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# Progress and perspective on multi-dimensional structured carbon nanomaterials for cathodes in aqueous zinc-based energy storage

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## ABSTRACT

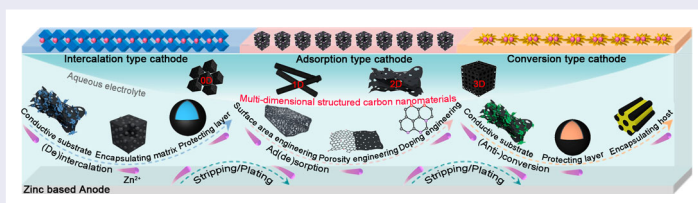
Aqueous zinc-based devices (AZDs) are considered as a promising candidate for next-generation energy storage due to high safety, economic benefit, and environmental benignity. However, the wide-spread application of AZD cathodes still faces challenges such as inferior energy density and cycling life. This manuscript focuses on the key design parameters for AZD cathodes and highlights the diverse functions of well-designed carbon architectures in AZD cathodes. The emerging opportunities are also presented to guide future endeavors towards high-performance AZD cathodes.

## ARTICLE HISTORY

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## KEYWORDS

Aqueous zinc-based devices; cathodic electrochemistry; cathode materials; carbon nanomaterials; multi-dimensional structure



## IMPACT STATEMENT

This manuscript is organized from the typical cathodic electrochemistry to discuss the progress and perspective of multi-dimensional structured nanocarbons for cathodes in Zinc-based energy devices.

## 1. Introduction

Employing aqueous rechargeable battery systems provides opportunities to eliminate the safety hazard and unaffordable cost issues associated with the commercial lithium-ion batteries (LIBs) [1,2]. The dominant aqueous solvent in the electrolyte effectively settles the security concern originating from the flammable and volatile aprotic electrolyte, while reducing the battery assembly cost. Additionally, the presence of water naturally roles out water- and air-sensitive raw alkaline metals as electrodes [3,4], and the multivalent metals emerge [5]. Therefore, aqueous AZDs stand out from the numerous candidates. The motivation mainly stems from the high affordability (USD \$2 kg<sup>-1</sup> of Zn vs. \$19 kg<sup>-1</sup> of Li) [6,7], intrinsic abundance (almost five times as much as Li resources) [8], low redox potential (−0.76 V vs. standard hydrogen electrode (SHE)) and high theoretical capacity (820 mAh g<sup>-1</sup>, 5851 mAh cm<sup>-3</sup>) of zinc metal [5,9–12]. The pure zinc metals directly acting as anode

enables AZDs to eliminate the price of excess weight posed by electrochemically inactive components. However, the naked zinc in electrolytes suffers from heterogeneous plating/stripping electrochemistry [13,14]. These are usually ascribed as the notorious dendrite formation and parasitic side reaction especially in the alkaline medium [15]. At present, the near neutral or mild acidic (pH of 3.6–6.0) electrolytes (or with additives) optimized from the early alkaline ones are commonly used for AZDs owing to the suppressed byproducts and the alleviated dendrite formation [16,17].

The cathodes of AZDs determine holistic cathodic electrochemistry, thereby attracting even more attention. To date, there have been diverse but well-classified cathodes, including manganese- [18–22], vanadium- [23–27], prussian blue analogs (PBA)- [28,29], chalcogens- [30–34], and carbon-based materials [35–37], etc. The most essential difference among these cathodes lies on the ion storage mechanism, which can be categorized

into intercalation-, adsorption-, conversion-type mechanism. Intercalation-type cathodes rely on the typical ion insertion/extraction, and usually suffer from inadequate specific capacities and unstable cyclability. These limit the energy density of AZDs to 50–300 Wh kg<sup>-1</sup> [18,24,29,38,39], which is even less than those of commercial LIBs (e.g. 387 Wh kg<sup>-1</sup> for LiCoO<sub>2</sub>/Graphite battery) [40]. The discrepancy between theoretical and practical values is attributed to the poor electrical conductivity, slow transfer kinetics, inferior structural stability caused by volumetric strain, and dissolution of active materials [9,41]. Introducing capacitive storage electrochemistry to cathode sides enables AZDs with high power capability and ultralong life-span, due to facile kinetics of ions adsorption/desorption absent of the bulk ions insertion/extraction [42–45]. Adsorption-type electrodes are expected to have adequate specific surface area (SSA), rich microstructure as well as the synergy of Faradic/non-Faradic storage for both electrical double-layer capacitance (EDLC) and pseudocapacitance. These cathodes make the AZDs with capacitor characteristic in nature and improved power/cycling performances. However, capacity concerns still remain due to the energy density of even less than 200 Wh kg<sup>-1</sup>. On the other hand, conversion-type cathodes are promising to break capacity bottlenecks of AZDs, especially with the emergence of multi-electron transfer type cathodes (e.g. S, Se, Te). For instance, the two-electron transfer process of chalcogens-based cathodes delivers extremely high energy density over 700 Wh kg<sup>-1</sup> (specific capacities over 1000 mAh g<sup>-1</sup><sub>chalcogens</sub>) [30–33,46], which are superior to both intercalation- and adsorption-type cathodes. Nevertheless, these proposed promising cathodes still suffer from the restricted electron/ion transport and volume expansion as the intercalation-type cathodes, which lead to unsatisfactory capacity retention and cycling life.

Currently, the focus of performance challenges mainly lies on the architecture design of existing cathodes, e.g. nano technology [47–49], defective engineering [50,51], and interlayer expansion [48,52,53]. Carbon nanomaterials with abundant resources, adjustable morphology, and porosity, as well as graphitic microstructure, can adapt to different charge storage scenarios [54–59]. Thus, building carbonaceous architecture is a feasible and promising approach to stimulate cathode for better performances. In this regard, lots of pioneering papers reveal the functionality of carbon nanomaterials in cathodes with various dimensions, e.g. 0D carbon quantum dots (QDs) [37,60–62], 1D carbon nanotubes (CNTs) [25,63–69] and carbon nanofibers (CNFs) [39,70–73], 2D graphene [20,74,75] and carbon nanosheets (CNSs) [76–78], and 3D hierarchical porous carbon (PC) [79–82]. Figure 1(a) exhibits that

the publication of AZDs has increased six-fold in the past decade, and nearly ten-fold for carbon-based AZDs. Carbon nanomaterials are reported to participate in host–guest electrochemistry in both intercalation and conversion-type materials as shown in Figure 1(b,c). Nanocarbons play an important role to bridge the gap of kinetics transfer and structural stability of active materials, resulting in improved rate capacities (~10–100% increase at low rate, and ~20–400% increase at high rate) and cyclability (~10–300% increase). Furthermore, the selected carbons with special surface chemistry and microstructure can autonomously activate capacitive process as adsorption-type cathodes. Consequently, advanced carbonaceous architecture has captured a surge of interest and has been attempted in all three types of cathodes.

Despite the booming research on the carbons in AZDs, there are few comprehensive overviews covering from the storage models to the application of carbons in AZDs. In this review, we start with a critical discussion on the typical cathodic electrochemistry and discuss the key design parameters on high-performance cathodes. Then we outline the progress of multi-dimensional structured carbon nanomaterials in three types of cathodes. The functionality of carbon is discussed and the critical scientific/technical issues are identified in both non-all-carbon based intercalation- and conversion-type electrodes, and the all-carbon based adsorption-type electrodes. Finally, we conclude with perspectives and suggestions for advanced carbon designers towards high-performance AZDs.

## 2. Fundamental electrochemistry of cathodes

Cathodic electrochemistry is a descriptor for internal migration patterns of anions/cations upon charge-discharge processes. This descriptor distinctly conveys the electrode reaction route regarding structure evolution, discharging potential plateau, and electron transfer number of redox couples. Thus, the fundamental electrochemistry of the cathode is closely associated with overall energy/power-cyclability performances. Figuring out the influence of key parameters on performance and the original discrepancy of cathodic electrochemistry are an essential focus of the electrode architecture design. Here we first discuss the typical cathodic electrochemistry. The respective fundamental principles, and performances as well as the current issues for typical cathodes will be discussed in this part.

### 2.1. Intercalation-type electrochemistry

Figure 2(a) shows the typical configuration of intercalation-type electrochemistry in AZDs. The cathode

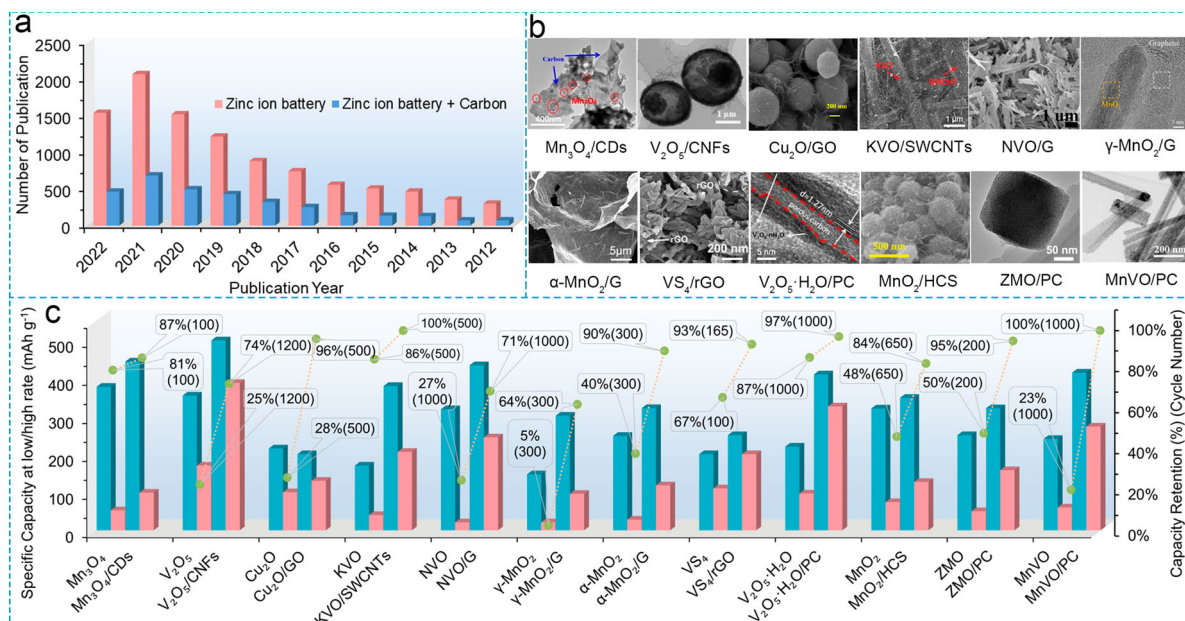


**Figure 1.** (a) Statistics of the number of publications from January 1st 2012 to September 1st 2022 by indexing the keywords of ‘zinc ion battery’ and ‘zinc ion battery and carbon’ in the Web of Science. (b) Microtopography of carbon composite in selected cases ( $\text{Mn}_3\text{O}_4/\text{CDs}$ : Reproduced with permission. Copyright 2022, Wiley-VCH [60].  $\text{V}_2\text{O}_5/\text{CNFs}$ : Reproduced with permission. Copyright 2022, Elsevier [83].  $\text{Cu}_2\text{O}/\text{GO}$ : Reproduced with permission. Copyright 2022, Elsevier [84].  $\text{KVO}/\text{SWCNTs}$ : Reproduced with permission. Copyright 2020, American Chemical Society [66].  $\text{NVO}/\text{G}$ : Reproduced with permission. Copyright 2019, Elsevier [23].  $\gamma\text{-MnO}_2/\text{G}$ : Reproduced with permission. Copyright 2020, Elsevier [85].  $\alpha\text{-MnO}_2/\text{G}$ : Reproduced with permission. Copyright 2020, American Chemical Society [86].  $\text{VS}_4/\text{rGO}$ : Reproduced with permission. Copyright 2018, Royal Society of Chemistry [87].  $\text{V}_2\text{O}_5\cdot\text{H}_2\text{O}/\text{PC}$ : Reproduced with permission. Copyright 2021, Wiley-VCH [88].  $\text{MnO}_2/\text{HCS}$ : Reproduced with permission. Copyright 2020, Royal Society of Chemistry [89].  $\text{ZMO}/\text{PC}$ : Reproduced with permission. Copyright 2022, Wiley-VCH [21].  $\text{MnVO}/\text{PC}$ : Reproduced with permission. Copyright 2021, Elsevier [90]. (c) Rate and cycling performance comparison of the selected samples (as indicated in Figure 1(b)) with or without carbon assistance.

undergoes  $\text{Zn}^{2+}$  intercalation into crystal and reduction of the associated elements upon discharge. The reversed deintercalation occurs with oxidation of the principal elements during charge. This storage mechanism in AZDs on the reversible  $\text{Zn}^{2+}$  insertion/extraction into/from  $\text{MnO}_2$  was first proposed in 2012 [91]. Since then, a suite of in-depth and innovative studies of AZDs boomed in this decade. Thereinto, the advances of intercalation-type electrochemistry can be divided into four sub-categories: exclusive  $\text{Zn}^{2+}$  intercalation,  $\text{H}^+$  and  $\text{Zn}^{2+}$  co-intercalation, displacement- and hybrid-type intercalation. Currently, the electrochemistry of various sub-types motivated continuous enrichment of major cathode family for AZDs. The existing cathodes could be classified into several categories: Mn-based materials (e.g.  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ -birnessite,  $\text{ZnMn}_2\text{O}_4$ ) [49,92–96], V-based materials (e.g.  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Zn}_2\text{V}_2\text{O}_7$ ,  $\text{NaV}_3\text{O}_8\cdot 1.5\text{H}_2\text{O}$ ,  $\text{Ag}_{0.4}\text{V}_2\text{O}_5$ ) [24,74,97–99], and PBA-based materials (e.g.  $\text{KCuFe}^{\text{III}}(\text{CN})_6$ ) [28].

However, the performances of those cathodes still fall behind expectations as exhibited in Figure 2(d). For instance, the Mn-based materials can deliver moderate capacities of 250–300  $\text{mAh g}^{-1}$  associated with

high discharge voltage (1.2–1.4 V vs.  $\text{Zn}^{2+}/\text{Zn}$ ) [93], while the pursuit of high energy is harder for V- and PBA-based materials due to mutually exclusive access of capacity and discharge voltage (300–400  $\text{mAh g}^{-1}$  and < 1 V (vs.  $\text{Zn}^{2+}/\text{Zn}$ ) for V-oxides, < 100  $\text{mAh g}^{-1}$  and 1.5–1.8 V ( $\text{Zn}^{2+}/\text{Zn}$ ) for PBA) [10]. To improve the electrochemical performances, we should start with identifying the key parameters of electrochemistry process and the drawbacks of existing cathodes. Firstly, the solvation shell formed outside of  $\text{Zn}^{2+}$  via Coulombic interaction enlarges the radius by more than five times (4.3 Å for  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  vs. 0.74 Å for  $\text{Zn}^{2+}$ ) [4,9], which means more energy consumption is required to break  $\text{Zn}^{\text{II}}\text{-H}_2\text{O}$  bonds for  $\text{Zn}^{2+}$  intercalation. Additionally, the steric hindrance from continuous insertion results in unstable kinetics. The strong electrostatic interactions between the host and divalent  $\text{Zn}^{2+}$  further make the extraction harder in a reversible way. The above factors lead to decreased ion transfer rate and reduced cathode efficiency. Secondly, the oxides-based cathodes are troubled by electron transport efficiency as well. Metal oxides species (e.g.  $10^{-5} \sim 10^{-6} \text{ S cm}^{-1}$  for  $\text{MnO}_2$  [100],  $10^{-2} \sim 10^{-3} \text{ S cm}^{-1}$  for  $\text{V}_2\text{O}_5$  [101]) exhibit unsatisfied electrical conductivity compared with

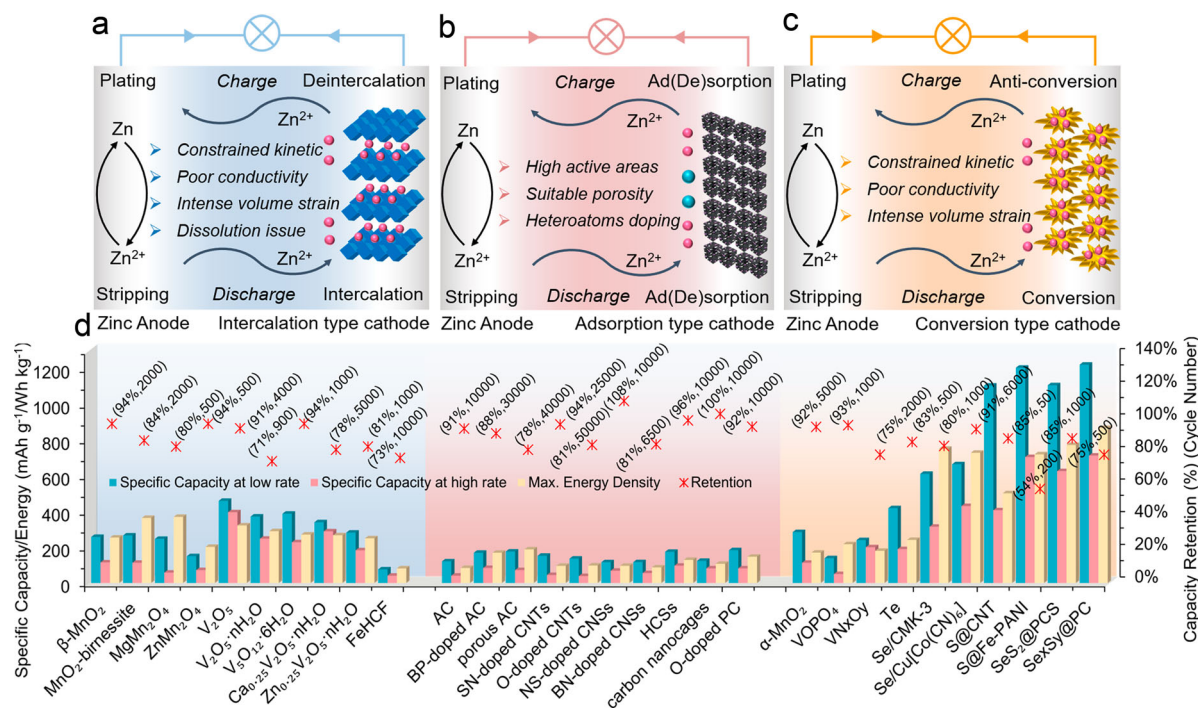


**Figure 2.** Schematic illustration of the cell configurations, mechanisms and key parameters of the limiting factors for performance of AZDs based on zinc anode and (a) intercalation-, (b) adsorption-, (c) conversion-type cathodes. (d) A representative exhibition of specific capacities at low/high rates, maximum energy densities and cycling performances of various reported cathodes respectively based on intercalation- [48,94,95,116–122], adsorption- [37,61,65,70,108,123–127], and conversion-type electrochemistry as shown in Figure 2a–c [31–34,46,103,112,113,115,128].

highly conductive carbons (e.g.  $10^6 \text{ S cm}^{-1}$  for graphene [7]). The sluggish electrochemical kinetics causes the low utilization of active materials, and consequently poor rate capacity and power performances. Thirdly, the ions insertion/extraction leads to volume variation of cathode material upon discharge/charge process. For instance, after exclusive  $\text{Zn}^{2+}$  insertion,  $\gamma\text{-MnO}_2$  composed of a tunnel structure was transformed to layered-type  $\text{Zn}_x\text{MnO}_2$  with volume expansion of 9.21% [102]. The drastic volumetric strain calls for structure robustness to maintain capacity during cycling. Fourthly,  $\text{Mn}^{2+}$  dissolution in the electrolyte causes irreversible capacity loss. Typical  $\text{MnO}_2$  working between 1 and 1.8 V (vs.  $\text{Zn}^{2+}/\text{Zn}$ ) prefer to exist stably as  $\text{Mn}^{2+}$  in a neutral or mild acidic system [103,104]. This explains that the formed  $\text{Mn}^{3+}$  species likely convert to  $\text{Mn}^{2+}$  via disproportionation reaction ( $2\text{Mn}^{3+}(\text{s}) \rightarrow \text{Mn}^{4+}(\text{s}) + \text{Mn}^{2+}(\text{aq})$ ) [103], thus causing Mn loss due to the high solubility of  $\text{Mn}^{2+}$  (70 g  $\text{MnSO}_4$  per 100 mL  $\text{H}_2\text{O}$  at  $7^\circ\text{C}$ ) [16,38]. The dissolved  $\text{Mn}^{2+}$  cannot participate in the sequent redox reduction, leading to irreversible capacity loss and short cycling life. To sum up, the intercalation-type electrochemistry has sparked many keen interests and greatly boosted the progress of cathodes. However, critical challenges need to be addressed for the pursuit of high-performance cathodes.

## 2.2. Adsorption-type electrochemistry

Figure 2(b) displays reversible ions adsorption/desorption in the adsorption-type electrochemistry. This mechanism in AZDs can be dated back to 2016 [64], but carbonaceous materials have been skyrocketed since activated carbon (AC) was reported in 2018 [61]. Ion storage based on this electrochemistry relies mainly on both physical and chemical models [54,105]. The physical model refers to the routine EDLC by physical electronic attraction. While the chemical adsorption/desorption of  $\text{Zn}^{2+}/\text{H}^+$  generally activated by heteroatomic sites (e.g. O doped graphitic sites) on carbons, which provide extra pseudocapacitance [106]. The adsorption-type electrochemistry relates to both cations and anions in the electrolyte. This dual-ions adsorption means that different charge carrier functions at respective regions which can be defined by zero charge potential. The cathodic electrochemistry below critical point is mainly attributed to cations, while the contribution of anions takes place at higher potential regions. These two models feature fast kinetics due to the absence of bulk insertion/extraction. Therefore, the AZDs assembled using carbon cathodes exhibit remarkable rate capability ( $> 20 \text{ A g}^{-1}$ ) and durability (over 10,000 cycles). The achieved power density of more than  $30 \text{ kW kg}^{-1}$  is superior to other types of

cathodes. Regardless of the incomparable power density, even the state-of-the-art carbons deliver low energy density of less than  $200 \text{ Wh kg}^{-1}$  (specific capacities less than  $300 \text{ mAh g}^{-1}$ ) as shown in Figure 2(d).

