Sodium-ion batteries (SIBs) are promising next-generation alternatives due to the low cost and abundance of sodium sources. Yet, developmental electrodes in SIBs such as transition metal sulfides have huge volume expansion, sluggish Na\(^+\) diffusion kinetics, and poor electrical conductivity. Here, bimetallic sulfide (Co\(_9\)S\(_8\)/ZnS) nanocrystals embedded in hollow nitrogen-doped carbon nanosheets are demonstrated with a high sodium diffusion coefficient, pseudocapacitive effect, and excellent reversibility. Such a unique composite structure is designed and synthesized via a facile sulfidation of the CoZn-MOFs followed by calcination and is highly dependent on the reaction time and temperature. The optimized Co\(_1\)Zn\(_1\)-S(600) electrode exhibits excellent sodium storage performance, including a high capacity of 542 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\), good rate capability at 10 A g\(^{-1}\), and excellent cyclic stability up to 500 cycles for half-cell. It also shows potential in full-cell configuration. Such capabilities will accelerate the adoption of sodium-ion batteries for electrical energy applications.

1. Introduction

Lithium-ion batteries (LIBs) have permeated energy storage market from portable electronics to electric vehicles in view of their high energy density and long cycle life.\(^{[1]}\) Nevertheless, it is still expensive to scale up due to the limited Li sources.\(^{[2]}\) In contrast, sodium-ion batteries (SIBs), with similar energy storage mechanism to LIBs, have recently attracted more attention for large-scale energy storage systems because of the natural abundance and low cost of sodium.\(^{[3]}\) However, the larger size of the Na\(^+\) (≈1.09 Å) leads to sluggish electrochemical reaction kinetics, unstable solid electrolyte interphase (SEI) layer, and severe structural distortion of the host materials,\(^{[4]}\) giving rise to inferior electrochemical performance. Therefore, the key point to SIBs lies in the development of electrode materials, especially the stable anode materials,\(^{[5]}\) to enable good sodium storage capability.

Compared to the intercalation SIBs anodes such as carbon (hard carbon),\(^{[6]}\) sodium super ion conductor (NASICON)-structured materials (NaTi\(_2\)(PO\(_4\))\(_3\), KTi\(_2\)(PO\(_4\))\(_3\), Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)),\(^{[7]}\) VS\(_2\),\(^{[8]}\) and TiS\(_2\),\(^{[9]}\) transition metal sulfides (TMSs) with conversion reaction or alloy-dealloying reaction have higher theoretical gravimetric and volumetric specific capacities.\(^{[10]}\) Therefore, the conversion mechanism, metal sulfides are reduced by Na\(^+\) ion to form the representative metal and Na\(_2\)S,\(^{[5]}\) for example, Co\(_9\)S\(_8\) converts to metal Co dispersed in an Na\(_2\)S matrix.\(^{[11,12]}\) The alloy-dealloying reaction of metal sulfides always follow the conversion reaction at a lower redox potential, depending on the alloy formation ability of the metal and sodium.\(^{[13]}\) These TMSs beyond the intercalation chemistry suffer from severe volume changes upon sodiation/desodiation, sluggish Na\(^+\) diffusion kinetics, and poor electrical conductivity, leading to large irreversible capacity, limited cycle life, and inferior rate performance.\(^{[15]}\)

One solution to address these issues is to design nanostructures with interior vacancy, which could shorten the Na\(^+\) diffusion pathways and buffer the volume changes simultaneously.\(^{[16]}\) Introducing bimetallic sulfides (or multiphase) with abundant phase boundaries enables small crystalline domains also hosts promising.\(^{[17]}\) It avoids deeply solid-state diffusion with fast ions diffusion kinetics and produces significant pseudocapacitance effect.\(^{[18,19]}\) Moreover, bimetallic sulfides exhibit higher electronic conductivity and richer redox reactions when compared to the monometal sulfides,\(^{[20]}\) which can significantly enhance the electrochemical performance.

