactor. Diethylzinc (DEZ) and water were used as precursors. A typical ALD sequence includes DEZ pulse (50 ms), waiting time (2 s), N₂ purge (20 s), H₂O pulse (30 ms), waiting time (2 s), and N₂ purge (20 s). Nitrogen (N₂) gas served as both the carrier and purge gas with a flow rate of 20 sccm. After deposition, a uniform ZnO layer was coated on all the exposed surfaces of the template (Fig. S1b and c†). Then, the samples were annealed at 700 °C for 3 h under an O₂ flow to remove the polymer template, and they changed from yellow to white (Fig. S1a†). A freestanding ZnO porous structure was simultaneously formed, and after crashing the porous structure, a large amount of ZnO NMs were obtained (Fig. S1d†). The NMs were washed with ethanol and deionized water to remove the residual organic material and inorganic salt.

Preparation of carbon foam. A melamine-based polymer was pyrolyzed at 700 $^{\circ}$ C in a quartz reactor under a N₂ flow (600 mL min⁻¹) for 3 h.

Preparation of the C/ZnO NM foam composite. A ZnO NM suspension with a concentration of 5.0 mg mL⁻¹ in alcohol was prepared and then treated by ultrasonication to obtain a uniformly dispersed solution. Then, the carbon foam was immersed in the suspension. After drying at room temperature, the samples were re-pyrolyzed under an inert atmosphere to make the ZnO NMs adhere to the carbon foam framework.

ZnO deposited on carbon foam by ALD. ALD was carried out at 150 °C in a homemade reactor. Diethylzinc (DEZ) and water were used as precursors. A typical ALD sequence includes DEZ pulse (20 ms), waiting time (5 s), N₂ purge (20 s), H₂O pulse (15 ms), waiting time (5 s), and N₂ purge (20 s). Nitrogen (N₂) gas served as both the carrier and purge gas with a flow rate of 20 sccm.

Microstructural characterization

The morphologies of the samples were investigated *via* scanning electron microscopy (SEM, Phenom Prox) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin). The crystallinity and phase composition of the samples were characterized by X-ray diffraction (XRD) analysis using a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Nitrogen sorption isotherms were obtained using a QuadraSorb SI MP Station. Thermogravimetric analysis (TGA) was performed using SDT Q600 in the range of 25–900 °C (heating rate: 10 °C min⁻¹) under an air flow. Raman spectra were obtained using a Jobin Yvon LabRAM HR800 spectrometer under excitation by a 632.8 nm He–Ne laser with a laser spot size of $\sim 1 \ \mu m^2$.

Electrochemical measurements

Electrochemical tests were performed using a coin-type 2032 half-cell. The samples (*e.g.*, carbon foam and the C/ZnO NM foam composite) were directly used as the working electrode. No additive (binder and conductive agent) was used. The electrolyte used for the Li-ion half cells consisted of a 1 M LiPF₆ solution in a 1 : 1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (Shenzhen Kejing Star Technology CO., LTD). The two-electrode systems were assembled into a cell in an

argon-circulating glove box (H₂O and O₂ < 1 ppm). A pure ZnO NM electrode was also prepared for comparison. The working electrode was composed of 80 wt% active material (ZnO NMs), 10 wt% conductive additive agent (Super-P), and 10 wt% binder (polyvinylidene difluoride in *N*-methyl-2-pyrrolidone (NMP)). The electrolyte used was same as that in the case of the C/ZnO NM foam composite. Galvanostatic charge/discharge tests were carried out using a battery testing system (LAND CT2001A) in the voltage window of 0.01–3 V ν s. Li⁺/Li at different current rates. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Zennium/IM6 electrochemical workstation in the frequency range from 1 MHz to 1 mHz at an amplitude of 5 mV. Cyclic voltammetry (CV) tests were also carried out at a scan rate of 0.2 mV s⁻¹ from 0 to 3 V using a Zennium/IM6 electrochemical workstation.

