Co$_3$ZnC@NC Material Derived from ZIF-8 for Lithium-Ion Capacitors
Yongfu Tang, Haiwei Li, Ruonan Zhang, Wenfeng Guo, and Meiqi Yu*

**ABSTRACT:** Metal–organic framework (MOF)-derived carbon materials were widely reported as the anodes of lithium-ion capacitors (LICs). However, tuning the structure and electrochemical performance of the MOF-derived carbon materials is still challenging. Herein, metal carbide materials of Co$_3$ZnC@NC-8:2 were obtained by the pyrolysis of the MOF materials of Co$_{0.2}$Zn$_{0.8}$ZIF-8 (Zn/Co ratio of 8:2). A half-cell assembled with the Co$_3$ZnC@NC-8:2 electrode exhibits a discharge capacity of the electrode material of 598 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. After 100 cycles, the retention rate of discharge specific capacity is about 90%. The high performance of Co$_3$ZnC@NC-8:2 is ascribed to its high crystalline degree and well-defined structure, which facilitates the intercalation/deintercalation of lithium ions and buffers the volume change during the charge/discharge process. The high capacitance contribution ratio calculated by cyclic voltammetry (CV) curves at different scanning rates indicates the pseudocapacitance storage mechanism. LICs constructed from the Co$_3$ZnC@NC-8:2 material have a rectangular CV curve, while the charge–discharge curve has a symmetrical triangular shape. This study indicates that MOF-derived carbon is one of the promising materials for high-performance LICs.

1. INTRODUCTION

Fossil fuel shortage and environmental pollution have seriously affected the development of human society. Development and application of clean energy technology are imperative. Currently, lithium-ion batteries (LIBs) and electrochemical supercapacitors (SCs) are the most widely used rechargeable energy storage techniques among all electrochemical energy storage methods. LIBs have been widely applied in consumer electronics, electric vehicles, and energy storage due to their high energy density, long cycle life, and environmental friendliness.1–3 Due to the low diffusion rate of lithium ions in positive and negative electrode materials, the low power density of LIBs cannot meet the high-power startup and acceleration requirements.4 SCs have the advantages of high power density, long cycle life, and excellent stability,5 while their disadvantages are low energy density and large self-discharge loss in pure electric applications.6,7 Lithium-ion capacitors (LICs) are new hybrid energy storage devices combining LIBs and SCs, which endow them with the advantages of both LIBs and SCs, such as high energy density, high power density, excellent safety, and cycle stability.

Mesoporous carbon materials,8–10 metal carbides,11 MXene-based materials,12,13 reduced graphene oxide-based materials,14,15 three-dimensional (3D) graphene including their hybrid derivatives,6,17 MnO$_2$-based materials,18 and so on are widely used as electrode materials for LICs and exhibit high capacitive performances. Porous carbon and 3D graphene have been attracting more attention as active materials for LICs due to their high surface areas, which offer more sites for lithium ion storage.9,17 Meanwhile, the impressive electrochemical activity of MXene makes it one of the most potential electrode materials in rechargeable batteries and supercapacitors.12,13 Among these advanced materials, metal carbides are considered one of the most promising electrode materials for electrochemical storage devices19 due to their high con-
ductivity and robust mechanics to alleviate volume changes. Metal–organic frameworks (MOFs) are one of the promising precursors for the synthesis of carbon materials and metal carbides.\textsuperscript{20} Metal carbides derived from MOFs\textsuperscript{21–24} have been attracting much research interest due to the following advantages: (1) metal-based nanoporous carbon materials derived from MOFs with robust carbon frameworks effectively alleviate the volume expansion and structure damage during discharge/charge cycles;\textsuperscript{25–28} (2) shortened Li ion transport path and enlarged electrode/electrolyte contact area due to small particle size and the porous structure can promote the diffusion and transfer rate of both Li ions and electrons during the high-rate discharge/charge process;\textsuperscript{29–31} and (3) doped N atoms in carbon-based structures from the ligands of MOFs efficiently increase the storage capacity for lithium ions.\textsuperscript{32–34} Chaikittisilp et al.\textsuperscript{35} used the porous carbon material prepared by directly pyrolyzing zeolitic imidazolate framework-8 (ZIF-8) in a supercapacitor, and its specific capacitance was as high as 251 F g\textsuperscript{−1}. Kim et al.\textsuperscript{36} prepared porous carbon with a specific surface area up to 350 m\textsuperscript{2} g\textsuperscript{−1} using MOFs as a precursor, which exhibited a specific capacitance of 272 F g\textsuperscript{−1}. The above examples have indicated that the electrode made of the MOF-derived carbon material has better double-layer capacitance performance and can be used as a capacitor-type positive electrode in LICs.

In this paper, MOF-derived N-doped carbon-coated Co\textsubscript{x}ZnC materials (Co\textsubscript{x}ZnC@NC) with different Zn/Co ratios\textsuperscript{37} in precursors were synthesized via a two-step route, including the preparation of Co\textsubscript{x}ZnCo-ZIF-8 and the post carbonization process. At a Zn/Co ratio of 8:2, the morphologies of Co\textsubscript{x}ZnCo-ZIF-8 and Co\textsubscript{x}ZnC-8:2 were the most well-defined structures. Co\textsubscript{x}ZnC@NC materials with different bimetallic ratios in precursors were assembled into half-cells, and the electrochemical properties were analyzed and characterized. Co\textsubscript{x}ZnC-8:2 exhibits the best rate capability and cycle performance among these MOF-derived metal carbides. In addition, the charge storage mechanism of the batteries was analyzed via cyclic voltammetry and galvanostatic discharge/charge curves. The results show that the capacity of the battery is mainly derived from the pseudocapacitance mechanism of the material. Thus, the Co\textsubscript{x}ZnC@NC material was assembled into LICs and electrochemical performance measurements were conducted. The results show that Co\textsubscript{y}ZnC-8:2 has the best rate capability and cycle stability.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis and Characterization of Co\textsubscript{x}ZnC@NC