Therefore, this inadequate energy density calls for more efficient and controllable carbons to boost performance. Firstly, a key criterion for estimating the availability of carbons is the active surface areas because it determines the charge accumulation of EDLC and pseudocapacitance [54]. A proof example is that AC with the highest SSA delivers a higher capacity ( $1923 \text{ m}^2 \text{ g}^{-1}$  for  $121 \text{ mAh g}^{-1}$ ) compared with counterparts with low SSA (e.g.  $1408 \text{ m}^2 \text{ g}^{-1}$  for  $78 \text{ mAh g}^{-1}$ ,  $142 \text{ m}^2 \text{ g}^{-1}$  for  $9 \text{ mAh g}^{-1}$ ) [61]. Therefore, designing carbon cathodes with high SSA is beneficial for capacitive applications. Secondly, although the high SSA is helpful to improve capacity, no exact relationship was observed. Additionally, the calculated theoretical capacity values for carbons with SSA of  $1000\text{--}3000 \text{ m}^2 \text{ g}^{-1}$  can reach  $300\text{--}500 \text{ F g}^{-1}$  but the achieved experimental values are only  $100\text{--}250 \text{ F g}^{-1}$  [42,54]. This means that uncontrollable factors such as inaccessible pores, poor compatibility between electrolyte ions and pore sizes, and surface wettability make the attainable SSA far less than the theoretical value. Therefore, elaborately designed pore structure is quite necessary for easy access of ions accumulation and high SSA utilization. The focus should be on understanding the different roles of various nanopores in ion storage and optimizing the overall pore size distribution for rapid dynamics transfer [107,108]. Thirdly, well-established modification strategies (e.g. doping engineering [106,107,109], chemical activation [36,110]) allow carbons with good surface functionality. Adequate sites that activate pseudocapacitance are used to compensate traditional EDLC, while the chemical adsorption relies on the affinity of approachable electrochemical sites with charge carriers. Therefore, adjusting the doping amount and species meanwhile amplifying the synergistic effect of each component require careful consideration. Fourthly, the capacity of the cathode should be as large as possible to match the paired zinc counterpart with high theoretical capacity. Thus, simultaneous increase of both capacity and tap density of active materials are required to achieve high energy density on the cell level. In brief, although the adsorption-type electrochemistry has made a great contribution to efficient cathodes, more and higher requirements for materials themselves are set to achieve high energy performances.

### 2.3. Conversion-type electrochemistry

Figure 2(c) shows the conversion-type electrochemistry in which the ions react with active materials to form a

new substance upon discharge. In terms of conversion-type electrochemistry, the consecutive conversion reaction for ions storage is free from the rigid framework of host and saturation of active sites. This enables those cathodes to achieve high capacity. The electrochemistry of the conversion reaction can be distinguished as cationic- and anionic-redox. Cationic-redox refers to the oxidation/reduction of transition metal elements in Mn-based oxides (e.g.  $\alpha\text{-MnO}_2$ ,  $\text{Mn}_3\text{O}_4$ ) [103,111]. Anionic-redox mainly involves non-metallic elements (e.g. oxygen, nitrogen) in V-based compounds (e.g.  $\text{VOPO}_4$ ,  $\text{VN}_x\text{O}_y$ ) [112,113]. Although single electron transfer type Mn- and V-based cathodes can hardly achieve any breakthrough in terms of performance, chalcogens-based cathodes with anionic-redox present an opportunity due to the multiple-electron transfer. The representatives of S and Se undergo a conversion reaction with two electrons transfer ( $\text{S} + \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{ZnS}$ ,  $\text{Se} + \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{ZnSe}$ ) [31,33,114]. Another aqueous Zn-Te system was based on a two-step solid-to-solid conversion with the successive formation of  $\text{ZnTe}_2$  and  $\text{ZnTe}$  ( $2\text{Te} + \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{ZnTe}_2$ ,  $\text{ZnTe}_2 + \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow 2\text{ZnSe}$ ) [34]. These chalcogen-based cathodes experienced the similar electrochemical processes but different plateaus voltages and capacities. For both Zn-Te and Zn-S systems, the distinct voltage plateau is usually below  $0.6 \text{ V}$  vs.  $\text{Zn}^{2+}/\text{Zn}$  [31,34], which is far less than the value of Zn-Se system ( $> 1.1 \text{ V}$  vs.  $\text{Zn}^{2+}/\text{Zn}$ ) [33]. To date, the Zn-Te battery using bare Te nanosheets as cathodes delivered a capacity of  $419 \text{ mAh g}^{-1}_{\text{Te}}$  ( $241 \text{ Wh kg}^{-1}_{\text{Te}}$ ) [34]. According to the Figure 2(d), the reported maximum capacities for Zn-S system with supporting of carbon host on cathode side were in the range of  $800\text{--}1600 \text{ mAh g}^{-1}_{\text{s}}$  ( $250\text{--}1100 \text{ Wh kg}^{-1}_{\text{s}}$ ) [30–32,114]. Meanwhile, a typical Zn-Se system assembled by CMK-3 encapsulated Se cathode delivered energy of  $751 \text{ Wh kg}^{-1}_{\text{Se}}$  ( $611 \text{ mAh}^{-1}_{\text{Se}}$ ) owing to the advantage of high voltage [33].

Despite high capacities, the conversion-type cathodes suffer from poor cycle stability and rate performance, which requires more comprehensive investigation (Figure 2(d)). First of all, the poor electronic conductivity of chalcogens-based materials (e.g.  $10^{-7} \text{ S cm}^{-1}$  for S,  $10^{-5} \text{ S cm}^{-1}$  for Se,  $2 \text{ S cm}^{-1}$  for Te) necessitates the incorporation of conductive host such as carbon [32,34,115]. The sluggish diffusion kinetics in the solid-solid reaction further exacerbated the poor power performance. The unsatisfied kinetics performance of both ions and electrons results in the underutilization of active materials. On the other hand, the negligible solubility constant of product rules out the dissolution issue ( $1.2 \times 10^{-23}$  for ZnS,  $3.6 \times 10^{-26}$  for ZnSe in aqueous electrolyte) [115]. However, the drastic volume changes

(53% for S to ZnS, 62% for Se to ZnSe, 49% for Te to ZnTe) in conversion reactions still cause low efficiency and rapid capacity decay upon cycling. Generally, the conversion-type cathodes especially the emerging chalcogens hold great promise for improving the energy density of AZDs, but the existing intractable challenges deserve more in-depth considerations.

### 3. Carbon nanomaterials for cathode

Carbons, known as rich dimensionality and diversity of existence forms (using alone or in combination), are emerging as the promising materials in cathodes. The well-established processing technologies and theories allow the produced carbon with diverse properties, such as large SSA, abundant porosity, and functional surfaces. This makes nanocarbon suitable for applying in the existing cathodes, which is revealed by numerous pioneering works. Therefore, this section systematically summarizes the applications of multi-dimensional structured carbon nanomaterials (0D-3D) in three types of cathodes as shown in Figure 3. We first summarize recent works on carbons in the intercalation-type cathodes to construct the non-all-carbon based cathodes, followed by the design of all-carbon based cathodes in the adsorption-type cathodes. Finally, we overview non-all-carbon based conversion-type cathodes, with attention emphatically being given to chalcogen-based species.

#### 3.1. Carbon in intercalation-type cathode

The previously mentioned issues of intercalation-type cathodes could be well addressed by introducing functional carbon nanomaterials with controllable physico-chemical properties and microtopography. Carbon can assist intercalation-type species to construct non-all-carbon based cathodes. Here we outline the progress of multi-dimensional structured carbons applied in intercalation-type cathodes in terms of specific functions of conductive substrate, encapsulating matrix and protecting layer.

##### 3.1.1. Conductive substrate

Conductive substrate is the most economically and technically feasible function of carbons for intercalation-type cathodes due to the advantages of special micro-textures and functional surfaces. The non-all-carbon electrode design can facilitate efficient ion/electron transport and accommodate volume changes. To date, great progress has been made using this strategy.

0D carbon dots (CDs) of a few nanometers in size can serve as substrates with the structural merits of graphitized cores and functional surfaces. In the example of  $\text{Mn}_3\text{O}_4/\text{CDs}$  composites, N-doped CDs-derived carbon skeleton was constructed as a conductive substrate [60]. The carbon skeleton demonstrated good affinity to Mn species and guided uniform arrangement to eliminate the discontinuous aggregation according to the TEM images comparison in Figure 4(a,b). The native

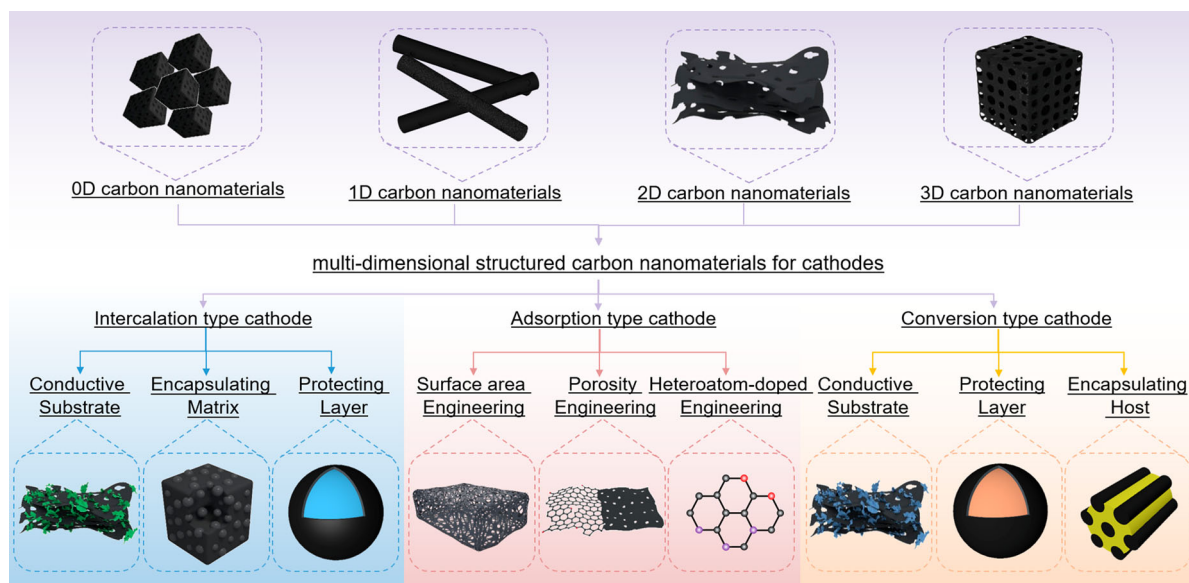


**Figure 3.** An illustration showing vital roles of multi-dimensional structured carbon nanomaterials (0D-3D) for intercalation-, adsorption- and conversion-type cathodes application in AZDs.

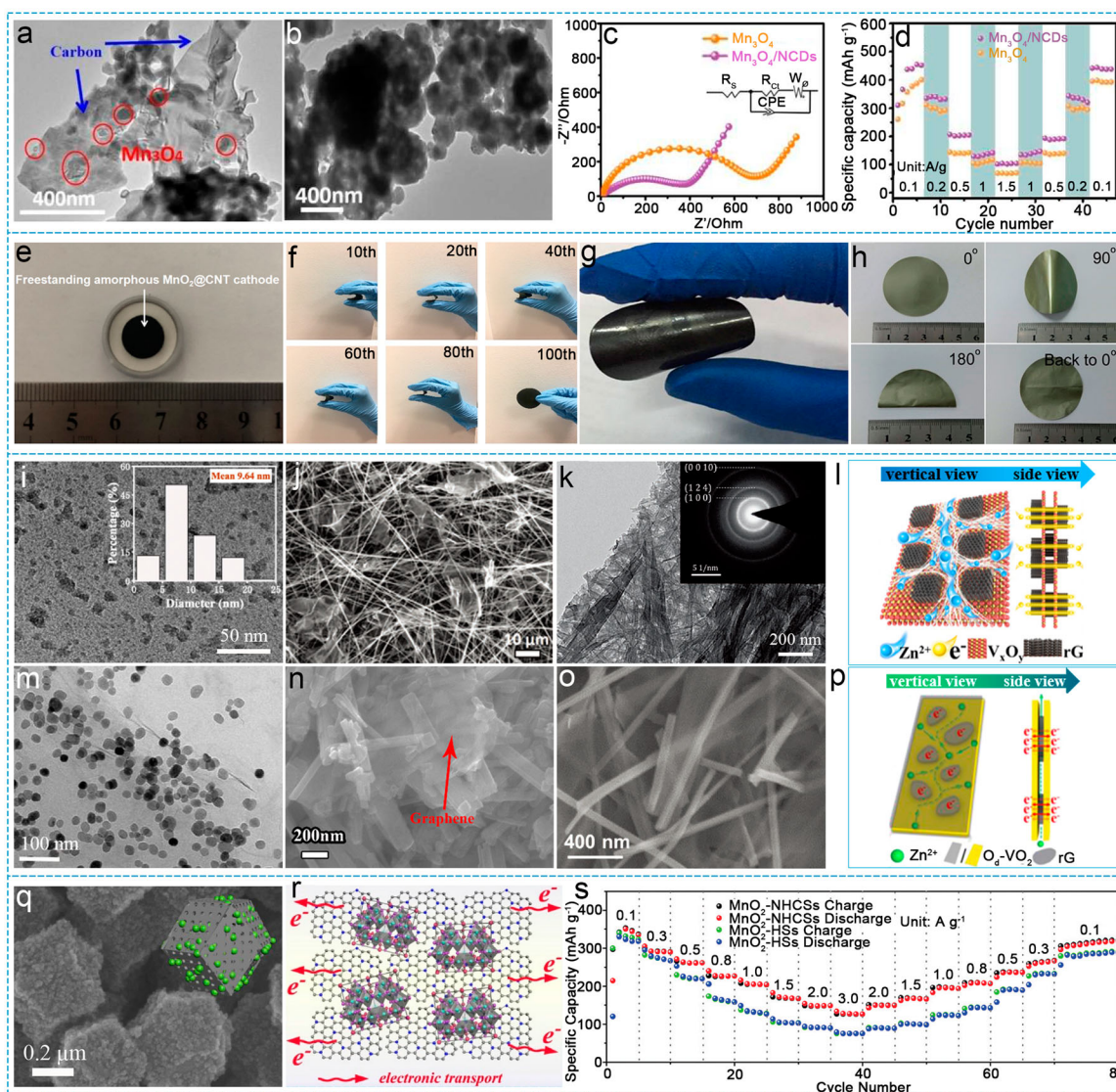


**Figure 4.** Transmission electron microscopy (TEM) images of (a)  $\text{Mn}_3\text{O}_4/\text{CDs}$  and (b) pure  $\text{Mn}_3\text{O}_4$ . (c) Electrochemical impedance spectroscopy (EIS) and (d) rate properties of  $\text{Mn}_3\text{O}_4/\text{CDs}$  and pure  $\text{Mn}_3\text{O}_4$ . Reproduced with permission. Copyright 2022, WILEY-VCH [60]. (e) Optical image of the free-standing cathode of amorphous  $\text{MnO}_2/\text{CNT}$ . Reproduced with permission. Copyright 2020, Elsevier [129]. (f) The mechanical stability of (f)  $\text{V}_2\text{O}_5$  nanoparticles/CNT, reproduced with permission, copyright 2019, Royal Society of Chemistry [130], (g)  $\text{V}_2\text{O}_5$  nanofibers/CNT, reproduced with permission, copyright 2020, Elsevier [25], and (h)  $\text{KVO}$  nanobelts/CNT free-standing electrode, reproduced with permission, copyright 2020, American Chemical Society [66]. (i) TEM image of  $\text{ZnMn}_2\text{O}_4/\text{rGO}$  and corresponded particle size distribution of  $\text{ZnMn}_2\text{O}_4$ . Reproduced with permission. Copyright 2020, Elsevier [131]. (m) TEM image of  $\text{ZnMn}_2\text{O}_4/\text{NG}$ . Reproduced with permission. Copyright 2019, Elsevier [132]. Scanning electron microscope (SEM) images of (j)  $\text{MnO}_2$  nanowires/rGO, reproduced with permission, copyright 2022, WILEY-VCH [20], (n)  $\text{H}_2\text{V}_3\text{O}_8$  nanorods/graphene, reproduced with permission, copyright 2020, American Chemical Society [133], and (o)  $\text{H}_2\text{V}_3\text{O}_8$  nanowires/graphene, reproduced with permission, copyright 2018, WILEY-VCH [134]. (k) TEM image of 1D  $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ /graphene. Reproduced with permission. Copyright 2018, WILEY-VCH [48]. Schematic illustration of the architectural frame structure of (l) 2D  $\text{VO}_2$  nanobelts/rGO, reproduced with permission, copyright 2021, Elsevier [135], and (p)  $\text{O}_d\text{-VO}_2$  nanobelts/rGO, reproduced with permission, copyright 2020, Elsevier [136]. (q) SEM image of  $\text{ZMO@PCPs}$ . (r) Schematic diagram of electronic transport of  $\text{ZMO@PCPs}$  cathodes. Reproduced with permission. Copyright 2020, Elsevier [137]. (s) Rate performances of  $\text{MnO}_2/\text{NHCS}$  and pure  $\text{MnO}_2$ . Reproduced with permission. Copyright 2020, Royal Society of Chemistry [89].

hydrophilic interface of substrate with heteroatomic site contributed greatly to immobilize the active species. Moreover, the hydrophilic groups and high SSA on

carbon also improved wettability and conductivity of the cathode, leading to fast ion and electron kinetics. The electrochemical characterizations in Figure 4(c,d)

validated that the  $\text{Mn}_3\text{O}_4/\text{CDs}$  exhibited a much smaller electrochemical resistance and higher rate capacities in contrast with pure  $\text{Mn}_3\text{O}_4$ .

1D carbon nanomaterials possess a well-defined unidirectional spatial structure to carry active materials. For typical CNFs, a hierarchical core-shell structure of  $\text{CNF@birnessite-MnO}_2$  was reported in which  $\text{MnO}_2$  nanosheet shells were vertically aligned on CNF core [71]. In this case, the hydrophobic surfaces of commercial CNFs are far less effective in anchoring active species than the N-doped carbon mentioned above. But an ingenious strategy proposed by the authors was pre-grinding CNFs with  $\text{KMnO}_4$  powder, which endows the CNFs with hydrophilicity and reactivity. The small  $\text{MnO}_x$  nuclei or domains produced on the CNFs surface induced the growth of  $\text{MnO}_2$  tightly and uniformly [71]. For substrate function, the key point are the firmness and denseness of anchoring sites. Careful consideration should be given to enhancing surface functionality of substrate because it is related to the loading mass and density as well as even the availability of substrates [138]. Another advantage to employ 1D carbon nanomaterials is to fabricate free-standing electrodes. 1D carbon can act as both conductive agent and binding material to improve flexibility of the electrode and utilization of the active material. The unwanted cost and weight of metal current collectors are also eliminated in the free-standing electrodes [107]. The CNT with 1D hollow structure acting as conductive substrate shows the advantage of this strategy [101]. Interlaced 1D CNT monomers can be integrated into packed 3D macroscopic architectures, and the tight anchoring makes loaded species undergo a post-densified procedure to obtain free-standing sample. Furthermore, the binding effect from interconnected conductive skeleton not only alleviates aggregation and accommodates volume change, but also contributes to fast electron/ion transfer. Inspired by this, there are a number of intercalation-type materials that are assembled into free-standing electrodes with the support of CNT, such as amorphous  $\text{MnO}_2$  (Figure 4(e)) [129],  $\text{V}_2\text{O}_5$  nanoparticles (Figure 4(f)) [130],  $\text{V}_2\text{O}_5$  nanofibers (Figure 4(g)) [25], and  $\text{KV}_3\text{O}_8 \cdot 0.75\text{H}_2\text{O}$  (KVO) nanobelts (Figure 4(h)) [66]. Thereinto, simple vacuum filtering is often adopted as processing method. In fact, the solution formula for filtration habitually follows the slurry ratio in conventional electrode preparation. However, the mass ratio between active species with high capacity and carbon with high conductivity needs to be optimized to maximize the overall energy density without losing the free-standing structure.