Results and discussion

Fig. 1a shows the fabrication process of the 3D C/ZnO NM foam. Initially, the carbon foam was obtained by pyrolyzing melamine-based polymer foam under a N_2 atmosphere. Subsequently, the carbon foam was anchored to the ZnO NMs by immersing it in a ZnO NM suspension and then subjected to a re-pyrolyzing process. The composite was directly used as working electrodes without any additives (right panel in Fig. 1a). The carbon foam used herein is freestanding and shows good mechanical strength; thus, it can be folded and compressed

(Fig. 1b–e). As obviously seen in the SEM image, the carbon foam shows an interconnected network with high porosity (Fig. 1c). This continuous network is retained even after the carbon foam is compressed (Fig. 1e and red arrows therein). The pore diameter is about 200 μ m (Fig. 1c), which decreases after compression. The surface area of the porous carbon foam was also measured and determined to be ~50 m² g⁻¹ (Fig. S2†). Moreover, Raman spectroscopy was carried out to study the nature of the carbon foam. The obtained spectra (Fig. S3†) present two distinct peaks at about 1339 (D band) and 1595 cm⁻¹ (G band). The D band is associated with disordered carbon, and the G band is ascribed to graphite-type carbon.^{31,32} It can be seen that the intensity of the D band is much stronger than that of the G band; this indicates an overall amorphous carbon structure.³³

ZnO NMs were synthesized using a scalable templateassisted ALD approach.³⁰ The ZnO NM is uniform and shows ultrathin and flexible properties (Fig. 1f). Its lateral size is about two orders of magnitude larger than its thickness (Fig. S4†), demonstrating its remarkable flexibility.¹² Fig. 1g shows the high-resolution TEM (HRTEM) image of the ZnO NMs, which indicates that ZnO is crystalline, and the distance of the lattice fringes is determined to be 0.28 nm, corresponding to the (100) planes of ZnO. Due to the large contact area of the twodimensional ZnO NMs, they are prone to adhere to surfaces they contact by physisorption.^{34–36} Thus, after immersing the carbon foam in the ZnO NM suspension, the ZnO NMs easily



Fig. 1 (a) Schematic of the synthetic procedure for the C/ZnO NM foam electrode. (b) Images of the freestanding carbon foam and carbon foam being folded (scale bar is 1 cm). (c) An SEM image of the interconnected framework. The inset shows an enlarged image with a scale bar of 50 μ m. (d) Images of the carbon foam being compressed. (e) An SEM image of the interconnected framework under compression. The inset shows an enlarged image under compression (scale bar: 10 μ m). (f) An SEM image of ZnO NM obtained with 200 ALD cycles. The inset shows the ZnO NMs in a vial. (g) An HRTEM image of ZnO NM. (h) An SEM image of C/ZnO NM foam composite electrode. (i) XRD patterns of carbon foam, ZnO NMs, and C/ZnO NM foam composite.

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anchored onto the surface of the carbon foam (Fig. 1h).³⁴ The treatment at high temperatures facilitates their tight adhesion. In addition, in this composite, its open pores enable good permeation of liquid electrolyte and provide channels for Li⁺ transport.^{37,38} To further prove the coexistence of both carbon material and ZnO in the C/ZnO NMs foam, we conducted XRD measurements. As shown in Fig. 1i, the results indicate the amorphous character of the carbon foam and the hexagonal phase of ZnO (PDF #36-1451). The peaks at $2\theta = 31.769^{\circ}$, 34.421° , 36.252° , 47.538° , 56.602° , and 62.862° are associated

with the (100), (002), (101), (102), (110), and (103) lattice planes of hexagonal ZnO, respectively.^{7,9}

Fig. 2a and b show the first five CV curves of the anode assembled using the C/ZnO NM foam (with 45% ZnO, Fig. S5†) and pure carbon foam at a scan rate of 0.2 mV s⁻¹, respectively. For the composite foam, in the first cathodic scan, three peaks are observed at 0.72, 0.63, and 0.36 V. The peak at 0.72 V presumably originates from the conversion reaction between ZnO and Li⁺ to form Zn and Li₂O and lithiation into amorphous carbon.³⁹ The broad peak at 0.36 V is ascribed to the multistep