Zn\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (2.4 g) and 0.72 g of cobalt acetylacetonate (Zn/Co molar ratio of 8:2) were mixed into 40 mL of methanol to prepare solution A. Dimethyl imidazole (6.5 g) was dissolved into 80 mL of methanol to prepare solution B. Solution B was quickly dropped into solution A and stirred rigorously for 24 h at room temperature. After the completion of the reaction, the product was washed with ethanol several times to remove the impurities and then dried under vacuum at 80 °C to obtain a light purple solid. Moreover, Co\textsubscript{y}ZnCo-ZIF-8 samples with different Zn/Co molar ratios of 9:1, 7:3, and 6:4 were synthesized by the same method. The obtained light purple solid was pyrolyzed in a tube furnace under a N\textsubscript{2} atmosphere at 800 °C for 1 h to obtain the Co\textsubscript{x}ZnC@NC sample. The phase structure and morphology of the obtained ZIF-8 and Co\textsubscript{x}ZnC@NC samples were characterized using an X-ray diffractometer (XRD, Max-2500, Rigaku Corp., Japan), a transmission electron microscope (TEM, HT-7700, Hitachi Corp., Japan), a high-resolution TEM (HRTEM, Titan TEM 300, FEI Corp.), and a V-SoB 2800P surface area and pore size distribution analyzer (Brunauer–Emmett–Teller, BET).

2.2. Preparation of Electrodes and Electrochemical Measurements of LICs

In the preparation of lithium-ion battery electrodes, the active material poly(vinylidene fluoride) (PVDF) and Super P were mixed at a mass ratio of 8:1:1 and ground for approximately 20 min in a mortar. After mixing, 1-methyl-2-pyrrolidone (NMP) was added dropwise and then ground continuously until a uniform slurry was formed. Then, the slurry was coated evenly onto a clean copper foil (neatly placed on a glass plate). Next, the coated electrode was dried in a vacuum drying oven at 80 °C for 12 h. After drying, the electrode was cut into several spherical electrode sheets with a diameter of 11 mm. Several blank copper foil sheets were cut via the same process. The prepared electrodes and the blank copper foils were weighed three times to obtain their weights. The mass of active materials was obtained by subtraction between the masses of the prepared electrodes and blank copper foils and then multiplication by 0.8.

Before assembling LICs, the Co\textsubscript{y}ZnC@NC materials with different bimetallic ratios in precursors need to be assembled into half-cells to evaluate their electrochemical performance. When assembling the half-cells, both the oxygen and water contents in a glovebox were maintained below 0.01 ppm. Charged electrode sheets were used as working electrodes, metallic lithium foils as counter electrodes, Celgard as the separator, and the solution mixed with LiPF\textsubscript{6} (EC/DEC/DMC = 1:1:1) as the electrolyte. Coin-type lithium-ion half-cells were assembled with the order of working electrodes, electrolyte, separator, electrolyte, and lithium foils in a CR2032 battery container. After finishing the assembly, the half-cells were sealed on the sealing machine at a pressure of 50 MPa. Before the electrochemical properties were tested, the battery was placed in an incubator at 25 °C for 12 h to ensure that the electrodes and the separator were completely wet by the electrolyte. The half-cells were clamped on a galvanostatic discharge–charge tester in the incubator for the electrochemical property test.

To assemble the LICs, the graphite electrodes were prelithiated to act as lithium-containing electrodes.\textsuperscript{48} The assembled half-cells were precycled three times at a voltage range of 0–3 V with a cutoff voltage of 0 V. The lithium-ion half-cells were disassembled to obtain the prelithiated graphite electrodes as the anodes for LICs. The Co\textsubscript{y}ZnC@NC electrodes were used as cathodes. The glass fiber film with a diameter of 16 mm and the solution mixed with LiPF\textsubscript{6} (EC/DEC/DMC = 1:1:1) were used as the separator and the electrolyte, respectively. The LICs were assembled in the order of prelithiated graphite electrode, glass fiber film, electrolyte (approximately 150 μL), and nonlithiated Co\textsubscript{x}ZnC@NC electrode. After finishing assembly, the batteries were sealed on a sealing machine at a pressure of 50 MPa. Before the electrochemical properties were tested, the batteries were kept in an incubator at 25 °C for 12 h.

3. RESULTS AND DISCUSSION

3.1. XRD, Raman Spectra, and X-ray Photoelectron Spectroscopy (XPS) Analysis of Co\textsubscript{y}ZnCo-ZIF-8 and Co\textsubscript{y}ZnC@NC

XRD patterns of CoZIF-87, Co\textsubscript{y}ZnCo-ZIF-8, ZnZIF-8, Co@NC, Co\textsubscript{y}ZnC@NC, and Zn@NC are shown in Figure 1. Figure 1a shows the XRD patterns of CoZIF-87,
Figure 1. (a) XRD patterns of CoZIF-67, Co$_x$Zn$_y$ZIF-8, and ZnZIF-8. (b) XRD patterns and (c) Raman spectra of Co@NC, Co$_3$ZnC@NC, and Zn@NC. (d) Survey XPS spectra of Co$_3$ZnC@NC-8:2.

