Constructing Advanced Aqueous Zinc-Ion Batteries with 2D Carbon-Rich Materials

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As a promising electrochemical energy storage system (EESS), aqueous zinc-ion batteries (AZIBs) hold the potential to achieve energy storage with low-cost and nonpollution merits. However, the intrinsic defects of these systems block their further development severely, including dendrite growth, structural deterioration, parasitic reactions, and sluggish charge/discharge kinetics. Herein, the application of 2D carbon-rich materials against the drawbacks of AZIBs is introduced. Advantages of each representative 2D carbon-rich material (i.e., graphdiyne, graphene, 2D covalent organic frameworks, 2D metal organic frameworks, and 2D conductive polymers) are thoroughly discussed, along with recent progress of AZIB cathodes, anodes, separators, and electrolytes utilizing 2D carbon-rich materials. Finally, the features of various 2D carbon-rich materials are summarized and several perspectives on optimization of 2D carbon-rich materials, development of characterization techniques, and the practical use of AZIBs in the future are given.

1. Introduction

The urgent demand for clean, economical, and sustainable energy has promoted the development of electrochemical energy storage systems (EESSs) as an alternative solution to fossil fuels.[1] The past few decades have witnessed the rise of commercial lithium-ion batteries (LIBs) as predominant rechargeable energy storage systems with lightweight, adequate capacity, and long cycling life,[2] which greatly stimulated the passion of researchers for creating next-generation EESSs including sodium-ion batteries (SIBs),[3] potassium-ion batteries (PIBs),[4] magnesium-ion batteries (MIBs),[5] zinc-ion batteries (ZIBs),[6] aluminum-ion batteries (AIBs),[7] etc. Among all the candidates, aqueous zinc-ion battery (AZIB) has attracted tremendous attention owing to the outstanding advantages of zinc anode like abundant reserves, low cost, high theoretical capacity (5855 mAh cm$^{-3}$/820 mAh g$^{-1}$), environmental friendliness, intrinsic stability against water and air, along with the extraordinary safety, high ion conductivity, and easy controllability of aqueous electrolyte.[8]

The main components of a typical AZIB system are cathode, anode, separator, and electrolyte. During the discharging process, Zn$^{2+}$ ions dissolve from anode to electrolyte, along with the directed migration to cathode and the subsequent combination with cathode material. Simultaneously, electrons pass through the external circuit, generating external current from cathode to anode. When the battery is being charged, reversed process happens and the system recovers from the discharged state. According to the charging–discharging mechanism, researchers have developed a series of materials that meet the demand of each component. Cathode materials are the predominant topic among all the AZIB researches. Ever since the first prototype of AZIB in 2011,[8] a great number of cathode materials have been carefully checked for zinc storage such as manganese-based materials,[6] vanadium-based materials,[9] Prussian blue analogs,[10] organic quinone materials,[11] polyanionic frameworks,[12] layered sulfides and selenides,[13] etc. These cathode materials, however, share the same limitations during the long-term cycling process:[14] including 1) poor conductivity that results in sluggish electron transfer and low coulombic efficiency,[14a] 2) dissolution and volume change of cathode materials in aqueous electrolytes during long cycling process,[14b] and 3) parasitic reactions between cathodes and aqueous electrolyte that generates inert by-products like Zn$_4$(OH)$_6$SO$_4$·nH$_2$O (ZHS).[14c] As for anodes, zinc foils are directly utilized in most situation, which suffer from side reactions like hydrogen evolution reaction as well, caused by the contact between zinc metal and aqueous electrolyte.[80]. Another serious problem of zinc anode is dendrite growth after long-term cycling that causes short circuit and low coulombic efficiency. The zinc deposition process is mainly controlled by ion diffusion on the electrode/electrolyte interface. Therefore, the unevenly distributed electric field as well as Zn$^{2+}$ concentration field will

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Inevitably lead to the aggregation of zinc nucleation and eventually dendrite growth.\[35\] Moreover, although the formation of passive by-products like ZnO and Zn(OH)\(_2\) is well suppressed by using neutral or mild acidic aqueous electrolyte, the solvation/desolvation process of Zn\(^{2+}\) will need extra energy, resulting in the sluggish kinetics on the electrode/electrolyte interfaces.\[36,37\] These drawbacks severely hamper the practical use of AZIBs.

Fortunately, the introduction of 2D carbon-rich materials perfectly satisfies the demand for fabricating better AZIBs. 2D carbon-rich material is a combination of “2D material”\[37\] and “carbon-rich material”,\[18\] referring to 2D sheet-like carbonaceous material where carbon is the major or the most composition. Graphdiyne, graphene, and 2D carbon-rich polymers including 2D covalent organic frameworks (2D COFs), 2D metal organic frameworks (2D MOFs), and 2D conductive polymers are typical 2D carbon-rich materials, which will be further discussed later (Scheme 1). Mere 2D carbonaceous materials with low carbon content (like MXenes), or carbon-rich materials without 2D properties (like carbon nanotubes, i.e., CNTs) do not match this concept and thus will not be included in this article.

Compared to bulk materials, 2D materials possess superb mechanical strength and flexibility, large specific surface area, and admirable processability.\[37\] while as carbon-rich materials, they own carbon-based covalent structure with excellent chemical stability, fine electric conductivity, and manageable functions.\[18\] Up to now, the utilization of versatile 2D carbon-rich materials has successfully solved the problems mentioned above. Specifically, highly conductive carbon-rich materials with large specific surface area significantly enhance the conductivity of cathode and efficiently regulate the distribution of electric filed by forming heterostructure; their intrinsic stability enables prolonged cycling lifespan as they form protective layers to block direct contact between electrodes and electrolyte; the processability of 2D carbon-rich materials that can be easily fabricated into different shapes with multiple functions meets the need under various conditions.

In this review, we first introduce recent advances in AZIBs using representative 2D carbon-rich materials including graphdiyne, graphene, 2D COFs, 2D MOFs, and 2D conductive polymers. We especially focus on the ideas of rationally designing various 2D carbon-rich materials facing certain problems. Then, we summarize the characteristics of each material and give some future perspectives on further development of AZIBs based on 2D carbon-rich materials.

### 2. Graphdiyne

As a novel allotrope of carbon, graphdiyne (GDY) was first synthesized by us in 2010 through a cross-coupling reaction.\[19\] The structure of graphdiyne is composed of two acetylenic groups (sp\(^2\) hybridized carbon) as the linkage between two adjacent benzene rings (sp\(^3\) hybridized carbon). Such a unique combination brings graphdiyne 2D framework layers, large \(\pi\)-conjugation, uniformly distributed porous structure (with pore size of 0.55 nm), admirable stability, and tunable semiconductivity (\(\approx 10^{-4} \text{S m}^{-1}\)).\[19,20\] Furthermore, the property of graphdiyne can be easily adjusted by adding functional groups, doping heteroatoms, or adjusting the monomer. These attractive characteristics enable wide application of graphdiyne in different fields including semiconductor, catalysis, energy storage, physical separation, signal detection, and biotherapy.\[21\]

Graphdiyne and its derivatives have been successfully applied to energy storage systems like LIBs\[22\] and SIBs\[23\]. However, ZIBs using 2D graphdiyne materials are yet to be developed. Graphdiyne materials possess a series of features that are beneficial for AZIB fabrication: 1) expanded specific surface area that provides more active sites for chemical reaction; 2) enhanced conductivity that significantly increases the electron transportation; 3) uniform porous structure that effectively regulates the ion transportation; 4) intrinsic stability that offers robust protection to electrodes and separators against zinc dendrite and self-dissolution; and 5) tunable structure and variable functional groups that make it possible to achieve rational design of battery components with desired functions.\[24\] The features mentioned above demonstrate the potential of graphdiyne materials as promising candidates for zinc-ion energy storage devices. In this section, we review previous studies of graphdiyne-based AZIBs where graphdiyne materials were applied to improve the performance of cathode, anode, and separator. Relationship among structure, function, and electrochemical performance is specifically focused to explain the roles of graphdiyne materials in zinc-ion energy storage systems.

Up to now, there are no reports of graphdiyne materials for direct zinc-ion storage as AZIB cathodes or anodes. However, graphdiyne cathode substrates or protective artificial interface layers (AIL) have already shown up. For instance, the large specific surface area efficiently increases the amount of reaction sites, and the tunable porous structure forms tunnels for fast

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**Scheme 1.** Structural models of representative 2D carbon-rich materials. a) 2D layered graphdiyne. The blue spheres represent C atoms. b) 2D layered graphene. The green spheres represent C atoms. c) 2D TpPa-SO\(_3\)Zn\(_{0.5}\) COF. The purple and gray spheres represent Zn\(^{2+}\) and TpPa-SO\(_3\)\(^-\) ions, respectively. Reproduced with permission.\[100\] Copyright 2020, Royal Society of Chemistry.
ion diffusion. As substrates, appropriate functionalization can enhance the interaction between graphdiyne and cathode to form hybrid materials with superior performance; while for AILs, outstanding stability of graphdiyne materials provides robust protection during long-term cycling.

Recently, we designed an in situ growth method to obtain MnO2@graphdiyne oxide (GDYO) hybrid 3D nanoflowers as AZIB cathode (Figure 1a). GDYO is an important derivative of graphdiyne. It retains the sp–sp2 carbon skeleton of 2D graphdiyne, while the terminal alkyne and a part of butadiyne structure are oxidized to oxygenic groups like carboxyl groups.24a The hydrophilic oxygenic groups of GDYO had strong coordination effect to Mn2+ ions, where the metal ions were firmly chelated and further oxidized to MnO2 nanosheets. Scanning electron microscope (SEM, Figure 1b), transmission electron microscope (TEM, Figure 1c), and energy-dispersive X-ray spectroscopy (EDS, Figure 1d) mapping images revealed that GDYO nanosheets were homogeneously and completely covered by the in situ grown MnO2 nanosheets to form a 3D nanoflower structure. The as-prepared MnO2@GDYO hybrid 3D nanoflowers owned enlarged specific surface area that shortened ion/electron diffusion pathways and increased active sites; nanopores from GDYO skeletal structure and mesopores between MnO2 nanosheets as tunnels for transportation; intimate interfacial connection between MnO2 and GDYO that enabled faster electron transfer and reaction kinetics; and enhanced integral mechanical stability for longer cycling life. AZIBs based on MnO2@GDYO hybrid 3D nanoflowers exhibited high reversible capacity (265.1 mAh g\(^{-1}\) at 0.1 C), superior rate capacity (253.7 mAh g\(^{-1}\) at 1 C and 80.6 mAh g\(^{-1}\) at 10 C), and long cycling life (1000 cycles at 5 C with 77.6% capacity retention and coulombic efficiency approaching 100%).24c

Interfacial engineering is an effective measure of cathode protection.14 We reported a hybrid K\(_{0.25}\)MnO2@graphdiyne nanowall cathode synthesized via a two-step in situ growth strategy. The K\(_{0.25}\)MnO2 nanowalls were prepared on titanium foil after hydrothermal treatment, followed by in situ growth of graphdiyne films via a facile polymerization process on K\(_{0.25}\)MnO2 nanowalls (Figure 2a). The K\(_{0.25}\)MnO2@graphdiyne cathode inherited the networks with large surface area of K\(_{0.25}\)MnO2 nanowalls that benefited the ion transport and interfacial charge transfer. The porous structure of graphdiyne film (average thickness of \(\approx 4\) nm, Figure 2b) allowed unhindered penetration of Zn\(^{2+}\) during the rapid insertion/extraction process in rate test, while the morphology change was also buffered by the robust protective layer. Besides, graphdiyne films around the K\(_{0.25}\)MnO2 nanowalls sufficiently buffered the oxygen evolution reaction. Theoretical calculation based on density functional theory (DFT) indicated an enhanced conductivity and an improved zinccophilicity of K\(_{0.25}\)MnO2@graphdiyne cathode, perhaps owing to the synergistic effect of this heterostructure. The as-constructed Zn–K\(_{0.25}\)MnO2@graphdiyne battery manifested a superior capacity of 520 mAh g\(^{-1}\) at 55 mA g\(^{-1}\), suggesting a near-full two-electron zinc storage mechanism. After 150 cycles at 550 mA g\(^{-1}\), K\(_{0.25}\)MnO2@graphdiyne cathode still delivered a high capacity of 221 mAh g\(^{-1}\), which illustrated its excellent stability and rate performance.25

As for anodes, Zhi et al. synthesized hydrogen-substituted graphdiyne (HsGDY) on zinc plate substrate (Zn@HsGDY) via the cross-coupling reaction of 1,3,5-triethynylbenzene (TEB) monomer (Figure 2c). The cyclization of TEB formed enlarged hexatomic rings that served as well-distributed sub-\(\text{Å}\)ngström level tunnels with the pore size of 1.3–1.5 nm (Figure 2d). The function of as-fabricated HsGDY layer during the zinc deposition process was predicted by the simulation of both electric field and Zn\(^{2+}\) concentration field. First, the HsGDY layer blocked the Zn\(^{2+}\) flow from the bulk electrolyte on the external surface. Second, Zn\(^{2+}\) ions were forced to homogeneously penetrate through the HsGDY layer, leading to a uniform distribution of Zn\(^{2+}\) along the transversal direction against the uneven electric field. Consequently, Zn\(^{2+}\) ions were regulated to deviate the original diffusion route directed by electric field and deposited with no aggregation nor dendrites in such a relatively uniform Zn\(^{2+}\) concentration field (Figure 2e). In addition, the butadiyne and aromatic rings of HsGDY possessed intrinsic stability of covalent bonds and \(\pi\)-conjunction to bear the distortion caused by zinc dissolution/deposition. The symmetric Zn@HsGDY cells therefore exhibited prolonged lifespan.