Herein, we report the In situ formation of Co\(_9\)S\(_8\)/ZnS nanocrystals embedded in hollow nitrogen-doped carbon...
nanes via a facile sulfidation of CoZn-MOFs followed by calcination. The formation mechanism of the bimetallic sulfides (Figure 1a) and the evolution of hollow structure (Figure 1b) were investigated in detail. This novel nanosheet with internal space serves as a rigid structure for the sodiation/desodiation reaction (Figure 1c). The abundant phase boundaries of Co9S8/ZnS create numerous extrinsic defects and active sites for fast electron and ion transportation, as illustrated in Figure 1d. Moreover, the nitrogen-doped carbon matrix, abundant in pyridinic and pyrrolic nitrogen in our case, can also greatly contribute to the pseudocapacitance effect and guarantee the fast the ions diffusion kinetics thus synergistically improves the rate performance and reversibility of the composite. Galvanostatic intermittent titration techniques (GITT) technology revealed that Na+ diffusion in the redox step was sluggish, and bimetallic sulfides with richer redox/conversion reactions exhibited higher sodium diffusion coefficient overall. The optimized Co9S8/ZnS exhibited a high capacity of 542 mA h g⁻¹ at 0.1 A g⁻¹, good rate capability at 10 A g⁻¹, and excellent cyclic stability up to 500 cycles. More importantly, Na1V4(PO4)₃|Co9Zn1-S full cell (CR2032) delivered a high reversible capacity and a good cyclic stability with the capacity retention of 93% after 500 cycles.

2. Results and Discussion

2.1. Formation Mechanism and Physical Characterization

We proposed in situ formation of Co9S8/ZnS nanocrystals embedded in hollow nitrogen-doped carbon nanosheets. Co-Zn leaf-shaped bimetallic zeolitic imidazolate framework (ZIF-L) with a molar ratio of Co²⁺:Zn²⁺ = 1:1 (named as Co1Zn1-ZIF-L) was sulfurized in thioacetamide (TAA) solution for different time, denoted as Co1Zn1-ZIF-L (Time). Scanning electron microscopy (SEM) images (Figure S1a–d, Supporting Information) show the gradual dissolution of inner organic framework. A sulfides shell on the Co1Zn1-ZIF-L surface was built up and became more significant with the increase of the reaction time. Transmission electron microscopy (TEM) images (Figure 2a–c) also demonstrate the enhancement in contrast between the center and the edge, indicating the gradual formation of the hollow structure. It could be deduced that sulfide ions reacted with metal ions on MOFs surface at the initial sulfidation process to form a thin sulfide layer (as illustrated in Figure 1b). It is believed that this buffer shell is the key factor for the hollow structure by preventing the direct contact between inner MOFs and outside S²⁻ ions. Apparently, the diffusion kinetic of the Zn/Co²⁺ ions in the buffer shell is faster than that of the S²⁻ ions due to the smaller ionic radius, indicating that the outward diffusion of Zn/Co²⁺ ions is much easier than the inward diffusion of the S²⁻ ions. Therefore, Zn/Co²⁺ ions released from the inner MOFs and diffuse to the outer surface of the shell to further react with S²⁻ ions. The dissolution of inner MOFs resulted in inner cavities, as demonstrated by the cracks under the shell (Figure 2c). High-resolution TEM (HRTEM) (Figure 2d–f) and selected area electron diffraction (SAED) (Figure 2g–i) provide further insight into the detailed structure. Few lattice fringes in Co1Zn1-ZIF-L (10 min) (Figure 2g) suggest few sulfuration reaction at the initial procedure compared to the HRTEM image of Co1Zn1-ZIF-L (Figure S2, Supporting Information). The lattice fringes and diffraction rings became more significant at prolonged sulfuration time, indicating the mass formation of sulfides. X-ray diffraction (XRD) patterns (Figure S1e, Supporting Information) indicate that Co1Zn1-ZIF-L was completely sulfurated after 30 min and converted to bimetallic sulfides of ZnS and Co9S8 (Figure 2e,f). However, the poor crystalline ZnS and Co9S8 required further thermal annealing.