Figure 2. TEM images of (a–d) Co$_x$Zn$_y$ZIF-8 with different Zn/Co ratios and (e–h) Co$_3$ZnC@NC after high-temperature pyrolysis of Co$_x$Zn$_y$ZIF-8 with different Zn/Co ratios (9:1, 8:2, 7:3, and 6:4).
ZnZIF-8, and Co3ZnC@NC-8:2 with different Zn/Co ratios, and the scanning range of the samples is 5–30° with a scanning rate of 2° min⁻¹. All samples show similar diffraction peaks, which correspond to the characteristic peaks of ZIF-8 in the literature. This shows that the addition of Co with different contents does not change the crystalline structure of Co3ZnC@NC-8:2. CoZIF-67 with pure Co metal exhibits a similar XRD pattern to that of Co3ZnC@NC-8:2. A negative shift of the peaks was observed with the increase of the Co content in CoZIF-67, corresponding to the lattice expansion with the increase of the Co content. It should be ascribed to the weaker interaction between Co ions and ligands than that between Zn ions and ligands. With the increase of the Co content, the intensity and crystallinity gradually decrease. Figure 1b shows the XRD patterns of the Co@NC, Co3ZnC@NC, and Zn@NC materials produced after high-temperature pyrolysis of CoZIF-67, Co3ZnZIF-8, and ZnZIF-8. The characteristic peaks of 41.9, 48.7, and 71.5° are assigned to the (111), (200), and (220) planes of Co3ZnC, respectively, with the standard JCPDS card number of 29-0524. Only the Co3Zn phase was formed, which may be ascribed to the loss of the additional Zn element under the pyrolysis process at high temperatures. The diffraction peaks located at 44.3, 51.4, and 75.8° in the Co@NC sample should be ascribed to the (111), (200), and (220) plane of metallic Co (Figure 1b), respectively. This result indicates that only metallic Co was formed during the pyrolysis of CoZIF-67. Within the range of 20–30°, there are diffraction peaks of carbon, which show the existence of amorphous carbon with a low graphitization degree. The diffraction peak intensity is increased with the increase of the Co content, which indicates that the content and crystallinity of Co3ZnC in the samples increase with the increase of Co in the precursors. The Raman spectra of Co@NC, Co3ZnC@NC, and Zn@NC were given to investigate the effect of the metal on the structure of the obtained materials. As shown in Figure 1c, the peaks located at 1324 and 1564 cm⁻¹ are assigned to the D and G bands of carbon. All of the Co3ZnC@NC materials exhibit a higher intensity ratio of the D and G bands (I_D/I_G) than 1.0, corresponding to rich structure defects, which may offer rich sites for lithium ion storage and provide high capacity. Figure 1d shows the survey XPS spectra of the Co3ZnC@NC-8:2 material. The peaks assigned to Co, Zn, C, and N are clearly observed in the spectra. This result indicates that the obtained materials are N-doped carbon-coated Co3ZnC materials, which is consistent with the literature. The element mapping of the Co3ZnC@NC-8:2 material (Figure S1) indicates the uniform distribution of Co, Zn, and C elements.

3.2. TEM Analysis of Co3ZnC@NC. TEM images of Co3ZnC@NC with different Zn/Co ratios are given in Figure 2. As shown, all of the Co3ZnC@NC samples with different Zn/Co ratios show a well-defined polyhedral structure (Figure 2a–d). The regularity of MOF materials is decreased with the increase of the Co content. The replacement of Zn²⁺ by a large amount of Co²⁺ causes the collapse of the framework of ZIF-8, which is consistent with the XRD pattern shown in Figure 1a. It is interesting that both CoZIF-67 and ZnZIF-8 exhibit higher particle sizes than that of Co3ZnC@NC-8:2, although the morphologies of both CoZIF-67 and ZnZIF-8 are similar to that of Co3ZnC@NC-8:2 (Figure S2a,b). This result indicates that the nanoparticle sizes of Co3ZnC@NC-8:2 composites were refined due to the addition of Co into ZnZIF-8. The pyrolyzed materials exhibited a similar tendency. As shown in Figure 2e–h, the regularity of the Co3ZnC@NC material is decreased with an increase in the Co content, and Co3ZnC@NC-8:2 shows the most well-defined structure. In addition, after heat treatment, the obtained Co3ZnC@NC materials and pristine Co3ZnC@NC-8:2 materials show similar polyhedral morphologies. Co3ZnC@NC-8:2 has the most well-defined polyhedral structure. However, the collapse of the morphology and the rough surface are caused by the decomposition of ligands and the migration of metal atoms during the high-temperature pyrolysis process, forming a bimetallic nitrogen-substituted polyhedral carbon nanocage with a rough surface. The TEM images of Co@NC and Zn@NC were also recorded to determine their morphologies (Figure S2c,d). Carbon nanotubes (CNTs) were observed in Co@NC, which should be the catalysis of Co nanoparticles on the formation of CNTs. The HRTEM images were recorded to further investigate the microstructure of Co3ZnC@NC-8:2 (Figure 3). A small nanoparticle with a lattice space of 0.371 nm, corresponding to the (100) plane of Co3ZnC, was coated with partially

![Figure 3. HRTEM images of (a) Co3ZnC particle and (b) N-doped carbon in Co3ZnC@NC-8:2.](https://example.com/figure3)
graphitized N-doped carbon (Figure 3a). Amorphous carbon was observed in the region far away from the Co\(_3\)ZnC nanoparticle (Figure 3b).

3.3. BET Analysis of Co\(_3\)ZnC. Figure 4a,b shows the nitrogen adsorption−desorption isotherms and pore size distribution of Co\(_{0.2}\)Zn\(_{0.8}\)ZIF-8, respectively. As shown in Figure 4a, the adsorption−desorption isotherm of Co\(_{0.2}\)Zn\(_{0.8}\)ZIF-8 exhibits a typical I-type behavior, corresponding to the existence of micropores. The specific surface area of Co\(_{0.2}\)Zn\(_{0.8}\)ZIF-8 is 1419.9 m\(^2\) g\(^{-1}\). From the pore size distribution, the pore size is concentrated around 1−2 nm (micropores), which is consistent with the isotherm. Figure 4c,d shows the nitrogen adsorption−desorption isotherm and pore size distribution of Co\(_3\)ZnC@NC-8:2, respectively. After high-temperature treatment, the specific surface area is reduced to 566.2 m\(^2\) g\(^{-1}\), and the N\(_2\) adsorption capacity is increased quickly at a low relative P/P\(_0\) value, which proves the existence of micropores. There is a hysteresis loop at P/P\(_0\) = 0.4−0.99, indicating the existence of mesopores formed by the high-temperature pyrolysis of Co\(_{0.2}\)Zn\(_{0.8}\)ZIF-8. The most probable pore size distribution is around 4 nm, confirming the existence of mesopores. The most probable pore in Co\(_3\)ZnC@NC-8:2 is larger than that of the solvated lithium ions, facilitating the diffusion of ions during the discharge/charge process.