2D carbon nanomaterials are also used as the conductive substrate, and the 2D spatial structure is more

suitable for *in-situ* growth and arrangement of loaded species compared to the 1D carbon. Graphene, as a typical 2D carbon, can be used both in conventional and flexible substrates. In conventional substrates, 0D  $\text{ZnMn}_2\text{O}_4$  nanoparticle/2D reduced graphene oxide (rGO) composite was proposed (denoted as  $\text{ZnMn}_2\text{O}_4/\text{rGO}$ ). The ultras-small  $\text{ZnMn}_2\text{O}_4$  nanodots (5–10 nm) uniformly anchored on rGO without agglomeration were shown in Figure 4(i). In the resultant composite, the small active nanoparticle was in favor of exposing sites and shortening the diffusion path, while the rGO contributed to the large surface area and high electrical conductivity. Therefore,  $\text{ZnMn}_2\text{O}_4/\text{rGO}$  delivered higher capacity than the  $\text{ZnMn}_2\text{O}_4$  microspheres [131]. The particle size was also well defined at 21 nm in another case of  $\text{ZnMn}_2\text{O}_4/\text{N-doped graphene}$  (denoted as  $\text{ZnMn}_2\text{O}_4/\text{NG}$ ) (Figure 4(m)). Moreover, lattice parameter quantitative calculation highlighted the weak distortion triggered by ion insertion/extraction in the hybrid electrode [132]. This also shows the prominent contribution of conductive substrate in terms of both size and volume limitation. Additionally, 1D nanomaterials with various morphology were rationally designed as 1D/2D hybrid by integrating with graphene. The representative examples include  $\text{MnO}_2$  nanowires/rGO (Figure 4(j)) [20],  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanowires/graphene (Figure 4(k)) [48],  $\text{H}_2\text{V}_3\text{O}_8$  nanorods/graphene (Figure 4(n)) [133],  $\text{H}_2\text{V}_3\text{O}_8$  nanowires/graphene (Figure 4(o)) [134], etc. In these cases, the graphene substrates were constructed into 3D interconnected conductive framework. This design is beneficial to not just productively alleviating the buildup of active materials, but also facilitating the rapid transfer of electrons/ions. Therefore, those hybrid electrodes can perform well even at ultrahigh rates as shown in Table 1. In terms of 2D active species/graphene hybrid, the bright spot is the face-to-face contact form. For example, the layer-by-layer architecture of  $\text{VO}_2$  nanobelts/rGO [135] and  $\text{O}_d\text{-VO}_2$  nanobelts/rGO were shown in Figure 4(l,p) [136]. Compared with point-to-face contact of 0D/2D and line-to-face contact of 1D/2D, the more intimately face-to-face contact guarantees fast kinetics and efficient control of volumetric strain. Simultaneously, dead volume was released and more sites were exposed because the stacking orientation was suppressed. For the flexible substrate, the vacuum filtration method is also effective for 2D graphene, such as in the case of  $\text{MnO}_2$  nanowires/rGO [20]. In addition, the flexible engineering can be operated on deformable carbon skeleton where active material *in situ* grows on the surface [139,140]. For example, a flexible skeleton was constructed by vertical multilayer graphene arrays growing on carbon cloth (CC), which offered the reliable deformation adaptability

**Table 1.** A summary of multi-dimensional structured carbon nanomaterials for intercalation-type cathodes.

| Carbon function      | Micro-dimensions of carbon | Cathode                                                    | Mass ratio of carbon (wt.%) | Mass loading (mg cm <sup>-2</sup> ) | Electrolyte (Voltage vs. Zn <sup>2+</sup> /Zn)                    | Specific capacity                                                                                      | Energy/power Density                               | Capacity retention                              | Ref. # & Publish year |
|----------------------|----------------------------|------------------------------------------------------------|-----------------------------|-------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|----------------------------------------------------|-------------------------------------------------|-----------------------|
| Conductive substrate | 0D                         | Mn <sub>3</sub> O <sub>4</sub> /NCDs                       | 3.9                         | 1.3                                 | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> (0.8–1.8 V)       | 443.2 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 98.8 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>   | /                                                  | 86.6% at 0.2 A g <sup>-1</sup> after 100 cycles | [60] 2022             |
|                      | 1D                         | MnO <sub>2</sub> /CNFs                                     | 17                          | 1.5–2.0                             | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (1.0–1.85 V)      | 297 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup> , 144 mAh g <sup>-1</sup> at 3 A g <sup>-1</sup>      | 406 Wh kg <sup>-1</sup> , 3.97 kW kg <sup>-1</sup> | 100% at 1 A g <sup>-1</sup> after 1500 cycles   | [71] 2021             |
|                      | 1D                         | V <sub>2</sub> O <sub>5</sub> /CNTs                        | 33                          | /                                   | 1 M ZnSO <sub>4</sub> (0.2–1.7 V)                                 | 312 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup> , 232 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>       | /                                                  | 81% at 1 A g <sup>-1</sup> after 2000 cycles    | [130] 2019            |
|                      | 1D                         | V <sub>2</sub> O <sub>5</sub> /CNTs                        | /                           | 3.0                                 | 2 M ZnSO <sub>4</sub> (0.2–1.6 V)                                 | 375 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 219 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>     | /                                                  | 98% at 1 A g <sup>-1</sup> after 100 cycles     | [25] 2019             |
|                      | 1D                         | amorphous MnO <sub>2</sub> /CNTs                           | 62                          | /                                   | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> (1.0–1.8 V)       | 308.5 mAh g <sup>-1</sup> at 0.97 C, 69.5 mAh g <sup>-1</sup> at 97.4 C                                | /                                                  | 100% at 32.5 C after 1000 cycles                | [129] 2020            |
|                      | 1D                         | KVO/SWCNTs                                                 | 20                          | 2.0                                 | 4 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.3–1.3 V) | 379 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 206 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>      | /                                                  | 91% at 5 A g <sup>-1</sup> after 10,000 cycles  | [66] 2020             |
|                      | 2D                         | ZnMn <sub>2</sub> O <sub>4</sub> /N-doped graphene         | 28.1                        | 1.3–1.6                             | 1 M ZnSO <sub>4</sub> + 0.05 M MnSO <sub>4</sub> (0.8–1.8 V)      | 238 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup> , 75 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>      | /                                                  | 97.4% at 1 A g <sup>-1</sup> after 2500 cycles  | [132] 2019            |
|                      | 2D                         | ZnMn <sub>2</sub> O <sub>4</sub> /rGO                      | /                           | /                                   | 1 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (1.0–1.8 V)       | 185 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 112 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>      | 266 Wh kg <sup>-1</sup> , 6.70 kW kg <sup>-1</sup> | /                                               | [131] 2020            |
|                      | 2D                         | MnO <sub>2</sub> / graphene                                | 30                          | 1.2                                 | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (1.0–1.9 V)       | 317 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 112 mAh g <sup>-1</sup> at 7.5 A g <sup>-1</sup>    | 436 Wh kg <sup>-1</sup> , 9.20 kW kg <sup>-1</sup> | 78% at 2 A g <sup>-1</sup> after 2000 cycles    | [20] 2020             |
|                      | 2D                         | V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O/ graphene | /                           | 2.5                                 | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.2–1.6 V) | 372 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup> , 248 mAh g <sup>-1</sup> at 30 A g <sup>-1</sup>     | 290 Wh kg <sup>-1</sup> , 12.2 kW kg <sup>-1</sup> | 71% at 6 A g <sup>-1</sup> after 900 cycles     | [48] 2017             |
|                      | 2D                         | H <sub>2</sub> V <sub>3</sub> O <sub>8</sub> / graphene    | 4.7                         | 1.0                                 | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.2–1.6 V) | 394 mAh g <sup>-1</sup> at 1/3 C, 270 mAh g <sup>-1</sup> at 20 C                                      | 168 Wh kg <sup>-1</sup> , 2.21 kW kg <sup>-1</sup> | 87% at 20 C after 2000 cycles                   | [134] 2018            |
|                      | 2D                         | H <sub>2</sub> V <sub>3</sub> O <sub>8</sub> / graphene    | 8.0                         | 10.7                                | 2 M ZnSO <sub>4</sub> (–1–0.6 V vs. SCE)                          | 372 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup> , 140 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>      | /                                                  | 73.3% at 2 A g <sup>-1</sup> after 200 cycles   | [133] 2020            |
|                      | 2D                         | VO <sub>2</sub> / graphene                                 | 28                          | 3.0                                 | 2 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.2–1.6 V) | 465 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 190 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>     | 312 Wh kg <sup>-1</sup> , 13.4 kW kg <sup>-1</sup> | 100% at 10 A g <sup>-1</sup> after 5000 cycles  | [135] 2021            |
|                      | 2D                         | (O <sub>d</sub> -VO <sub>2</sub> )/rGO                     | 22                          | 3.0                                 | 2 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.2–1.4 V) | 376 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 116 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>     | 296 Wh kg <sup>-1</sup> , 12 kW kg <sup>-1</sup>   | 88.6% at 10 A g <sup>-1</sup> after 5000 cycles | [136] 2020            |
|                      | 2D                         | P-MnO <sub>2-x</sub> @VMG                                  | /                           | 4.1                                 | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> (1.0–1.8 V)       | 302.8 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 150.1 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup> | /                                                  | 91.3% at 2 A g <sup>-1</sup> after 1000 cycles  | [140] 2020            |

(continued)

Table 1. Continued.

| Carbon function      | Micro-dimensions of carbon | Cathode                                             | Mass ratio of carbon (wt.%) | Mass loading (mg cm <sup>-2</sup> ) | Electrolyte (Voltage vs. Zn <sup>2+</sup> /Zn)                                                                    | Specific capacity                                                                                      | Energy/power Density                                 | Capacity retention                                | Ref. #&Publish year |
|----------------------|----------------------------|-----------------------------------------------------|-----------------------------|-------------------------------------|-------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|------------------------------------------------------|---------------------------------------------------|---------------------|
| Encapsulating matrix | 2D                         | V <sub>2</sub> O <sub>3</sub> /N-doped CNSs         | 8.7                         | /                                   | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.4–1.6 V)                                                 | 405 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 159 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>     | 367 Wh kg <sup>-1</sup> , /                          | 90% at 20 A g <sup>-1</sup> after 4000 cycles     | [27] 2022           |
|                      | 2D                         | V <sub>2</sub> O <sub>5</sub> /CNSs                 | 13.8                        | /                                   | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.3–1.6 V)                                                 | 415.4 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 325.3 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup> | /                                                    | 97.1% at 5 A g <sup>-1</sup> after 1000 cycles    | [88] 2021           |
|                      | 3D                         | ZnMn <sub>2</sub> O <sub>4</sub> /PC                | 21                          | /                                   | 1 M ZnSO <sub>4</sub> + 0.05 M MnSO <sub>4</sub> (0.8–1.8 V)                                                      | 176.8 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 88.7 mAh g <sup>-1</sup> at 4 A g <sup>-1</sup>   | /                                                    | 90.3% at 1 A g <sup>-1</sup> after 2000 cycles    | [137] 2020          |
|                      | 3D                         | MnO <sub>2</sub> /HCS                               | 10.2                        | 1.3–1.6                             | 3 M ZnSO <sub>4</sub> + 0.15 M MnSO <sub>4</sub> (1.0–1.85 V)                                                     | 348 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 149 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>      | 457 Wh kg <sup>-1</sup> , 3.31 kW kg <sup>-1</sup>   | 78.7% at 2 A g <sup>-1</sup> after 2000 cycles    | [89] 2020           |
|                      | 1D                         | Mn <sub>3</sub> O <sub>4</sub> /CNFs                | 12.7                        | 1.2                                 | 2 M ZnSO <sub>4</sub> + 0.15 M MnSO <sub>4</sub> (0.9–1.85 V)                                                     | 215.8 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup> , 115.7 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>  | 225.8 Wh kg <sup>-1</sup> , /                        | /                                                 | [22] 2020           |
|                      | 1D                         | V <sub>2</sub> O <sub>3</sub> /CNFs                 | 9.24                        | 1.8                                 | 3 M ZnSO <sub>4</sub> (0.3–1.6 V)                                                                                 | 451.0 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 258.9 mAh g <sup>-1</sup> at 25 A g <sup>-1</sup> | /                                                    | 91.7% at 10 A g <sup>-1</sup> after 4000 cycles   | [142] 2021          |
|                      | 1D                         | V <sub>2</sub> O <sub>5</sub> /CNFs                 | 60.6                        | /                                   | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (0–2.0 V)                                                         | 293 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup> , 91 mAh g <sup>-1</sup> at 4 A g <sup>-1</sup>      | /                                                    | /                                                 | [72] 2022           |
|                      | 1D                         | Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub> /CNFs | 25.8                        | 2.3–2.5                             | 1 M ZnSO <sub>4</sub> (0.4–1.4 V)                                                                                 | 162 mAh g <sup>-1</sup> at 8 A g <sup>-1</sup>                                                         | /                                                    | 93.1% at 8 A g <sup>-1</sup> after 2000 cycles    | [39] 2019           |
|                      |                            | V <sub>2</sub> O <sub>5</sub> /CNFs                 | 28.7                        | 2.3–2.5                             | 1 M ZnSO <sub>4</sub> (0.2–1.6 V)                                                                                 | 409 mAh g <sup>-1</sup> at 8 A g <sup>-1</sup>                                                         | /                                                    | 95.8% at 8 A g <sup>-1</sup> after 2000 cycles    |                     |
|                      | 2D                         | ZnMn <sub>2</sub> O <sub>4</sub> /CNSs              | 23.6                        | 2.0                                 | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (1.0–1.8 V)                                                       | 364 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 174 mAh g <sup>-1</sup> at 1.2 A g <sup>-1</sup>    | /                                                    | /                                                 | [143] 2020          |
| Protecting layer     | 3D                         | ZnMn <sub>2</sub> O <sub>4</sub> /PC                | 13                          | /                                   | 2 M ZnSO <sub>4</sub> (0.8–1.8 V)                                                                                 | 318.4 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 157.7 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>  | /                                                    | 86.4% at 1 A g <sup>-1</sup> after 1500 cycles    | [21] 2022           |
|                      | 3D                         | amorphous V <sub>2</sub> O <sub>5</sub> /PC         | 26                          | /                                   | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.3–1.9 V)                                                 | 620.2 mAh g <sup>-1</sup> at 0.3 A g <sup>-1</sup> , 72.8 mAh g <sup>-1</sup> at 200 A g <sup>-1</sup> | /                                                    | 91.4% at 40 A g <sup>-1</sup> after 20,000 cycles | [144] 2020          |
|                      | 1D                         | V <sub>6</sub> O <sub>13-δ</sub> nanowires/graphene | /                           | /                                   | ZnSO <sub>4</sub> ·7H <sub>2</sub> O, Na <sub>2</sub> SO <sub>4</sub> and H <sub>3</sub> BO <sub>3</sub> solution | 403.5 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup> , 380.4 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>  | /                                                    | 73% at 8 A g <sup>-1</sup> after 2000 cycles      | [51] 2020           |
|                      | 1D                         | α-MnO <sub>2</sub> nanowires/rGO                    | 3.6                         | /                                   | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> (1.0–1.8 V)                                                       | 301.2 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 165.7 mAh g <sup>-1</sup> at 3 A g <sup>-1</sup>  | 406.6 Wh kg <sup>-1</sup> , 9.45 kW kg <sup>-1</sup> | 94% at 3 A g <sup>-1</sup> after 3000 cycles      | [145] 2018          |
|                      | 2D                         | HAVO nanobelts/graphene                             | 11.9                        | 1.59                                | 2 M ZnSO <sub>4</sub> (0.4–1.4 V)                                                                                 | 305.4 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup> , 180.6 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>   | /                                                    | 91.5% at 5 A g <sup>-1</sup> after 500 cycles     | [146] 2019          |

|    |                                                                        |      |         |                                                                                             |                                                                                                        |                                                      |                                                   |            |
|----|------------------------------------------------------------------------|------|---------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|------------------------------------------------------|---------------------------------------------------|------------|
| 2D | V <sub>10</sub> O <sub>24</sub> ·12H <sub>2</sub> O nanosheets/ carbon | /    | /       | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.3–1.5 V)                           | 290.5 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 116.7 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup> | 195.4 Wh kg <sup>-1</sup> , 6.6 kW kg <sup>-1</sup>  | 94.1% at 10 A g <sup>-1</sup> after 10,000 cycles | [152] 2021 |
| 2D | δ-MnO <sub>2</sub> nanoflakes/ carbon                                  | /    | /       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> (1.0–2.0 V)                                 | 348.5 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 78.3 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>  | /                                                    | 96.8% at 6 A g <sup>-1</sup> after 2000 cycles    | [153] 2021 |
| 2D | VO <sub>2</sub> nanosheets/ carbon                                     | 21.4 | 1.0–1.5 | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.4–1.2 V)                           | 388 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 180 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>     | 349 Wh kg <sup>-1</sup> , /                          | 80% at 5 A g <sup>-1</sup> after 1000 cycles      | [151] 2021 |
| 3D | ZnMn <sub>2</sub> O <sub>4</sub> microspheres/ graphene                | 20.3 | 1.3–1.6 | 1 M ZnSO <sub>4</sub> + 0.05 M MnSO <sub>4</sub> (0.8–1.8 V)                                | 111 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 45 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>       | /                                                    | /                                                 | [154] 2019 |
| 3D | KMOH/HCS                                                               | /    | /       | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> (0.85–1.85 V)                               | 296.8 mAh g <sup>-1</sup> at 0.5 A g <sup>-1</sup> , 122.2 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup> | 579.3 Wh kg <sup>-1</sup> , 12.6 kW kg <sup>-1</sup> | /                                                 | [150] 2021 |
| 3D | α-MnO <sub>2</sub> nanoparticles/ carbon                               | 7.9  | /       | 1 M ZnSO <sub>4</sub> (1.0–1.8 V)                                                           | 272 mAh g <sup>-1</sup> at 0.066 A g <sup>-1</sup>                                                     | /                                                    | 69.5% at 0.066 A g <sup>-1</sup> after 50 cycles  | [148] 2017 |
| 3D | NaVPO <sub>4</sub> F nanoparticles/ carbon                             | 10.0 | 2.0     | 15 M NaClO <sub>4</sub> + 1 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.6–1.8 V) | 88.9 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup> , 66.4 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>   | 113 Wh kg <sup>-1</sup> , 5.75 kW kg <sup>-1</sup>   | 89.3% at 1 A g <sup>-1</sup> after 4000 cycles    | [149] 2021 |

for the loaded  $\text{MnO}_2$  [140]. In addition to graphene, there are also well-designed artificial CNS as conductive substrates to construct non-all-carbon electrodes, such as  $\text{V}_2\text{O}_3/\text{CNS}$  (derived from pentyl viologen dibromide) with layer-by-layer structure [27] and  $\text{V}_2\text{O}_5/\text{CNS}$  (derived from sodium citrate) with 2D sandwich structure [88]. Furthermore, the non-graphene CNSs are no less impressive for flexible electrode preparation. Xia et al. prepared a flexible substrate via growing N-doped CNSs arrays on CC to anchor active  $\text{MnO}_2$  [141]. Although the vacuum filtration used by CNT and graphene are not universally applicable to the common composite materials, reasonable structural design, such as the tight loading on flexible CC, is also applicable in the free-standing electrodes.

3D carbon nanomaterials are another choice for conductive substrates. Many 1D and 2D carbon substrates prefer to exist in an interconnected network rather than standing alone. The 3D structure is more durable upon the frequent insertion/extraction. Moreover, the associated efficient mass transfer is also well-expected. 3D carbon with naturally interconnected framework can offer the possibility of high mass loading but without losing the ability to control the volume changes. Meanwhile, the abundant porosity permits easy accessibility of electrolyte ions to ensure high utilization. For instance, Zhao et al. have employed (metal-organic framework) MOF-derived porous carbon polyhedrons as 3D skeleton to anchor  $\text{ZnMn}_2\text{O}_4$  nanoparticles (denoted as  $\text{ZMO@PCPs}$ ) (Figure 4(q)) [137]. As shown in Figure 4(r), the 3D conductive framework greatly promotes the efficient transport of electrons. Besides,  $\text{MnO}_2$  nanosheets grown on N-doped hollow carbon sphere (NHCS) also exhibited hollow structures in 3D skeleton construction [89]. As shown in Figure 4(s), the rate performances of  $\text{MnO}_2/\text{NHCS}$  were much higher than that of pure  $\text{MnO}_2$  hollow spheres. As for the flexible application, the above mentioned  $\text{ZMO/PCPs}$  composites were coated on carbon paper to prepare the electrode for assembling the flexible device. Such flexible post-treatment engineering can give deformable properties. However, this is quite different from 3D macroscopic stacking formed by vacuum filtration of CNT and graphene and *in-situ* growth on flexible CC, since the integrity and stability of the coated active material during operation need to be guaranteed to enable long cycling life.

### 3.1.2. Encapsulating matrix

Encapsulating matrix is another major function of carbon nanomaterials for intercalation-type cathodes, where the active ingredients are entirely embedded in the carbon. Going from cooperating with substrate to matrix,

the intercalation-type species undergo a transition from the surface to the interior in the micro-space of carbons. However, this function transition still maintains or even improves the contribution ability of carbons to electrical conductivity and mass transfer because of the huge omnidirectional contact. Moreover, the embedment strategy not only isolates the electrolyte from the active species to relieve dissolution issue, but also enhances the constraint on volumetric strain. Here we summarize the progress of 1-3D structured carbon nanomaterials as encapsulating matrix for intercalation-type species.