The followed calcination procedure was determined by the thermogravimetric (TG) analysis (Figure S3a, Supporting Information). Two exothermic peaks at ~285 and ~475 °C could be ascribed to the crystallization of ZnS and conversion of Co9S8 to stable phase Co9S8, respectively. XRD patterns (Figure S3b, Supporting Information) reveal that Co9S8 was formed after 500 °C. Further calcination at higher temperature results in better crystallinity. The sample obtained at 600 °C (Co1Zn1-S(600)) exhibits high purity with good crystallinity (Figure 3a). It clearly shows the cubic Co9S8 phase (PDF No. 73-1442) and cubic ZnS phase (powder diffraction file (PDF) No. 77-2100). Metallic Co phase (PDF No. 15-0806) was detected due to the remain of reduced Co during carbonization of Co1Zn1-ZIF-L (10 min),[28] as shown in Figure S3c in the Supporting Information. The coexistence of ZnS and metallic Co phase after the calcination of Co1Zn1-ZIF-L (20 min) further confirmed the prior sulfidation of Zn²⁺ ions. The reserved organic framework was in situ transferred to nitrogen-doped carbon during calcination.

X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the surface composition of Co1Zn1-S(600). The ZnS and Co9S8 components are clearly detected on the surface, as demonstrated by Figure 3b. The high resolution
of N1s spectrum exhibited mainly three nitrogen environments (Figure 3b) which are corresponding to pyridinic N (398.5 eV), pyrrolic N (399.7 eV), and graphitic N (401.0 eV), respectively.\(^{[29]}\) Interestingly, the N content in Zn-containing compounds is higher than that of Co\(_9\)S\(_8\), as summarized in Table S1 in the Supporting Information. The proportion of pyridinic/pyrrolic-type N in Co\(_{1}\)Zn\(_{1}\)-S(600) is as high as 75.5 wt%, which could create numerous extrinsic defects and active sites in carbon. This would greatly contribute to the ultrafast pseudocapacitive sodium storage,\(^{[22]}\) leading to fast reaction kinetic and good rate capability. SEM image (Figure 3c) showed the well-maintained hollow nanosheet, as further proven by TEM image (Figure 3d). Inset Figure 3c illustrated the hollow structure. The Co\(_{1}\)Zn\(_{1}\)-S(600) has a high specific Brunauer–Emmett–Teller surface area of 219.3 m\(^2\) g\(^{-1}\) (Figure S5, Supporting Information) with mainly pore diameter below 10 nm. High-angle annular dark-field scanning TEM and elemental mapping images (Figure 3e) reveals that Zn, Co, S, C, and N are evenly distributed in the hollow nanosheet. Interestingly, when the sulfide products were removed, it keeps a hollow carbon nanosheet structure (Figure S6, Supporting Information). HRTEM images (Figure 3f and Figure S7a, Supporting Information) show abundant phase boundaries between ZnS and Co\(_9\)S\(_8\) particles. Phase boundaries have been widely adopted in Ti-based materials for improving Li storage performance;\(^{[30]}\) however, the impact to the TMSs systems for SIBs is yet to be explored. The interfaces and the lattice mismatch (\(m\)) can be calculated using Equation (1)\(^{[17]}\)

\[
m = \frac{|d_i \sin \theta - d_j|}{0.5 \times (d_i \sin \theta + d_j)}
\]

For instance, lattice fringes of ZnS (220) plane and Co\(_9\)S\(_8\) (220) plane with a 40° angle, ZnS (220) plane and Co\(_9\)S\(_8\) (311) plane with a 90° angle exhibited \(m\) of 13.9% and 44.9%, respectively. The large amount of lattice distortion between the interfaces of bimetallic sulfides created more crystal defects for conductivity improvement and more active sites for Na\(^+\) storage. SAED pattern (Figure S7b, Supporting Information) further confirmed the coexistence of ZnS and Co\(_9\)S\(_8\) in Co\(_{1}\)Zn\(_{1}\)-S(600). The molar ratio of Zn: Co detected by energy dispersive X-ray analysis was 1.08 (Figure S7c, Supporting Information), which corresponded to the initial experimental design.