3.4. Electrochemical Performance of Co\(_3\)ZnC@NC. 3.4.1. Charge/Discharge Cycle Performance of Co\(_3\)ZnC@NC. To further evaluate the electrochemical performances of these materials, the rate performance and the cycle stability of the electrodes were tested. As shown in Figures 5a and S3, the first cycle specific discharge capacities of Co\(_3\)ZnC@NC at different Zn/Co ratios (9:1, 8:2, 7:3, and 6:4), Zn@NC, and Co@NC at 0.1 A g\(^{-1}\) are 540, 589, 425, 250, 442, and 232 mAh g\(^{-1}\), respectively. Co\(_3\)ZnC@NC-8:2 exhibits the highest specific discharge capacity, which should be ascribed to its most well-defined structure. The well-defined structure provides a short ion transportation path, which promotes the rapid diffusion of lithium ions. Furthermore, the doping of N atoms can add more active sites and increase the storage capacity of lithium ions. The specific charge capacities of Co\(_3\)ZnC@NC-8:2 at 0.1, 0.2, 0.5, and 1 A g\(^{-1}\) are 598, 551, 409, and 307 mAh g\(^{-1}\), respectively. The specific discharge capacity is restored to around 590 mAh g\(^{-1}\) at a charge/discharge current density of 0.1 A g\(^{-1}\), which demonstrates that the material has good rate performance. The long cycle stability of electrodes was tested at 0.1 A g\(^{-1}\). After 100 discharge/charge cycles at 0.1 A g\(^{-1}\), the Co\(_3\)ZnC-8:2 electrode exhibits a high discharge capacity retention of 90% (Figure 5b). After high-temperature treatment, the structural stability of the material is improved, enhancing the cycle stability. Figure 5c shows the charge/discharge curves of the 2nd, 25th, 50th, and 100th cycles of the electrode at 0.1 A g\(^{-1}\). The five curves are almost coincided, indicating good cycle stability, which corresponds to the performance of the long cycle. Figure 5d shows the high rate performance of Co\(_3\)ZnC@NC-8:2 at rates of 1, 2, 5, and 10 A g\(^{-1}\). A battery with the Co\(_3\)ZnC@NC-8:2 electrode exhibits good rate performance at high current densities. When the...
Figure 5. (a) Rate performance of Co$_3$ZnC@NC electrodes with different Zn/Co ratios. (b) Long cycle performance of Co$_3$ZnC@NC electrodes at 0.1 A g$^{-1}$. (c) Charge and discharge curves of the long cycle with different cycles at 0.1 A g$^{-1}$. (d) Rate performance curves of the Co$_3$ZnC@NC-8:2 electrode.

Figure 6. (a) Cyclic voltammetry and (b) the discharge/charge curves in the first three cycles of Co$_3$ZnC@NC-8:2 at 0.1 A g$^{-1}$. (c) CV curves of Co$_3$ZnC@NC-8:2 at different scanning rates. (d) Capacitance contribution ratio at a scanning rate of 0.5 mV s$^{-1}$. (e) Capacitance contribution ratio at different scanning rates. (f) Nyquist diagram of Co$_3$ZnC@NC electrodes before the cycling test.
current density was increased from 1 to 10 A g\(^{-1}\), the capacity of the Co\(_3\)ZnC@NC-8:2 electrode was still 80 mAh g\(^{-1}\) at 10 A g\(^{-1}\). When the current density was reduced to 1 A g\(^{-1}\) again, the performance was recovered fully, indicating the good high rate performance of Co\(_3\)ZnC@NC-8:2.

3.4.2. Cyclic Voltammetry of Co\(_3\)ZnC-8:2. To further investigate the electrochemical behavior of the material, cyclic voltammetry tests were performed on the half-cells. Figure 6a shows the first three cycles of cyclic voltammetry (CV) curves at 0.1 mV s\(^{-1}\) at a voltage range of 0–2.5 V. The area of the first cycle of cyclic voltammetry performance is significantly different from those of the second and third cycles. A strong cathode peak appears at around 0.7 and 1.5 V during the first discharge cycle, which corresponds to the plateau position in the charge–discharge curves shown in Figure 6b. In the second and third cycles, two reduction peaks observed in the first cycle disappear due to the formation of a solid electrolyte interphase (SEI) film during the first discharge process. The cathode peak at about 1.4 V is mainly ascribed to the synergistic effect of Co\(_3\)ZnC@NC, nitrogen doping, and polyhedral carbon nanocages; a set of wider anode peaks at 1.0–1.5 V correspond to the delithiation reaction in the carbon nanocages. Cyclic volt-ampere performances were tested at different scanning rates of 0.2, 0.5, 1.0, and 2.0 mV s\(^{-1}\) at a voltage range of 0–2.5 V to investigate the rate performance. As shown in Figure 6c, the oxidation peak and the reduction peak still exist in each cycle, corresponding to the high rate performance.

The charge storage mechanism of the battery is judged with different scanning rates and the resulted peak current responses, as given in eq 1.

\[
i = av^b
\]

where \(i\) is the peak current; \(v\) is the scanning rate, and \(a\) and \(b\) are adjustable parameters. When \(b\) is 1, the electrochemical system shows the capacitance behavior controlled by ionic adsorption or the surficial faradic reaction. When \(b\) is 0.5, the system shows an ion diffusion process controlled by lithium ion intercalation/deintercalation. In Figure 6c, the scanning rate and the logarithm of peak current were used as the abscissa and the ordinate, respectively, and \(b\) is the slope. In this case, \(b\) is 0.9296, the pseudocapacitance dynamics dominated the whole reaction process, suggesting that the material can be used as the electrode of LICs.

To further determine the capacitance contribution correlating to the scanning rate, the formula can be modified as eq 2.

\[
i = k_1v + k_2v^{1/2}
\]

where \(k_1\) and \(k_2\) are adjustable parameters. Both sides of the formula are divided by \(v^{1/2}\) to get the formula as eq 3.
At each voltage, $i/v^{1/2}$ and $v^{1/2}$ are fitted linearly to obtain a fitted $k_1v^{1/2}$ and $k_2v^{1/2}$, respectively. Capacitance values ($k_1v$) at different voltages ($V$) were connected to obtain the fitted capacitance contribution. The ratios between the areas of the fitted closed curve and the CV curve are the pseudocapacitance contribution ratios at different scanning rates. As shown in Figure 6e, at scanning rates of 0.2, 0.5, 1.0, and 2.0 mV s$^{-1}$, the capacitance contribution ratios are 55.1, 59.3, 67.8, and 71.1%, respectively. With the increase in the scanning rate, the capacitance contribution ratio is increased. As shown in Figure 6e, the pseudocapacitance accounts for the main contribution of the capacity, indicating that Li storage in the electrode is mainly attributed to the pseudocapacitance mechanism. The pseudocapacitance contribution should be ascribed to the intercalation of lithium ions in the Co$_3$ZnC nanoparticles and the graphitic structure coating on the Co$_3$ZnC nanoparticles, as shown in the HRTEM image (Figure 3a).