For 1D CNFs, the electrospinning is the most common technology to construct the core-shell structure with the embedded active species. In this design, the porous carbon skeleton shell acts as conductive matrix to not only prevent active nanoparticles from contacting the electrolyte, but also restrict aggregation and unlimited volume expansion. In this regard, the mass ratio is more of a concern than surface functionality in this matrix function. For instance,  $\text{Mn}_3\text{O}_4$  nanoparticles were encapsulated in hollow carbon fibers (HCFs) via coaxial electrospinning (denoted as  $\text{Mn}_3\text{O}_4@\text{HCFs}$ ) [22]. Polyacrylonitrile (PAN) precursors in electrospinning solutions were pre-designed with a series of concentration gradients to optimize the embedding effect.  $\text{Mn}_3\text{O}_4@\text{HCFs}$  with carbon content of 12.7 wt% did the best in encapsulating active nanoparticles and delivered most excellent performances. For another case of  $\text{V}_2\text{O}_3/\text{N}$ -doped carbon hybrid nanofibers (Figure 5(a)), the regulation of embedded species was achieved by the addition of different vanadium-containing precursors [142]. The rate performance in Figure 5(b) indicated the optimized embedding amount of  $\text{V}_2\text{O}_3$  was 85.3 wt% (denoted as S-VO85). CNFs can be woven into a dense stacking network by electrospinning to assemble into a free-standing film. For example, a flexible electrode consisting of carbon fiber cloth (CFC) and  $\text{V}_2\text{O}_5$  was fabricated via electrospinning method (denoted as  $\text{V}_2\text{O}_5/\text{CFC}$ , Figure 5(c)) [72]. By comparison of SEM images in Figure 5(c,d), the free-standing film exhibited good durability even after 100 cycles in which the overall structure with embedded  $\text{V}_2\text{O}_5$  was well maintained. Bi-continuous conductive network was also constructed using electrospinning approach [39]. As shown in Figure 5(e), morphology observation showed that the shell was composed of the hollow fibers, while the core was contributed to the inner porous network. These built bi-continuous conductive paths and porous networks provided the encapsulated nanoparticles with rapid electrons/ions transfer. Moreover, the robust 1D hierarchical carbon matrix endowed composites with good pliability and high flexibility. The design can also be applied to embed both  $\text{V}_2\text{O}_5$  and  $\text{Zn}_2\text{V}_2\text{O}_7$  nanoparticles (Figure 5(f,g)). The

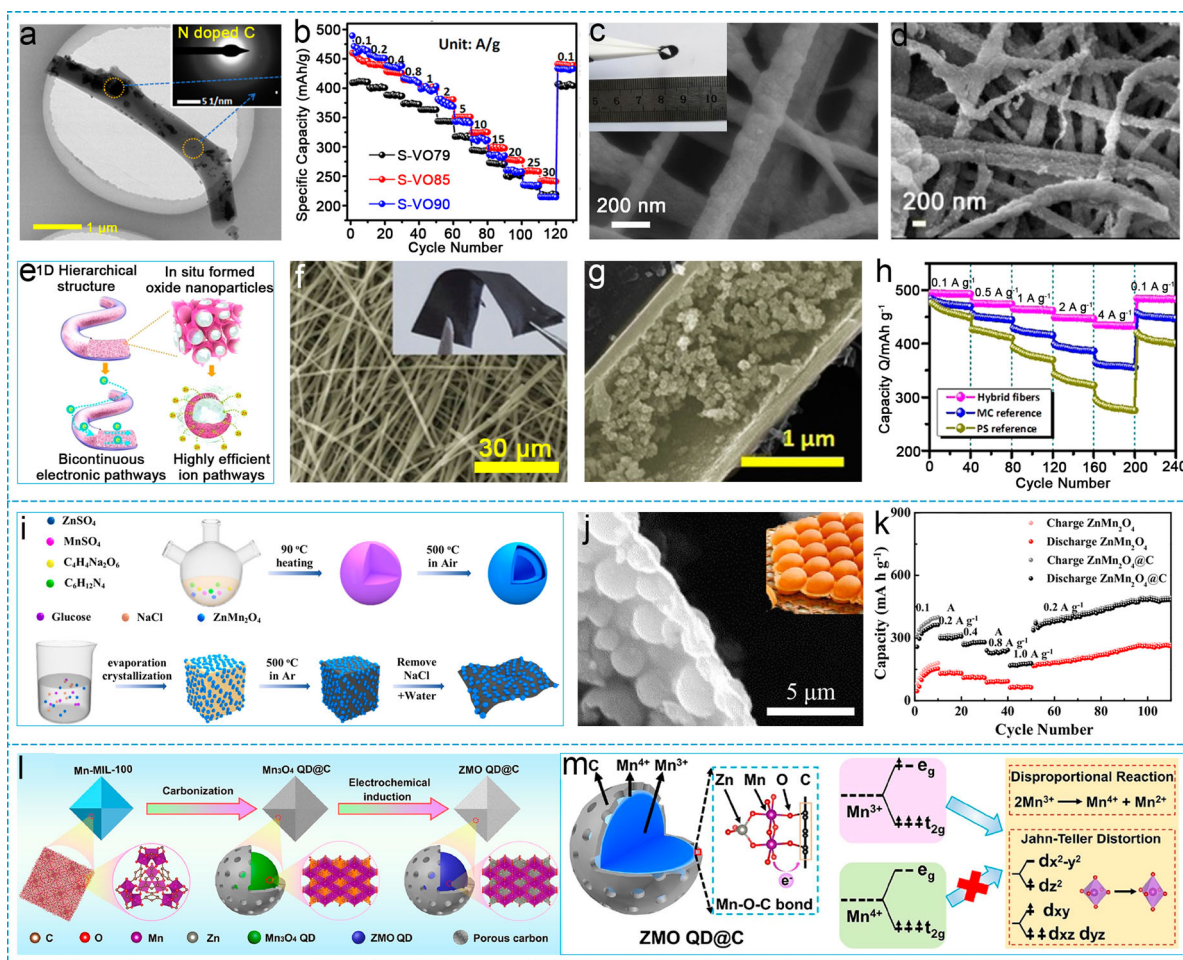


**Figure 5.** (a) TEM image of  $\text{V}_2\text{O}_3/\text{N}$ -doped carbon. (b) Rate capability of  $\text{V}_2\text{O}_3/\text{N}$ -doped carbon electrodes at various current densities. Reproduced with permission. Copyright 2021, Elsevier [142]. (c) SEM image of  $\text{V}_2\text{O}_5/\text{CFC}$  and digital photograph of free-standing electrode during the flexibility test (inserted). (d) SEM image of  $\text{V}_2\text{O}_5/\text{CFC}$  after the 100th cycle. Reproduced with permission. Copyright 2022, Elsevier [72]. (e) Scheme of the hierarchical structure of the hybrid fibers. (f) SEM and (g) TEM images of the 1D hierarchical hybrid fibers with embedded  $\text{Zn}_2\text{V}_2\text{O}_7$  nanoparticles. (h) Comparisons of the discharge capacities between hybrid fibers and reference samples with naked metals oxides (MC) or replaced by activated carbon (PS) at different current densities. Reproduced with permission. Copyright 2019, American Chemical Society [39]. (i) Schematic diagram of the synthesis steps of  $\text{ZnMn}_2\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4@\text{C}$  composites. (j) SEM image of  $\text{ZnMn}_2\text{O}_4@\text{C}$  and photographs of egg-waffle-like architecture (inserted). (k) Rate performance at different current densities and cycling performance of  $\text{ZnMn}_2\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4@\text{C}$ . Reproduced with permission. Copyright 2020, Elsevier [143]. (l) Schematic illustration of fabrication process of ZMO QD@C. (m) Illustration of the Mn valence state distribution in ZMO QD@C and the mechanism of the structural stability of ZMO QD@C. Reproduced with permission. Copyright 2022, WILEY-VCH [21].

self-supported composite delivered better performances than the reference samples with naked metals oxides or replaced by activated carbon according to the rate performances in Figure 5(h).

Theoretically, 2D carbon nanomaterials could also be used as the encapsulating matrix, but the micron-thickness unfortunately limits its practical application. Currently, there are only a few reports on 2D encapsulating matrix. Figure 5(i) showed egg waffle-like architecture consisting of double-shell  $\text{ZnMn}_2\text{O}_4$  hollow microspheres and CNS matrix (denoted as  $\text{ZnMn}_2\text{O}_4@\text{C}$ ). SEM image in Figure 5(j) indicated that the  $\text{ZnMn}_2\text{O}_4$  microspheres (1.5–3  $\mu\text{m}$  in size) were evenly embedded or anchored in/on the carbon matrix. Additionally, the

2D carbon matrix with high conduction and porous networks was beneficial for the fast kinetics and structure stability upon long cycles. The intuitive values of the electrical conductivity and SSA of  $\text{ZnMn}_2\text{O}_4@\text{C}$  were far greater than those of pure  $\text{ZnMn}_2\text{O}_4$  (1.96  $\text{S m}^{-1}$  vs. 0.0284  $\text{S m}^{-1}$ , 109.1  $\text{m}^2 \text{g}^{-1}$  vs. 32.2  $\text{m}^2 \text{g}^{-1}$ ). Therefore, the  $\text{ZnMn}_2\text{O}_4@\text{C}$  delivered higher capacities of 364  $\text{mAh g}^{-1}$  at 0.1  $\text{A g}^{-1}$  and 127  $\text{mAh g}^{-1}$  at 2  $\text{A g}^{-1}$  compared to those of pure  $\text{ZnMn}_2\text{O}_4$  (154  $\text{mAh g}^{-1}$  and 67  $\text{mAh g}^{-1}$ ) (Figure 5(k)). The remaining capacity of  $\text{ZnMn}_2\text{O}_4@\text{C}$  composite after 110 cycles was about 1.8 times that of the reference sample. CNS matrix with  $\text{ZnMn}_2\text{O}_4$  uniformly embedded also showed good structural stability as revealed by post morphological characterization after

100 cycles [143]. This egg waffle-like architecture sheds light on the design of 2D carbon matrix. A good match between the size of active species and the thickness of 2D carbon nanosheets is the key point to the successful operation. In addition, how to make full utilization of the flexible nature of the 2D matrix is also worth further exploration.

3D carbon nanomaterials as matrix can completely release the spatial limitations of embedding. A simple and feasible strategy for this is to induce the electrochemical transition of MOF-derived materials. For instance,  $\text{ZnMn}_2\text{O}_4$  QDs were introduced in 3D porous carbon framework (denoted as ZMO QD@C) via electrochemically inducing MOF-derived  $\text{Mn}_3\text{O}_4$ /carbon hybrid (Figure 1) [21]. The 3D porous carbon matrix with ultrasmall embedded QDs (5.6 nm) helped to expose more active sites and brought fast transport dynamics. In addition, the spatial confinement effectively avoided particle aggregation. The formed Mn–O–C bond between QDs and matrix greatly strengthened the inherent stability by altering the electron configuration of Mn. Therefore, the dissolution issue can be effectively eliminated (Figure 5(m)). In the pure  $\text{ZnSO}_4$  electrolyte, a superior rate capacity ( $157.7 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$ ) and cycle retention (86.4% retention after 1500 cycles) were delivered. A similar study on amorphous  $\text{V}_2\text{O}_5$ /3D carbon composite was reported [144]. The amorphous  $\text{V}_2\text{O}_5$  prepared from the MOF derived  $\text{V}_2\text{O}_3$ @C precursor favored isotropic diffusion paths and storage sites. The well-designed composite displayed extraordinary rate performance of  $72.8 \text{ mAh g}^{-1}$  at  $200 \text{ A g}^{-1}$  and record-breaking cyclability of 91.4% retention after 20,000 cycles at  $40 \text{ A g}^{-1}$  [144].

### 3.1.3. Protecting layer

Protecting layer function refers to carbon nanomaterials exist as a thin shell outside the active species. Such a protecting layer further shields active components from direction contact with electrolytes. Meanwhile, it also reduces the risk of structure collapsing and underutilization due to volume changes and over-embedding, respectively. However, kinetic transport in the carbon layer even with ultrathin thicknesses still plays a key role in the electrochemical performance of the electrode. Since the micro-morphology of carbon layer largely depends on active components wrapped inside, the progress of the carbon protecting layer is summarized by the microscopic dimension (1D–3D) of the internal materials in this section.

1D nanomaterials could be enwrapped in center of carbon layer to build a typical coaxial core-shell structure (Figure 6(a)). For this purpose, graphene with good

mechanical strength is appropriate for self-rolling outside the active fibers. For example, defect-rich  $\text{V}_6\text{O}_{13-\delta}$  (Figure 6(b)) [51] and  $\alpha\text{-MnO}_2$  [145] nanowires were coated with multi-layer graphene to form hybrid coaxial scrolls via time-controlled hydrothermal reactions. Per TEM images in Figure 6c, d, the overall diameter for coaxial core-shell structure of the two samples ranged from 50 to 250 nm and multi-layer graphene was in thickness of 5–10 nm. In the example of  $\text{V}_6\text{O}_{13-\delta}$ , the time-dependent product evolution in the hydrothermal reaction was investigated. The orientated growth of nanowires, self-assembly, and self-rolling of graphene occurred sequentially as time increased. In addition to morphological evolution, the dosage of added graphene was controlled to set reference samples. The difference in performance between the optimized samples and pristine active species was plotted in Figure 6(e) to highlight the effectiveness of the graphene layer. For advanced carbon design, the structural parameters of protective layer are worth paying attention to, and more experimental parameters need to be introduced beyond the mass ratio of carbon.

2D nanomaterials with carbon layer covering are in the form of face-to-face contact to construct the hybrid layers. The tight attachment on both sides of 2D structured composite maximizes contact areas without sacrificing control over volume variation and dissolution issue. Thereby, this design guarantees structured stability and dynamic transport. There are relevant examples of graphene-wrapped  $\text{H}_{11}\text{Al}_2\text{V}_6\text{O}_{23.2}$  nanobelt (denoted as HAVO@G) (Figure 6(f)) [146] and graphene oxide-wrapped  $\text{CuV}_2\text{O}_6$  nanobelts (denoted as GO/CVO) [147]. In both cases, blank sample with carbon-free was set for comparison. For HAVO@G, it exhibited better reversible capacity of  $280.2 \text{ mAh g}^{-1}$  after 200 cycles, while pure HAVO underwent significant capacity fading due to the partial dissolution and poor conductivity (Figure 6(g)). But in the case of  $\text{CuV}_2\text{O}_6$ , the designer's intention was to introduce GO with rich O-groups to enhance capacity. As expected, the GO/CVO sample achieved at least 30% of the capacity improvement compared with the blank sample as shown in Figure 6(h). This capacity increase can largely be attributed to the contribution of kinetic transport and conductivity by GO. The pseudocapacitance activated by O-groups may also contribute to the increased capacity, which needs to further clarification by systematically characterization. Besides graphene, other organic compounds-derived carbon can serve as protecting layer for 2D active materials including  $\text{VO}_2$  covered with polyethylene oxide-derived carbon [151], carbon-coated  $\text{V}_{12}\text{O}_{24} \cdot 12\text{H}_2\text{O}$  from hydrothermal treatment of ethanol and  $\text{V}_2\text{O}_5$  solution [152], and  $\text{MnO}_2$  coated with dopamine-derived carbon [153]. For the

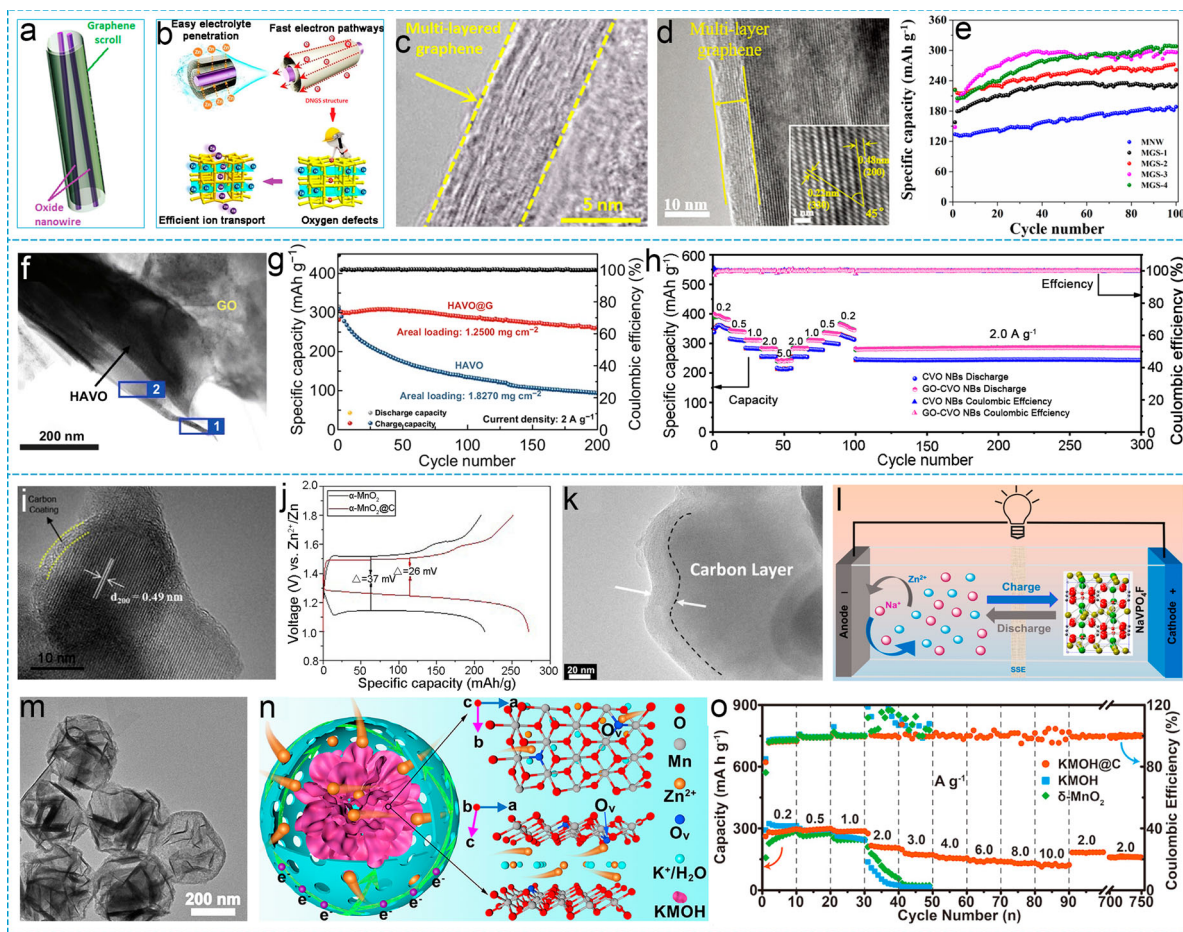


**Figure 6.** (a, b) Schematic illustration of 1D hybrid scrolls with core-shell structure. Reproduced with permission. Copyright 2020, Elsevier [51]. (c) TEM image of defect-rich  $V_6O_{13-8}$  coated with multi-layer graphene. Reproduced with permission. Copyright 2020, Elsevier [51]. (d) TEM image of  $\alpha$ - $MnO_2$  nanowires coated with multi-layer graphene. Reproduced with permission. Copyright 2018, WILEY-VCH [145]. (e) Cycling performance at  $0.3 \text{ A g}^{-1}$  of  $\alpha$ - $MnO_2$  nanowires coated by graphene with different mass ratio. Reproduced with permission. Copyright 2018, WILEY-VCH [145]. (f) TEM image of HAVO@G. (g) Cycling performances at  $2 \text{ A g}^{-1}$  of HAVO and HAVO@G. Reproduced with permission. Copyright 2019 Springer Nature [146]. (h) Rate performances at different current densities and cycling performances of GO/CVO and pure CVO. Reproduced with permission. Copyright 2019, American Chemical Society [147]. (i) TEM image of  $\alpha$ - $MnO_2$ @C sample. (j) Galvanostatic charge-discharge (GCD) profiles of the pristine  $\alpha$ - $MnO_2$  and  $\alpha$ - $MnO_2$ @C sample. Reproduced with permission. Copyright 2017, Elsevier [148]. (k) TEM image of carbon-coated  $NaVPO_4F$  sample. (l) Schematic illustration of the cell configuration and mechanism of aqueous zinc battery assembled using carbon-coated  $NaVPO_4F$  cathode. Reproduced with permission. Copyright 2021, American Chemical Society [149]. (m) TEM image of  $KMOH$ @C. (n) Schematic illustration of the  $Zn^{2+}$ /electron transport in  $KMOH$ @C. (o) Rate capability at various current densities of  $KMOH$ @C and reference samples. Reproduced with permission. Copyright 2021, Elsevier [150].

last case, the carbon-coated  $MnO_2$  was further vertically grown on flexible CC for flexible application. Moreover, the anti-dissolution function of protecting layer was analyzed in detail. Thereinto, the measured Mn content in electrolyte of the carbon-coated sample after 50 cycles was about  $4.70 \mu\text{g mL}^{-1}$ , approximately  $0.74 \mu\text{g mL}^{-1}$  lower than that of the unprotected sample.

3D nanomaterials covered with carbon layer are finally described. A typical sample is the carbon-coated  $\alpha$ - $MnO_2$  nanoparticles (denoted as  $\alpha$ - $MnO_2$ @C) prepared via simple gel formation and subsequent annealing. Morphology characterization in Figure 6(i) showed that micro-spherical  $MnO_2$  particles with size of 20 nm

were uniformly covered by carbon. The  $\alpha$ - $MnO_2$ @C exhibited a higher capacity in pure  $ZnSO_4$  electrolyte compared to bare  $MnO_2$  ( $272 \text{ mAh g}^{-1}$  vs.  $213 \text{ mAh g}^{-1}$ ) as shown in Figure 6(j), due to the effectiveness of the carbon layer to inhibit dissolution. In another example, chemical vapor deposition (CVD) was used to coat the pre-synthesized  $NaVPO_4F$  with a uniform and clear carbon layer of 20 nm thick (Figure 6(k)). Moreover, the high concentration of electrolyte ( $15 \text{ M NaClO}_4 + 1 \text{ M ZnCF}_3\text{SO}_3$ , Figure 6(l)) coordinated with carbon layer synergistically achieved the outstanding capacity retention of 94.5% after 4000 cycles. It can be observed that the above carbon layer design is based on

a two-step method. In this procedure, the size control of pre-synthesized materials in the first step is of decisive significance. The active particles with well-defined size make the subsequent covering process easy, while the fine regulation of the carbon layer is still necessary. Another example showed a yolk-shell structured K-birnessite ( $\text{K}_{0.48}\text{Mn}_2\text{O}_4 \cdot 0.49\text{H}_2\text{O}$ )@mesoporous carbon nanospheres (denoted as KMOH@C, Figure 6(m)). In this case, the outer carbon layer structure was of particular interest [150], because the carbon shells regulated the transport of reaction ions by surface charge and pore structure to induce target yolk-shell structure. And the customized hollow carbon spheres as conductive framework ensured fast transfer of ions/electrons in the electrochemical process (Figure 6(n)). Furthermore, the abundant void space between internal core and outside shell can effectively adjust the volume strain of KMOH nanosheets. Therefore, the KMOH@C delivered a better rate and cycling performances at various currents, while the capacities of reference samples declined to unacceptable values quickly (Figure 6(o)). These examples show the efficient operation of construct protecting layer for 3D structured materials. Yet careful controlling and deliberate design of carbon layer structure as depicted in KMOH@C sample must be employed to avoid excessive protection and improve the utilization. Furthermore, a stable layer design with certain mechanical strength to avoid collapse is critical for durability.