### 2.2. Electrochemical Na-Ion Storage Performance

The electrochemical performance was evaluated in a half cell using sodium foil as both counter and reference electrodes. Figure 4a shows the first three cyclic voltammetry curves of Co\(_{1}\)Zn\(_{1}\)-S(600) at a scan rate of 0.1 mV s\(^{-1}\) with multiple redox peaks, which is consistent with the galvanostatic
charge/discharge (GCD) curves (Figure 4b). In the initial scan, a minor cathodic peak at \( \approx 1.48 \) V versus Na\(^{+}\)/Na can be ascribed to the insertion of Na\(^{+}\) ions into the sulfide crystals to form sodiated metal sulfides.\(^{[31]}\) Further sodiation corresponded to the conversion reaction of bimetallic sulfides and the alloying reaction of Zn. The redox peak at round 0.58/1.73 V is ascribed to conversion reaction between Co\(_9\)S\(_8\) and Co/Na\(_2\)S,\(^{[11,32]}\) while the other pair of redox peak at around 0.17/0.95 V can be attributed to the formation of Co/Na\(_2\)S.\(^{[33]}\)

**Figure 4.** a) CV curves at 0.1 mV s\(^{-1}\) in the voltage range of 0.01–3.0 V versus Na\(^{+}\)/Na, b) representative galvanostatic charge/discharge curves, ex situ HRTEM images and SAED patterns of c) 1st full discharge state and d) 1st full charge state.
to the conversion reaction between ZnS and Zn/Na$_2$S, and alloying/dealloying transformation between Zn and NaZn$_{13}$, as distinguished by the representative pure metal sulfides phase (Figure S6, Supporting Information). Ex situ XRD and TEM were conducted to investigate the phase transformation upon cycling. At full discharge state, several weak diffraction peaks related to Na$_2$S (PDF No. 23-0441), Co (PDF No. 15-0806), and NaZn$_{13}$ (PDF No. 03-1008) are observed (Figure S10, Supporting Information), which were further confirmed by the ex situ HRTEM and SAED (Figure 4c with (200) and (400) planes for Na$_2$S, (111) for Co, (200), (420), and (422) planes for NaZn$_{13}$. The generated metal and alloy could enhance metallic conductivity of the electrode that allows for rapid electron transport. During the charge process, the peaks of Co$_9$S$_8$ and ZnS appeared again (also seen in Figure 4d), indicating the good reversibility of the electrode. The related reaction mechanism could be described as

Conversion reaction

$$x\text{Na}^+ + \text{Co}_9\text{S}_8 + xe^- \leftrightarrow \text{Na}_2\text{Co}_x\text{S}_y$$  \hspace{1cm} (2)

$$x\text{Na}^+ + \text{ZnS} + xe^- \leftrightarrow \text{Na}_2\text{ZnS}$$  \hspace{1cm} (3)

$$\text{Na}_2\text{Co}_x\text{S}_y + (16-x)\text{Na}^+ + (16-x)e^- \leftrightarrow 9\text{Co} + 8\text{Na}_2\text{S}$$  \hspace{1cm} (4)

$$\text{Na}_2\text{ZnS} + (2-x)\text{Na}^+ + (2-x)e^- \leftrightarrow \text{Zn} + \text{Na}_2\text{S}$$  \hspace{1cm} (5)

Alloying/dealloying reaction

$$13\text{Zn} + \text{Na}^+ + e^- \leftrightarrow \text{NaZn}_{13}$$  \hspace{1cm} (6)

The elemental mapping (Figure S11, Supporting Information) shows that small amount of Na was existed in the nanosheet after been fully charged. This is due to the formation of an SEI layer and a certain amount of sodium trapped in the bimetallic sulfides. The remaining sodium could enhance the ionic and electrical conductivity of the electrode, which are beneficial to the fast pseudocapacitive behavior and will be discussed later. The small crystalline of these products (Figure 4a,b) also produced significant pseudocapacitance effect. In addition, the intact nanosheets were preserved after cycling, revealing a peaceful evolution during sodiation/desodiation reaction. This is attributed to the different redox potentials of Co$_9$S$_8$ and ZnS that relieved the stress during sodiation/desodiation.