To further study the electrochemical properties of the material, the AC impedance measurement was performed at a frequency range of 0.1–10 000 Hz and an amplitude of 5 mV in this paper. Figure 6f shows the Nyquist plots of Co$_3$ZnC@NC with different Zn/Co ratios before the cycling performance. The resistance of the material was analyzed during the electrochemical reaction. The impedance diagram consists of two parts, corresponding to different impedances. The cross-connection between the plots and the real axis at a high-frequency area represents the ohmic impedance of the electrode, while the semi arc at medium frequency represents the charge-transfer resistance of the electrode. Co$_3$ZnC@NC-8:2 shows the lowest resistance, corresponding to its best performance. It is mainly due to the porous carbon nanocage structure, which facilitates the insertion and extraction of Li ions. The Nyquist plot of the Co$_3$ZnC@NC-8:2 electrode after 100 cycles was also conducted to investigate the cycling stability of the Co$_3$ZnC@NC-8:2 electrode. As shown in Figures 6f and S4, both the ohmic and charge-transfer resistances did not increase after the cycling test, which contributed to the high cycling performance of the Co$_3$ZnC@NC-8:2 electrode. The SEM images of the Co$_3$ZnC@NC-8:2 electrode after the cycling test indicate that the electrode remains stable after cycling (Figure S5).

### 3.4.3. Electrochemical Performance of LICs

To avoid the imbalance of electrochemical kinetics and the capacity between the cathode and the anode of LICs, the cathode material was changed from activated carbon and graphite to the same material as the anode to improve the performance of the entire capacitor by increasing the capacity of the cathode material. In addition, during the charge and discharge processes, lithium ions were inserted into carbon pores and N-containing active centers, while PF$_6^-$ were accumulated on carbon pores and the nitrogen-doped surface, which improved the electrochemical performance of the battery.

Figure 7 shows the electrochemical performance of LICs configured with Co$_3$ZnC@NC and pretreated graphite electrodes (Co$_3$ZnC@NC/graphite LIC), in which the graphite electrode exhibits suitable electrochemical properties (Figure S6). Figure 7a shows the cyclic volt-amperic curves of LICs at a voltage range of 1–3 V and scanning rates of 2, 5, 10, and 20 mV s$^{-1}$. With the increase in the scanning rate, the shape of the CV curve presents a rectangular shape, indicating the good capacitive characteristic of the LIC. Figure 7b shows the charge and discharge curves of LICs at current densities of 0.1, 0.2, 0.5, 1, 2, and 5 A g$^{-1}$, showing a relatively symmetrical triangular shape and suggesting the dynamics matching of the cathode and the anode. As shown in Figure 7c, the specific discharge capacities at 0.1, 0.2, 0.5, 1, 2, and 5 A g$^{-1}$ are 53.55, 45.77, 40.15, 30.3, 20.14, and 3.24 F g$^{-1}$, respectively. The result indicates good rate performance. Ragone plots of the Co$_3$ZnC@NC/graphite LIC cell (Figure S7) show high energy densities of 67.1 and 4.1 Wh kg$^{-1}$ at power densities of 120 W kg$^{-1}$ and 1.48 kW kg$^{-1}$, respectively, which are comparable to the reported LICs with different electrodes at low power densities. Figure 7d shows the good cycle stability of the LIC during 1000 discharge/charge cycles.

### 4. CONCLUSIONS

In this paper, Co$_3$ZnC@NC materials were synthesized by the pyrolysis of Co$_3$Zn,ZIF-8 materials at 800 °C with different Zn/Co ratios in precursors. Co$_3$Zn,ZIF-8 materials with different Zn/Co ratios show similar diffraction peaks in XRD. Co$_{0.2}$Zn$_{0.8}$ZIF-8 with a Zn/Co ratio of 8/2 exhibits the highest crystalline degree. However, the crystalline degree of the Co$_3$ZnC material derived from the Co$_3$Zn,ZIF-8 MOF material increased with the increase of the Co content. The rate performance of Co$_3$ZnC@NC-8:2 is the best. After 100 cycles, the specific discharge capacity retention rate of the material is maintained at approximately 90%. The high performance is ascribed to its high crystalline degree and well-defined structure, which facilitates the insertion and extraction of lithium ions and buffers the volume change of the material during the charge and discharge processes. The charge storage mechanism of the battery was investigated by CV curves at different scanning rates. The pseudocapacitance accounts for the main contribution of Li storage in the electrode. LICs configured with Co$_3$ZnC@NC-8:2 show a rectangular CV curve and a relatively symmetrical triangular charge and discharge curve at different rates, indicating good kinetic matching of the cathode and the anode to achieve equilibrium.

### ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02271.

- SEM image and element mapping; TEM images; rate performance of electrodes; EIS spectra of the electrode; SEM images of the material after cycling; electrochemical properties of the graphite electrode; and Ragone plots of LiCs (PDF)

### AUTHOR INFORMATION

**Corresponding Author**
Meiqi Yu – Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P. R. China; orcid.org/0000-0001-8122-998X; Email: meiqiyu@ysu.edu.cn

**Authors**
Yongfu Tang – Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering.

ACS Omega 2021, 6, 28528–28537

https://doi.org/10.1021/acsomega.1c02271

28535
Haiwei Li — Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P. R. China

Ruonan Zhang — Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P. R. China

Wenfeng Guo — Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02271

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the selective funding for provincial postdoctoral research projects (B2019003018), Fok Ying-Tong Education Foundation of China (No. 171064), and the Natural Science Foundation of Hebei Province (B2018203297).