Figure 1. AZIB cathodes using graphdiyne substrate. a) Schematic illustration of synthesis procedure of MnO2@GDYO hybrid 3D nanoflowers. b) SEM image and c) TEM image of MnO2@GDYO hybrid 3D nanoflowers. d) Elemental EDS mapping images of Mn, O, and C. Reproduced with permission.24c Copyright 2021, Royal Society of Chemistry.
of over 2400 h at from 0.5 to 2 mA cm\(^{-2}\) with well-preserved HsGDY layer and smooth zinc surface.\(^{[24b]}\) Another strategy for anode AIL fabrication was proposed by Zhang et al. who introduced a radio frequency (RF) heating strategy to synthesize few-layered graphdiyne (average thickness of 1–2 nm) on zinc foil. By selectively heating the metal substrate, RF irradiation created temperature gradient from metal surface to solvent, making dissolved monomers selectively coupled on the solid/liquid interface. The as-prepared Zn-GDY plate exhibited flatter and smoother surface morphology as well as better hydrophilicity than bare zinc plate. These graphdiyne films possessed fine electrical conductivity, uniform pore size, and improved hydrophilicity, which not only decreased the nucleation overpotential, but also controlled the migration of Zn\(^{2+}\) ions and formed an evenly distributed Zn\(^{2+}\) concentration field. As a result, the growth of zinc dendrites was significantly suppressed. Electrochemical test of Zn-GDY using copper as counter electrode showed a higher coulombic efficiency (over 98% at the current density ranging from 2 to 20 mA cm\(^{-2}\) for \(\approx 200\) cycles), lower nucleation overpotential, and an extended lifespan (over 400 h at 4 mA cm\(^{-2}\) / 4 mAh cm\(^{-2}\)).\(^{[26]}\)

Figure 2. AZIB cathodes and anodes using graphdiyne AILs. a) Schematic illustration of synthesis procedure of Ti@K\(_{0.25}\)MnO\(_2\)@graphdiyne with SEM images in each step. Insets show optical images of electrodes in each step. b) High-resolution TEM image of K\(_{0.25}\)MnO\(_2\)@graphdiyne. Reproduced with permission.\(^{[25]}\) Copyright 2021, Springer Nature. c) Schematic illustration of the cross-coupling reaction of TEB. d) Schematic illustration of sub-ångström ion tunnels of HsGDY on zinc substrate. e) Cross-sectional SEM image of Zn@HsGDY. Reproduced with permission.\(^{[24b]}\) Copyright 2020, John Wiley and Sons.

Compared to cathode and anode, researches on AZIB separator are still in the early stage. Except for avoiding short circuit, separator also controls the ion diffusion and regulates the electron transfer between anode and cathode. Therefore, the porous structure and semiconducting property of graphdiyne perfectly meet the demand of separator construction. Furthermore, graphdiyne-based membrane is expected to display high stability against the penetration of zinc dendrites. Besides, the functionalization of graphdiyne enhances the interaction between ions and graphdiyne derivatives. These virtues make graphdiyne materials ideal candidate for AZIB separator. As it is well known, GDYO contains oxygenic groups like carboxyl groups, while the main skeleton of graphdiyne is well retained. To further explore the application of GDYO in AZIBs, we took a vacuum-filtration method to prepare GDYO membranes on polytetrafluoroethylene (PTFE). GDYO showed uniform and porous morphology composed of compactly stacked GDYO nanosheets (Figure 3a), with an average thickness of \(\approx 30\) μm (Figure 3b). We chose birnessite-type MnO\(_2\) nanosheets as cathode material, which underwent a H\(^+\)-insertion mechanism. Such a proton-dominated process specifically favored the abundant hydrophilic oxygenic groups of GDYO. Thus, a multifunctional GDYO membrane on the cathode side was applied as separator in Zn–MnO\(_2\) batteries: the mesopores of GDYO membrane could regulate the transport of Zn\(^{2+}\) as ion tunnels; semiconductive GDYO could enhance the electron transfer of MnO\(_2\); oxygenic groups could accommodate the proton behavior; and the densely stacked GDYO nanosheets with high mechanical strength could protect cathode material from dissolution or degradation. Cyclic voltammetry (CV) tests indicated that the introduction of GDYO membrane and MnSO\(_4\) electrolyte additive affected little during the
redox process of MnO₂ (Figure 3c). This novel AZIB exhibited ultrahigh specific capacity of 300 mAh g⁻¹ at 1 C over 50 cycles (Figure 3d), long lifespan, and remarkable rate capability of 100 mAh g⁻¹ at 10 C over 1000 cycles. Symmetric cell test using GDOY membrane also displayed better reversibility (over 800 h at 0.1 mA cm⁻²), indicating the regulation of zinc deposition by GDOY membrane.²⁴α Very recently, Zhi et al. prepared a cellulose (CS)@N-modified graphdiyne (NGDY) separator by cross-coupling reaction of triacetylenyl-based triazine monomer. In situ pH detection indicated that CS@NGDY membrane sufficiently suppressed the pH change at zinc anode in symmetric cell. Further investigation and simulation revealed that the desolvation of hydrated Zn²⁺ ions was enhanced by N atoms of NGDY, resulting in the direct electron transfer from current collector to desolvated Zn²⁺. The split of O–H bonds was thus prevented, with a stabilized pH at zinc/electrolyte interface. Symmetric batteries with CS@NGDY membranes exhibited a prolonged lifespan (116 times compared to batteries with CS membrane), while the Zn//V₆O₁₃ full cell maintained stable after 1000 cycles at 20.65 mA cm⁻².²⁴β

3. Graphene

Since first discovered in 2004, graphene has been widely studied as a promising material in various fields.²⁶α Its covalent π-conjugated honeycomb plane that consists of pure sp² hybridized carbon enables fine structural stability and ultrafast electron transfer. Therefore, graphene is usually considered to be a representative 2D material with unexpected properties like great electrical conductivity (≈107 S m⁻¹), high intrinsic mobility of 200 000 cm² V⁻¹ s⁻¹, high theoretical specific surface area of 2630 m² g⁻¹, and great mechanical strength (with Young’s modulus of ≈1.0 Tpa).²⁷α which are especially favored in energy storage systems such as LIBs²⁸α and SIBs²⁸β. Nevertheless, the carbon skeleton of graphene can be rationally modified to fabricate functionalized graphene or heteroatom-dopped graphene that meets different demands.²⁹α

Recent years have seen great efforts into graphene-based AZIBs, where graphene and its derivatives participated in cathodes, anodes, electrolytes, and separators fabrication. In most cases, graphene and its derivatives served as additives or conductive substrates that enabled rapid and homogeneous electron transfer. Besides, the excellent mechanical strength and flexible property of graphene materials made it feasible to protect electrodes from byproducts and volume change. Herein, we systematically review recent development of AZIBs containing graphene or its derivatives. The pioneering studies and characteristic researches are especially concentrated to provide an overall perspective of graphene-based AZIBs.

3.1. Cathode

Based on the above discussion, 2D graphene materials possess large specific surface area, excellent electrical conductivity, and attractive mechanical properties. The first application of graphene materials in aqueous zinc storage system could date back to 2015 when Wu et al. assembled a hybrid Zn²⁺/Li¹⁺ battery based on zinc anode and graphene-wrapped LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode.³₀α However, it was not until 2018 that studies focusing on graphene and its derivatives in AZIBs began to significantly boost, among which graphene-based cathodes attracted the most attention. Up to now, different types of cathodes combined with graphene material in AZIBs have been designed and synthesized. To form an organized manner, we divided graphene-based cathodes into five parts here: direct zinc storage cathodes, conductive additives, cathode substrates, protective layers, and current collectors. The essential points of cathode design and synthesis are also discussed below.

Although theoretical simulations showed pessimistic attitude toward defect-free graphene monolayers being zinc anodes,³¹α chemical modification has already made it possible for functionalized graphene to reversibly store Zn²⁺ ions as cathode. Liu et al. synthesized a holey graphene electrode with high conductivity and dual-ion storage ability. In this case, GO was first oxidized by H₂O₂ solution to form artificial holes and then treated with diazotized sulfanilic acid to get functionalized holey graphene (FHG) electrode. During the battery cycling, the sulfonic groups (–SO₃H) and secondary amino groups (–NH⁻) of amide structure could reversely combine Zn²⁺ and SO₄²⁻, respectively. The as-synthesized FHG cathode exhibited interconnected network morphology of stacked 2D FHG nanosheets that formed electron and proton transport matrix. AZIB using FHG as cathode and holey graphene protected zinc foil as anode showed admirable specific capacity with good rate performance (234 mAh g⁻¹ at 0.1 A g⁻¹ and 43% retention at 10 A g⁻¹) and long cycling life (98% capacity retention after 4000 cycles at 10 A g⁻¹).³²α This creative work explored the new application
of graphene materials and confirmed their ability for direct zinc storage.