Co$_1$Zn$_1$-S(600) electrode exhibited a high discharge and charge capacity of 745 and 529 mA h g$^{-1}$ with a high initial coulombic efficiency of 71% at 0.1 A g$^{-1}$. The subsequent GCD curves show no significant change, rendering good reversibility of Co$_1$Zn$_1$-S(600). Figure 5a shows a reversible capacity of 542 mA h g$^{-1}$ with an excellent retention of 97.8% after 100 cycles at 0.1 A g$^{-1}$. Moreover, it maintains a considerable capacity of 219.3 mA h g$^{-1}$ (88% retention) after 500 cycles at 10 A g$^{-1}$ (Figure 5c) In contrast, the GCD curves of monometal sulfides (Co$_9$S$_8$ and ZnS) showed gradual decrease in capacity (Figure S12, Supporting Information). The Co$_1$Zn$_1$-S(600) composite also exhibits a high rate capability of 258.6 mA h g$^{-1}$ at 10 A g$^{-1}$, which was obviously better than those of other metal sulfides with different ratio of Co and Zn (Figure S13e, Supporting Information). The low

Figure 5. Sodium-ion half-cell electrochemical performance. a) Cycling performance at 0.1 A g$^{-1}$ (0.065 mA cm$^{-2}$), b) rate capability from 0.1 to 10 A g$^{-1}$ (0.077 to 7.7 mA cm$^{-2}$), and c) long cycling performance at 10 A g$^{-1}$ (6.7 mA cm$^{-2}$) of Co$_1$Zn$_1$-S(600).
capacity provided by carbon nanosheet electrodes (Figure S14, Supporting Information) demonstrates that the capacity of Co1Zn1-S(600) is mainly from the sulfide products. In other words, this rigid carbon nanosheet plays a role in improving the stability and conductivity of electrode material.

To further verify the practical application of Co1Zn1-S(600), full-cell with Co1Zn1-S(600) anode and Na3V2(PO4)3 cathode was assembled (Figure 6a). A presodiation procedure for Co1Zn1-S(600) was carried on to compensate the loss of sodium during the initial cycle in half-cell. In addition, to ensure the maximized material utilization and reasonably evaluate the electrochemical property of the Co1Zn1-S(600), the full-cell in this work was assembled based on the capacity ratio of ≈1.2:1 between the Na3V2(PO4)3 cathode and Co1Zn1-S(600) anode and the cell capacity was calculated based on the weight of anode material only. The full-cell exhibits a complete discharge plateau at 2.3 V with no capacity fading after 50 cycles at 0.17 mA and coulombic efficiencies of ≈100% (Figure 6b). It also has a high-rate capability (Figure S15, Supporting Information) and a long-term cyclic performance with 93% capacity retention after 500 cycles at a high current of 1.65 mA (Figure 6c). We also compared Co1Zn1-S(600) electrode with other Co/Zn-based metal sulfides reported previously (Table S2, Supporting Information), rendering that the Co1Zn1-S(600) is an extremely promising anode materials for sodium-ion batteries.

2.3. Na Reaction Kinetics

To interpret the excellent sodium storage performance of Co1Zn1-S(600), the electrochemical kinetics was analyzed by CV measurements at different sweep rates from 0.1 to 1.0 mV s⁻¹ (Figure 7a). The measured current (i) and sweep rates (v) obey the following power-law relationship (7)[23]

\[ i = av^b \]

where a and b are adjustable values. The b value provides insight into the charge storage mechanism, meaning that the b value of 0.5 indicates a diffusion-controlled process, whereas 1.0 represents a surface capacitive-controlled process. The b values calculated by slope of the log(v)–log(i) plots (Figure 7b) for peak 1, 2, 3, and 4 are 0.81, 0.86, 0.86, and 0.97, respectively, indicating that the kinetics for Co1Zn1-S(600) were mainly surface capacitive-controlled. The b values of monometal sulfides Co9S8 and ZnS were also calculated (Figure S16 and Table S3, Supporting Information). The pseudocapacitive contribution is quantified by Equations (8) or (9)[19,25,33]