REFERENCES

(1) Zhou, S.; Huang, P.; Xiong, T.; Yang, F.; Yang, H.; Huang, Y.; Li, D.; Deng, J.; Balogun, M.-S. Sub-Thick Electrodes with Enhanced Transport Kinetics via In Situ Epitaxial Heterogeneous Interfaces for High Areal-Capacity Lithium Ion Batteries. Small 2021, No. 2100778. (2) Huang, Y.; Yang, H.; Xiong, T.; Adekoya, D.; Qiu, W.; Wang, Z.; Zhang, S.; Balogun, M.-S. Adsorption energy engineering of nickel oxide hybrid nanosheets for high areal capacity flexible lithium-ion batteries. Energy Storage Mater. 2020, 25, 41–51.

(3) Li, G.; Ouyang, T.; Xiong, T.; Jiang, Z.; Adekoya, D.; Wu, Y.; Huang, Y.; Balogun, M.-S. All-carbon-frameworks enabled thick electrode with exceptional high-areal-capacity for Li-Ion storage. Carbon 2021, 174, 1–9.

(4) Getman, R. B.; Bea, Y. S.; Wilmer, C. E.; Snurr, R. Q. Review and Analysis of Molecular Simulations of Methane, Hydrogen, and Acetylene Storage in Metal-Organic Frameworks. Chem. Rev. 2012, 112, 703–723.

(5) Xiong, T.; Su, H.; Yang, F.; Tan, Q.; Appadurai, P. B. S.; Afuwape, A. A.; Guo, K.; Huang, Y.; Wang, Z.; Balogun, M.-S. Harmonizing self-supportive VN/ MoS2 pseudocapacitance core-shell electrodes for boosting the areal capacity of lithium storage. Mater. Today Energy 2020, 17, No. 100461.

(6) Dong, M. J.; Zhao, M.; Ou, S.; Zou, C.; Wu, C. D. A Luminescence Dye@MOF Platform: Emission Fingerprint Relationships of Volatile Organic Molecules. Angew. Chem., Int. Ed. 2014, 53, 1575–1579.

(7) Jiang, H. L.; Feng, D.; Liu, T. F.; Li, J. R.; Zhou, H. C. Pore Surface Engineering with Controlled Loadings of Functional Groups via Click Chemistry in Highly Stable Metal-Organc Frameworks. J. Am. Chem. Soc. 2012, 134, 14690–14693.

(8) Zhang, K.; Lee, T. H.; Khalilzadeh, M. A.; Varma, R. S.; Choi, J.; Wang, J.; Hwang, R. H.; Shokouhimehr, M. Rendering Redox Reactions of Cathodes in Li-Ion Capacitors Enabled by Lanthanides. ACS Omega 2020, 5, 1634–1639.

(9) Cai, P.; Zou, K.; Zou, G.; Hou, H.; Ji, X. Quinone/ester-based oxygen functional group incorporated full carbon Li-ion capacitor for enhanced performance. Nanoscale 2020, 12, 3677–3685.

(10) Zou, K.; Cai, P.; Deng, X.; Wang, B.; Liu, C.; Li, J.; Hou, H.; Zou, G.; Ji, X. Revealing dual capacitive mechanism of carbon cathode toward ultrafast quasi-solid-state lithium ion capacitors. J. Energy Chem. 2021, 60, 209–221.

(11) Yi, S.; Wang, L.; Zhang, X.; Li, C.; Liu, W.; Wang, K.; Sun, X.; Xu, Y.; Yang, Z.; Cao, Y.; Sun, J.; Ma, Y. Cationic intercalates assisted self-assembly two-dimensional TiC2/TiO2@rGO hybrid nanoflakes for advanced lithium-ion capacitors. Sci. Bull. 2021, 66, 914–924.

(12) Zhang, X.; Wang, L.; Liu, W.; Li, C.; Wang, K.; Ma, Y. Recent Advances in MXenes for Lithium-Ion Capacitors. ACS Omega 2020, 5, 75–82.

(13) Liu, F.; Jin, S.; Xia, Q.; Zhou, A.; Fan, L.-Z. Research on progress in energy and storage performance of MXene heterostructures. J. Energy Chem. 2021, 62, 220–242.

(14) Bazan-Aguilar, A.; Ponce-Vargas, M.; Caycho, C. L.; La Rosita-Toro, A.; Baena-Moncada, A. M. Highly Porous Reduced Graphene Oxide-Coated Carbonized Cotton Fibers as Supercapacitor Electrodes. ACS Omega 2020, 5, 32149–32159.

(15) Li, C.; Zhang, X.; Lv, Z.; Wang, K.; Sun, X.; Chen, X.; Ma, Y. Scalable combustion synthesis of graphene-welded activated carbon for high-performance supercapacitors. Chem. Eng. J. 2021, 414, No. 128781.

(16) Li, L.; Zhang, D.; Hou, Y.; Fang, J.; Kang, Q.; Feng, R.; Liang, Z.; Deng, J. Lithium/sodium-ion capacitors based on 3D graphene-based materials. Energy Storage 2021, No. 4010282.

(17) Liu, C.; Ren, Q.-Q.; Wang, S.-W.; Yin, B.-S.; Que, L.-F.; Zhao, L.; Sui, X.-L.; Yu, F.-D.; Li, X.; Gu, D.-M.; Wang, Z.-B. High energy and power lithium-ion capacitors based on MnO2/3D graphene as anode and activated polyaline-derived carbon nanorods as cathode. Chem. Eng. J. 2019, 370, 1485–1492.

(18) Moon, J. S.; Nula, A.; Hwang, Y. G.; Nula, V.; Sohn, K. Y. Facile Synthesis of Porous Cobalt-Doped lambda-MnO2 Nanarchitectures as a High-performance Anode Material for Li-Ion Batteries and Li-ion Hybrid Supercapacitors. ChemistrySelect 2021, 6, 7012–7024.

(19) Gao, X. T.; Liu, Y. T.; Zhu, X. D.; Yan, D. J.; Wang, C.; Feng, Y. J.; Sun, K. N.V2O5 nanoparticles confined in Three-Dimensionally organized, porous Nitrogen-Doped graphene frameworks: Flexible and Free-Standing cathodes for high performance lithium storage. Carbon 2018, 140, 45–51.

(20) Li, Y.; Xia, Y.; Liu, K.; Ye, K.; Wang, Q.; Zhang, S.; Huang, Y.; Liu, H. Constructing Fe-MOF-Derived Z-Scheme Photocatalysts with Enhanced Charge Transport: Nanointerface and Carbon Sheath Synergistic Effect. ACS Appl. Mater. Interfaces 2020, 12, 25494–25502.