Considering that most existing cathode materials suffer a lot from poor conductivity, conductive additives with lightweight and large surface area are essential for AZIB cathodes. Compared to conventional conductive additives like carbon black (3D) and carbon nanotube (1D), 2D graphene owns the largest specific surface area which enables efficient electron transfer between redox-active materials and current collectors.\[36\] Hence, graphene materials are alternative additives that can combine with AZIB cathode materials via simple physical mixing. For instance, Niu et al. constructed a flexible all-in-one AZIB consisted of reduced graphene oxide (rGO)/polyaniline (PANI) cathode, cellulose nanofiber (CNF) separator, and exfoliated graphene (EG)/Zn anode. The rGO/PANI cathode was synthesized via simple stirring and ultrasonication of GO and PANI suspension, followed by the reduction of GO. GO additive formed porous structure with good flexibility for cathode, resulting in a flexible AZIB with excellent flexibility and great stability against physical bending.\[37\] Analogous operations were performed by Yang et al. who utilized the electrostatic self-assembly of vanadium nitride (VN) and GO to form VN@GO compounds which were reduced subsequently into VN@rGO as AZIB cathode.\[38\] Besides, graphene is especially favorable in photorechargeable systems because of its appropriate energy level. Boruah et al. proposed a series of photocathodes using a mixture of photosensitive vanadium oxide and rGO for photo-AZIBs. rGO was found crucial in such systems, as it supports the charge separation and transports the photoexcited electrons from vanadium oxide to the current collector (Figure 4a,b). The authors’ first work of photorechargeable V2O5-poly (3-hexylthiophene-2,5-diy)-rGO AZIB delivered a boosted capacity of ≈370 mAh g−1 at 50 mA g−1 in light condition (compared to ≈190 mAh g−1 in the dark) with a photoconversion efficiencies of ≈1.2%.\[39\] Subsequent study of the photosensitive VO2@rGO cathode exhibited a high illuminated rate capacity of ≈315 mAh g−1 at 200 mA g−1 and ≈134 mAh g−1 at 2000 mA g−1 (compared to 282 and 71 mA g−1 in the dark, respectively).\[40\]

Although physical mixture of active materials and additives is widely employed as a simple approach to fabricate AZIB cathodes, it usually leads to inadequate contact between each component and inescapable aggregation. To achieve compact and binder-free cathodes via physical method, vacuum filtration is often adopted. Zhou et al. first demonstrated binder-free MnO2/rGO cathode using vacuum filtration method in 2018 (Figure 4c). The as-prepared free-standing cathode showed good flexibility and intimate interface among MnO2, rGO, and carbon cloth substrate, which improved the electrical conductivity and increased the cathode stability. The Zn–MnO2/rGO batteries exhibited ultrahigh capacity of 332.2 mAh g−1 at 0.3 A g−1 and a capacity retention of 96% after 500 cycles at 6 A g−1, which was significantly better than conventional MnO2 cathodes.\[43\] The same preparation strategy was also adopted for other redox-active inorganic materials including 6-NaxV2O5·xH2O,\[42\] NaV2O4·1.5H2O,\[43\] MnO2 nanosheets,\[44\] and MnO2 nanowire.\[45\] Besides, Li et al. proposed a flexible organic cathode supported by GO and carbon nanotubes via vacuum filtration. The carboxyl groups of GO, in this case, served as proton source for PANI to deal with the capacity deterioration problems. The close contact between GO and PANI enabled sufficient transfer of protons from GO to PANI (Figure 4d), resulting in a high reversible capacity of 233 mAh g−1.\[46\] According to these works, vacuum filtration can be applied to a variety of cathode materials to physically obtain compacted GO-cathode combination.

Besides above physical strategies, in situ chemical reactions in the presence of certain substrates are also widely adopted to reach this goal. As we mentioned before, the intimate contact between conductive additives and active cathode materials significantly shortens the electron transfer pathways and thus enhances the rate performance, increases the available capacity, and achieves the effective utilization of active sites. Like graphdiyne oxides,\[24c\] graphene materials can participate in the cathode synthesis process as cathode substrates, providing not only binder-free contact with vague boundaries but also macroscopic/mesoscopic cross-linked networks for fast ion transport with excellent stability. The basic point of utilizing graphene materials as substrates is adding graphene materials into chemical reactions to obtain certain products. As typical examples, Zhu et al. developed an in situ synthetic method of layered δ-MnO2, where 2D GO was oxidized by KMnO4 as a self-sacrificing template in aqueous solution,\[47\] and Chen et al. further applied this strategy in molten salt method to synthesize MnO2 nanocomposite for AZIBs.\[48\] Fortunately, most conventional synthetic methods like solution-phase method, hydrothermal method, and microwave method can be successfully carried

Figure 4. Graphene additives for AZIB cathodes. a) Schematic illustration of the photocharging mechanism of photo-AZIBs. b) SEM image of V2O5 nanofibers with an inset of high-resolution TEM image. Reproduced under the terms of the CC-BY license.\[39\] Copyright 2020, The Authors. Published by Royal Society of Chemistry. c) Schematic diagram of the vacuum filtration. Reproduced under the terms of the CC-BY license.\[41\] Copyright 2018, The Authors. Published by Springer Nature. d) Schematic illustration of proton transfer process of GO doping PANI. Reproduced with permission.\[46\] Copyright 2020, Elsevier.
out with well-preserved graphene materials under controlled conditions because of their excellent chemical stability. The raw materials, uniformly dispersed with graphene, form binder-free and homogenous hybrids in the subsequent reaction.

In 2016, Yang et al. synthesized Na3V2(PO4)3 (NVP) cathode co-incorporated by carbon and rGO for a hybrid Zn2+/Na+ battery. The procedure of Na3V2(PO4)3 synthesizing was modified by adding citric acid as carbon source and GO suspension as rGO source. NVP particles with diameter of 50–150 nm were uniformly distributed on the rGO nanosheets, delivering a capacity of 92 mAh g\(^{-1}\).[49] Afterward, solution-phase synthesis of Mn1O4 nanoparticles,[50] Mn2O3 nanosheets,[51] ZnMn2O4 nanodots,[52] and V2O5 nanoparticles[53] with graphene substrates was studied to acquire hybrid cathodes for AZIBs with improved conductivity and enhanced stability. Tian et al. applied solution-phase synthesized FeVO/reduced holey graphene oxide (rHGO) hybrids into 3D printable ink. The 3D printed cathode possessed macroscopical open channels for ion transport and intimately contacted FeVO and rHGO nanosheets, which paved a new way to rationally design the shape of AZIB cathode for better performance.[54] Wu et al. designed an amorphous V2O5/graphene (A-V2O5/G) 2D heterostructure using single-layer graphene as 2D templates via solution-phase reaction (Figure 5a). The layer-by-layer 2D heterostructure with large surface area enabled fast ion/electron transport during the cycling. An outstanding capacity of 447 mAh g\(^{-1}\) at 0.3 A g\(^{-1}\) was observed, along with a long lifespan of 20 000 cycles.[55] The same structure was also achieved via freeze-drying and annealing method by the authors, with a similar electrochemical performance.

Hydrothermal method is broadly employed to synthesize cathode materials including manganese-based cathodes,[56] vanadium-based cathodes,[57] MoS2-based cathodes,[58] and others.[59] The first research that synthesized cathode-graphene hybrid via hydrothermal reaction was proposed by Yang et al. in 2018, where rGO served as both cathode substrate and reactant to obtain VS4@rGO nanocomposite.[57m] Up to now, plenty of researches utilizing hydrothermal reactions to grow certain cathode materials on different graphene substrates have been reported, most of which selected GO as oxidant to acquire rGO-supported cathodes or graphene as reductant to obtain GO-supported cathodes. To introduce heteroatoms into graphene materials, Yang et al. proposed a ZnMn2O4/nitrogen-doped rGO (NG) cathode by adding a small amount of ammonia into the hydrothermal system containing Zn2+, Mn2+, and GO.[56d] Liu et al. further introduced nickel and cobalt into the ZnMn2O4 lattice framework to synthesize nickel and cobalt co-substituted ZnMn2O4@N-rGO via similar procedure.[56e] Compared to rGO, NG provided more active sites via coordination and limited the excess growth or aggregation of ZnMn2O4 nanoparticles. Moreover, graphene substrates are usually demonstrated as capacitive components without faradic activities, which means that graphene can only participate in ion transport and electron transfer. However, Mai et al. reported an abnormal VO\(_x\) subnanometer cluster/rGO heterostructure cathode synthesized by hydrothermal reaction between V2O5 and rGO. The synthesized cathode, composed of interfacial V–O–C bonds, exhibited a unique Zn2+ storage mechanism in the interface between VO\(_x\) and rGO surface (Figure 5b). rGO was found reduced during the discharging process, with a significant increase of \(\pi\) electrons and decoupled transport of Zn2+ and electrons. This rGO-dominated redox mechanism was enabled by the heterogeneous structure where Zn2+ reversibly broke the V–O–C bonds to form V–O–Zn bonds during Zn insertion and reconstructed the V–O–C bonds during the Zn extraction. Owing to the fast interfacial Zn2+ diffusion, the VO\(_x\)/rGO

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**Figure 5.** Graphene substrates for AZIB cathodes. a) Schematic illustration of synthesis procedure of 2D A-V2O5/G heterostructures using graphene as 2D templates. Reproduced with permission.[55] Copyright 2020, Elsevier. b) Atomic-resolution high-angle annular dark-field STEM image of the VO\(_x\)-G heterostructure in the discharged state, indicating the zinc storage sites. c) Cycling performance of the VO\(_x\)-G heterostructure, VO2–G, and VO2+G, and VO2 varying from 0.1 to 100 A g\(^{-1}\). Reproduced with permission.[57b] Copyright 2021, John Wiley and Sons. d) Schematic illustration of synthesis procedure of V3O7·1.5H\(_2\)O nanobelts via microwave method. Reproduced with permission.[60] Copyright 2021, John Wiley and Sons.
cathode delivered a high rate capacity of 174.4 mAh g\(^{-1}\) at 100 A g\(^{-1}\) (Figure 5c).\[^{[25]}\]

Except for the above widely adopted strategies, researchers also explored the other synthetic methods with graphene substrates. Mossin et al. added GO solution into microwave reactor with VOSO\(_4\)-xH\(_2\)O to synthesize V\(_2\)O\(_7\)-1.5H\(_2\)O nanobelts/rGO composites (Figure 5d), whose electron transfer kinetics and cycling stability were significantly promoted in the presence of rGO.\[^{[60]}\] Fan et al. synthesized a 2D hierarchical Mn\(_3\)O\(_4@\)graphene cathode by molten salt method. The vertical growth of numerous Mn\(_3\)O\(_4\) nanosheets on 2D hierarchical graphene possessed large surface area and high exposure of open edges for Zn\(^{2+}\) storage. AZIB using Mn\(_3\)O\(_4@\)graphene cathode showed an outstanding capacity of 850.4 mAh g\(^{-1}\) at 300 mA g\(^{-1}\).\[^{[61]}\] We do believe that graphene materials can be applied into other synthetic techniques to fabricate cathodes with various structure and multiple functions.

Structural and morphological engineering enables well-controlled combination of cathode materials and graphene, technically making graphene materials capable for cathode protection. Indeed, the large specific surface area and flexible property of lightweight 2D graphene are especially favored in this area. Graphene-based protective layers usually serve as multifunctional shields. They maintain the basic functions of graphene substrates (i.e., conductive cross-linked networks that improve the ion transport and electron transfer and avoid aggregation), but feature additional properties for cathode protection as they inhibit the direct contact between cathodes and electrolytes to suppress cathode dissolution as well as buffer the volume change during the charge/discharge process. Most graphene protective layers were acquired via hydrothermal methods. For example, Mai et al. synthesized graphene scroll-coated \(\alpha\)-MnO\(_2\) nanowires. After 12 h hydrothermal treatment, MnO\(_2\) particles gradually transformed into nanowires covered by preabsorbed rGO sheets with an average width of 5 nm (Figure 6a,b), which efficiently enhanced the electron transfer and suppressed the structural deterioration. The as-assembled AZIB showed high capacity (362.2 mAh g\(^{-1}\)) and prolonged lifespan (94% retention after 3000 cycles).\[^{[62]}\] This work strongly influenced the following studies. Zhu et al. explored the relationship between cathode wettability and electrochemical performance of \(\alpha\)-MnO\(_2\) by adjusting the ratio of hydrophobic graphene and amphiphilic cellulose nanowhiskers (CNWs) in the scroll-coating layer. The hydrophobic graphene protective layers were found beneficial to the desolvation of hydrated Zn\(^{2+}\) but detrimental to the Zn\(^{2+}\) diffusion, resulting in the first increase and then decrease of the battery performance.\[^{[63]}\] Zhao et al. constructed a N-doped graphene sheet on chain-like MnO cathode using hydrothermal and subsequent annealing strategy. The electrochemical performance MnO@N-doped graphene scrolls was greatly enhanced compared to pure MnO, delivering a high capacity of 269 mAh g\(^{-1}\%) \text{and} 98% \text{capacity retention at 0.5 A g}^{-1}\) after 300 cycles.\[^{[64]}\] Moreover, graphene-wrapped cathodes including oxygen-deficient \(\beta\)-MnO\(_2\),\[^{[65]}\] MOFs-derived MnO/C,\[^{[66]}\] defect-rich V\(_6\)O\(_{11.6}\),\[^{[67]}\] H\(_2\)V\(_3\)O\(_8\) nanowire,\[^{[68]}\] Cu\(_2\)V\(_6\)O\(_{15}\) nanobelt,\[^{[69]}\] and H\(_2\)Al\(_2\)V\(_6\)O\(_{21.2}\) were also obtained via hydrothermal reactions. Solid-phase method via freeze-drying and calcination was also adopted for graphene layers. Zhou et al. dispersed hydrothermal synthesized Na\(_{1.1}\)V\(_3\)O\(_7\) nanoribbons in GO solution. The mixture was first freeze-dried and then calcined in the air. Na\(_{1.1}\)V\(_3\)O\(_7\) nanoribbons wrapped by rGO films showed enhanced conductivity and fine integrity, achieving \(\approx 92.5\% \text{capacity retention at 1 A g}^{-1}\) after 500 cycles.\[^{[70]}\] Furthermore, physical treatments like self-assembling and spray-drying methods played important roles in cathode protection. For instance, rGO-wrapped hollow ZnMn\(_2\)O\(_4\) microspheres