### 3.2. Carbon in adsorption-type cathode

The adsorption-type cathodes mainly depend on the conventional EDLC at effective electrode interfaces and compensative Faradic pseudocapacitances occurred at functional groups. This means that the carbon cathodes are expected to feature with the large SSA to increase the exposure, rich heteroatomic groups to activate pseudocapacitance, and abundant porosity to facilitate ion transfer. Thereby, these typical features spontaneously become the accepted considerations for advanced carbon designs. In this section, we focus on the carbon design engineering of surface area, porosity, and heteroatom-doping, and summarize the progress of all-carbon based cathodes with different microscopic dimension (1D–3D).

#### 3.2.1. Surface area engineering

A large surface area can contribute sufficient sites for both physical electrostatic attraction and Faradic chemical adsorption, thereby being regarded as the key parameter of carbon design. For typical 1D CNTs, the chemical oxidation treatment increased SSA from 120 to 211  $\text{m}^2 \text{g}^{-1}$ , meanwhile enriched the surface oxygen content [64]. These heteroatomic oxygen groups activated the

chemical adsorption on oxidized CNTs to offer pseudo-capacitances. The enlarged SSA not only provided more EDLC, but also exposed sufficient heteroatomic sites to ensure high utilization. Therefore, oxidized CNT delivered higher capacitances compared to the untreated sample [64]. Except for the harsh chemical treatment mentioned above, surface area engineering can also be operated via the moderate alignment strategy. As an example, a carbon fiber composite consisting rGO and CNTs was assembled hydrothermally to increase SSA [155]. Figure 7(a) gave the schematic illustration of the synthesis of rGO/CNT and the assembled Zn-ion hybrid fiber capacitor (ZnFC). In this design, the inserted single-walled CNTs among rGO nanosheets can effectively inhibit the completing rGO restacking, which enabled the rGO/CNT fibers with a sizeable accessible SSA ( $265 \text{ m}^2 \text{g}^{-1}$ ) for ion storage (Figure 7(b)). In comparison, the SSA of hydrothermally assembled pure rGO fibers without CNTs was only  $24 \text{ m}^2 \text{g}^{-1}$ . Moreover, the compact architecture endowed CNT/rGO fibers with outstanding self-supporting mechanical strength (127 MPa) that can satisfy the requirements for flexible wearable devices (Figure 7(c)). One of the advantages of fiber-shaped device is that they can be integrated into sophisticated energy storage units. Several as-assembled ZnFCs can be integrated in series or parallel to realize more extensive operating voltage windows or higher effective currents to meet the energy needs of the practical equipment. Thus, an energy storage unit was constructed by connecting five assembled ZnFCs in parallel first, and then integrating four of such assemblies in series. Thanks to the energy advantage brought by high SSA of the rGO/CNT electrode, this energy storage unit can power a light-emitting diode (LED) panel or a digital watch. Furthermore, the energy unit also showed good deformation adaptability under bending and twisting conditions, highlighting the great potential for flexible wearable devices.

2D carbon materials could also be carried out by alignment strategy for surface area engineering [75]. Referring to the case in Figure 7(d), GO was reduced thermally by the hydrazine hydrate/ammonia to act as interlayer mediator (named as  $\text{N}_2\text{H}_4$ -Graphene, NHG). This mediator exhibited typically reduction feature and crumple geometric configuration. Therefore, the interspacing of laminate graphene films was extended via tailoring ratio of crumple NHG mediator. The resulting interlayer spacing could be customized in range of 0.72–0.81 nm (Figure 7(e–f)), thereby facilitating the transfer kinetics of hydrated  $\text{Zn}^{2+}$  with large size. Furthermore, as shown in Figure 7(g), the interlayer expansion by regulating the ratio of NHG made the SSA increase from 12.5 to  $325.1 \text{ m}^2 \text{g}^{-1}$ , and the corresponding packing density decrease from 1.58 to  $1.0 \text{ g cm}^{-3}$ . Combined with

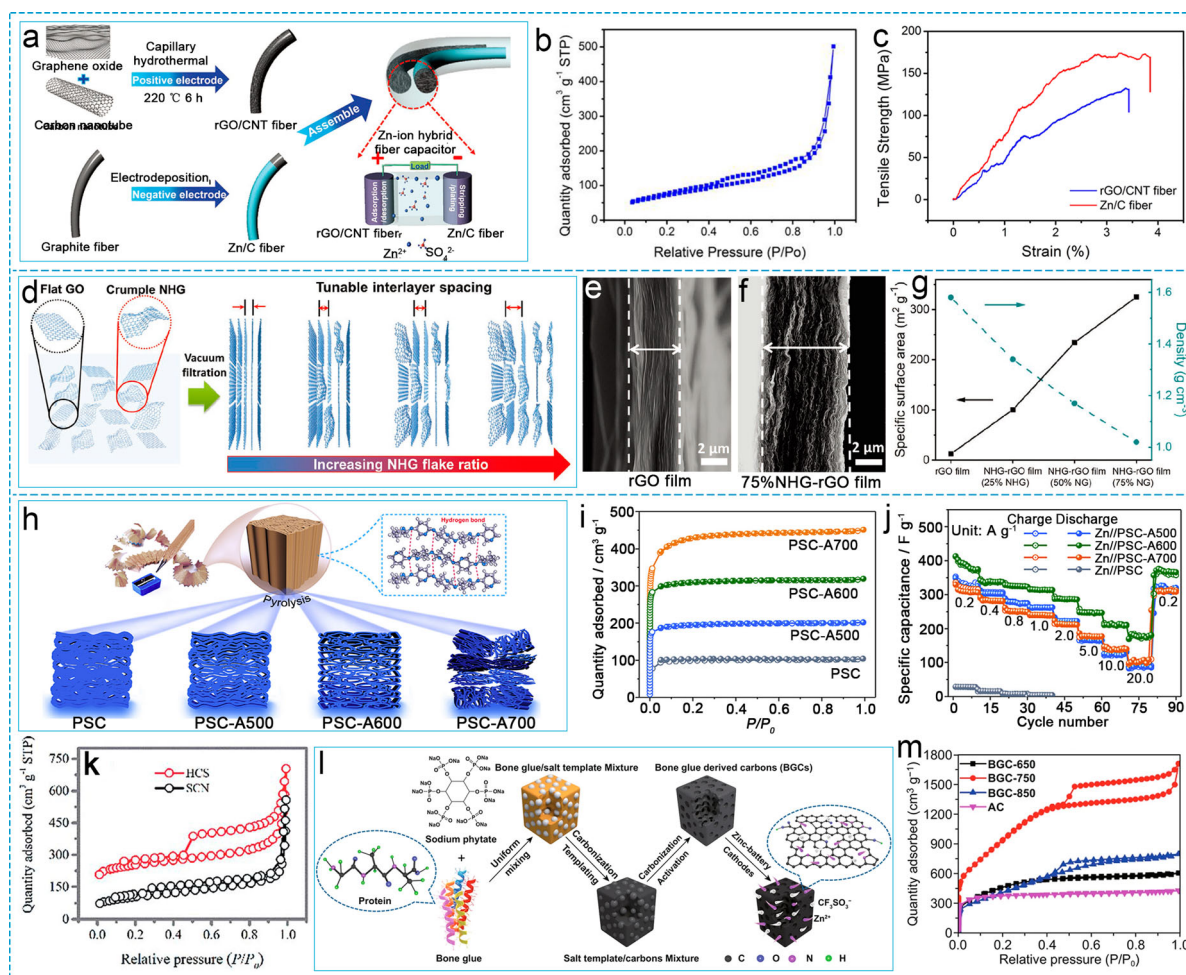


**Figure 7.** (a) Schematic illustration of the synthesis of rGO/CNT hybrid fiber and Zn-coated graphite fiber for assembling a Zn-ion hybrid fiber capacitor. (b) N<sub>2</sub> adsorption-desorption isotherm of rGO/CNT hybrid fiber. (c) The stress-strain curves of rGO/CNT fiber and Zn-coated/graphite fiber. Reproduced with permission. Copyright 2019, Wiley-VCH [155]. (d) Schematic of the preparation of NHG-GO films from GO and NHG solutions with a tunable ratio of NHG to GO. (e) Cross-sectional SEM images of (f) rGO and 75%NHG-rGO films. (g) Tradeoff relationship between SSA and density of rGO and NHG-rGO films. Reproduced with permission. Copyright 2022, Wiley-VCH [75]. (h) Schematic preparation, (i) N<sub>2</sub> adsorption/desorption isotherms and (j) rate capability of PSC and PSC-Ax. Reproduced with permission. Copyright 2020, Elsevier [127]. (k) N<sub>2</sub> adsorption and desorption isotherms of HCS and SCN. Reproduced with permission. Copyright 2019, Royal Society of Chemistry [79]. (l) The schematic illustrating the preparation procedure of the BGCs. (m) N<sub>2</sub> adsorption and desorption isotherms of BGCs. Reproduced with permission. Copyright 2022 Springer Nature [107].

electrolyte engineering to tailor the solvation structure of Zn<sup>2+</sup>, the optimized sample showed a remarkable cyclability of 93.9% retention over 100,000 cycles and a preeminent volumetric capacitance of 235.4 F cm<sup>-3</sup>.

3D carbon nanomaterials are usually operated via chemical activation for SSA engineering. Precursors are usually selected carefully because of their direct association with the final product. For example, a hydrothermal-assisted biomass precursor mixing strategy with chemical activation was proposed [110]. The as-obtained carbon integrates both advantages of SSA and conductivity of carbons derived from bagasse and coconut shell precursor. Therefore, the resultant carbon delivered higher rate capacitances than the carbon derived from a single precursor. Another wood-based pencil shavings biomass

was employed as a precursor to study the effect of pyrolysis temperature on carbon during KOH activation (Figure 7(h)) [127]. Figure 7(i) showed the N<sub>2</sub> adsorption/desorption isotherms of carbons activated at different temperatures. The sample at 600 °C (denoted as PSC-A600) with moderate SSA (948 m<sup>2</sup> g<sup>-1</sup>) but stable porous structure delivered better rate performances than the under-activated sample at 500 °C (598 m<sup>2</sup> g<sup>-1</sup>) and over-activated sample at 700 °C (1293 m<sup>2</sup> g<sup>-1</sup>) (Figure 7(j)). This also indicated that SSA is not the only dominant factor of capacity. In addition, Liu et al. have investigated the effect of activator dosage by means of phenanthrene molecules precursor. The performance comparison showed that the optimized sample with moderate dosage of activator exhibited the highest SSA and

best performances [156]. Employing excessive activator addition or over-temperature carbonization to pursue high SSA at the expense of stable structure are inefficient and counter-productive. Meanwhile, an ultrahigh SSA and low activator dosage are mutually exclusive and intractable to achieve simultaneously in traditional activation process. A recent report indicated that a liquid-liquid micro-mixing strategy of activator and precursor can endow carbon with higher SSA using extremely low dosage of KOH (mass ratio of 0.42:1). Compared with the grinding-assisted solid-solid mixing technique, it achieved homogeneous mixing between precursor and activator at the microscopic level, thereby leading to a higher activation efficiency. The feasibility of this facile strategy was well-verified by operating on both precursors of silkworm cocoon and mushroom stalk [157]. Apart from the single activator, there is also report on the synergistic effect of dual activators to obtain high SSA [158]. The concomitant requirement is that the activator species and formulations need to be carefully decided. Another strategy for SSA engineering is the template approach. For example, a 3D HCSs (denoted as HCS) were fabricated by carbonizing polyaniline-co-polypyrrole employing a surfactant as the soft template, which exhibited a high SSA of  $819.5 \text{ m}^2 \text{ g}^{-1}$ , far higher than that of the free-template ( $246.7 \text{ m}^2 \text{ g}^{-1}$ , denoted as SCN) with solid nanoparticle morphology [79] (Figure 7(k)). Furthermore, according to our previous experience [107], the templating/activating co-assisted carbonization processing strategy also helped us transform a routine protein-rich biomass to 3D carbon (denoted as BGCs) with ultrahigh SSA of  $3657.5 \text{ m}^2 \text{ g}^{-1}$  (Figure 7(l,m)).

Although it is believed that high SSA is beneficial for electrochemical performances, there are many samples (as listed in Tables 2–3) with similar SSA delivered vastly different capacitances, even low SSA for higher performances. The fruitful surface area engineering also indicates that both SSA and electrochemical performances are affected by multiple factors. Therefore, pursuing high SSA meanwhile giving a comprehensive consideration to the overall structure of carbon are meaningful to boost performances.

### 3.2.2. Porosity engineering

Although the pursuit of high SSA can be satisfied in various nanocarbons, the internal pore structure greatly affects the practical utilization of SSA. Tortuous paths in the interconnected nanopores make the inside materials easily shielded by the external part, which inevitably introduces invalid SSA. Advanced nanostructure design for high performances should be characterized by appropriate SSA cooperating with well-developed porosity.

**Table 2.** Radius and hydrated radius of representative electrolyte ions.

| Ion                                          | Ion radius (Å) | Hydrated radius (Å) | Ref.#     |
|----------------------------------------------|----------------|---------------------|-----------|
| H <sup>+</sup>                               | 0.17           | 2.82                | [167]     |
| Li <sup>+</sup>                              | 0.76           | 3.82                | [167]     |
| Na <sup>+</sup>                              | 0.95           | 3.58                | [167]     |
| Zn <sup>2+</sup>                             | 0.74           | 4.30                | [168]     |
| Mn <sup>2+</sup>                             | 0.86           | 4.38                | [168]     |
| NH <sub>4</sub> <sup>+</sup>                 | 1.48           | 3.31                | [42]      |
| OH <sup>−</sup>                              | 1.76           | 3.00                | [167]     |
| SO <sub>4</sub> <sup>2−</sup>                | 2.90           | 3.79                | [167]     |
| NO <sub>3</sub> <sup>−</sup>                 | 2.64           | 3.35                | [167]     |
| CF <sub>3</sub> SO <sub>3</sub> <sup>−</sup> | 2.70           | > 5.80              | [169,170] |
| ClO <sub>4</sub> <sup>−</sup>                | 2.66           | 3.94                | [171]     |
| F <sup>−</sup>                               | 1.36           | 3.52                | [167]     |
| CH <sub>3</sub> COO <sup>−</sup>             | 1.62           | 2.96                | [172,173] |
| Cl <sup>−</sup>                              | 1.81           | 3.32                | [167]     |
| Br <sup>−</sup>                              | 1.95           | 3.30                | [167]     |
| I <sup>−</sup>                               | 2.16           | 3.31                | [167]     |

Both porosity and SSA engineering are closely related to each other. Here we are going to discuss the advanced design porosity engineering of multi-dimensional structured carbon nanomaterials.

Generally accepted classification of nanopores includes micropore (< 2 nm), mesopore (2–50 nm), and macropore (> 50 nm). In practice, the pore size distribution of the prepared carbon is usually not precisely concentrated in a range. A hierarchical architecture with various nanopores in carbon nanomaterials is common. For example, a designed B, N dual-doped 1D carbon microtubes (denoted as BN-CMT) were prepared using polypyrrole as precursor and H<sub>3</sub>BO<sub>3</sub> as salt assistant (Figure 8(a)) [159]. The N<sub>2</sub> adsorption/desorption isotherm of BN-CMT in Figure 8(b) showed typical II and IV curves, indicating the existence of mesopores and macropores. The macropores can be attributed to the hollow structures, while the mesopore should be related to the activation effect. Moreover, the salt assistant can play dual roles of chemical activator and B dopant, which contributed to both the increase of SSA and the introduction of B-doping (Figure 8(c,d)). In the other case of 1D carbon, a surface engineering strategy based on two-step activation was employed to design hierarchically porous structure on fibrous carbon surface [160]. The first steam-activated carbon fiber (denoted as MPCF) showed a micropore-dominated pore structure. Further chemical activation endowed the carbon fiber (denoted as HPCF) with hierarchical porous structure consisting of micropores, mesopores and macropores, and larger SSA. The discharge capacity of HPCF cathode was higher than that of MPCF at low rate (141 vs. 85 mAh g<sup>−1</sup> at 0.1 A g<sup>−1</sup>) associated with the advantage of SSA (2000 vs. 810 m<sup>2</sup> g<sup>−1</sup>). The MPCF sample underwent a dramatical decrease in the capacity at high rate, while that of HPCF still remained at a relatively high level. This is because

**Table 3.** A summary of multi-dimensional structured carbon nanomaterials for adsorption-type cathodes.

| Carbon design engineering | Micro-dimensions of carbon | Cathode                        | SSA ( $\text{m}^2 \text{g}^{-1}$ ) | Mass loading ( $\text{mg cm}^{-2}$ ) | Electrolyte                                                     | Specific capacity                                                                                                  | Energy/power density                                    | Capacity retention                                  | Ref. #&Publish year |
|---------------------------|----------------------------|--------------------------------|------------------------------------|--------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------|---------------------|
| Surface area engineering  | 1D                         | rGO/CNT hybrid fibers          | 265                                | /                                    | 2 M $\text{ZnSO}_4$ /PAA hydrogel electrolyte (0–1.8 V)         | $104.5 \text{ F cm}^{-3}$ at 0.4 A $\text{cm}^{-3}$ , $76.7 \text{ F cm}^{-3}$ at 8 A $\text{cm}^{-3}$             | $48.5 \text{ mWh cm}^{-3}$ , $3.60 \text{ W cm}^{-3}$   | 98.5% at 3.2 A $\text{cm}^{-3}$ after 10,000 cycles | [155] 2019          |
|                           | 2D                         | graphene films                 | 325.1                              | /                                    | 2 M $\text{ZnCl}_2$ (0.2–1.7 V)                                 | $235.4 \text{ F cm}^{-3}$ at 0.1 A $\text{g}^{-1}$ , $157 \text{ F cm}^{-3}$ at 100 A $\text{g}^{-1}$              | $73.6 \text{ Wh kg}^{-1}$ , /                           | 94.05% at 5 A $\text{g}^{-1}$ after 40,000 cycles   | [75] 2022           |
|                           | 3D                         | dual-biomass derived carbon    | 3401                               | 0.9                                  | 2 M $\text{ZnSO}_4$ + 1 M $\text{Na}_2\text{SO}_4$ (0.01–1.8 V) | $305 \text{ mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , $101 \text{ mAh g}^{-1}$ at 5 A $\text{g}^{-1}$                | $118 \text{ Wh kg}^{-1}$ , $3.16 \text{ kW kg}^{-1}$    | 94.9% at 2 A $\text{g}^{-1}$ after 20,000 cycles    | [110] 2019          |
|                           | 3D                         | pencil shavings derived carbon | 948                                | 2.0                                  | 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.2–1.8 V)           | $183.7 \text{ mAh g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , $81.8 \text{ mAh g}^{-1}$ at 20 A $\text{g}^{-1}$            | $147 \text{ Wh kg}^{-1}$ , $5.7 \text{ kW kg}^{-1}$     | 92.2% at 10 A $\text{g}^{-1}$ after 10,000 cycles   | [127] 2020          |
|                           | 3D                         | silkworm cocoon derived carbon | 3009                               | 1.6                                  | 2 M $\text{ZnSO}_4$ + 1 M $\text{Na}_2\text{SO}_4$ (0.01–1.8 V) | $344 \text{ mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , $152 \text{ mAh g}^{-1}$ at 5 A $\text{g}^{-1}$                | /                                                       | 98.5% at 3 A $\text{g}^{-1}$ after 10,000 cycles    | [157] 2020          |
|                           | 3D                         | lotus-shaped porous carbon     | 1786.6                             | 4.3                                  | 1 M $\text{ZnSO}_4$ (0.2–1.8 V)                                 | $1688.5 \text{ mF cm}^{-2}$ at $0.215 \text{ mA cm}^{-2}$ , $1370.6 \text{ mF cm}^{-2}$ at $86 \text{ mA cm}^{-2}$ | $686.6 \text{ mWh cm}^{-2}$ , /                         | 98.9% at 5 A $\text{g}^{-1}$ after 20,000 cycles    | [156] 2022          |
|                           | 3D                         | N, S co-doped PC               | 1384.7                             | 2.5                                  | 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0–1.8 V)             | $136.3 \text{ mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , $86.5 \text{ mAh g}^{-1}$ at 20 A $\text{g}^{-1}$            | $122.6 \text{ Wh kg}^{-1}$ , $14.46 \text{ kW kg}^{-1}$ | 99.5% at 5 A $\text{g}^{-1}$ after 15,000 cycles    | [158] 2022          |
|                           | 3D                         | HCS                            | 819.5                              | 1.0–1.2                              | $\text{ZnSO}_4$ /PAM hydrogel electrolyte (0.15–1.95 V)         | $86.8 \text{ mAh g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , $47.1 \text{ mAh g}^{-1}$ at 4 A $\text{g}^{-1}$              | $59.7 \text{ Wh kg}^{-1}$ , /                           | 98% at 1 A $\text{g}^{-1}$ after 15,000 cycles      | [79] 2019           |
|                           | 3D                         | bone glue derived carbon       | 3657.5                             | 1.0                                  | 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.1–1.8 V)           | $257 \text{ mAh g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , $72 \text{ mAh g}^{-1}$ at 100 A $\text{g}^{-1}$               | $168 \text{ Wh kg}^{-1}$ , $61.7 \text{ kW kg}^{-1}$    | /                                                   | [107] 2021          |
| Porosity engineering      | 1D                         | B, N doped carbon microtube    | 101.24                             | 1.0                                  | 1 M $\text{ZnSO}_4$ + 0.001 $\text{ZnI}_2$ (0.2–1.8 V)          | $416.6 \text{ mAh g}^{-1}$ at 1 A $\text{g}^{-1}$ , $73.6 \text{ mAh g}^{-1}$ at 10 A $\text{g}^{-1}$              | $472.6 \text{ Wh kg}^{-1}$ , $16 \text{ kW kg}^{-1}$    | 99.1% at 10 A $\text{g}^{-1}$ after 10,000 cycles   | [159] 2019          |
|                           | 2D                         | porous carbon nanoflakes       | 1770                               | 0.8                                  | 1 M $\text{ZnSO}_4$ (0.1–1.7 V)                                 | $177.7 \text{ mAh g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , $85.5 \text{ mAh g}^{-1}$ at 20 A $\text{g}^{-1}$            | $142.2 \text{ Wh kg}^{-1}$ , $15.39 \text{ kW kg}^{-1}$ | 90% at 10 A $\text{g}^{-1}$ after 10,000 cycles     | [162] 2020          |
|                           | 2D                         | Starch derived CNS             | 2671.9                             | 1.0                                  | 1 M $\text{ZnSO}_4$ (0.1–1.7 V)                                 | $149 \text{ mAh g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , $75 \text{ mAh g}^{-1}$ at 20 A $\text{g}^{-1}$                | $119 \text{ Wh kg}^{-1}$ , $15.98 \text{ kW kg}^{-1}$   | 91% at 10 A $\text{g}^{-1}$ after 10,000 cycles     | [163] 2020          |
|                           | 2D                         | N-doped mesoporous CNS         | 642.3                              | 1.1                                  | 2 M $\text{ZnSO}_4$ (0.15–1.7 V)                                | $262 \text{ mAh g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , $115 \text{ mAh g}^{-1}$ at 10 A $\text{g}^{-1}$               | $198.2 \text{ Wh kg}^{-1}$ , /                          | 118.2% at 5 A $\text{g}^{-1}$ after 10,000 cycles   | [165] 2022          |
|                           | 2D                         | N, O co-doped CNS              | 1248                               | 6.0                                  | 2 M $\text{ZnSO}_4$ (0.2–1.8 V)                                 | $111 \text{ mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , $63.9 \text{ mAh g}^{-1}$ at 3 A $\text{g}^{-1}$               | $109.5 \text{ Wh kg}^{-1}$ , $6.75 \text{ kW kg}^{-1}$  | 92.7% at 2 A $\text{g}^{-1}$ after 50,000 cycles    | [164] 2021          |