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

or

\[ i/v^{1/2} = k_1v^{1/2} + k_2 \]

where \( k_1 \) and \( k_2 \) are constants for a given potential. The \( k_1v \) represents the capacitive-controlled contribution, whereas \( k_2v^{1/2} \) stands for diffusion-controlled contribution. The capacitive-controlled contribution was calculated to be 84.2% for Co1Zn1-S(600) at 0.2 mV s⁻¹ as illustrated by the shaded area (Figure 6c). It is higher than that of Co9S8 and ZnS due to

Figure 6. Sodium-ion full-cell electrochemical performance. a) Schematic of Na3V2(PO4)3||Co1Zn1-S(600) full-cell, b) capacity retention at 0.17 mA and inset: discharge/charge profiles of full-cell, and c) long cycling performance at 1.65 mA of full-cell.
the two phases with abundant phase boundaries that enables small crystalline domains and rich pyridinic/pyrrolic-type nitrogen and high surface area as discussed above (Figure S16 and Table S3, Supporting Information). In addition, the enhanced metallic conductivity and small crystalline of the reaction products also contribute to the pseudocapacitive effect. Figure 7d shows that the proportion of the pseudocapacitive contribution gradually improves from 79.7% to 90.3% with the increases of scan rate. It is revealed that the majority of charge storage in Co1Zn1-S(600) appears to be the pseudocapacitive processes, which is characterized by the fast electrochemical kinetics.

GITT (see details in the Supporting Information) was performed to elucidate the effect of multistep sodiation/desodiation reaction of Co1Zn1-S(600) on ion diffusion and conductivity properties. The diffusion coefficient varies at the course of discharge/charge, with the minima appears at the each redox plateau (Figure 8 and Figure S18, Supporting Information), where the Na⁺ was deeply diffused into/from the crystalline framework. The higher Na⁺ diffusion coefficient of the Co1Zn1-S(600) is attributed to the nanocrystalline domains, which shorten the solid-phase diffusion length. Furthermore, the Na⁺ diffusion coefficient in Co1Zn1-S(600) was minor fluctuant and higher than that in monometal sulfides as a whole, suggesting ion diffusion and conductivity enhancement by the two phase bimetallic sulfides. On the one hand, phase boundaries restrict the growth of crystalline domains and create crystal defects and active sites for fast ion diffusion; On the other hand, different redox potentials and out-of-step reactions of two phase sulfides would relieve the stress during the sodiation/desodiation, which is helpful for the diffusion of Na⁺.

Electrochemical impedance spectra (EIS) were conducted at various voltage states to study the resistance changes during cycling. All the Nyquist plots (Figures S19–S21, Supporting Information) show a depressed semicircle followed by an inclined line, which can be fitted by an equivalent circuit (inset in Figure 9). The initial EIS spectra (Figure S19, Supporting Information) show that charge-transfer resistance $R_{CT}$ of Co1Zn1-S(600) was lower than that of monometal sulfide electrodes, further demonstrating the advantage of the two phase bimetallic sulfides. As shown in Figure 9, the electrolyte resistance ($R_S$) was small and remained as a constant (4–7 Ω). $R_{SEI}$, the resistance of the SEI layer, increased during initial the discharge process (maximum $≈$ 78 Ω) and then decreased gradually to a stable value (10–20 Ω), suggesting formation of a stable SEI layer after the initial discharge process. Charge-transfer resistance $R_{CT}$ decreased from 554 Ω in the initial discharge process and further decreased in the subsequent charge process, reaching a minimum value (79 Ω) at the full charge state (3 V). The $R_{CT}$ increased and reached a maximum value (204 Ω) at the end of the 2nd discharge process and decreased again with the depth of the 2nd charge. It exhibited a regular change between full discharge and charge states afterward, further demonstrating excellent reversibility of the Co1Zn1-S(600) electrode. In addition, $R_{CT}$ value after 1st discharge process became smaller, suggesting the improvement in the reaction kinetic as forming a stable SEI layer, which contributes to
the excellent cyclic performance. Noting that the change of sloping line in the lower frequency region with the depth of charge and discharge suggests the variation of the electronic conductivity of the electrode. A similar behavior has been reported in previous works. [34] As revealed in Figure S21 in the Supporting Information, the electrode showed semi-conductive properties at initial or fully charged state, which means that electronic conductivity became the limiting factor. The metal-like material appeared at fully discharged state in which the ionic conductivity was limiting factor as the maximum value of $R_{CT}$.