![Graphene protective layers and current collectors for AZIB cathodes.](image)

Figure 6. Graphene protective layers and current collectors for AZIB cathodes. a) TEM image with an inset of selected area electron diffraction and b) High-resolution TEM image of graphene scroll-coated \(\alpha\)-MnO\(_2\) nanowires. Reproduced with permission.\[^{[62]}\] Copyright 2018, John Wiley and Sons. c) SEM image of rGO@HM-ZMO. Reproduced with permission.\[^{[72]}\] Copyright 2019, Elsevier. d) SEM image 3D MNWs@GNSs microflowers. Reproduced with permission.\[^{[73]}\] Copyright 2020, Elsevier. e) Cross-sectional SEM image and f) high-resolution cross-sectional SEM image of MnO\(_2@\)graphene film. Reproduced with permission.\[^{[74]}\] Copyright 2021, Elsevier. g) SEM image of P-MnO\(_2-x@VMG\) arrays. Reproduced with permission.\[^{[75]}\] Copyright 2020, John Wiley and Sons. h) SEM image of Na:MnO\(_2\)/GCF cathode. Reproduced with permission.\[^{[76]}\] Copyright 2020, John Wiley and Sons.
(rGO@HM-ZMO) were designed by Yang et al. via electrostatic assembly (Figure 6c). The cross-linked rGO conductive network on the surface of HM-ZMO greatly enhanced the conductivity. With the synergistic effect of hollow microspheres that could withstand the volume swelling, rGO@HM-ZMO cathode exhibited specific capacity of 146.9 mAh g⁻¹ at 0.3 A g⁻¹ and 72.7 mAh g⁻¹ at 1 A g⁻¹ after 650 cycles.²⁷¹ Spray-drying method was adopted by Yan et al. for the scalable synthesis of 3D MnO₂ nanowires (MNWs)@graphene nanosheets (GNSs) nanoflowers (Figure 6d). The spontaneous assembled GNSs driven by the capillary force from rapid solvent evaporation formed crumpled protective layers for intertwined MNWs, enabling fast ion/electron transfer and well-maintained structural integrity. MNWs@GNSs cathode exhibited ≈97.5% capacity retention after 10 000 cycles at 2 A g⁻¹, with a high discharge capacity of 306.8 mAh g⁻¹.²⁷² The synthetic methods mentioned above show good promise for protective layers, while new techniques and precise mechanisms of cathode protection are still needed.

The high conductivity and 2D planar structure of graphene make it possible to serve as current collector. Compared to traditional metal current collectors, graphene materials own several advantages like close combination with cathode materials, lightweight, designable structure, and high electrochemical stability. A direct strategy was proposed by An et al. who synthesized graphene film via conventional doctor-blade method from a mixture of graphene, polyvinylidene difluoride (PVDF), and N-methyl-2-pyrrolidone (NMP). After functionalized by HCl, the graphene film was floated on the acidic aqueous solution of KMnO₄ to obtain free-standing MnO₂ particles on the hydrophilic graphene film with superior flexibility and good electrochemical performance (Figure 6e,f).²⁷³ Previous studies have demonstrated graphene-based current collectors in different shapes, including 3D porous graphene networks,²⁷⁵ vertical graphene arrays,²⁷⁶ and graphene films.²⁷⁶ For example, Niu et al. synthesized a free-standing graphene foam with VO₂ via freeze-drying and calcination method as cathode. rGO sheets constructed 3D porous conductive network with pores of micrometer and submicrometer size. The large inter-space between rGO nanosheets could afford rapid diffusion of electrolytes and accommodate a huge loading of cathode materials (in this case, VO₂) with no aggregation. Besides, the lightweight free-standing rGO/VO₂ cathode was free of external binder or metal current collector, delivering an energy density of 65 Wh kg⁻¹ at a power density of 7.8 kW kg⁻¹ with a long lifespan of over 1000 cycles.²⁷⁶ Fan et al. synthesized 3D conductive porous graphene foam via chemical vapor deposition (CVD) to support both cathode and anode for a quasi-solid-state AZIB, which exhibited recorded energy density of ≈115 Wh kg⁻¹ and a peak power density of ≈5.1 kW kg⁻¹.²⁷⁴ Another 3D porous graphene network, graphene aerogel (GA), which is usually synthesized via hydrothermal method, was also adopted as current collector. Ye et al. combined poly(3,4,9,10-perylenetetracarboxylic dianhydride) (PPTCDA) and GA to form a PPTCDA/GA cathode where PPTCDA uniformly embedded in the graphene nanosheets. The 3D GA provided highly conductive networks for the insulative polymer to achieve excellent electrochemical performance. The as-prepared cathode exhibited capacity of 281 mAh g⁻¹ with a conspicuous capacitive contribution of 41.7%, indicating the high-rate ability enabled by GA networks.²⁷⁵ Similar strategies were also applied to MnO₂,²⁷⁴,²⁷₅ PANI,²⁷₆,²⁷₆,²⁷₉ 2,3,6,7,10,11-hexahydroxynaphthoquinone (HTTP),²⁷₆ and polydopamine (PO).²⁷₆ Recently, vertical graphene (VG) arrays were introduced for cathode current collectors. The vertical growth of interconnected graphene sheets on carbon cloth or carbon fiber fabrics via microwave plasma-enhanced CVD method endows large exposed surface area and pores of submicrometer size.²⁷⁸ Xia et al. first reported vertical multilayer graphene (VMG) arrays with uniform hydrothermal MnO₂ deposition. The MnO₂@VMG arrays were phosphorized in the following step to obtain P-MnO₂-x@VMG with oxygen defects and rougher surface (Figure 6g). VMG provided high conductivity and numerous ion transport channels for the in situ grown P-MnO₂-x nanosheets, showing a high capacity of 302.8 mAh g⁻¹ at 0.5 A g⁻¹, great rate capacity of 150.1 mAh g⁻¹ at 10 A g⁻¹ with 91.3% retention after 1000 cycles.²⁷⁶a Wang et al. fabricated conductive polymer encapsulating layers of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) on VG-MnO₂ cathodes to encapsulate the electrode, which delivered an enhanced capacity of 367.4 mAh g⁻¹.²⁷⁶b VO₂ cathode was treated with the same method by He et al. with abundant exposed edges for fast charge transfer.²⁷⁶c Electrochemical exfoliated graphite is another candidate for current collector with their graphene-like 3D structure because graphene is originally separated from graphite. For instance, Song et al. used 0.5 M KOH solution to electrochemically exfoliate carbon paper as highly conductive current collectors. The as-prepared exfoliated carbon paper (EC) consisted of 3D-interconnected porous graphite/graphite network. EC was successively activated by HNO₃ and LiCl for further electrochemical deposition of MnO₂. The hierarchical structure of EC layer hosted MnO₂ microspheres with a mass loading of ≈9.5 mg cm⁻², which delivered an excellent areal capacity of 5.1 F cm⁻² and a high areal capacity of 3.78 mAh cm⁻².²⁷⁷a Cai et al. exfoliate graphite paper in concentrated H₂SO₄ to acquire 2D/3D graphene-like carbon film (GCF) as the substrate for electrochemical deposition of Birnessite Na₂MnO₂ cathode (Figure 6h), which showed a high capacity (313.7 mAh g⁻¹ at 100 mA g⁻¹) and an unprecedented energy density (511.9 Wh kg⁻¹ at power density of 137 W kg⁻¹).²⁷⁷b Although the lightweight graphene-based current collectors significantly increase the power density of AZIB devices, conflicts between achieving high mass loading and avoiding cathode aggregation remain unsolved. Thus, strategies for abundant and uniformly distributed cathodes in graphene-based current collectors are still in demand.

3.2. Anode

The formation of zinc dendrite and byproduct severely prohibits AZIB anodes from long cycling stability and high coulombic efficiency. Great efforts have been expended to deal with these problems. In 2016, an early work reported by Santhanam et al. confirmed that graphene quantum dots (GQDs) could combine with zinc metal after electrochemical deposition, which achieved higher coulombic efficiency with zinc flakes rather than
dendrites.\(^7^9\) Following studies illustrated that graphene materials could serve as current collectors or protective AILs for zinc anodes because of their excellent conductivity and various functional groups.

The basic idea of designing current collectors for AZIB anodes is to redistribute the electric field for homogeneous zinc deposition without dendrite formation. Thus, current collectors adopted for cathode like VG arrays,\(^7^6^a,7^6^d\) 3D porous graphene networks,\(^7^5^a,8^0\) and graphene films\(^8^4,7^7^b\) are able to support zinc deposition as well because they deliver high conductivity with large specific surface area. For example, Guan et al. constructed N-doped VG nanosheets to manage the zinc deposition process. Besides the dispersed electric field on the surface of 3D porous arrays, the coordination interaction between Zn\(^{2+}\) and nitrogen-containing groups of N-doped VG effectively reduced the nucleation overpotential, which led to a prolonged cycling lifespan compared with directly composited Zn on bare carbon cloth.\(^7^6^d\) Very recently, Xie et al. created a MXene/graphene aerogel (MGA) scaffold for zinc deposition (Figure 7a). The fluoro groups of Ti,\(_3\)C\(_2\)T\(_x\) MXene formed solid electrolyte interface (SEI) with Zn\(^{2+}\) resulting in the uniform deposition of zinc and the separation between zinc particles and aqueous electrolyte. Symmetric battery based on MGA anode delivered a long cycling lifespan of over 1000 h at 10 mA cm\(^{-2}\) (Figure 7b).\(^8^1\) Moreover, new concepts of anode designing were proposed by researchers. In 2019, Archer et al. achieved well-oriented epitaxial growth of zinc platelets on parallelly aligned graphene flakes. Electrodeposition of zinc on graphene substrates exhibited heteroepitaxial property, followed by the homoepitaxy of zinc which eventually achieved layer-by-layer growth of zinc platelets (Figure 7c). This epitaxial deposition was proved reversible, as the electrode yielded high coulombic efficiency (\(\approx 99.7\%\)) over 2000 cycles.\(^8^2\) This work provided a brand-new perspective on zinc anode construction. In addition, Fan et al. synthesized an organic anode with zinc storage ability by assembling perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) on rGO (Figure 7d). DFT simulation indicated a high LUMO energy level of \(-0.2247\) eV of PTCDI, corresponding to its low discharge platform potential of 0.38 V versus Zn\(^{2+}\)/Zn. By reversibly forming Zn-PTCDI rather than zinc metal, PTCDI eliminated zinc dendrites from the source.\(^8^3\)