Fig. 2 CV curves of the (a) C/ZnO NM foam composite and (b) carbon foam in the potential window of 0-3 V at a scanning rate of 0.2 mV s⁻¹. The rate performance of the (c) C/ZnO NM foam composite and (d) carbon foam at different current densities. (e) Cycling performance of the C/ZnO NM foam composite. All capacities were calculated using the total mass of the electrode.

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alloying process between Zn and Li⁺ to generate Li_xZn.⁴⁰ The peak at 0.63 V is ascribed to the decomposition of the electrolyte to generate an SEI layer.^{41,42} In the subsequent cathodic scans, a sharp peak at 0.87 V gradually stables, corresponding to the conversion reaction between ZnO and Li⁺ to form Zn and Li₂O and lithiation into amorphous carbon. Subsequently, the peak associated with an SEI layer disappears; this proves that there is no continuous growth of the SEI layer. The first anodic scan consists of two small peaks at 0.67 and 0.94 V and a broad peak at 1.33 V. The oxidation peaks at 0.67 and 0.94 V represent the dealloying reaction of the LirZn alloy to form Zn, and the peak at 1.33 V indicates the oxidation of Zn to generate ZnO.39 Moreover, the peak at 0.67 V represents delithiation of the carbon foam.4,7,11 The anodic curve shows almost no change in peak shape after 3 cycles, suggesting the high reversibility of the composite electrode. CV analysis of the anodes fabricated using carbon foam and ZnO NMs were also conducted to further understand the electrochemical process. For the pure ZnO NM anode (Fig. S6[†]), in the first cathodic scan, there is a strong peak at 0.61 V, related to the reduction of ZnO into Zn and the growth of the SEI layer.43 There are also three small peaks located at 0.48, 0.42, and 0.27 V, corresponding to the multistep alloying process of Li⁺ and Zn.⁴³ In the first anodic scan, the peak located at 0.76 V is associated with the dealloying process of Li_xZn, and the peak at 1.3 V is caused by the oxidation of Zn to generate ZnO.²⁸ The weak peak at 2.5 V corresponds to the conversion of Zn to ZnO and disappears in the subsequent scan. In the subsequent cycles, the peak located at 1.0 V is related to the reduction of ZnO to Zn, and the broad peak at around 0.5 V represents the alloying process and the continuous growth of the SEI layer.³⁹ Additionally, the small peak located at 0.25 V is ascribed to the alloying process of Zn and Li⁺. Accordingly, the electrochemical reactions of the ZnO-based electrode are proposed as follows:

> $ZnO + 2Li^+ + 2e^- \leftrightarrow Zn + Li_2O;$ $Zn + xLi^+ + xe^- \leftrightarrow Li_xZn (x < 1).$

For the carbon foam electrode (Fig. 2b), the first cathodic scan consists of two peaks located at 0.55 and 0.31 V, which present the lithiation of carbon and formation of the SEI layer, respectively.⁴² On the anodic side, the broad large peak located at 0.4 V is ascribed to delithiation. After the first cathodic-anodic cycle, a broad band centered at 0.61 V appears and becomes stable in the subsequent cycles, which corresponds to the lithiation of the carbon foam.⁴⁴