(21) Chen, J.; Mu, X.; Du, M.; Lou, Y. Porous rod-shaped Co3O4 derived from Co-MOF as high-performance anode materials for lithium ion batteries. Inorg. Chem. Commun. 2017, 84, 241–245.

(22) Li, S.; Chen, J.; Gong, X.; Wang, J.; Lee, P. S. Holey graphene-wrapped porous TiNbO2O6 microparticles as high-performance intercalation pseudo capacitive anode materials for lithium-ion capacitors. NPG Asia Mater. 2018, 10, 406–416.

(23) Poongsombate, A.; Iyimen, T.; Dittanet, P.; Embley, B.; Kongkachuyichay, P. Direct synthesis of dimethyl carbonate from CO2 and methanol by supported bimetallic Cu−Ni/ZIF-8 MOF catalysts. J. Taiwan Inst. Chem. Eng. 2017, 80, 16–24.

(24) Yu, H.; Xia, H.; Zhang, J.; He, J.; Guo, S.; Xu, Q. Fabrication of Fe-doped Co-MOF with mesoporous structure for the optimization of supercapacitor performances. Chin. Chem. Lett. 2018, 29, 834–836.

(25) Li, W.; Hu, S.; Luo, X.; Li, Z.; Sun, X.; Li, M.; Liu, F.; Yu, Y. Confined Amorphous Red Phosphorus in MOF-Derived N-Doped Carbon as Superior Anode for Sodium-Ion Battery. Adv. Mater. 2017, 29, No. 1605820.

(26) Li, Y.; Cai, X.; Chen, S.; Zhang, H.; Zhang, K. H. L.; Hong, J.; Chen, B.; Kuo, D. H.; Wang, W. Highly Dispersed Metal Carbide on ZIF-Derived Pyridinic-N-Doped Carbon for CO2 Enrichment and Selective Hydrogenation. ChemSusChem 2018, 11, 1040–1047.

(27) Zhang, X.; Zhang, T.; Wang, Y.; Li, J.; Liu, C.; Li, N.; Liao, J.; Yang, H.; Chen, T.; Peng, X.; Chen, J. Mixed-matrix membranes based on Zn/Ni-ZIF-8-PEBA for high performance CO2 separation. J. Membr. Sci. 2018, 560, 38–46.

(28) Xu, J.; Zhang, W.; Chen, Y.; Fan, H.; Su, D.; Wang, G. MOF-derived porous N-Co3O4@N-C nanododecahedra wrapped with

28536

https://doi.org/10.1021/acsomega.1c02271 ACS Omega 2021, 6, 28528–28537
reduced graphene oxide as a high capacity cathode for lithium-sulfur batteries. J. Mater. Chem. A, 2018, 6, 2797−2807.

(29) Zhang, G.; Hou, S.; Zhang, H.; Zeng, W.; Yan, F.; Li, C. C.; Duan, H. High-Performance and Ultra-Stable Lithium-Ion Batteries Based on MOF-Derived ZnO@ZnO Quantum Dots/C Core-Shell Nanorod Arrays on a Carbon Cloth Anode. Adv. Mater. 2015, 27, 2400−2405.

(30) Chen, M.; Han, L.; Zhou, J.; Sun, C.; Hu, C.; Wang, X.; Su, Z. Photoreduction of carbon dioxide under visible light by ultra-small Ag nanoparticles doped into Co-ZIF-9. Nanotechnology 2018, 29, No. 284003.

(31) Xu, X.; Cao, R.; Jeong, S.; Cho, J. Spindle-like Mesoporous α-Fe2O3@Anode Material Prepared from MOF Template for High-Rate Lithium Batteries. Nano Lett. 2012, 12, 4988−4991.

(32) Yu, F.; He, Z.; Qiang, S. Modification of cobalt-containing MOF-derived mesoporous carbon as an effective sulfur-loading host for rechargeable lithium-sulfur batteries. J. Alloys Compd. 2019, 772, 843−851.

(33) Shi, W.; Xu, X.; Zhang, L.; Liu, W.; Cao, X. Metal-organic framework-derived structures for next-generation rechargeable batteries. J. Mater. Chem. A 2018, 11, No. 1830006.

(34) Shrivastav, V.; Sundriyal, S.; Goel, P.; Kaur, H.; Tutega, S.; Vikrant, K.; Kim, K.; Tiwari, U.; Deep, A. Metal-organic frameworks (MOFs) and their composites as electrodes for lithium battery applications: Novel means for alternative energy storage. Coord. Chem. Rev. 2019, 393, 48−78.

(35) Yang, M.; Hu, X.; Fang, Z.; Sun, L.; Yuan, Z. Bifunctional MOF-Derived Carbon Photonic Crystal Architectures for Advanced Zn-Air and Li-S Batteries: Highly Exposed Graphitic Nitrogen Matters. Adv. Funct. Mater. 2017, 27, No. 1701971.

(36) Li, X.; Sun, Q.; Liu, J.; Xiao, B.; Li, R.; Sun, X. Tunable porous structure of metal organic framework derived carbon and the application in lithium-sulfur batteries. J. Power Sources 2016, 302, 174−179.

(37) Zhou, J.; Yu, X.; Fan, X.; Wang, X.; Li, H.; Zhang, Y.; Li, W.; Zheng, J.; Wang, B.; Li, X. The impact of the particle size of a metal−organic framework for sulfur storage in Li−S batteries. J. Mater. Chem. A 2015, 3, 8272−8275.

(38) Zhang, X.; Ou-Yang, W.; Zhu, G.; Lu, T.; Pan, L. Shuttle-like carbon-coated FeP derived from metal-organic frameworks for lithium-ion batteries with superior rate capability and long-life cycling performance. Carbon 2019, 143, 116−124.

(39) Huang, M.; Mi, K.; Zhang, J.; Liu, H.; Yu, T.; Yuan, A.; Kong, Q.; Xiong, S. MOF-derived bi-metal embedded N-doped carbon polyhedral nanocages with enhanced lithium storage. J. Mater. Chem. A 2017, 5, 266−274.