Compared to graphdiyne, graphene materials possess better conductivity but lack intrinsic nanopores. Therefore, besides building uniform electric fields for evenly distributed nucleation sites, graphene-based protective layers own extra ability of inhibiting the direct contact between anode and electrolyte as well as regulating the ion diffusion process on the macro/mesoscale. A convenient approach to applying AILs on Zinc anodes is doctor-blade method.\(^8^4\) As a typical example, Xie et al. coated N-doped graphene (NGO) onto the zinc foil as protective AIL (Figure 7e). Zinc deposition was found guided by nitrogen in the interface, resulting in a flat morphology and low overpotential. Symmetric battery test exhibited extra electrochemical stability over 500 h with no side reactions like hydrogen evolution, mainly caused by the physical isolation of NGO-AIL.\(^8^4a\) Moreover, previous study illustrated that GO could realize spontaneous reduction and assembly on zinc and other metal substrates.\(^8^3\) Such a concept was adopted by Xie et al.\(^5^7u\) and Liu et al.\(^8^6\) The former constructed 3D graphene networks on zinc anode for Zn-V\(_2\)O\(_7\) AZIB, which exhibited a long cycling lifespan with a capacity retention of 79% after 1000 cycles. The latter obtained layer-by-layer 2D conductive rGO films on zinc foil with large surface area for homogeneous zinc deposition, delivering a decreased overpotential of \(\approx 20\) mV at 1 mA cm\(^{-2}\) and fine cycling stability with no dendrite growth within 5000 cycles. Besides, Xie et al. designed a modified Langmuir–Blodgett (LB) method to coat NGO on zinc foil (Figure 7f). The amphiphilic NGO on zinc foil was found parallelly oriented, which could induce an oriented deposition on the (002) crystal plane of zinc. The smooth morphology of zinc foil was well maintained over 1200 cycles at 1 mA cm\(^{-2}\) without byproducts like H\(_2\) or Zn(OH)\(_2\)\(^{2-}\), indicating the superior protection endowed by NGO LB layer.\(^8^7\)

**Figure 7.** Graphene current collectors and AILs for AZIB anodes. a) Cross-sectional SEM of MGA@Zn after plating 5 mAh cm\(^{-2}\). b) Cycling performance of symmetric cells using Cu@Zn and MGA@Zn electrodes at 10 mA cm\(^{-2}\)/1 mAh cm\(^{-2}\). Reproduced with permission.\(^8^1\) Copyright 2021, John Wiley and Sons. c) Schematic illustration of the stacked epitaxial deposition of zinc on graphene. Reproduced with permission.\(^8^2\) Copyright 2019, American Association for the Advancement of Science (AAAS). d) TEM image of PTCDI/rGO. Reproduced under the terms of the CC-BY license.\(^8^3\) Copyright 2020, The Authors. Published by John Wiley and Sons. e) Cross-sectional SEM of NGO@Zn anode. Reproduced with permission.\(^8^4\) Copyright 2021, American Chemical Society. f) Optical image of bare Zn foil and NGO@Zn. Reproduced with permission.\(^8^5\) Copyright 2021, John Wiley and Sons.
3.3. Separator

Current researches on graphene-based separators mainly focus on suppressing zinc anode dendrites, making graphene membranes, to some extent, serve as protective AILs exhibiting less adhesion or interaction with zinc anodes. For example, Sun et al. modified commercial glass fiber separator via in situ CVD growth of conductive VG carpet with large specific area and porous structure to develop a Janus separator for AZIB (Figure 8a). The VG scaffold on the anodic side offered well-distributed electric/Zn\(^{2+}\) concentration field which led to the even deposition of zinc.\(^{88}\)

Besides, the orientation effect of graphene reported by Archer et al.\(^{82}\) encouraged the exploration of graphene-induced epitaxial zinc deposition. For instance, the locked orientation of zinc position was also achieved by Zhu et al. using a mixture of cellulose nanowhisker and graphene (CNG) as separator. CNG membrane was assembled by the CH–π interaction with multiple functions (Figure 8b). On the one hand, graphene guided the epitaxial zinc deposition; on the other hand, negatively charged cellulose nanowhiskers could regulate the selective cation diffusion by blocking the migration of anions (Figure 8c). Therefore, CNG separator enabled a long cycling life of \(\approx 5500\) h.\(^{89}\) The same strategy was adopted by Qin et al.\(^{90}\) Moreover, Qin et al. illustrated that the epitaxial deposition could be guided by using glass fiber modified with vacuum filtered GO powder as well.\(^{91}\) Researches on regulating cathode behavior via graphene-based separators, however, remain vacant, which definitely needs more attention.

3.4. Electrolyte

Graphene materials have been applied in AZIB electrolytes as functional additive.\(^{92}\) On the one hand, the highly conductive graphene materials can sufficiently promote the formation of well-distributed electric field; on the other hand, graphene materials with considerable mechanic strength can firmly support the solid electrolytes like gel electrolyte. For example, Zhang et al. reported that the electrochemical performance of conventional aqueous ZnSO\(_4\) electrolyte was greatly enhanced by adding GO as electrolyte additive. The electric field on the surface of electrodes was redistributed by homogeneously dispersed conductive GO powder, resulting in a reduced nucleation overpotential and fast charge transfer process. Symmetric battery using such hybrid electrolyte achieved a cycling lifespan of over 650 h, indicating the suppressed dendrite growth.\(^{92a}\) Adding hydrophilic GQDs into ZnSO\(_4\) electrolyte also benefited the zinc anode, reported by Hou et al. very recently.\(^{92b}\) Besides, previous studies demonstrated that graphene materials could also regulate ion transport by constructing 3D microporous networks. Thus, Chen et al. added GO and ethylene glycol (EG) additives while synthesizing antifreezing polyacrylamide (PAM) gel electrolyte (Figure 8d). The oxygenic groups of GO formed plenty of hydrogen bonds with EG and PAM chains, constructing a 3D network with great mechanical stability and freezing resistance. Ion conductivity of PAM/GO/EG gel electrolyte was also enhanced by the synergistic effect of GO and EG, achieving a high specific capacity of 183.2 mAh g\(^{-1}\) at \(-20^\circ\)C.\(^{92c}\)

4. 2D Carbon-Rich Polymers

Up to now, there are only a limited number of researches on AZIBs utilizing other 2D carbon-rich materials. In this section, we review works related to 2D carbon-rich polymers including 2D COFs, 2D MOFs, and 2D conductive organic polymers.\(^{93}\) We summarize the attractive features and explain the zinc storage/transport mechanism of 2D COFs in particular.

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**Figure 8.** Graphene separators and electrolytes for AZIB anodes. a) Schematic illustration of synthesis procedure of Janus separator. Reproduced with permission.\(^{88}\) Copyright 2020, John Wiley and Sons. b) Model of CNG membrane. The white, brown, and red spheres represent H, C, and O atoms of cellulose nanowhiskers, respectively, while the black spheres below represent C atoms of graphene. c) The epitaxial zinc deposition induced by CNG membrane without byproducts after 15 min at 4 mA cm\(^{-2}\). Reproduced with permission.\(^{89}\) Copyright 2021, Royal Society of Chemistry. d) Optical images of PAM/GO/EG gel at normal state (top) and bending state (down). Reproduced under the terms of the CC-BY license.\(^{92b}\) Copyright 2020, The Authors. Published by Frontiers Media S.A.
4.1. 2D COFs

COFs are a series of crystalline porous organic polymers that feature specific structure and controllable synthetic methods. Using certain planar organic molecules as monomers can easily fabricate COFs connected by covalent bonds on a 2D plane, which is the predominate aspect of the COF field.\textsuperscript{93b} 2D COFs combine the advantages of both polymers and small organic molecules, which possess abundant functional groups evenly dispersing on the 2D plane as well as intrinsic insolubility and stability. Furthermore, the polymer skeleton forms abundant pores whose topology and distribution can be well predicted and tailored. Therefore, 2D COFs have attracted growing attention in many fields. When it comes to energy storage, 2D COFs are especially favorable owing to the high specific surface area and numerous pores from the 2D porous structure, as well as the manageable functional groups and predesignable covalent structure.\textsuperscript{93a}

Considering the features mentioned above, 2D COFs show great potential in AZIB systems.

Unlike graphdiyne or graphene, the abundant functional groups of 2D COFs with high order provide considerable zinc storage sites, making them capable for direct zinc storage as cathodes and anode. In 2019, Banerjee et al. first introduced 2D COF cathode into AZIB systems. The authors chose 2,5-diaminohydroquinone dihydrochloride (Hq) and 1,3,5-triforylmethylphloroglucinol (TP) as monomers to synthesize HqTP COF by a solid-state mechano-mixing method. HqTP displayed β-ketoenamine structure connected by hydroquinone units, which was full of redox-active carbonyl groups (Figure 9a). As a result, the CV profile of Zn/HqTP batteries displayed a pair of sharp redox peaks at 1.12/1.0 V versus Zn\textsuperscript{2+}/Zn, representing the redox procedure of quinone (Figure 9b). This reversible electrochemical reaction indicated the coordination of carbonyl groups and Zn\textsuperscript{2+}. Galvanostatic charge-discharge test announced a high
discharge capacity of 276.0 mAh g\(^{-1}\) at 125.0 mA g\(^{-1}\), excellent rate performance, along with a capacity retention of 95% and coulombic efficiency of 98% after 1000 cycles. DFTB calculations predicted that the π-π stacked 2D HqTp COF could accommodate Zn\(^{2+}\) between the 2D planes owing to the intermolecular interactions of C=O...Zn (distance of 2.3 Å) and Zn...N=H (distance of ≈2 Å), while only the carbonyl groups of quinone units were presumed to exhibit redox activity (Figure 9a).\(^{94}\)

Eddaoudi et al. proposed another zinc storage mechanism achieved by phenanthroline functional groups of a novel phenanthroline COF (PA-COF). PA-COF could be categorized as a new 1,4,5,8,9,12-hexaazatriphenylene (HAT) derivative with plenty of C=C=N functional groups as redox active sites. The authors designed a solvothermal condensation method of hexaketocyclohexane and 2,3,7,8-phenazinetetramine to introduce nitrogen-rich phenanthroline parts into the aromatic framework. Aqueous zinc-hexane and 2,3,7,8-phenazinetetramine to introduce nitrogen-rich groups by the interaction between Zn \(^{2+}\). The authors then proved a Zn\(^{2+}\)/H\(^{+}\) cointercalation mechanism that the cations were hosted between the 2D layers of PA-COFs. Theoretical simulation illustrated that Zn\(^{2+}\) ions passed through the channels of PA-COF and were accommodated at the nitrogen sites of phenanthroline groups by the interaction between Zn\(^{2+}\) and C=C=N functional groups densely distributed in the π-conjugated frameworks as ion-storage sites. These features, however, suggest that 2D COFs may also serve as cathode substrates or protective AILs to provide increased kinetics and extra stability. Indeed, Nagarale et al. combined redox-active 7,7,8,8-tetracyanoquinodimethane (TCNQ) with 2D COF (synthesized from cyanuric chloride and pyrene, marked as CCP) material by mechano-mixing. TCNQ was found confined in the nanopores in CCP with π-π stacking interaction between electron deficient TCNQ and electron surplus cyanuric groups of CCP. Moreover, nanochannels of CCP facilitated the shuttling of Zn\(^{2+}\). The introduction of multifunctional CCP additive effectively improved the electrochemical performance, leading to a boosted capacity of up to 171 mA h\(^{-1}\) with longer cycling stability versus pure TCNQ cathode.\(^{97}\) Grzybowski et al. reported a systematic work of 2D COF-protected zinc anodes using a series of 1,3,5-triphenylglucitol (TPF)-based COFs (labeled as a DIP series). The authors designed a dip-coating method to fabricate large self-assembling COF films (30 × 12 cm\(^2\)) on zinc and other substrates (Figure 9c) with a controllable thickness varying from 5 to over 100 nm. The imine and ketone functional groups of DIP-COFs exhibited strong affinity to Zn\(^{2+}\), leading to an enhanced ion transport ability and a lower nucleation overpotential. Asymmetric DIP-@stainless-steel/Zn and symmetric DIP-@Zn/Zn batteries achieved an ultralong lifespan of over 420 h at 1 mA cm\(^{-2}\) with a stable polarization voltage; DIP-@Zn//MnO\(_2\) full batteries delivered a better capacity retention of 88.5% after 300 cycles at 2 A g\(^{-1}\). Further examination of zinc deposition process indicated that DIP-@Zn formed well-distributed and compact zinc particles during the deposition originated from the confined 2D zinc diffusion and decoupled growth of adjacent nuclei under the integrated DIP-COF AIL. Therefore, the formation of zinc dendrites or inactive byproducts was sufficiently suppressed.\(^{98}\)