(continued)

Table 3. Continued.

| Carbon design engineering    | Micro-dimensions of carbon | Cathode                                | SSA ( $\text{m}^2 \text{g}^{-1}$ ) | Mass loading ( $\text{mg cm}^{-2}$ ) | Electrolyte                                                  | Specific capacity                                                                                       | Energy/power density                                   | Capacity retention                                   | Ref. # & Publish year |
|------------------------------|----------------------------|----------------------------------------|------------------------------------|--------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|--------------------------------------------------------|------------------------------------------------------|-----------------------|
| Heteroatom-doped engineering | 3D                         | mesoporous structured activated carbon | 2527                               | /                                    | 2 M $\text{ZnSO}_4$ (0.3–1.8 V)                              | 176 $\text{mAh g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , 72 $\text{mAh g}^{-1}$ at 10 A $\text{g}^{-1}$       | 188 $\text{Wh kg}^{-1}$ , 10.67 $\text{kW kg}^{-1}$    | 78% at 10 A $\text{g}^{-1}$ after 40,000 cycles      | [37]2020              |
|                              | 3D                         | N-doped carbon nanocage                | 2526                               | 2.0                                  | 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.2–1.8 V)        | 124 $\text{mAh g}^{-1}$ at 0.25 A $\text{g}^{-1}$ , 81.7 $\text{mAh g}^{-1}$ at 20 A $\text{g}^{-1}$    | 107.3 $\text{Wh kg}^{-1}$ , 16.65 $\text{kW kg}^{-1}$  | 100% at 10 A $\text{g}^{-1}$ after 10,000 cycles     | [126]2021             |
|                              | 3D                         | Mesoporous HCS                         | 1275                               | 1.0                                  | 2 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 174.7 $\text{mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , 96.9 $\text{mAh g}^{-1}$ at 10 A $\text{g}^{-1}$   | 129.3 $\text{Wh kg}^{-1}$ , 13.7 $\text{kW kg}^{-1}$   | 96% at 1 A $\text{g}^{-1}$ after 10,000 cycles       | [125]2020             |
|                              | 3D                         | Mesoporous HCS                         | 800                                | 3.0–4.0                              | 2 M $\text{ZnSO}_4$ + 1 M $\text{Na}_2\text{SO}_4$ (0–1.6 V) | 212.5 F $\text{g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , 100 F $\text{g}^{-1}$ at 20 A $\text{g}^{-1}$        | 75.4 $\text{Wh kg}^{-1}$ , 16 $\text{kW kg}^{-1}$      | 99.4% at 2 A $\text{g}^{-1}$ after 2500 cycles       | [178]2020             |
|                              | 1D                         | O-doped CNFs                           | 276.6                              | 0.9–1.2                              | 1 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 136.4 $\text{mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , 38.8 $\text{mAh g}^{-1}$ at 20 A $\text{g}^{-1}$   | 97.7 $\text{Wh kg}^{-1}$ , 9.9 $\text{kW kg}^{-1}$     | 81% at 5 A $\text{g}^{-1}$ after 50,000 cycles       | [70]2021              |
|                              | 1D                         | N, O-doped CNFs                        | 1980.8                             | /                                    | 2 M $\text{ZnCl}_2$ (0.2–1.8 V)                              | 402.7 F $\text{g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , 148 F $\text{g}^{-1}$ at 20 A $\text{g}^{-1}$        | 143.2 $\text{Wh kg}^{-1}$ , 10.0 $\text{kW kg}^{-1}$   | 94% at 10 A $\text{g}^{-1}$ after 10,000 cycles      | [174]2022             |
|                              | 1D                         | N, S, O-doped CNFs                     | 589.2                              | /                                    | 2 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 152.6 $\text{mAh g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , 44.5 $\text{mAh g}^{-1}$ at 40 A $\text{g}^{-1}$   | 95.9 $\text{Wh kg}^{-1}$ , 19.17 $\text{kW kg}^{-1}$   | 93.5% at 5 A $\text{g}^{-1}$ after 25,000 cycles     | [65]2022              |
|                              | 2D                         | glycerol derived mesoporous CNS        | 1666.8                             | /                                    | 2 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 132.9 $\text{mAh g}^{-1}$ at 0.2 A $\text{g}^{-1}$ , 88.9 $\text{mAh g}^{-1}$ at 5 A $\text{g}^{-1}$    | 106.4 $\text{Wh kg}^{-1}$ , 40 $\text{kW kg}^{-1}$     | 94.7% at 15 A $\text{g}^{-1}$ after 20,000 cycles    | [76]2021              |
|                              | 2D                         | potassium citrate derived O-doped CNS  | 1259.7                             | 1.5                                  | 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.2–1.8 V)        | 169.4 $\text{mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , 97.6 $\text{mAh g}^{-1}$ at 20 A $\text{g}^{-1}$   | 125.1 $\text{Wh kg}^{-1}$ , 16.1 $\text{kW kg}^{-1}$   | 93.1% at 10 A $\text{g}^{-1}$ after 60,000 cycles    | [175]2021             |
|                              | 2D                         | N, P, O-doped CNSs                     | 1644                               | 1.77–2.12                            | 1 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 103.2 $\text{mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , 52.8 $\text{mAh g}^{-1}$ at 20 A $\text{g}^{-1}$   | 81.1 $\text{Wh kg}^{-1}$ , 13.37 $\text{kW kg}^{-1}$   | 101.8% at 5 A $\text{g}^{-1}$ after 10,000 cycles    | [77]2021              |
|                              | 2D                         | N, P co-doped graphene                 | 168.3                              | /                                    | 1 M $\text{ZnSO}_4$ (0–1.8 V)                                | 210.2 F $\text{g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , 107.2 F $\text{g}^{-1}$ at 5 A $\text{g}^{-1}$       | 94.6 $\text{Wh kg}^{-1}$ , 4.5 $\text{kW kg}^{-1}$     | 82% at 10 A $\text{g}^{-1}$ after 15000 cycles       | [179] 2022            |
|                              | 3D                         | rubidium-activated PC                  | 1527.7                             | 1.0                                  | 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.2–1.8 V)        | 260.4 $\text{mAh g}^{-1}$ at 0.5 A $\text{g}^{-1}$ , 72.2 $\text{mAh g}^{-1}$ at 120 A $\text{g}^{-1}$  | 178.2 $\text{Wh kg}^{-1}$ , 72.3 $\text{kW kg}^{-1}$   | 99.8% at 10 A $\text{g}^{-1}$ after 20,000 cycles    | [35]2022              |
|                              | 3D                         | N, O-doped PC                          | 2762.7                             | 1.0–1.2                              | 1 M $\text{ZnSO}_4$ (0–1.8 V)                                | 177.8 $\text{mAh g}^{-1}$ at 4.2 A $\text{g}^{-1}$ , 08.2 $\text{mAh g}^{-1}$ at 33.3 A $\text{g}^{-1}$ | 107.3 $\text{Wh kg}^{-1}$ , 24.9 $\text{kW kg}^{-1}$   | 73.6% at 16.7 A $\text{g}^{-1}$ after 100,000 cycles | [106]2019             |
|                              | 3D                         | B, S, O-doped PC                       | 2364                               | 0.83–1.58                            | 1 M $\text{ZnSO}_4$ (0.2–1.8 V)                              | 183.6 $\text{mAh g}^{-1}$ at 0.1 A $\text{g}^{-1}$ , 74 $\text{mAh g}^{-1}$ at 20 A $\text{g}^{-1}$     | 292.16 $\text{Wh kg}^{-1}$ , 16.91 $\text{kW kg}^{-1}$ | 96.2% at 5 A $\text{g}^{-1}$ after 15,000 cycles     | [176] 2022            |

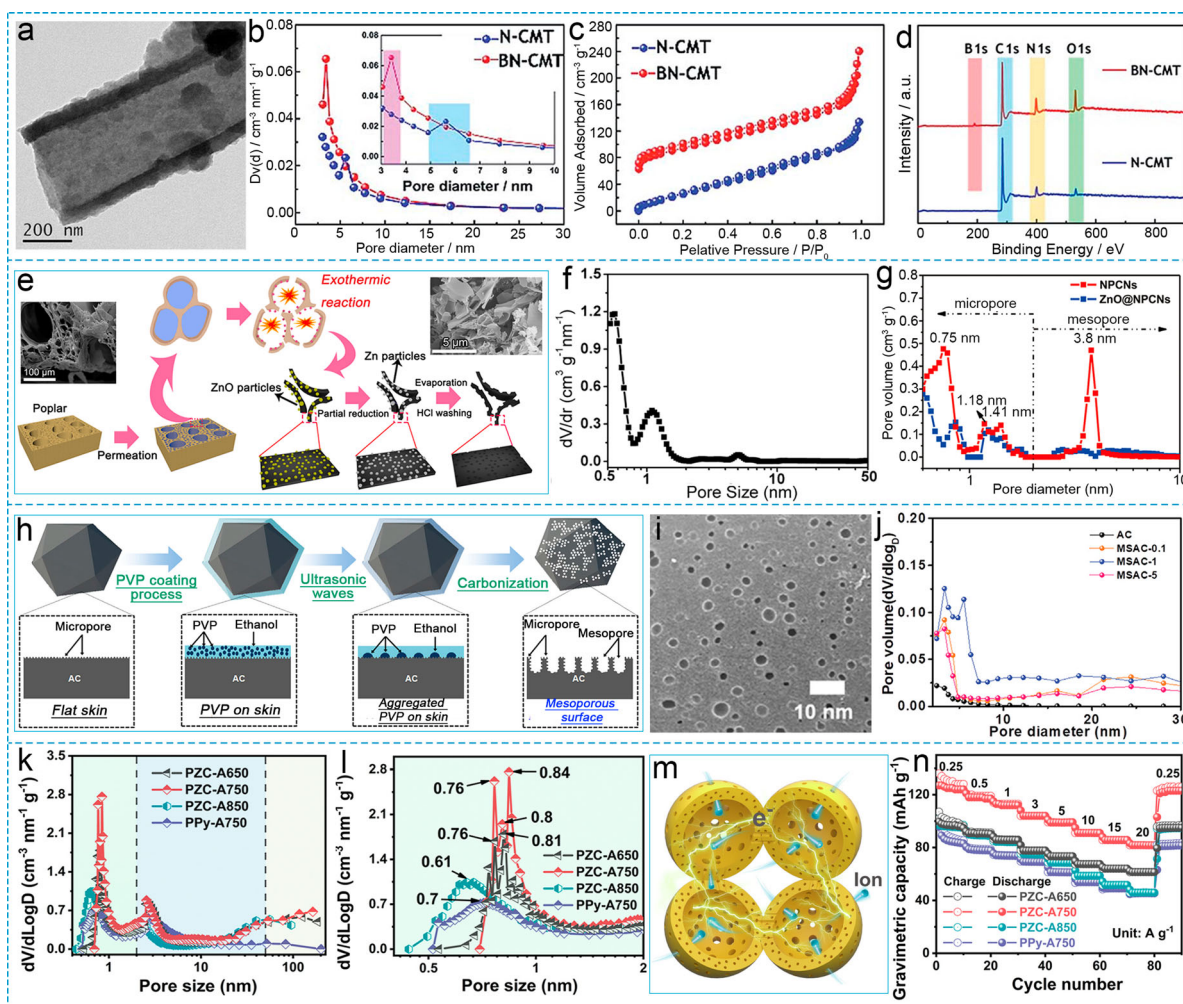


**Figure 8.** (a) TEM image of BN-CMT. (b) PSD curves, (c)  $N_2$  adsorption/desorption isotherms and (d) X-ray photoelectron spectroscopy (XPS) survey spectra of N doped and B, N doped carbon microtube. Reproduced with permission. Copyright 2019, Royal Society of Chemistry [159]. (e) The formation mechanism of porous CNSs based on  $Zn(NO_3)_2$  and urea. (f) PSD curve of poplar wood powder derived CNSs. Reproduced with permission. Copyright 2021, Elsevier [164]. (g) PSD curve of polyvinylpyrrolidone derived CNSs. Reproduced with permission. Copyright 2022, WILEY-VCH [165]. (h) Schematics of the step-by-step fabrication process for the MSAC. (i) High-magnification SEM image of MSAC-1. (j) Pore size distribution (PSD) curve of MSACs and AC samples. Reproduced with permission. Copyright 2020, Elsevier [37]. (k, l) PSD curves and (n) rate performances of PZC-Ax and reference samples. (m) Schematic illustration for the transportation of ions and electrons. Reproduced with permission. Copyright 2021, Elsevier [126].

the micropores are more favorable to charge adsorption in capacitors due to their contribution to the active site, and the meso-/macropores can guarantee a superior rate capacity by serving as ions reservoir to shorten transport path [161].

In an example of 2D carbon nanomaterials, sodium polyacrylate was transformed into carbon nanoflakes using  $KHCO_3$  as activator. In this case, optimizing the dosage of activator can not only induce the formation of 2D morphology, but also effectively adjust the pore size distribution [162].  $KHCO_3$  activator with low content was mainly associated with micropores, while more mesopores were generated by a higher amount of activator. The optimized sample with well-developed nanoflakes morphology, appropriate

mesopore proportions (42.4%), large pore volume, and SSA achieved the best performances. A similar phenomenon was observed in starch-derived 2D CNSs using  $KNO_3$  assisted KOH activation strategy. The suitable ratio of micropores/mesopores resulted from the moderate amount of  $KNO_3$  promoted transfer dynamic and ensured a large SSA [163]. Therefore, a well-balanced pore distribution in stable hierarchical structure is critical for the efficient coordination of ion transport and storage. The high activity and strong etching effect of activators are admirable for pore engineering, but the precise control of pore size is insufficient. Thereby, the salt-assisted template method is more advantageous. For instance, the zinc nitrate-assisted pyrolysis strategy was employed to transform biomass precursor into porous

2D CNSs [164,165]. As shown in Figure 8(e), the redox reaction between zinc nitrate and urea additives released a lot of high-temperature gases to induce sheet morphology. Moreover, *in-situ* generated zinc species (e.g. ZnO and metal Zn) from zinc nitrate can penetrate and diffuse into the carbon matrix. The removal of these template species produced abundant nanopores with defined sizes in the resultant CNSs. The ammonia gas from urea and oxygen species from precursor were associated with the N, O dual-doped structure. Thereby, the poplar wood and polyvinylpyrrolidone (PVP) precursors derived CNSs by this strategy possessed hierarchically porous structure, which was consisted of micropores and abundant mesopores (Figure 8(f,g)).

In terms of 3D carbon nanomaterials, AC as a typical micropore-dominated nanocarbon has already showed the availability for adsorption-type cathode [61]. However, the micropore-enriched nanostructure is also subject to drawbacks of deficient ion diffusion and poor wettability, which leads to rapid capacity and life fading at high rates. As shown in Figure 8(h), a PVP coating-assisted dehydrogenation process was proposed to synthesize mesoporous structured AC (denoted as MSAC) [37]. The aggregated PVP on the AC consumed partial carbon during dehydrogenation to increase the pore size (see SEM image in Figure 8(b)). The MSAC showed higher fraction of mesopores (51% vs. 7%) (Figure 8(j)) and oxygen groups (47 wt% vs. 7 wt%) compared to the microporous structured AC, which improved ion diffusion efficiency and surface wettability. Thereby, MSAC delivered an ultra-long life of over 40,000 cycles with capacity retention of 78%. In addition, the 3D N-doped carbon nanocages (denoted as PZC-Ax) were fabricated via carbonizing and activating polypyrrole on the supporting platform of ZIF-8. This resultant hierarchical porous structure synchronously integrated micropores, mesopores, and macropores (Figure 8(k)) [126]. Specifically, macropores were mainly generated by confinement pyrolysis of the ZIF-8, while the micropores and mesopores can be attributed to KOH activation and precursor carbonization. Generally, the macropores can be regarded as ions buffering reservoirs and transportation channels for facilitating electrolyte into the smaller pores. Mesopores are notable for providing rapid ion transport paths, whereas micropores donate large accessible SSA to expose sufficient active sites, thus playing a crucial role in ion storage. In addition, it can be observed that the micropore sizes of the obtained PZC samples were concentrated at 0.76, 0.8, and 0.84 nm (see zoom-in PSD curves in Figure 8(l)). Gogotsi and Simon argued that the pore size being optimized close to the ion diameters could endow the EDLC with an anomalous increase [166]. Thereby the expected micropores are modulated to

exceed 0.8 nm in view of the diameter of hydrated  $\text{Zn}^{2+}$  (0.86 nm) [43,127]. Consequently, the specific capacities of optimized PZC sample were up to 124 mAh  $\text{g}^{-1}$  and 81.7 mAh  $\text{g}^{-1}$  at 0.25 and 20 A  $\text{g}^{-1}$  (Figure 8(n)) benefited from the 3D hierarchical framework architecture. Despite the hierarchical porous structure with several advantages, the suitable ratio of the possible nanopores with different sizes is critical for the combination of efficient ion diffusion and storage. While for the specific nanopores (mainly micropores), the size compatibility between electrolyte ions and existing nanopores also needs to be considered carefully. Advanced carbon design should take both into account. Furthermore, available ions for adsorption are not only  $\text{Zn}^{2+}$ , but also various anions in aqueous electrolyte. At this point, we summarized the representative electrolyte ions with original and hydration ion radius in Table 2 to serve as a reference for carbon design.

### 3.2.3. Heteroatom-doped engineering

The conventional Helmholtz layer capacitance for carbon cathodes is inadequate, but a synergistic contribution of Faradic/non-Faradic charge storage is highly desired. Heteroatom-doped engineering can enrich the functionality of carbon surface to activate the Faradic behaviors for extra pseudocapacitance. Accordingly, heteroatoms such as O, N, B, P, S have been attempted to dope in carbon skeleton with single or multiple forms in the reports of all-carbon based cathodes. Thereby, this section is organized by multi-dimensional structured carbons with various elements doped to present the advanced heteroatom-doped engineering.