(40) Li, M.; Wang, J.; Jiao, C.; Wang, C.; Wu, Q.; Wang, Z. Magnetic porous carbon derived from a Zn/Co bimetallic metal-organic framework as an adsorbent for the extraction of chlorophenols from water and honey tea samples. J. Sep. Sci. 2016, 39, 1884−1891.

(41) Li, R.; Ren, X.; Feng, X.; Li, X.; Hu, C.; Wang, B. A highly stable metal- and nitrogen-doped noncomposite derived from Zn/Ni-ZIF-8 capable of CO2 capture and separation. Chem. Commun. 2014, 50, 6894−6897.

(42) Thanh, M. T.; Thien, T. V.; Du, P. D.; Hung, N. P.; Khieu, D. Q. Iron doped zeolitic imidazolate framework (Fe-ZIF-8): synthesis and photocatalytic degradation of RDB dye in Fe-ZIF-8. J. Porous Mater. 2018, 25, 857−869.

(43) Xiao, M.; Zhu, J.; Ma, L.; Jin, Z.; Ge, J.; Deng, X.; Hou, Y.; He, Q.; Li, J.; Jia, Q.; Mukerjee, S.; Yang, R.; Jiang, Z.; Su, D.; Liu, C.; Xiong, W. Microporous Framework Induced Synthesis of Single-Atom Dispersed Fe-N-C Acidic ORR Catalyst and Its in Situ Reduced Fe-N4 Active Site Identification Revealed by X-ray Absorption Spectroscopy. ACS Catal. 2018, 8, 2824−2832.

(44) Yang, T.; Yang, D.; Liu, Y.; Liu, J.; Chen, Y.; Bao, L.; Lu, X.; Xiong, Q.; Qin, H.; Ji, Z.; Ling, C. D.; Zheng, R. MOF-derived carbon-encapsulated cobalt sulfides orostachys-like micro/nano-structures as advanced anode material for lithium ion batteries. Electrochim. Acta 2018, 290, 193−202.

(45) Chaikittisilp, W.; Hu, M.; Wang, H.; Huang, H.-S.; Fujita, T.; Wu, K. C.-W.; Chen, L.-C.; Yamauchi, Y.; Ariga, K. Nanoporous carbons through direct carbonization of a zeolitic imidazolate framework for supercapacitor electrodes. Chem. Commun. 2012, 48, 7259−7261.

(46) Kim, H.; Park, K.-Y.; Cho, M.-Y.; Kim, M.-H.; Hong, J.; Jung, S.-K.; Roh, K. C.; Kang, K. High-Performance Hybrid Supercapacitor Based on Graphene-Wrapped Li4Ti5O12 and Activated Carbon. ChemElectroChem 2014, 1, 125−130.

(47) Li, Z.; Li, C.; Ge, X.; Ma, J.; Zhang, Z.; Li, Q.; Wang, C.; Yin, L. Reduced graphene oxide wrapped MOFs-derived cobalt-doped porous carbon polyhedrons as sulfur immobilizers as cathodes for high performance lithium sulfur batteries. Nano Energy 2016, 23, 15−26.

(48) Sun, C.; Zhang, X.; Li, C.; Wang, K.; Sun, X.; Ma, Y. High-efficiency sacrificial prelithiation of lithium-ion capacitors with superior energy-storage performance. Energy Storage Mater. 2020, 24, 160−166.

(49) Song, X.; Jiang, Y.; Cheng, F.; Earnshaw, J.; Na, J.; Li, X.; Yamauchi, Y. Hollow Carbon-Based Nanoarchitectures Based on ZIF: Inward/Outward Contraction Mechanism and Beyond. Small 2021, 17, No. 2004142.

(50) Zhou, H.; He, D.; Saana, A. I.; Yang, J.; Wang, Z.; Zhang, J.; Liang, Q.; Yang, S.; Zhu, J.; Mu, S. Mesoporous-silica induced doped carbon nanotube growth from metal−organic frameworks. Nanoscale 2018, 10, 6147−6154.

(51) Singla, G.; Bhanage, S. N.; Mahajan, M.; Kurungot, S. Facile synthesis of CNT interconnected PVP-ZIF-8 derived hierarchically porous Zn/N co-doped carbon frameworks for oxygen reduction. Nanoscale 2021, 13, 6248−6258.

(52) Wang, Q.; Ina, T.; Chen, W.-T.; Shang, L.; Sun, F.; Wei, S.; Sun-Waterhouse, D.; Telfer, S. G.; Zhang, T.; Waterhouse, G. I. N. Evolution of Zn(II) single atom catalyst sites during the pyrrolysisis-induced transformation of ZIF-8 to N-doped carbons. Sci. Bull. 2020, 65, 1743−1751.

(53) Cheng, G.; Si, C.; Zhang, J.; Wang, Y.; Yang, W.; Dong, C.; Zhang, Z. Facile fabrication of cobalt oxide nanosstructures with superior specific capacitance and super-long cycling stability. J. Power Sources 2016, 312, 184−191.

(54) Vijayan, B. L.; Misnon, I. I.; Karuppaiyah, C.; Kumar, G. A.; Yang, S.; Yang, C. C.; Jose, R. Thin metal film on porous carbon as a medium for electrochemical energy storage. J. Power Sources 2021, 489, No. 229522.

(55) Wang, G.; Lu, C.; Zhang, X.; Wan, B.; Liu, H.; Xia, M.; Gou, H.; Xin, G.; Lian, J.; Zhang, Y. Toward ultrafast lithium ion capacitors: A novel atomic layer deposition seeded preparation of Li4Ti5O12/graphene anode. Nano Energy 2017, 36, 46−57.

(56) Jin, L.; Guo, X.; Shen, C.; Qin, N.; Zheng, J.; Wu, Q.; Zhang, C.; Zheng, J. P. A universal matching approach for high power-density and high cycling-stability lithium ion capacitor. J. Power Sources 2019, 441, No. 22711.

(57) Sun, W.; Tao, X.; Du, P.; Wang, Y. Carbon-coated mixed-metal sulfide hierarchical structure: MOF-derived synthesis and lithium-storage performances. Chem. Eng. J. 2019, 366, 622−630.