Direct anodic zinc storage was achieved by Feng et al. in 2020. Except for abundant redox active sites that reversibly host Zn\(^{2+}\), zinc storage in 2D COF-based anodes requires a slightly higher redox potential than Zn\(^{2+}\)/Zn potential. However, most 2D COFs deliver much higher potential, making them capable for cathode materials. As we mentioned above, PTCDI was successfully applied in anode fabrication.\(^{83}\) Inspired by this work, a 2D polyaniline COF (PI-COF) was synthesized on carbon cloth via the condensation reaction of 1,4,5,8-naphthalene tetracarboxylic dihydride (NTCDA) and tri(4-aminophenyl) amine (TAPA) mixed with CTXs. The as-synthesized PI-COF anode operated at 0.06–0.96 V versus Zn\(^{2+}\)/Zn exhibited a two-step pseudocapacitive mechanism for zinc storage. DFT simulation and in situ Raman spectroelectrochemistry revealed that Zn\(^{2+}\) ions were coordinated by carbonyl O atoms of the negative enolates between two 2D layers stepwisely during the charging process. Furthermore, Zn\(^{2+}\) diffusion and electron conduction were significantly enhanced by the nanochannels and AA parallel stacked of 2D porous PI-COF. As a result, a specific capacity of 332 C g\(^{-1}\)/92 mAh g\(^{-1}\) at 0.7 A g\(^{-1}\) was acquired with a rate capability of 79.8% at 7 A g\(^{-1}\) and a prolonged cycling lifespan of 4000 cycles (85% retention, Figure 9d). PI-COF//MnO\(_2\) full battery showed a threefold higher capacity retention than Zn//MnO\(_2\) batteries with no dendrites growing, indicating an optimized performance of PI-COF anode.\(^{99}\)
Another work reported by Jeong et al. proposed a unique single-ion conducting COF electrolyte that enabled single Zn$^{2+}$ transport by well-distributed sulfonates. The 2D anionic COF, TpPa-SO$_3$Zn$_{0.25}$, was synthesized by the solvothermal method to connect 1,3,5-triformylphloroglucinol (Tp) with 1,4-phenylenediamine-2-sulfonic acid (Pa-SO$_3$H) and followed by the cation exchange between H$^+$ and Zn$^{2+}$. TpPa-SO$_3$Zn$_{0.25}$ delivered a high zinc conductivity ($\sigma = 2.2 \times 10^{-4}$ S cm$^{-1}$, Figure 9e) with single ion conducting behavior (a zinc-ion transference number of 0.91) and excellent stability (owing to the chemically stable \(\beta\)-ketoenamine groups). Molecular dynamics (MD) simulations predicted a uniform ion distribution in TpPa-SO$_3$Zn$_{0.25}$ electrolyte compared to the randomly distributed anions in liquid electrolyte. This significant difference originated from the fixed sulfonate groups along the directional pores of TpPa-SO$_3$Zn$_{0.25}$, which established the anionic channels and thus guided the homogeneous Zn$^{2+}$ flow. Symmetric cell test revealed a stable cycling performance for 500 h, while the full cell of Zn/TpPa-SO$_3$Zn$_{0.25}$/MnO$_2$ exhibited 73% capacity retention after 800 cycles at 0.6 A g$^{-1}$. The morphology of both Zinc anode and MnO$_2$ cathode was well preserved, indicating a possible ionicomeric buffer layer characteristic of TpPa-SO$_3$Zn$_{0.25}$ electrolyte. This study created a brand-new approach to achieve electrochemical stability by engineering electrolyte.$^{[100]}$

Essentially, 2D COFs are enlarged organic molecules (compared to small organic molecules) with highly ordered and robust structure. That is, the mechanism of Zn$^{2+}$ storage in 2D COFs is similar to that of small organic molecules, while 2D COFs are free of the negligible structural deterioration that small organic molecules suffer. Like graphdiyne, researches on 2D COF-based AZIBs are still in its early stage. Although researchers have confirmed that 2D COFs possess several attractive features for zinc storage, problems like electric insulation and inadequate usage of redox active sites still block the way to better AZIBs.

### 4.2. 2D MOFs and Conductive Organic Polymers

MOFs are a series of crystalline inorganic–organic hybrid porous materials composed of organic-coordinated metal ions or clusters.$^{[93d]}$ Although plenty of researches on 3D MOF-based EESSs have emerged, 2D MOFs are relatively rare and require further study. In 2019, Stoddart et al. reported a 2D conductive MOF, Cu$_3$(HTTP)$_2$, for AZIB cathode ($\text{HTTP} = 2,3,6,7,10,11$-hexahydroxytriphenylene, Figure 10a). 4-Coordinated Cu–quinoid structure served as redox-active site in this 2D COF-like porous framework (Figure 10b,c), which facilitated the hydrated Zn$^{2+}$ insertion with high diffusion rate. Besides, the intrinsic insolubility of this 2D MOF material enabled the integrity of cathode during the cycling. In the following electrochemical tests, Cu$_3$(HTTP)$_2$ exhibited a high reversible capacity of 228 mAh g$^{-1}$ at 50 mA g$^{-1}$ and excellent capacity retention of $\approx$75% at 4000 mAh g$^{-1}$ after 500 cycles.$^{[101]}$ Another research based on 2D conductive poly-pyrrole (ppy) was reported by Xue et al. The researchers designed a solution-phase method to achieve epitaxial polymerization of pyrrole around the 2D MnO$_x$ nanosheets and form a MnO$_x$/ppy network with superior electron-transfer rate and intimate contact between 2D planes (Figure 10d). Moreover, flexible ppy network could regulate the volume change of MnO$_x$ as mechanical buffer layer, and the interfacial resistance was significantly reduced because of the coordinate interaction between Mn and N atoms. Consequently, the MnO$_x$/ppy cathode delivered a reversible capacity of 408 mAh g$^{-1}$ at 1 C with remarkable capacity retention (78% after 2800 cycles at 5 C).$^{[102]}$ Indeed, AZIBs based on novel 2D carbon-rich materials possess great potential. We believe that these 2D carbon-rich materials will undoubtedly solve certain problems of AZIBs with rational design.

![Figure 10. Application of 2D MOFs and conductive organic polymers in AZIBs. a) Schematic illustration of the rechargeable Zn-2D MOF cell and b) the structure of Cu$_3$(HTTP)$_2$ viewed down the c axis. The cyan, red, and gray spheres represent Cu, O, and C atoms, respectively. The H atoms are omitted for the sake of clarity. c) Expected redox process in the coordination unit of Cu$_3$(HTTP)$_2$. Reproduced under the terms of the CC-BY license.$^{[101]}$ Copyright 2019, The Authors. Published by Springer Nature. d) AFM images of MnO$_x$/ppy. The order I–IV represents the gradual formation of 2D configuration of MnO$_x$/ppy nanosheets. Reproduced with permission.$^{[102]}$ Copyright 2020, American Chemical Society.](image-url)
5. Conclusion and Perspective

5.1. Characteristics of Various 2D Carbon-Rich Materials

As a summary, we collected previous works into three tables (Table 1–3) to demonstrate the electrochemical performance of various 2D carbon-rich materials in AZIB systems. The 2D carbon-rich materials we review (i.e., graphdiyne, graphene, 2D COFs, 2D MOFs, and 2D conductive polymers) share a few features in common: excellent flexibility, large specific surface area with 2D plane, and structural stability originated from their x-conjugated covalent structure. Owing to these mutual merits, all the 2D carbon-rich materials can support redox-active materials in both electrodes and help maintain the integrity of the batteries. On the other hand, it is the diversities between different 2D carbon-rich materials that endow them with potential in various fields. Table 4 summarizes the properties of 2D carbon-rich materials we review in this article, along with the assessment of the merits and drawbacks of each material.

Previous researches have illustrated the successful application of graphene materials in AZIBs where graphene participated in nearly every component of the AZIB system, that is, the capability of graphene materials in AZIBs has been comprehensively evaluated. Compared to other 2D carbon-rich materials, graphene possesses the highest conductivity, making it ideal conductive additive and current collector. However, the porosity of graphene materials is limited owing to the integrity of sp² carbon skeleton, as it only constructs mesoscopic holes in graphene-based frameworks. Although chemical modulations like oxidation are widely adopted to synthesize holey graphene materials, the inhomogeneous distribution of pore size and position seriously blocks their hierarchical porosity. Indeed, conventional modification of graphene materials relies heavily on top-down strategies like chemical functionalization and heteroatomic doping. These strategies, yet convenient, are hardly controllable at atomic level.

Considering the programmable synthesis of predictable 2D structure, graphdiyne and 2D crystalline porous polymers (COFs and MOFs) stand out for their bottom-up synthetic strategies. As we discussed before, 2D COFs are well-predictable crystalline frameworks with uniform porous structure. The functional groups and pore size of 2D COFs can be easily tuned via rational design of monomers, making them excellent protective layers and quasi-solid-state electrolytes. As for direct zinc storage, the development of 2D COFs heavily relies on the achievement of small organic molecules. Moreover, 2D COFs suffer from the same problem, poor conductivity, with conventional cathode materials. Relative to insulated 2D COFs, the emerging conductive 2D MOFs may provide solutions for high rate performance cathodes. Unfortunately, the redox-active sites in such conductive MOFs are usually coordinated metal ions that are essential for maintaining the 2D MOF skeleton, resulting in rigid structure with little possibility for further functionalization. Besides, the introduction of heavy metal atoms possibly decreases the specific capacity and power density of AZIBs.

Among all the 2D carbon-rich materials, graphdiyne may exhibit the most promising properties as it combines the attractive advantages of the others. As semiconductor, graphdiyne possesses considerable electric conductivity that enables faster electron transfer than 2D COFs. Moreover, its intrinsic porous structure with tunable pore size helps construct graphdiyne networks with both nanoscopic and mesoscopic pores. The ion diffusion and transport process can thus be enhanced, making graphdiyne suitable for electrode protection and electrolyte regulation. Besides, although consisting of all-carbon skeleton, graphdiyne is obtained by bottom-up strategies. Such a unique synthetic methodology makes a variety of modification methods suitable for graphdiyne. The sp–sp² carbon skeleton of graphdiyne can undergo edge modification and heteroatom doping process like graphene, while the designability of monomers enables structurally manageable construction of graphdiyne derivatives like 2D COFs and MOFs. In addition, the lightweight graphdiyne materials usually contribute little to the capacity, exhibiting their outstanding electrochemical stability as substrates. The main problem that hampers the application of graphdiyne materials might be the complex synthetic procedure. The bottom-up synthesizing of graphdiyne is, though structurally controllable, relatively high cost compared to other 2D carbon-rich materials. Designing new strategies for synthesizing graphdiyne materials with lower costs, endowing pristine graphdiyne materials with new structure and functional groups, as well as regulating the contact between graphdiyne and electrode materials are the main directions for their future development.

5.2. Future Perspectives and Outlook

Functionalization of 2D carbon-rich materials, which we emphasized a lot in previous discussion, is the predominant strategy to obtain high-quality battery components. To date, synthesizing 2D carbon-rich materials in an ordered manner is still challenging, especially when applying top-down strategies on graphene and graphdiyne materials. The development of functionalization strategies should focus on controllability that endows pristine 2D carbon-rich materials with homogeneously distributed functional groups and predictable structures, in order to avoid ambiguous property, mechanism, or electrochemical performance.

Another issue about functionalization is the variation of physical properties, especially the change in hydrophilicity of 2D carbon-rich materials. Raw carbon-rich materials are usually hydrophobic substances that hardly disperse in water owing to the limited number of hydrophilic groups. Such a character may block the ion diffusion process and cause poor rate performance when aqueous electrolytes are employed. After functionalized with oxygenic groups, the hydrophilicity of carbon-rich materials is improved, bringing about enhanced wettability, fast ion transport, and promoted dispersibility. However, the hydrophobic nature of raw carbon-rich materials was found beneficial to the desolvation process of hydrated zinc ions, indicating the possibility of controlling electrode behavior by adjusting its hydrophilicity. Studies on explaining and regulating the hydrophilic/hydrophobic nature of functionalized 2D carbon-rich materials are still in demand, while the same goes for researches on other physical properties including dispersibility, electrostatic interaction, etc.