Fig. 2c displays the rate performance of the composite. The C/ZnO NM foam electrode shows a relatively low initial coulombic efficiency (ICE) due to the large surface area of the formed SEI layer,⁴⁵ and an improved coulombic efficiency is observed upon decreasing the initial current density (Fig. S7†).⁴⁶ The coulombic efficiency manifested a rapid increase, which exceeded 95% in the second cycle and sustained 99.5% in the subsequent cycles. The rapid stable coulombic efficiency is mainly ascribed to the superior structure of the electrode structure. The porous and flexible carbon foam provides

sufficient space for the ZnO NMs to release the strain by deformation rather than by cracking. This would prevent the further growth of the SEI layer and thus enable a high coulombic efficiency during the following cycles. Moreover, the open pores and interconnected framework could remarkably improve the electronic and ionic transport throughout the electrode, facilitating the reversible lithiation/delithiation of Li⁺.⁴⁷ On the contrary, a poor coulombic efficiency is observed for the pure ZnO NM electrode due to the fracture of ZnO and excessive growth of the SEI layer (see Fig. S8 and S9 in the ESI[†]).^{48,49} High steady discharge capacities of 450, 375, 288, 175, and 80 mA h g^{-1} are observed at a current density of 250, 500, 1000, 2000, and 4000 mA g^{-1} , respectively. The charge/ discharge profiles are shown in Fig. S10.[†] When the current density switches back to 250 mA g^{-1} , an average capacity of about 450 mA h g^{-1} is recovered. It is notable that herein, the specific capacity is given based on the total mass of the electrode. If only the mass of ZnO is calculated, the capacities are up to 1000, 833, 640, 388, and 177 mA h g⁻¹, which are higher than those previously reported for C/ZnO composite anodes (Fig. S11[†]). The capacity of the composite is higher than the theoretical capacity of the ZnO anode due to the contribution of the carbon foam. Therefore, the electrochemical lithium storage performance of the carbon foam was further evaluated (Fig. 2d). Coin cells were fabricated by directly using the carbon foam as the electrode without any additives. The battery exhibited the capacities of 300, 255, 225, 200, and 175 mA h g^{-1} at a current density at 40, 80, 160, 320, and 640 mA g^{-1} . The capacity retention is 58% with the current increasing by 16 times the original current. The excellent rate is enabled by the fast electron transport through the continuous framework, good permeation of the liquid electrolyte, and fast Li⁺ diffusion due to the open pores. Moreover, the carbon foam electrode maintains a long-term stable capacity of 220 and 170 mA h g^{-1} at 240 and 640 mA g^{-1} , respectively, with no apparent capacity decay after 600 cycles (Fig. S12[†]). Thus, when the carbon foam is composited with the ZnO NMs, the composite electrode manifests both the superiority of the carbon foam and ZnO NMs, as illustrated in the long cycling performance in Fig. 2e. The composite electrode was further cycled at 2000 mA g^{-1} for 700 cycles and at 5000 mA g^{-1} for 500 cycles, with a capacity at around 260 and 180 mA h g^{-1} based on the electrode mass (577 and 400 mA h g^{-1} based on ZnO mass, much higher than the theoretical capacity of the commercially used graphite anode), respectively. No apparent capacity loss is observed during the first 800 cycles, and the coulombic efficiency remains constant at approximately 100%. At an even higher current of 5000 mA g^{-1} , a stable capacity of 180 mA h g^{-1} is still measured after 500 cycles with an 8% capacity loss, illustrating excellent stability. In addition, we should mention that the composition of the composite affects its electrochemical properties.⁵⁰ Thus, a C/ZnO NM electrode with a lower ZnO content (23%) was also prepared. This electrode possessed better conductivity due to its higher carbon content; thus, better capacity reversibility was observed (Fig. S13[†]).

We considered that the excellent electrochemical performance of the C/ZnO NM foam composite was related to its unique structure features in several aspects. ZnO in the form of 2D NMs shows superior mechanical properties. The 2D NMs could release the strain of lithiation/delithiation by deformation rather than by cracking.¹²⁻¹⁴ In the composite, the porous and flexible carbon foam structure provides sufficient space for the ZnO NMs to release the strain, which is favorable for longlife batteries. As illustrated in Fig. 3a and b, after 100 cycles at 640 mA h g^{-1} , the carbon foam maintains its initial structure, the composite inherits this merit, and the ZnO NMs still anchor to the framework of the carbon foam tightly (inset of Fig. 3a). However, the pure ZnO NM electrode suffers from fast capacity fading in the first 10 cycles (Fig. S8[†]). This may be caused by the structure fracture of the ZnO NMs due to volume change (Fig. S9[†]). A thin SEI layer was formed during the first discharge procedure, but it was too thin to stand the volume change of ZnO. Nanocracks may occur and expose the inside of ZnO, thus causing continuous growth of the SEI layer.48,49 This led to gradual capacity decay due to Li consumption. The structure fracture is proven by the structural changes in the electrode before and after cycling (shown in Fig. S9[†]). In addition, the