3. Conclusions

In summary, we have in situ synthesized the Co$_9$S$_8$/ZnS nanocrystals embedded in hollow nitrogen-doped carbon nanosheets via a facile sulfidation of CoZn-MOFs and subsequent calcination. The internal space of this rigid nanosheet could accommodate the volume expansion during sodiation/desodiation. The abundant phase boundaries of bimetallic sulfides and rich pyridinic/pyrrolic-type nitrogen in carbon shell improve the electronic and ionic conductivity, thereby enhance the reversibility of sodiation/desodiation. Moreover, Co$_1$Zn$_1$-S(600) electrode appeared to pseudocapacitive behavior and higher sodium diffusion coefficient, which exhibited fast electrochemical kinetics and high rate capability. In addition, the excellent reversibility of Co$_1$Zn$_1$-S(600) guaranteed its long-term stability. As a result, the optimum Co$_1$Zn$_1$-S(600) exhibited excellent electrochemical performance for both half-cell and full-cell. For instance, a high capacity of 542 mA h g$^{-1}$ with an excellent retention of 97.8% after 100 cycles at 0.1 A g$^{-1}$, a high rate capability of 10 A g$^{-1}$, and excellent cyclic stability up to 500 cycles at 10 A g$^{-1}$ were obtained for half-cell. More importantly, the Na$_3$V$_2$(PO$_4$)$_3$‖Co$_1$Zn$_1$-S(600) full cell exhibits a high-rate capability and a long-term cyclic performance with 93% capacity retention after 500 cycles.

4. Experimental Section

Sample Synthesis: Co-/Zn-MOFs nanosheets were synthesized as the previous reports.[35] Two steps were conducted to synthesize Co$_9$Zn$_1$-S(600).
First, 40 mL ethanol (C₂H₅OH >99.7%) containing 100 mg CoZn(1:1)-MOFs nanosheets and 400 mg TAA (≥99%) were placed in oil-bath device at 90 °C for 20 min. Second, the powders were collected and thermally treated at 600 °C under an Ar flow for 2 h with a heating rate of 2 °C min⁻¹. The other Co₆Zn₆S₆(T) samples were also synthesized in similar way for comparison. Na₃V₂(PO₄)₃ was prepared through a similar method of our group.[9]

**Structure Characterization:** The XRD data were collected using a Rigaku D/max2500 powder diffractometer (Cu Kα, λ = 0.15405 nm). SEM (FEI Nova NanoSEM 230, 10 kV) was performed to scan HRTEM images, SAED patterns, and energy dispersive spectrometer mapping. XPS spectra were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher). The thermogravimetric curve was collected by thermal gravimetric analyzer (NETZSCH STA 449 C).

**Electrochemical Measurements:** The electrochemical performances of the samples were carried out via stainless-steel coin cells (CR2016). Working electrodes were prepared by coating a slurry mixed 70% active materials, 20% super P, and 10% sodium carboxymethylcellulose in deionized water onto a copper foil and dried at 100 °C in vacuum overnight. Glass fiber filter paper was used as a separator. The electrolyte was 1 M LiPF₆ in carbonate/dimethyl carbonate (1:1 wt%) with 5% fluoroethylene carbonate.

**Supplementary Information**

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by National Natural Science Foundation of China (Grant No. 51374255, 51502323, and 51572299), Innovation-Driven Project of Central South University (No. 2018CKX004), and Hunan Provincial Innovation Foundation For Postgraduate (Grant No. CX2017B045).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

bimetallic sulfides, ion diffusion coefficient, metal-organic frameworks, pseudocapacitive effect, sodium-ion batteries