The combination of conventional battery components like cathode, anode, electrolyte, and separator with 2D carbon-rich
| Cathode         | Modification strategy                  | Capacity [mAh g⁻¹ at A g⁻¹] | Capacity retention | References |
|-----------------|----------------------------------------|------------------------------|--------------------|------------|
| K₀.₂₅·MnO₂@CDY  | Protective layer                       | 520 at 0.055                 | 221 mAh⁻¹ at 550 mA g⁻¹ (150 cycles) | [25]       |
| MnO₂@CDYO       | Cathode substrate                      | 265.1 at 0.031, 253.7 at 0.308 | 77.6% at 1.5 A g⁻¹ (1000 cycles) | [24]       |
| FHG             | Direct zinc storage cathode             | 234 at 0.1                   | 98% at 10 A g⁻¹ (4000 cycles) | [35]       |
| rGO/PANI        | Conductive additive                    | 175.5 at 0.1                 | 94.6% at 1 A g⁻¹ (500 cycles) | [37]       |
| VN@rGO         |                                        | 267 at 1, 125.6 at 20        | 94.68% at 1 A g⁻¹ (585 cycles), 91.24% at 20 A g⁻¹ (10 900 cycles) | [38]       |
| P₃HT/V₂O₅/rGO  |                                        | ≈190 at 0.050 in the dark, ≈370 at 0.050 under light | ≈90% at 1 A g⁻¹ (1000 cycles, in the dark) | [39]       |
| V₂O₅/rGO       |                                        | 282 at 0.200 in the dark, 315 at 0.200 under light | 96% at 6 A g⁻¹ (500 cycles) | [40]       |
| MnO₃/rGO       |                                        | 332.2 at 0.3, 172.3 at 6     | 92% at 2 A g⁻¹ (4000 cycles) | [41]       |
| rGO/Sn3V₂O₇·nH₂O|                                        | 374.9 at 0.1                 | 94% at 5 A g⁻¹ (2000 cycles) | [42]       |
| rGO/NVO        |                                        | 410 at 0.1                   | 67% at 0.308 A g⁻¹ (500 cycles) | [43]       |
| MnO₂/EG        |                                        | 300 at 0.0616               | 78% at 2 A g⁻¹ (2000 cycles) | [44]       |
| MnO₂/rGO       |                                        | 317 at 0.1                   | 96% at 10 A g⁻¹ (4000 cycles) | [45]       |
| PANI/GO/CNT     |                                        | 233 at 0.1, 100 at 5         | 100 mAh⁻¹ at 3 A g⁻¹ (2500 cycles) | [46]       |
| Layered α-MnO₂  | Cathode substrate                      | 133 at 0.100, 85 at 0.500    | 133 mAh⁻¹ at 100 mA g⁻¹ (100 cycles) | [47]       |
| α-MnO₂·Mn₂O₃   |                                        | 322.1 at 0.2, 213.6 at 3     | 86.2% at 3 A g⁻¹ (1000 cycles) | [48]       |
| NVP/rGO        |                                        | 92 at 0.050, 60 at 2         | 64% at 50 mA g⁻¹ (150 cycles) | [49]       |
| Mn₃O₄/rGO      |                                        | 215.6 at 0.1                 | 85.0% at 1 A g⁻¹ (500 cycles) | [50]       |
| MnO₂/rGO       |                                        | 260 at 0.1                   | 98.8% at 500 mA g⁻¹ (1000 cycles) | [51]       |
| ZnMnO₃ NDs/rGO |                                        | 207.6 at 0.2                 | 113.7 mAh⁻¹ at 1 A g⁻¹ (400 cycles) | [52]       |
| V₂O₅/GO       |                                        | 525 at 0.1, 114 at 40        | 90.8% at 20 A g⁻¹ (10 000 cycles) | [53]       |
| 3DP-FeVO₄/rGO  |                                        | 344.8 at 0.1                 | 93.3% at 2 A g⁻¹ (650 cycles) | [54]       |
| V₂O₅/rGO       |                                        | 447 at 0.3, 202 at 30        | 83% at 30 A g⁻¹ (20 000 cycles) | [55]       |
| MnS/rGO        |                                        | 289 at 0.100, 62 at 1.000    | 70.8% at 1000 mA g⁻¹ (1000 cycles) | [56a]      |
| MnO/rGO/MWCNTs |                                        | 267.4 at 0.2                 | 96.2% at 0.5 A g⁻¹ (200 cycles), 94.7% at 1.2 A g⁻¹ (550 cycles) | [56b]      |
| γ-MnO₂/G       |                                        | 301 at 0.5, 95.8 at 10       | 64.1% at 20 mA cm⁻² (300 cycles) | [56c]      |
| ZnMnO₃/NG      |                                        | 221 at 0.100                 | 97.4% at 1000 mA g⁻¹ (2500 cycles) | [56d]      |
| ZnNiₓCoᵧMn₂₋ₓ₋ₓO₄@N- rGO |                       | 200.5 at 0.010          | 79% at 1000 mA g⁻¹ (900 cycles) | [56e]       |
| VS@rGO        |                                        | 450 at 0.5, 313.8 at 10      | ≈82% at 10 A g⁻¹ (1500 cycles) | [57a]      |
| rGO/VSe₂      |                                        | 238 at 0.1, 190 at 5         | 93% at 5 A g⁻¹ (1000 cycles) | [57b]      |
| VO₄/rGO       |                                        | 443 at 0.100, 174.4 at 100   | –                   | [57c]       |
| H₂V₂O₇/rGO    |                                        | 401 at 0.2, 170 at 2         | 73.3% at 2 A g⁻¹ (200 cycles) | [57d]      |
| CaVOH/rGO     |                                        | 409 at 0.05                  | 90% at 4.0 A g⁻¹ (2000 cycles) | [57e]      |
| O₂HVO/rGO     |                                        | 428.6 at 0.1, 186 at 20      | 197.5 mAh⁻¹ at 10 A g⁻¹ (2000 cycles) | [57f]     |
| VOG           |                                        | 423 at 0.25                  | 87% at 8 A g⁻¹ (1000 cycles) | [57g]      |
| FeVO₄·nH₂O@rGO |                                        | ≈300 at 0.2, first cycle     | 100 mAh⁻¹ at 1.0 A g⁻¹ (1000 cycles) | [57h]      |
| O₂V₂O₇·rGO    |                                        | 376 at 0.1, 116 at 20        | 88.6% at 10.0 A g⁻¹ (5000 cycles) | [57i]      |
| VOH·rGO       |                                        | 466 at 0.1, 190 at 20        | 100% at 10 A g⁻¹ (5000 cycles) | [57j]      |
| rGO/VSe₂      |                                        | 221.5 at 0.5                 | 91.6% at 0.5 A g⁻¹ (150 cycles) | [57k]      |
| Ag₂V₂O₇·H₂O@rGO |                                      | 437 at 0.170                | 72% at 2 A g⁻¹ (1000 cycles) | [57l]      |
| VS@rGO       |                                        | 180 at 1                     | 93.3% at 1 A g⁻¹ (165 cycles) | [57m]      |
| MnVOH/rGO     |                                        | 361 at 0.1, 323 at 2         | 80% at 0.1 A g⁻¹ (100 cycles) | [57n]      |
| V₁₀O₄·nH₂O@rGO-PVA |                                   | 533 at 0.1, 194 at 0.5      | 78% at 0.5 A g⁻¹ (300 cycles) | [57o]      |
| V₃O₇/rGO     |                                        | 275.6 at 1.0                 | 79.6% at 1.0 A g⁻¹ (200 cycles) | [57p]      |
Table 1. Continued.

| Cathode                                      | Modification strategy | Capacity [mAh g\(^{-1}\) at A g\(^{-1}\)] | Capacity retention References |
|----------------------------------------------|-----------------------|------------------------------------------|-------------------------------|
| V_{2}O_{5} nanobelts/rGO                    |                       | 113 at 1                                 | 135 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) (200 cycles) [57a] |
| LaVO/rGO                                    |                       | 298 at 0.3, 166 at 8                     | 88% at 1 A g\(^{-1}\) (6000 cycles) [57b] |
| NVO/rGO/CNT                                 |                       | 459.1 at 0.5, 352.5 at 10                | 83.1% at 10 A g\(^{-1}\) (1800 cycles) [57c] |
| rGO/n-NVO                                   |                       | 433.5 at 0.1, 244.1 at 5                 | 70.5% at 2 A g\(^{-1}\) (1000 cycles) [57d] |
| V_{2}O_{5}H_{2}O/rGO                        |                       | Power density of 8400 W kg\(^{-1}\) at 77 Wh kg\(^{-1}\) | 79% at 1500 mA g\(^{-1}\) (1000 cycles) [57e] |
| MoS_{2}/rGO                                 |                       | 108.3 at 5                               | 88% at 5 A g\(^{-1}\) (1000 cycles) [57f] |
| MoS_{2}/G                                   |                       | 285.4 at 0.05, 141.6 at 5                | 88.2% at 1 A g\(^{-1}\) (1800 cycles) [57g] |
| Na LDH+rGO                                  |                       |                                         | 80.1% at 2 mA cm\(^{-2}\) (1000 cycles) [57h] |
| POLA/G                                      |                       | 225 at 0.1, 152 at 20                    | 90% at 10 A g\(^{-1}\) (5000 cycles) [57i] |
| PONEA/G                                     |                       | 329 at 0.1, 277 at 20                    | 85% at 10 A g\(^{-1}\) (4000 cycles) [57j] |
| V_{2}O_{5}H_{2}O/rGO                        |                       | 410.7 at 0.5, 385.7 at 4                 | 99.6% at 4 A g\(^{-1}\) (1000 cycles) [57k] |
| Mn_{2}O_{3}/rGO                              |                       | 850.3 at 0.300                           | 125 mAh g\(^{-1}\) at 7000 mAh g\(^{-1}\) (5000 cycles) [57l] |
| α-MnO_{2}/rGO scroll                        | Protective layer       | 382.2 at 0.3                             | 94% at 3 A g\(^{-1}\) (3000 cycles) [57m] |
| MnO_{2}/C@CNWs                              |                       | 384 at 0.308                             | 108 mAh g\(^{-1}\) at 6.16 A g\(^{-1}\) (5000 cycles) [57n] |
| MnO@NGS                                     |                       | 288 at 0.1                               | 98% at 0.5 A g\(^{-1}\) (300 cycles) [57o] |
| β-MnO_{2}/rGO                               |                       | 278.2 at 0.308                           | ≈129.6 mAh g\(^{-1}\) at 1.23 A g\(^{-1}\) (2000 cycles) [57p] |
| MnO/C@rGO                                   |                       | 314.9 at 0.1                             | 170.6 mAh g\(^{-1}\) at 500 mA g\(^{-1}\) (300 cycles) [57q] |
| V_{2}O_{5}-rGO scroll                       |                       | 403.5 at 0.2, 380.4 at 2                 | 97% at 13 A g\(^{-1}\) (4 A g\(^{-1}\)) (1000 cycles) [58a] |
| H_{2}V_{2}O_{5} NW/G                        |                       | 394 at 0.100, 270 at 6.00                | 87% at 6000 mA g\(^{-1}\) (2000 cycles) [58b] |
| GO-CuO_{2}O                                 |                       | 427 at 0.1                               | 99.3% at 5 A g\(^{-1}\) (3000 cycles) [58c] |
| HAVO@G                                      |                       | 305.4 at 1, 180.6 at 10                  | 131.7 mAh g\(^{-1}\) at 2 A g\(^{-1}\) (400 cycles) [58d] |
| Na_{2}V_{2}O_{7}rGO                         |                       | 220 at 0.300                             | 84.8 mAh g\(^{-1}\) at 1 A g\(^{-1}\) (500 cycles) [58e] |
| rGO@HM-ZMO                                  |                       | 150 at 0.3                               | 72.7 mAh g\(^{-1}\) at 1 A g\(^{-1}\) (650 cycles) [58f] |
| 3D MnO\(_{2}\)Ns@GNSs                       |                       | 306.8 at 0.1                             | ≈97.5% at 2 A g\(^{-1}\) (10 000 cycles) [58g] |
| MnO_{2}@G film                              | Current collector      | ≈204 at 0.100                           | ≈89% at 4000 mA g\(^{-1}\) (2000 cycles) [58h] |
| ZOV@G foam                                  |                       | 280 at 0.1                               | 99% at 4 A g\(^{-1}\) (1000 cycles) [58i] |
| rGO/V_{2}O_{2} foam                         |                       | 280 at 0.1                               | 99% at 4 A g\(^{-1}\) (1000 cycles) [58j] |
| HTTCA/DA/G                                  |                       | 281 at 0.100                             | 100% at 100 mA g\(^{-1}\) (300 cycles) [58k] |
| MnO\(_{2}\)/NCA                              |                       | 275.8 at 0.1                             | 93.6% at 3 A g\(^{-1}\) (1000 cycles) [58l] |
| CH/PANI                                     |                       | 154 at 0.1                               | 80.5% at 5 A g\(^{-1}\) (6000 cycles) [58m] |
| MnO_{2}/GO@PANI                             |                       | 241.1 at 0.1                             | 82.7% at 1 A g\(^{-1}\) (600 cycles) [58n] |
| GA-MnO_{2}                                  |                       | 321 at 0.0616                            | 91% at 0.924 A g\(^{-1}\) (300 cycles) [58o] |
| GH-HHTP                                     |                       | 225 at 0.05                              | 90% at 10 A g\(^{-1}\) (7000 cycles) [58p] |
| PC/GH                                       |                       | 355 at 0.0500, 171 at 5.00               | 74.4% at 1000 mA g\(^{-1}\) (3000 cycles) [58q] |
| β-MnO_{2}/@VMC                              |                       | 302.8 at 0.5                             | >90% at 2 A g\(^{-1}\) (1000 cycles) [58r] |
| VG-MnO_{2}/PEDOT:PSS                        |                       | 367.4 at 0.5                             | 73.7% at 5.0 A g\(^{-1}\) (1000 cycles) [58s] |
| V_{2}O_{5}/VC/CC                            |                       | 370 at 0.2                               | 85% at 2 A g\(^{-1}\) (5000 cycles) [58t] |
| MnO_{2}/@VG@CC                              |                       | ≈80 at 2                                 | 80% at 2 A g\(^{-1}\) (300 cycles) [58u] |
| MnO_{2}/EC                                  |                       | 368 at 20 mA cm\(^{-2}\)                | 50% at 0.2 A g\(^{-1}\) (300 cycles) [58v] |
| Na:MnO_{2}/GCF                              |                       | 381.8 at 0.100                          | 188.0 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\) (1000 cycles) [58w] |
| HQTP-COF                                    | Direct zinc storage    | 276 at 0.125                             | 98% at 3750 mA g\(^{-1}\) (1000 cycles) [58x] |
| PA-COF                                       |                       | 247 at 0.1                               | 0.38% decay per cycle at 1.0 A g\(^{-1}\) (10 000 cycles) [58y] |
| HAQ-COF                                      |                       | 344 at 0.1                               | 85% at 5 A g\(^{-1}\) (10 000 cycles) [58z] |
| TCNQCCP                                     | Cathode substrate     | 171 at 1                                 | 134.3 mAh g\(^{-1}\) at 1 A g\(^{-1}\) (100 cycles) [58a] |