Fig. 3 SEM images of the (a) carbon foam electrode and (b) C/ZnO NM foam composite electrode after 100 cycles at 640 mA h g⁻¹. The insets show the corresponding magnified images with a scale bar of 3 μ m.

electrode synthesized by directly depositing ZnO on carbon foam *via* ALD sustained severe capacity fading (Fig. S14[†]) due to fracturing and finally pulverization of the continuous fixed ZnO layer deposited on the carbon foam (inset in Fig. S14[†]).

To gain more insight into the superior performance of the composite electrode, EIS measurements were carried out, and Fig. 4 illustrates the Nyquist plots of the C/ZnO NM foam electrode before and after the galvanostatic charge/discharge cycles. Before lithiation, the plot exhibits a single semicircle at high-tomedium frequencies, followed by the appearance of a straight line at low frequencies. The single semicircle is assigned to the charge transfer process, whereas the sloping straight line represents the typical Warburg behavior, which is associated with the diffusion of lithium in the electrode.4,51 A second semicircle is observed in the charge state, which is commonly attributed to the formation of a surface layer on the electrode due to the decomposition of the electrolyte at a low discharge potential.52 The diameter of the second semicircle gradually stabilizes in the charge state battery. Herein, an equivalent circuit was used to fit the Nyquist plots, as depicted in the upper panel of Fig. 4. Herein, $R_{\rm e}$, $R_{\rm SEI}$, and $R_{\rm ct}$ represent electrolyte resistance (e), SEI resistance, and charge transfer resistance (ct), respectively.53 CPE is the respective constant-phase element accounting for the depressed semicircle in the experimental spectra. $W_{\rm s}$ is the Warburg impedance, and $C_{\rm int}$ is the intercalation capacitance. The fitted R_{ct} is 110 Ω for the as-prepared anode. After 1, 3, and 4 cycles, the fitted values of R_{ct} are 115,



Fig. 4 EIS spectra of the C/ZnO NM foam composite electrode before and after galvanostatic charge/discharge. The upper panel shows the equivalent circuit used to fit the experimental results. Herein, $R_{\rm e}$, $R_{\rm SEI}$, and $R_{\rm ct}$ represent electrolyte resistance (e), SEI resistance, and charge transfer resistance (ct), respectively. CPE is the respective constantphase element accounting for the depressed semicircle in the experimental spectra. $W_{\rm s}$ is the Warburg impedance and $C_{\rm int}$ is the intercalation capacitance.

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135, and 135 Ω , and the fitted values of R_{SEI} are 260, 225, and 210 Ω , respectively. The gradually stabilized R_{SEI} demonstrates the formation of a stable SEI layer on the ZnO NMs surface, indicating the good stability of the present composite.