Since porous carbon generally undergoes low-temperature carbonization and activation, introduction of oxygen to carbon surface is inevitable. Common doped oxygen can activate the Faradic pseudocapacitive reaction and optimize the physicochemical properties of carbon. For instance, oxygen-enriched 1D porous flexible CNFs (denoted as OPCNFs) were synthesized via the electrospinning and acid-assisted oxidation technology [70]. After oxidation treatment, the new peak appearing in FTIR spectra at 1728  $\text{cm}^{-1}$  indicated that the carbonyl ( $\text{C}=\text{O}$ ) and carboxyl ( $\text{COOH}$ ) groups were introduced (Figure 9(a)). Oxidation time was optimized to balance the oxidation degree. The CNFs after 20 h treatment with a moderate oxygen content showed the best conductivity and hydrophilicity. The reversible composition change observed from *ex-situ* XPS characterization during discharge/charging process indicated that both  $\text{C}=\text{O}$  and  $\text{COOH}$  were involved in pseudocapacitive reaction (Figure 9(b)). The effect of the type of oxygen functional groups on CNT's electrochemical

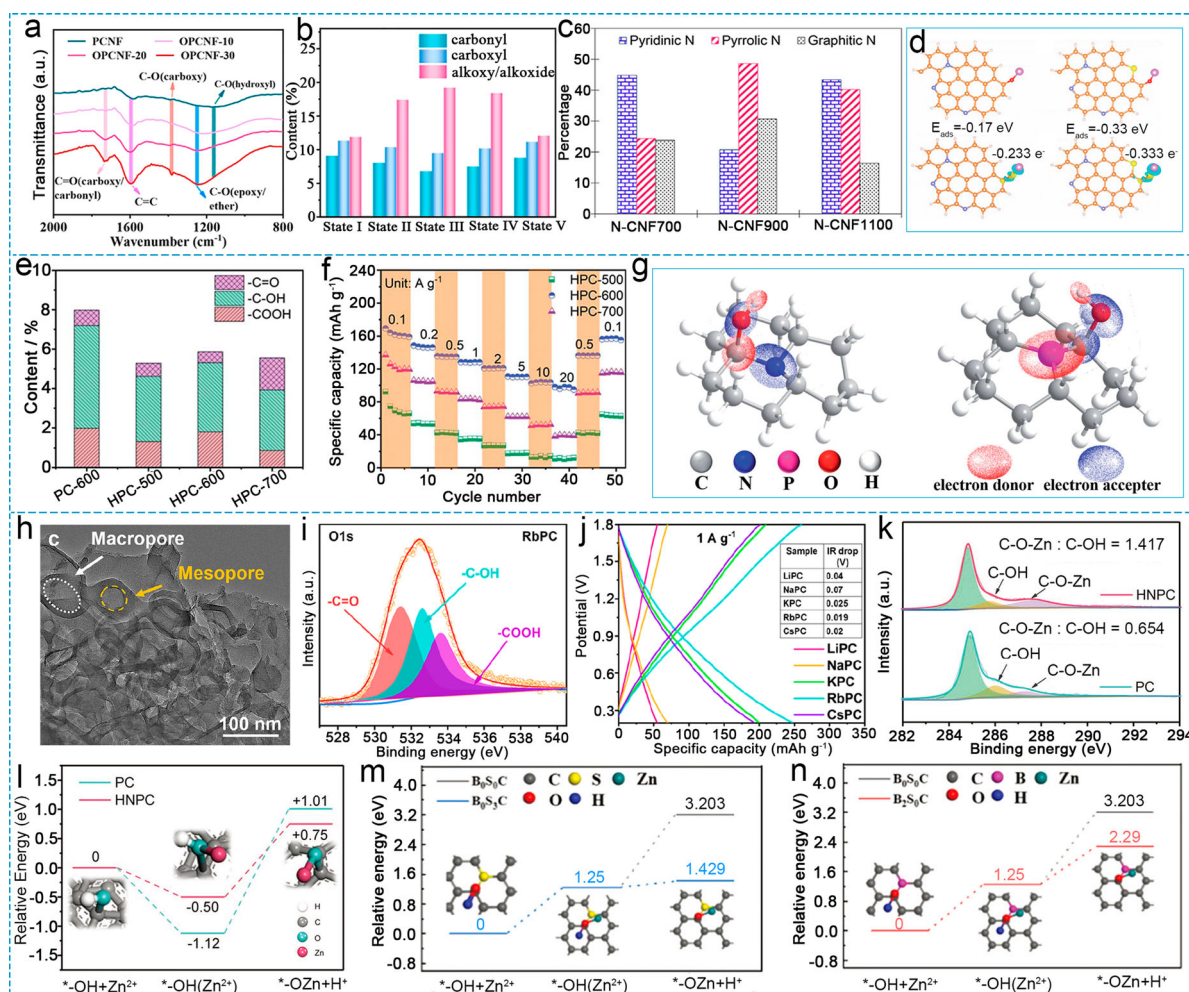


**Figure 9.** (a) Fourier transform infrared spectroscopy (FTIR) spectra of PCNF and OPCNF-x. (b) Oxygen functional group ratios of OPCNF sample based on *ex-situ* XPS fitting results during the discharge (state I-III) and charge process (state III-V). Reproduced with permission. Copyright 2021, Elsevier [70]. (c) Chemical composition of N, O doped CNF samples. Reproduced with permission. Copyright 2022, Elsevier [174]. (d) The configurations of Zn adsorption on the N-PCNTs and SN-PCNTs as well as corresponding adsorption energy and calculated charge density difference. Reproduced with permission. Copyright 2022, Royal Society of Chemistry [65]. (e) The contents of oxygen bonding configurations in PC-600 and HPC-x. (f) Rate capability of HPC-x at different current density. Reproduced with permission. Copyright 2021, Royal Society of Chemistry [175]. (g) Charge pattern of N-C-O-H and P-C-O-H in CNPK sample. Reproduced with permission. Copyright 2021, Royal Society of Chemistry [77]. (h) TEM image of RbPC. (i) High-resolution O 1s XPS spectra of RbPC. (j) GCD curves at 1 A g<sup>-1</sup> of RbPC and contrast samples. Reproduced with permission. Copyright 2022, American Chemical Society [35]. (k) C 1s XPS spectra at full-discharge state and (l) relative energy profiles along the reaction pathway of PC and HNPC. Reproduced with permission. Copyright 2019, WILEY-VCH [106]. Relative energy values of (m) B<sub>0</sub>S<sub>3</sub>C and (n) B<sub>2</sub>S<sub>3</sub>C in the reaction process compared with B<sub>0</sub>S<sub>3</sub>C. Reproduced with permission. Copyright 2022, Royal Society of Chemistry [176].

behaviors was further elucidated by different functionalized CNTs (i.e. *c*-CNTs, *p*-CNTs, *h*-CNTs) [177]. XPS characterization confirmed the existence of hydroxyl and carboxyl groups on the surface of *h*-CNT and *c*-CNT, respectively, but *p*-CNT contained almost no oxygen. It argued that the number of hydroxyl groups on the *h*-CNTs surface is larger than that of carboxyl groups on the *c*-CNTs since there two have similar oxygen content but hydroxyl monomer in *h*-CNT requires less oxygen atoms. The similar structure of the three CNTs highlights the contribution of oxygen groups to capacity. A

significant amount of hydroxyl groups of *h*-CNT can not only activate chemical adsorption ( $\text{C-O} + \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{C-O}\cdots\text{Zn}$ ) for extra pseudocapacitance, but also endow the *h*-CNTs with better hydrophilic feature. Thus, the *h*-CNTs cathode delivered higher ion storage ability than others. As for 2D carbon nanomaterials, oxygen functionalized CNSs (denoted as HPC-x) were prepared via the direct pyrolysis of potassium citrate [175]. In this case, regulation of oxygen doping was achieved efficiently by controlling the pyrolysis temperature. The sample pyrolyzed at 600 °C (denoted as HPC-600) showed the

highest proportion of hydroxyl group (C-OH) among the HPC samples as depicted in Figure 9(e). Comprehensive characterizations showed that the chemisorption of  $\text{Zn}^{2+}$  mainly occurred at C-OH and COOH groups to form C-O-Zn and C-OO-Zn. Thereby, benefiting from the high content of C-OH groups to offer abundant interaction sites, HPC-600 delivered the best rate performances (Figure 9(f)). In the 3D carbon material, an oxygen-doped porous carbon was prepared by annealing the tetra-alkali metal pyromellitic acid salts [35]. The highly reactive alkali metal ions (Li, Na, K, Rb, and Cs) can lead to the self-activation phenomenon. As shown in Figure 9(h), the optimized Rb-activated carbon (denoted as RbPC) exhibited well-developed porosity and abundant lattice defects. Moreover, XPS fitting results showed that RbPC possessed a high percentage of  $\text{C}=\text{O}$  and  $\text{C}-\text{OH}$  groups, which can effectively enhance the chemical adsorption and surface wettability (Figure 9(i)). Thus, the RbPC delivered the highest capacity compared with other samples (Figure 9(j)).

The doped oxygen is usually not alone in carbon, but accompanied by other heteroatomic elements. The first need to mention should be nitrogen. The outstanding contributions in optimizing physicochemical properties and boosting chemisorption inspired a series of studies on N doping engineering. As a typical example, N, O riched-1D CNFs were obtained by KOH activating and following N doping [174]. N doping process was operated at various pyrolysis temperature (700–1100°C) in which the maximum N doping concentration and electrical conductivity were achieved at 900°C (denoted as N-CNF900). Moreover, as shown in Figure 9(c), the N-CNF900 with highest content of pyrrolic N and graphitic N showed the best performances, thereby highlighting the contribution of these configurations to improve capacity. In addition, the 2D CNSs with N, O dual doping were prepared by carbonizing glycerol assisted by zinc acetate template and urea. The optimization of template dosage not only dominated the morphology, pore structure and SSA, but also affected the content of O and N [76]. The optimized sample with medium doping levels but highest SSA and rich mesopores performed better than others. This also indicates that SSA and porosity need to be considered in heteroatoms-doped engineering. For 3D carbon nanomaterials, a hierarchical porous carbon with N doping (denoted as HNPC) was constructed for the purpose of enhancing the chemical adsorption of  $\text{Zn}^{2+}$  on oxygen groups [106]. XPS fitting results showed that N doping increases the strength ratio of C-O-Zn and C-OH from 0.654 of contrast sample (PC) to 1.417 of HNPC at full-discharge state

(Figure 9(k)). Moreover, as revealed by theoretical simulations in Figure 9(l), N doping engineering can significantly decrease the energy barrier for forming C-O-Zn bonding (1.25 eV for PC vs. 2.13 eV for HNPC), thus effectively boosting the chemical adsorption of  $\text{Zn}^{2+}$  at the carbon surface.

Except for single N, Zhang et al. presented S incorporated N, O-rich porous carbon nanotubes (denoted as SN-PCNTs) [65]. The sulfur incorporation can effectively modulate absorption kinetics and electron transfer behaviors to boost  $\text{Zn}^{2+}$  storage capability, which was well confirmed by higher  $\text{Zn}^{2+}$  diffusion coefficient of SN-PCNTs than that of S-free sample (N-PCNTs) ( $1.21 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  vs.  $9.78 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ). According to the density functional theory (DFT) simulations (Figure 9(d)), the adsorption energy of  $\text{Zn}^{2+}$  for SN-PCNTs was 0.33 eV, while only 0.17 eV for N-PCNTs. Furthermore, the O-doped 2D CNSs with incorporated N and P heteroatoms (denoted as CNPK) were proposed [77]. As revealed by DFT calculation, the N and P doping effectively boosted the chemisorption of  $\text{Zn}^{2+}$  on O-groups through significantly decreasing the energy barrier (1.09, 0.78, and 2.06 eV for N-doped, P-doped, and non-doped sample, respectively). Additionally, the Bader charge analysis indicated that N introduction can endow O-H in N-C-O-H with stronger polarization, thereby being conducive to breaking O-H and forming C-O-Zn bond (Figure 9(g)). The P-doping can give O atoms in P-C-O-H more negative charges for easily attracting and reacting with  $\text{Zn}^{2+}$ . Therefore, the CNPK performed better than non-doped samples (103.2 vs. 52.9 mAh  $\text{g}^{-1}$  at 0.1 A  $\text{g}^{-1}$ , 52.8 vs. 21.4 mAh  $\text{g}^{-1}$  at 20 A  $\text{g}^{-1}$ ). Another 3D spongy-like hierarchically porous carbon with B, S co-doping was similarly analyzed by means of DFT calculation (Figure 9(m,n)) [176]. The energy barrier for B-doped ( $\text{B}_2\text{S}_0\text{C}$ ) and S-doped ( $\text{B}_0\text{S}_3\text{C}$ ) samples were much lower than those for samples without doping ( $\text{B}_0\text{S}_0\text{C}$ ) (2.290 and 1.429 eV vs. 3.203 eV).

Although the role of oxygen played in heteroatom-doped engineering for boosting pseudocapacitance is remarkable, the specific mechanism of dominant heteroatomic configuration (e.g. C-OH,  $\text{C}=\text{O}$  and  $\text{-COOH}$ ) remains to be further studied. Moreover, maximizing the contribution of doping engineering requires that many heteroatoms work together. However, in the existing multiple-atom doping cases, the contributions of non-oxygen heteroatoms doping are only highlighted to boost the pseudocapacitive behaviors of O-groups. Therefore, further research is still needed on the effects of doping level, functional configuration of these non-oxygen doped atoms on adsorption behaviors and electrochemical performances.

### 3.3. Carbon in conversion-type cathode

Current conversion-type cathodes include traditional Mn-, V-based materials and emerging chalcogens. For traditional Mn- and V-based materials, the transformation of storage mechanism is unable to bypass the intrinsic drawbacks of poor conductivity, dynamic transport and severe volume expansion. Therefore, the functionality of nanocarbons in intercalation-type cathodes can be inherited as well. While the emerging chalcogens also suffer from these challenges, which inevitably include a carbon host. In this part, we largely inherited summary rules based on functionality of carbons in intercalation-type cathodes to discuss the progress of multi-dimension structured carbons, but only including limited number of reports according to our thorough research (Table 4).

#### 3.3.1. Conductive substrate

Carbon nanomaterials as conductive substrates to anchor active species can not only contribute to facilitating kinetics of both ions and electrons, but also improving structural stability and even endowing composite with flexibility. Although some of the Mn and V-based materials were already verified to rely on the conversion-type mechanism, these materials have not been reported to be constructed as non-all-carbon based electrodes. Here we can only discuss the limited number of the existing cases. For example, active  $\text{Co}_3\text{O}_4$  nanosheets array arranged on 1D carbon nanotube fibers (CNTFs) were constructed via oxidation treatment of Co-based MOF on CNTF (denoted as  $\text{Co}_3\text{O}_4@\text{CNTFs}$ ) [180]. The evenly distributed  $\text{Co}_3\text{O}_4$  nanosheets with porous and ultrathin structure were conducive to the exposure of reactive sites and permeation of electrolyte. Line resistance comparison of CNTF and  $\text{Co}_3\text{O}_4@\text{CNTF}$  ( $23.00 \Omega \text{ cm}^{-1}$  vs.  $53.53 \Omega \text{ cm}^{-1}$ ) showed that the  $\text{Co}_3\text{O}_4@\text{CNTF}$  inherited the excellent conductivity of pristine CNTF. Moreover, Figure 10(a,b) indicated that the flexible fiber-shaped  $\text{Co}_3\text{O}_4@\text{CNTF}$  electrode showed good deformation adaptability upon  $0\text{--}150^\circ$  bending with negligible resistance change. A pair of redox peaks was observed in cyclic voltammetry (CV) curves, which was attributed to the reversible conversion reactions ( $\text{Co}_3\text{O}_4 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 3\text{CoO} + \text{H}_2\text{O}$ ). Further analysis indicated the fitting slope  $b$  by plotting the relationship between  $\log i$  (peak current) and  $\log v$  (scan rate) was  $0.82\text{--}0.88$  (Figure 10(c)). And capacitance contribution was as high as  $72.67\%$  at high scan rate of  $7 \text{ mV s}^{-1}$  (Figure 10(d)). This efficient pseudocapacitive behavior is benefited from the fast ion/electron transport in self-supported 3D structure of the  $\text{Co}_3\text{O}_4@\text{CNTF}$  with high conductive CNTF framework.

Another typical conversion-type V-based cathode (VN) was supported by 2D CNSs [78]. Specially, as shown in Figure 10(e), the hybrid nanosheets (denoted as VN/NC) with layer-by-layer stacked structure consist of VN nanocrystals and N doped CNSs, which were fabricated via *in-situ* thermal conversion of  $\text{V}_2\text{O}_5$  with pyrolyzing pentyl viologen (PV) intercalated. During the pyrolysis, the  $\text{V}_2\text{O}_5$  nanosheets were converted into VN nanocrystals, while the intercalated PV molecules were synchronously carbonized into N-doped CNSs. The blank sample of pure VN was fabricated via pyrolyzing  $\text{V}_2\text{O}_5$  without PV, which showed sheet-like morphology and stacked into porous blocks. It was observed that the CNSs can inhibit the two-dimensional growth of VN crystals and serve as support to induce the formation of VN nanocrystals. The VN/NC with a stable structure consisting of ultrasmall VN and conductive substrate delivered more excellent rate capacity than pure VN. Moreover, the CNS can offer robust support for VN nanocrystals to restrain volume variation and self-aggregation, thus minimizing the damage to crystal structure during cycling. Therefore, the hybrid nanosheets with nanocrystals anchored were well maintained after long-cycling while VN blocks were broken into small pieces (see the SEM images in Figure 10(f,g)). Consequently, VN/NC sample showed better cyclability compared to pure VN.

In regarding the substrate function, reasonable arrangement of reactive species with optimized morphology on the substrate is crucial to improve utilization and structural stability. In the above two examples,  $\text{Co}_3\text{O}_4$  was anchored on the substrate with an ultrathin 2D nanosheet, while VN was as nanocrystal. Both of these are helpful for exposing active sites and increasing utilization. In addition, further expand study for carbon substrate is also urgently needed because of the conversion-type cathodes are not carefree in rate/cycling performances.

#### 3.3.2. Protecting layer

In the case of above-mentioned  $\text{Co}_3\text{O}_4@\text{CNTFs}$ , the additional  $\text{CoSO}_4$  solvent in electrolyte contributed to the excellent performance of  $\text{Co}_3\text{O}_4@\text{CNTF}$  by inhibiting dissolution behaviors [180]. This suggests that dissolving concerns also come with some conversion-type species, therefore, using the protective layer to isolate the electrolyte should be considered. In a typical example,  $\text{V}_2\text{O}_3$  with the coated carbon layer (denoted as  $\text{V}_2\text{O}_3@\text{C}$ ) was fabricated via carbothermic reduction of polyaniline-coated  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  [181]. TEM image showed that the thickness of this carbon shell was about  $4.9 \text{ nm}$  (Figure 10(h)). Moreover, the introduction

**Table 4.** A summary of multi-dimensional structured carbon nanomaterials for conversion-type cathodes.

| Carbon function      | Micro-dimensions of carbon | Cathode                                               | Mass ratio of carbon (wt.%) | Mass loading (mg cm <sup>-2</sup> ) | Electrolyte (voltage)                                                            | Specific capacity                                                                                                                                                                | Energy/power Density                                                 | Capacity retention                                | Ref. #&Publish year |
|----------------------|----------------------------|-------------------------------------------------------|-----------------------------|-------------------------------------|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|---------------------------------------------------|---------------------|
| Conductive substrate | 1D                         | Co <sub>3</sub> O <sub>4</sub> /carbon nanotube fiber | /                           | /                                   | 2 M ZnSO <sub>4</sub> + 0.0005 M CoSO <sub>4</sub> (0.8–2.1 V)                   | 158.7 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup> , 86.19 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>                                                                             | /                                                                    | 97.27% at 5 A g <sup>-1</sup> after 10,000 cycles | [180]2021           |
|                      | 2D                         | VN/N-doped CNS                                        | 18.8                        | 2.11–3.16                           | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.2–1.8 V)                | 566 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup> , 136 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>                                                                               | 386 Wh kg <sup>-1</sup> , /                                          | 85% at 10 A g <sup>-1</sup> after 1000 cycles     | [78]2022            |
| Protecting layer     | 3D                         | V <sub>2</sub> O <sub>3</sub> /carbon                 | 25.5                        | /                                   | 3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (0.3–1.6 V)                | 472.4 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup> , 217 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>                                                                             | 302 Wh kg <sup>-1</sup> , 6.5 kW kg <sup>-1</sup>                    | /                                                 | [181] 2022          |
| Encapsulating host   | 1D                         | S@CNTs                                                | 50.0                        | 3.0–5.0                             | 1 M Zn(CH <sub>3</sub> COO) <sub>2</sub> + 0.05 wt.% I <sub>2</sub> (0.05–1.6 V) | 1105 mAh g <sup>-1</sup> <sub>S</sub> at 0.1 A g <sup>-1</sup> , 407 mAh g <sup>-1</sup> <sub>S</sub> at 4 A g <sup>-1</sup>                                                     | 502 Wh kg <sup>-1</sup> <sub>S</sub> , /                             | 85% at 1 A g <sup>-1</sup> after 50 cycles        | [31]2020            |
|                      | 2D                         | SeS <sub>2</sub> @CNSs                                | 39.0                        | 3.0–5.0                             | 1 M Zn ZnSO <sub>4</sub> + 0.1 wt.% I <sub>2</sub> (0.1–1.3 V)                   | 1107 mAh g <sup>-1</sup> <sub>SeS<sub>2</sub></sub> at 0.1 A g <sup>-1</sup> , 626 mAh g <sup>-1</sup> <sub>SeS<sub>2</sub></sub> at 5 A g <sup>-1</sup>                         | 772 Wh kg <sup>-1</sup> <sub>SeS<sub>2</sub></sub> , /               | 85% at 5 A g <sup>-1</sup> after 1000 cycles      | [128]2021           |
|                      | 3D                         | Se@CMK-3                                              | 49.9                        | 2.1                                 | 2 M ZnTFSI/PEG/water (0–2 V)                                                     | 611 mAh g <sup>-1</sup> <sub>Se</sub> at 0.1 A g <sup>-1</sup> , 315 mAh g <sup>-1</sup> <sub>Se</sub> at 5 A g <sup>-1</sup>                                                    | 751 Wh kg <sup>-1</sup> <sub>Se</sub> , /                            | 80.3% at 1 A g <sup>-1</sup> after 1000 cycles    | [33]2021            |
|                      | 3D                         | Se <sub>x</sub> S <sub>y</sub> /carbon foams          | 50.0                        | /                                   | 3 M Zn ZnSO <sub>4</sub> + 0.1 wt.% I <sub>2</sub> (0.1–1.3 V)                   | 1226 mAh g <sup>-1</sup> <sub>Se<sub>x</sub>S<sub>y</sub></sub> at 0.2 A g <sup>-1</sup> , 713 mAh g <sup>-1</sup> <sub>Se<sub>x</sub>S<sub>y</sub></sub> at 5 A g <sup>-1</sup> | 867.6 Wh kg <sup>-1</sup> <sub>Se<sub>x</sub>S<sub>y</sub></sub> , / | 75% at 4 A g <sup>-1</sup> after 500 cycles       | [115]2021           |