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| Cathode Material | Modification Strategy | Capacity [mAh g\(^{-1}\) at A g\(^{-1}\)] | Capacity Retention | References |
|------------------|------------------------|------------------------------------------|-------------------|------------|
| Cu\(_3\)(HHTP)\(_2\)-MOF | Direct zinc storage cathode | 228 at 0.050 | 75.0% at 4000 mA g\(^{-1}\) (500 cycles) | [101] |
| 2D MnO\(_2\)/PPy | Cathode substrate | 408 at 0.308 | 78% at 1.54 A g\(^{-1}\) (2800 cycles) | [102] |

### Table 2. Summary of AZIB anodes based on 2D carbon-rich materials.

| Anode | Modification Strategy | Coulombic Efficiency | Cycling Stability | References |
|-------|-----------------------|----------------------|-------------------|------------|
| Zn@HsCDY | Protective layer | \(\approx 100\%\) (50 000 cycles, full cell) | \(>2400\ h\) at 0.5–2 mA cm\(^{-2}\) | [24b] |
| Zn-N-GDY | >95% (\(\approx 200\) cycles) | \(>2000\ h\) at 2 mA cm\(^{-2}\) | [26] |
| Zn@GQD | Current collector | \(>99.86\%\) | = | [79] |
| Zn@VMG | – | 91.3% retention at 2.0 A g\(^{-1}\) (1000 cycles, full cell) | [76a] |
| Zn/N-VG@CC | >95% at 5 mA cm\(^{-2}\) | 150 cycles at 0.5 mA cm\(^{-2}\) | [76d] |
| Zn@G foam | \(\approx 95\%\) at 410 mA g\(^{-1}\) (full cell) | 280 cycles at 1 mA cm\(^{-2}\) | [75a] |
| Zn/EG | – | 67% retention at 820 mA g\(^{-1}\) (500 cycles, full cell) | [44] |
| Zn/GCF | \(\approx 100\%\) at 0.2 mA cm\(^{-2}\) | \(>100\ h\) at 0.2–1.0 mA cm\(^{-2}\) | [77b] |
| MXene/C@Zn | Mxene/C@Zn | \(\approx 99.67\%\) at 10 mA cm\(^{-2}\) (\(\approx 600\) cycles) | \(>1000\ h\) at 10 mA cm\(^{-2}\) | [81] |
| GSS | \(\approx 99.7\%\) at 3.2 mA cm\(^{-2}\) (\(>2000\) cycles) | \(>2000\) cycles at 3.2 mA cm\(^{-2}\) | [82] |
| PTCDI/rGO | \(\approx 100\%\) at 3000 mA g\(^{-1}\) (1500 cycles) | 96% retention at 3000 mA g\(^{-1}\) (\(>1500\) cycles) | [83] |
| NGO@Zn | Protective AIL | \(>99\%\) at 820 mA g\(^{-1}\) (\(\approx 600\) cycles, full cell) | \(>500\ h\) at 1 mA cm\(^{-2}\) | [84a] |
| PEDOT-PSS/GS@Zn | – | \(>98\%\) at 1 mA cm\(^{-2}\) (100 cycles) | \(>500\ h\) at 1 mA cm\(^{-2}\) | [84b] |
| Zn/N-GDY | >95% at 4100 mA g\(^{-1}\) (1000 cycles, full cell) | 200 cycles at 1–10 mA cm\(^{-2}\) | [57a] |
| Zn/C | \(\approx 100\%\) at 1 A g\(^{-1}\) (5000 cycles, full cell) | 300 h at 0.2–1 mA cm\(^{-2}\) | [86] |
| NGO@Zn | \(\approx 98.5\%\) at 820 mA g\(^{-1}\) (178 cycles, full cell) | 1200 h at 1 mA cm\(^{-2}\), 300 h at 5 mA cm\(^{-2}\) | [87] |
| COF@Zn | Protective AIL | \(>99.95\%\) at 2 A g\(^{-1}\) (300 cycles) | \(>420\ h\) at 1 mA cm\(^{-2}\) | [98] |
| Pi-COF | Direct zinc storage anode | – | 85% retention at 10 mV s\(^{-1}\) (\(>4000\) cycles) | [99] |

### Table 3. Summary of AZIB separators and electrolytes based on 2D carbon-rich materials.

| Role of 2D carbon-rich materials | Cathode | Capacity [mAh g\(^{-1}\) at A g\(^{-1}\)] | Cycling Performance | References |
|----------------------------------|---------|------------------------------------------|---------------------|------------|
| Separator | MnO\(_2\) | 300 at 0.308 | 93% at 3080 mA g\(^{-1}\) (2000 cycles, full cell) | [24a] |
| Separator | V\(_2\)O\(_3\) | 306 at 0.5 | 500 cycles at 5 mA cm\(^{-2}\) (zinc anode), 205 mA h g\(^{-1}\) at 8 A g\(^{-1}\) (750 cycles, full cell) | [27] |
| Separator | V\(_2\)O\(_5\) | 231 at 0.3 | 75% at 5 A g\(^{-1}\) (1000 cycles, full cell) | [88] |
| Separator | MnO\(_2\) | 307 at 0.308 | \(\approx 5500\ h\) at 0.25 mA cm\(^{-2}\) (Zn anode), 87.8% at 1.54 A g\(^{-1}\) (5000 cycles, full cell) | [89] |
| Separator | MnO\(_2\)/graphite | 214 at 0.1 | \(>1750\ h\) at 2 mA cm\(^{-2}\) & 400 h at 20 mA cm\(^{-2}\) (Zn anode), 95.3% at 1 A g\(^{-1}\) (800 cycles, full cell) | [90] |
| Separator | MnO\(_2\) | 126 at 0.1 | 500 cycles at 0.5–20 mA cm\(^{-2}\) (Zn anode), >75% at 0.5 A g\(^{-1}\) (500 cycles, full cell) | [91] |
| Electrolyte | MnO\(_2\) | 57 at 5 | \(>650\ h\) at 1 mA cm\(^{-2}\) (Zn anode), 93% at 5 A g\(^{-1}\) (250 cycles, full cell) | [92a] |
| Electrolyte | MnO\(_2\) | 284.8 at 0.2 (20°C), 225.8 at 0.2 (0°C), 183.2 at 0.2 (−20°C) | 95.0% at 0.2 A g\(^{-1}\) (100 cycles, full cell) | [92c] |
| Electrolyte | Ag\(_2\)O | 204.3 at 0.01 | – | [92d] |
| Electrolyte | Na\(_2\)V\(_2\)O\(_5\)-H\(_2\)O | 164.3 at 1 | 2200 h at 0.8 mA cm\(^{-2}\) (zinc anode), 68.03% at 1 A g\(^{-1}\) (600 cycles, full cell) | [92b] |
| Electrolyte | MnO\(_2\) | 196.0 at 0.6 | 73% at 0.6 A g\(^{-1}\) (800 cycles, full cell) | [100] |
Table 4. Summary of Properties of various 2D carbon-rich materials.

| Properties                  | Graphdiyne | Graphene | 2D COFs | 2D MOFs | 2D conductive polymers |
|-----------------------------|------------|----------|---------|---------|------------------------|
| Mechanical strength         | Good       | Good     | Good    | Good    | Varies                 |
| Flexibility                 |            |          | All the 2D carbon-rich materials possess good flexibility |
| Relative density            | Low        | Low      | Low     | Relatively high | Low                   |
| Conductivity                | Semiconductive | Conductive | Insulative | Conductive         |
| Specific surface area       |            |          | All the 2D carbon-rich materials possess large specific surface area |
| Porosity                    | Good       | Poor     | Good    | Good    | Good                   |
| Synthesis                   | Bottom-up coupling | Top-down and bottom-up (industrialized) | Bottom-up polymerization | Bottom-up polymerization | Bottom-up polymerization |
| Functionalization           | Top-down and bottom-up | Top-down | Bottom-up polymerization | Bottom-up | Bottom-up               |
| Cost                        | High       | Relatively low | Relatively high | Relatively high | Relatively high         |

Generally speaking, the surge of 2D carbon-rich materials in last few years has illustrated their capability of enhancing the overall performance of AZIBs. Nevertheless, researches of many 2D carbon-rich materials are still in the early stage. How to cope with the challenges like impreciseness of functionalized structures, inadequate use of their merits and complex synthetic procedure will dominate the evolution of 2D carbon-rich materials in next decade. We are pretty sure that future studies on these 2D carbon-rich materials will definitely impel the process toward advanced AZIBs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous zinc-ion batteries, crystalline porous polymers, graphdiyne, graphene, 2D carbon-rich materials

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