The importance of areal capacity for practical batteries needs to be particularly emphasized. A high areal mass loading is a critical requirement for high areal capacity. However, many previous studies only focused on improving the gravimetric capacity and cycling life based on a low mass loading of the active material. Herein, an areal capacity of up to 4.3 mA h cm $^{-2}$ at 80 mA g^{-1} was obtained, which satisfied the typical areal capacity requirement (4 mA h cm^{-2}) for practical applications. Moreover, it is the highest areal capacity reported to date for a C/ZnO composite electrode (Fig. 5).15,16,29,39,40,54 To demonstrate the potential application of the composite electrode in electrical devices requiring high-power and energy density, the Ragone plot (Fig. S15[†]) of the composite electrode was further studied. All data were calculated based on the total mass of the electrode. At a current density of 80 mA g^{-1} , the cell demonstrates a maximum gravimetric energy density of 330 W h kg⁻¹ at which the power density is still around 64 W kg^{-1} . Even if the current density increases to 2560 mA g^{-1} , the energy density remains 126 W h kg⁻¹ with the corresponding highest power density of 2980 W kg⁻¹. These values are significantly high to satisfy the applications in various fields. However, for its potential application in full cells, due to the low ICE of the C/ ZnO NM foam, an extra cathode or cathode additives are required to compensate the loss of cathode capacities in the formation of the SEI on the C/ZnO NMs foam anode, which will sacrifice the energy density of the battery. However, this could be suppressed by pre-solidating the C/ZnO NM foam by galvanostatic cycling in the half-cell.55 Moreover, specially designed electrolytes (e.g., gel-like electrolyte48) and surface modification using thin oxides⁵⁶ are efficient strategies to improve the ICE; the high areal capacity, high stability, and further improvement of ICE will make the C/ZnO NM foam promising for use in batteries.



Fig. 5 Comparison of the overall areal capacity of the C/ZnO NM foam composite electrode with those of the C/ZnO composites reported in recent studies.

The good performance obtained is ascribed to the unique composite structure. The large surface area (50 m² g⁻¹, Fig. S2^{\dagger}) due to the volumetric porosity (95%) of the carbon foam provides sufficient space for a high mass loading of ZnO NMs $(3-4 \text{ mg cm}^{-2})$. However, the bearing mass of ZnO on a unit area is much smaller (2 orders of magnitude) than that on a normal flat substrate because of the large surface area of the carbon foam. This avoids the active material from peeling off the current collector and eliminates charge transport resistance that usually occurs in conventional thick electrodes.^{21,24,35} For comparison, a conventional ZnO electrode with a close areal capacity was also prepared via a typical traditional slurry-based processing on a flat current collector. The thickness of the electrode is close to 500 µm, and this thick electrode easily detaches from the current collector (Fig. S16[†]) due to its weak bonding strength and high mechanical strain during processing. This would dramatically inhibit electron transfer from the current collector to the electrode materials. In contrast, electron transfer from the conductive carbon foam to the ZnO NMs is more effective in the C/ZnO NM foam. In addition, the carbon foam in the composite electrode is not just a conductive medium, but also provides reasonable lithium storage capacity (see Fig. 2d and S12[†]). The high areal mass loading, absence of inactive components, and superior structure characteristics of the C/ZnO NM foam composite electrode finally lead to a significant areal energy density.

Conclusion

Herein, we introduced a new composite anode consisting of an interconnected carbon foam anchored with flexible ZnO NMs at a high mass loading (C/ZnO NMs foam). Initially, the new electrode architecture endowed long cycles life. Upon cycling at 2000 mA h g^{-1} for 700 cycles and 5000 mA h g^{-1} for 500 cycles, the capacity remained stable at 270 and 160 mA h g^{-1} , respectively, without apparent decay (based on the total mass of the electrode). Moreover, an areal capacity of up to 4.3 mA h cm^{-2} was achieved using a ZnO NM mass loading of 3-4 mg. The large surface area of the carbon foam made the bearing mass of ZnO per area much smaller than that in the case of a flat electrode. This effectively eliminated the charge diffusion limitation and detachment of the electrode from a flat current collector. It should be emphasized that the carbon foam used herein not only functions as a current collector, but also contributes to the total capacity. The absence of inactive components, high area mass loading, and superior structure characteristic in the composite electrode led to a long cycle life and an enhanced areal energy density. Our ingenious C/ZnO composite exhibits the merits of an ideal electrode. This approach is expected to be expandable to other active materials and therefore has important application potentials in many fields.

Conflicts of interest

There are no conflicts to declare.

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