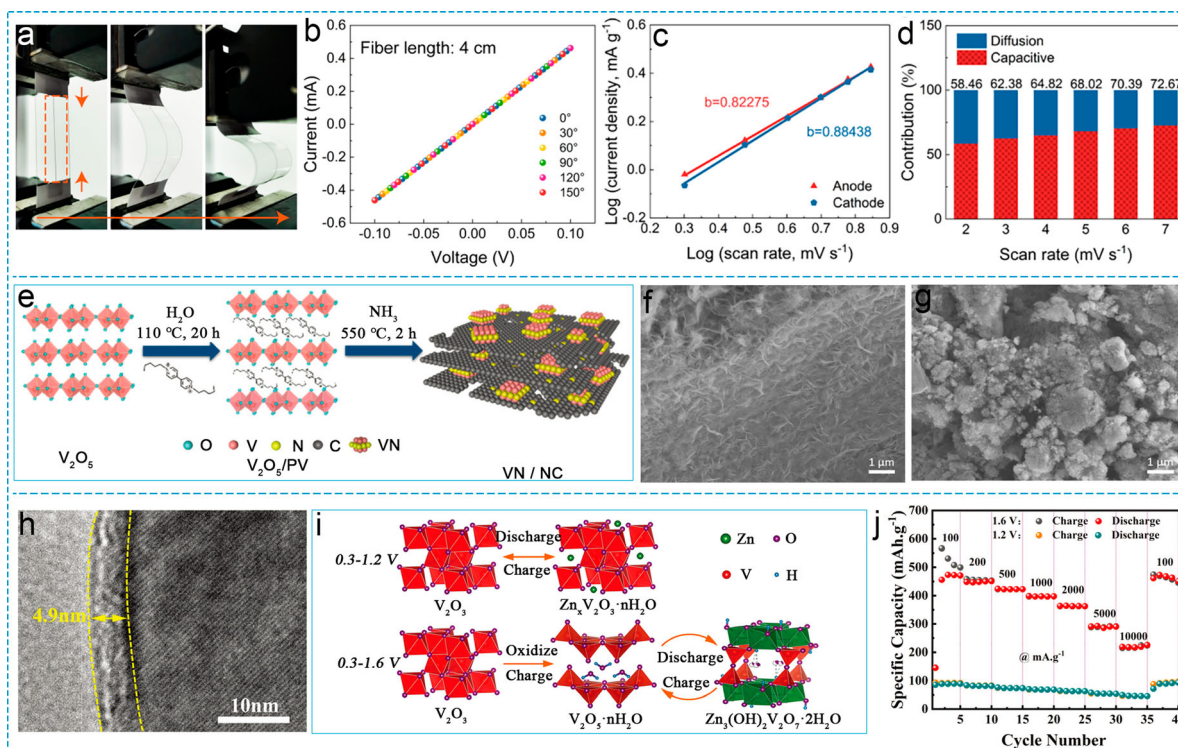


**Figure 10.** (a) Photographs of the bending process of the  $\text{Co}_3\text{O}_4/\text{CNTF}$  cathode. (b) I-V measurements of  $\text{Co}_3\text{O}_4/\text{CNTF}$  at various bending angles. (c)  $b$  values determined by the relationship between the scan rate and peak current densities. (d) Normalized contribution ratio of the capacitive and diffusion-controlled capacities at different scan rates. Reproduced with permission. Copyright 2021, American Chemical Society [180]. (e) Schematic of the synthetic procedure for the VN/NC hybrid nanosheets. The SEM images of (f) VN-control and (g) VN/NC after 500 cycles at 10  $\text{A g}^{-1}$ . Reproduced with permission. Copyright 2022, Royal Society of Chemistry [78]. (h) TEM image of  $\text{V}_2\text{O}_3/\text{C}$ . (i) Schematic illustration of energy storage mechanism and (j) rate capability of  $\text{V}_2\text{O}_3/\text{C}$  in voltage ranges of 0.3–1.2 V and 0.3–1.6 V. Reproduced with permission. Copyright 2022, Royal Society of Chemistry [181].

of carbon layer ( $\sim 25.52 \text{ wt\%}$ ) endowed the composite with a high SSA of  $106.7 \text{ m}^2 \text{ g}^{-1}$  and abundant mesopores, which can contribute to efficient ion transport. Interestingly, as depicted in Figure 10(i), a distinct phase transition from the original  $\text{V}_2\text{O}_3$  to  $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  occurred during the initial discharge in the extended high-voltage region (0.3–1.6 V). Moreover, the electrode exhibited a highly reversible conversion reaction between  $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  during the following charge/discharge process. The as-assembled system operated at 0.3–1.6 V also exhibited lower charge transfer resistance ( $186.8 \Omega$  vs.  $306.4 \Omega$ ) and larger  $\text{Zn}^{2+}$  diffusion coefficients ( $4.39 \times 10^{-10}$ – $4.15 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  vs.  $1.88 \times 10^{-10}$ – $3.35 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ). Thereby, the delivered capacity of  $472.4 \text{ mAh g}^{-1}$  was approximately five times higher than that of the original  $\text{V}_2\text{O}_3$  at 0.3–1.2 V (Figure 10(j)). The protecting carbon layer can not only restrict dissolution issue, but also support and stabilize the electrochemically induced phase transitions.

Notwithstanding the aforementioned progress, the studies on carbon layer for conversion-type cathodes are few. Although the isolation of electrolyte by the carbon layer is beneficial to alleviate the dissolution and volume

change, it also poses a challenge to the carbon separator between the electrolyte and the active species. The precise regulation on the thickness, internal pore structure and SSA of carbon layer is critical for ensuring the efficient transport of ions across the carbon layer as described in the carbon layer for intercalation-type cathodes.

### 3.3.3. Encapsulating host

In this section, we focus on the chalcogens-based cathodes. Due to the high theoretical capacity and multi-electron transfer processes, those cathodes are superior to other types of active species in terms of capacity and energy density. But it inevitably requires the introduction of a carbon to ease the concerns on electronic conductivity and volume expansion. Here the active species are generally encapsulated into nanopores of carbon by melting diffusion. This is not exactly the same function as conductive matrix, thereby the title of ‘host’ for carbon is more accurate.

In a report of 1D CNTs, the infiltration of active S was achieved via melting-diffusion strategy (160 °C for 16 h) [31]. The first concern is to examine the effect of

electrolyte with different types of anions to electrochemical behaviors in which the focus was on multiple electrochemical performances. Based on the comprehensive comparison of reversible capacity, Coulombic efficiency and voltage hysteresis, the CNTs supported 50 wt% sulfur (denoted as S@CNT-50) preferred to work in the  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolyte with 0.05 wt%  $\text{I}_2$  as additive (pH of 6.6). Thereinto, the additive of 0.05 wt%  $\text{I}_2$  made S@CNT-50 show a smaller voltage hysteresis of 0.72 V and higher reversible capacity of  $1105 \text{ mAh g}^{-1}$  (Figure 11(a)). Such case can be attributed to that  $\text{I}_2$  served as medium of  $\text{Zn}^{2+}$  to reach lower reaction barrier. Then, another concern of S content was considered. Figure 11(b) showed the electrochemical performances of S@CNT samples with different content of active S. Despite the highest capacity and the smallest overpotential, S@CNTs-30 (S content of 30 wt%) still suffered severe parasitic reaction during the charge. While for S@CNTs-60, the lowest capacity and high overpotential caused by severe underutilization were unsatisfied. Thereinto, S@CNTs-50 with relatively high capacity and low overpotential was most appropriate based on comprehensive consideration. Moreover, it also showed the

excellent cyclability with capacity retention of 85% over 50 cycles at  $1000 \text{ mA g}^{-1}$  (Figure 11(c)). It should be noted that S@CNTs-50 with 5 wt% Pt catalyst addition delivered a higher capacity of  $1193 \text{ mAh g}^{-1}$  and a smaller voltage hysteresis of 0.6 V (Figure 11(d)). This provides valuable information that introduction of catalysts into the host may improve the electrochemical behavior of S, as being well verified in some non-carbon hosts [32,46].

For 2D carbon nanomaterials, the concern on spatial restriction such as those in the carbon encapsulating matrix are totally freed because the active molecules are encapsulated into nanopores. For example, the P-doped porous carbon sheets (denoted as PCS) were prepared to encapsulate the active  $\text{SeS}_2$  (Figure 11(e)) [128]. The PCS showed specific surface area of  $1828.5 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $1.03 \text{ cm}^3 \text{ g}^{-1}$ . The flourishing porous structure can afford adequate accommodation for the encapsulation of  $\text{SeS}_2$  and the infiltration of electrolyte. As shown in Figure 11(f), the sharp decrease of SSA from 1828.5 to  $381.9 \text{ m}^2 \text{ g}^{-1}$  and pore volume from 1.03 to  $0.19 \text{ m}^2 \text{ g}^{-1}$  can be described as the penetration of nanopores by  $\text{SeS}_2$ . Thermogravimetric analysis (TGA) indicated that

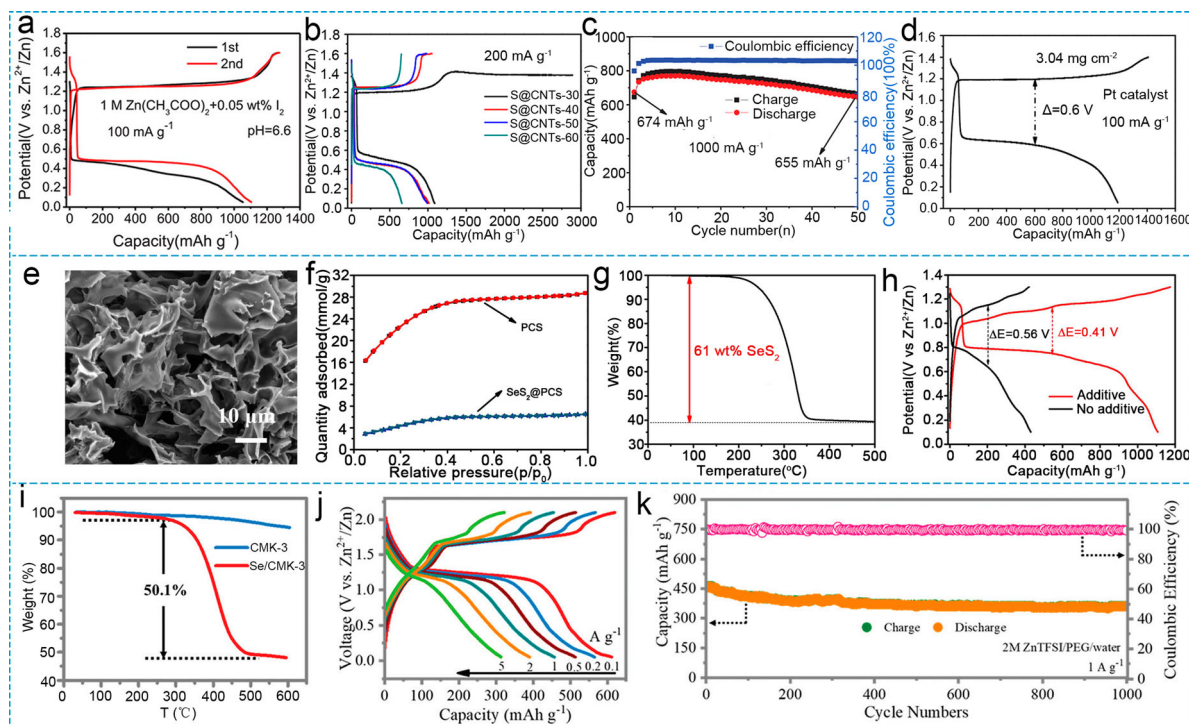


**Figure 11.** GCD curves of (a) S@CNTs-50 cathode at  $100 \text{ mA g}^{-1}$  and (b) S@CNTs with different sulfur contents at  $200 \text{ mA g}^{-1}$  in  $1 \text{ M Zn}(\text{CH}_3\text{COO})_2$  with 0.05 wt%  $\text{I}_2$  as additive. (c) Cycling performance of S@CNTs-50 cathode at a current density of  $1000 \text{ mA g}^{-1}$  (d) GCD curve of S@CNTs-50 with 5 wt% Pt at  $100 \text{ mA g}^{-1}$ . Reproduced with permission. Copyright 2020, WILEY-VCH [31]. (e) SEM image of  $\text{SeS}_2$ @PCS. (f)  $\text{N}_2$  adsorption/desorption isotherms of PCS and  $\text{SeS}_2$ @PCS. (g) TGA curve of  $\text{SeS}_2$ @PCS. (h) GCD curves of  $\text{SeS}_2$ @PCS in  $1 \text{ M ZnSO}_4$  with or without additive. Reproduced with permission. Copyright 2021, Elsevier [128]. (i) TGA curves of pure CMK-3 and the Se/CMK-3 composite. (j) GCD curves under different current densities and (k) cycling performance under  $1 \text{ A g}^{-1}$  of Se/CMK-3 composite based on  $2 \text{ M ZnTFSI/PEG/water}$  aqueous electrolyte. Reproduced with permission. Copyright 2021, Royal Society of Chemistry [33].

the mass content of  $\text{SeS}_2$  was 61 wt% (Figure 11(g)). This report highlighted the  $\text{I}_2$  additive as redox mediator to boost the reversible capacity and kinetics (Figure 11(h)). While from the viewpoint of carbon, doping of non-metallic heteroatoms is also worthy of attention. It has been verified in the organic system that non-metallic doping can reduce the activation energy to accelerate conversion reaction. However, the catalytic potency of doping for redox reaction in aqueous systems remains to be theorized.

Nanopores are also worth attention to confine active molecules. For instance, the 3D mesopore-enriched CMK-3 carbon was employed as an encapsulating host for Se via melting-diffusion method [33]. As demonstrated by TG in Figure 11(i), the mass content of Se in Se/CMK-3 composite was up to 50.1 wt%. A significant decay in SSA and the disappearance of mesopores in CMK-3 host can be found after Se infiltration. The homogeneous encapsulation of Se in the ordered channels of CMK-3 ensured efficient utilization of the active substance and restriction for volume expansion. The Zn-Se system was operated in a 'molecule crowding' aqueous electrolyte in which the additive of 5 wt % polyethylene glycol (PEG) ensured a stable potential up to 2.2 V due to the reduced chemical activity of water. Thereby, it delivered a high specific capacity of  $611 \text{ mAh g}^{-1}_{\text{Se}}$  ( $751 \text{ Wh kg}^{-1}$ ) with the potential plateau of more than 1 V (Figure 11(j)) and retained  $365 \text{ mAh g}^{-1}_{\text{Se}}$  at  $1 \text{ A g}^{-1}$  after 1000 cycles with retention of 80.3% (Figure 11(k)).

These chalcogens-based cathodes are still in their infancy, consequently further research is urgently needed. Furthermore, the reported carbon hosts only include CNT and template-assisted carbon, and more porous carbons are worth considered as the encapsulating host. Moreover, the optimization of carbon host should not only focus on the mass ratio, and the pore structure and doped metallic/non-metallic heteroatoms with catalytic function deserve more attention for boosting the performances.

#### 4. Conclusions and perspectives

To sum up, we provide a comprehensive review covering the typical cathode storage models and highlighting the advanced carbon architecture designs to boost the cathode performances. The progress of multi-dimensional structured carbon nanomaterials for constructing the non-all-carbon based intercalation- and conversion-type electrodes, and the all-carbon based adsorption-type electrodes have been systematically discussed. However, some essential electrochemical details still remain to be elucidated. The pioneer carbon theories deserve more consideration to guide future endeavors of carbon-based

cathodes design. Meanwhile, advanced characterization techniques are expected to explore the underlying mechanism of the electrochemistry process. Particularly, considering further promotion of the carbon architecture in the cathodes, more explorations are expected in the following directions as shown in Figure 12.

For the intercalation-type cathodes, nanocarbons function by serving as conductive substrates, encapsulating matrixes, and protecting layers to boost the performances. In these scenarios, the direct contact between the employed carbons and the electrolyte is unavoidable. Meanwhile, in order to pursue higher conductivity and more stable combination, especially for conductive substrates, enriching surface functionality via the introduction of heteroatomic groups is highly favored. Most intercalation-type species work at the voltage region of 0.3–1.8 V (vs.  $\text{Zn}^{2+}/\text{Zn}$ ), which overlaps with the physicochemical (de)adsorption region of available electrolyte ions. These favorable conditions make the functional nanocarbon potentially contribute to the surface-controlled capacitive behaviors. Simply assessing the capacity contribution of carbons to blur out these behaviors is inadequate. Study is needed to figure out these ambiguous electrochemical behaviors with the support of advanced *in-situ* or *operando* techniques. For the carbon matrix and layer, isolation effect amplifies the dominance of carbon shell for overall dynamic transport. Further careful control and deliberate design of carbon shell structure (e.g. micromorphology, thickness, internal porosity, and SSA) are needed for efficient ion penetration. Furthermore, balance should be established on the accessibility and robustness of the carbon shell to prevent excessive protection for improving utilization and to ensure certain mechanical strength for durability.

For the adsorption-type cathodes, the critical parameters that guide the selection of nanocarbons are as follows: high SSA, well-developed pore geometry, and sufficient pseudocapacitive active sites. Various hierarchical porous carbons, noted for large SSA, have sprung up. However, the current capacity level of carbon cathodes is seriously mismatched with that of zinc anode counterpart. The loading mass of active nanocarbons at laboratory level on cathode is generally  $2 \text{ mg cm}^{-2}$ , corresponding to an areal specific capacity of approximately  $0.5 \text{ mAh cm}^{-2}$  (calculated with specific capacity of  $250 \text{ mAh g}^{-1}$ ). But the theoretical specific capacity of zinc anode with the thickness of  $100 \mu\text{m}$  in laboratory usage is as high as  $58.51 \text{ mAh cm}^{-2}$ . The energy density of the AZD device will plummet if being normalized by the total mass because anode is overused by more than 100 times. The extreme mass loads of active nanocarbons for electrochemical testing in the laboratory from some literatures can reach  $30\text{--}40 \text{ mg cm}^{-2}$ , but the drastic capacity

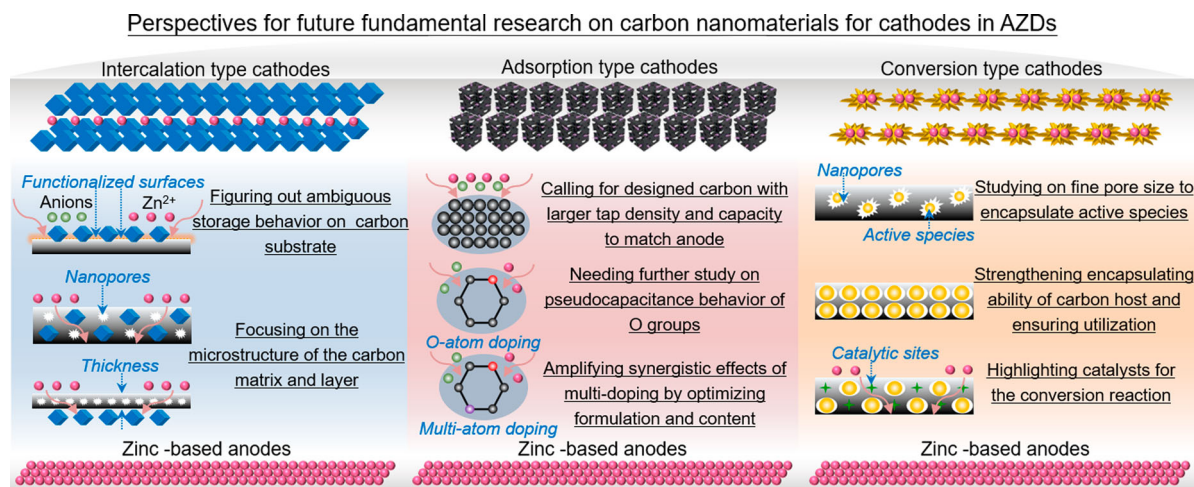


**Figure 12.** Perspectives for future fundamental research on carbon nanomaterials for intercalation, adsorption and conversion type cathodes in AZDs.

decay associated with underutilization is not acceptable. In terms of cathodes, future engineering on increasing mass loading, meanwhile maintaining the existing capacity level for active carbon is essential to driving practical applications. This calls for designed carbon with larger tap density and reasonable microstructure to ensure dynamic transport even at high mass loading. In addition, for the heteroatom-doping engineering, the high-profile but still controversial mechanisms for oxygen groups are worthy of further interpretation via *in-situ* techniques or simulation calculation. The synergistic effects of multi-atom doping also need to be continuously amplified by rational design of species collocation. The specific behaviors of the functional configuration for non-oxygen doped atoms in the electrochemical reaction are waiting to be theorized.

For the conversion-type cathodes, we're going to focus on the chalcogens-based conversion cathodes in which carbon emerges as the encapsulating host. Introducing carbon host mainly relies on the typical melting-diffusion operation to encapsulate active chalcogens species into the nanopores. So, pore structure is worth paying attention to. It has been verified in the organic system that the internal pore size in carbon host interferes with the allotrope formation of resolidified chalcogens species. Therefore, detailed exploration to deliberate the role of nanopore size played on encapsulating active species and concurrent perturbations of electrochemical behavior would be of great interest. Moreover, the proportion of carbon host should also be taken seriously. At present, the inactive host accounts for 20–50% of the total mass, which substantially diminishes the overall energy density even though most of the reported values so far are normalized by only chalcogens mass. Strengthening the encapsulating capability of carbon host to afford reduced

carbon usage is also urgently needed. Another point of concern is the sluggish kinetics of multiple-electron transfer. According to the sporadic inspired works in some non-carbon hosts, constructing the catalytic active sites in carbon host (e.g. metallic/non-metallic heteroatoms doping) to reduce the reaction energy barrier should be taken into further consideration.

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