

Reduced Graphene Oxide (rGO)-Based Hybrid Materials as Cathodes in Aqueous Zinc-Ion Batteries: Recent Progress

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Abstract

The growing global energy demand and increasing environmental concerns have created the need for the development of efficient, safe, and sustainable energy storage technologies. While lithium-ion batteries (LIBs) have dominated the energy storage market due to their high energy density and long cycle life, concerns regarding lithium resource scarcity, high cost, and safety risks associated with flammable organic electrolytes have motivated research on alternative batteries. In this context, aqueous zinc-ion batteries (AZIBs) have attracted significant attention as a promising next-generation energy storage system because of their inherent safety, resulting from the utilization of non-flammable aqueous electrolytes, and environmental friendliness, as well as natural abundance and low cost of zinc. Nevertheless, they face various challenges, which hinder their practical applications. Among them, the intrinsic limitations of the cathode materials, including their poor electronic conductivity, sluggish reaction kinetics and structural degradation during charge–discharge cycles, are considered particularly significant. Thus, the scientific community has explored various mitigation strategies, including the combination of cathode materials with carbon-based nanomaterials, such as reduced graphene oxide (rGO), with exceptional physicochemical properties. The present critical review discusses the most recent scientific work published in the literature during the last three years, referring to the combination of rGO with conventional cathode materials, such as manganese-based oxides, vanadium-based oxides, Prussian blue analogues, etc., for the development of next-generation AZIBs with superior electrochemical performance, long-term cycling durability, intrinsic safety, and enhanced sustainability.

Keywords: reduced graphene oxide (rGO); hybrid materials; cathodes; aqueous zinc-ion batteries (AZIBs)

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1. Introduction

1.1. Energy Storage Technologies

Nowadays, the world is undergoing an unprecedented transformation driven by the escalating global population, urbanization and technological advancements. Energy is fundamental to modern society, supporting nearly every aspect of daily life, from portable electronics and electric vehicles to smart grids and large-scale industrial systems. As the global energy demand continues to rise alongside increasing environmental concerns, the transition toward sustainable and efficient energy systems has become a critical pri-

ority, particularly considering the aim of the EU to achieve climate neutrality by 2050 through net-zero greenhouse gas emissions [1]. Consequently, there has been a growing focus on research efforts toward renewable energy alternatives, such as solar and wind. However, the integration of renewable energy sources has introduced significant challenges, as their intermittent and inherently unpredictable nature results in a mismatch between energy supply and demand. This imbalance poses serious risks to grid stability and reliability. In this context, energy storage technologies play a pivotal role in ensuring the efficient capture, management, distribution, and utilization of energy, especially in systems that depend on renewable sources [2].

Energy storage technologies could be classified into several categories, according to different criteria, such as the type of the stored energy, the employed technology, their capacity as well as their final application [3]. Figure 1 presents the five main categories: i. mechanical, ii. thermal, iii. electromagnetic, iv. chemical and v. electrochemical energy storage. Briefly, mechanical energy storage (MES) is among the most attractive technologies, in terms of environmental impact, cost and sustainability, and refers to systems that store energy as motion or gravitational potential energy. MES could be classified into three main categories: flywheel energy storage systems (FESSs), which store energy by utilizing the rotation of a high-speed rotor, pumped hydro energy storage (PHES), where water is elevated to a higher reservoir and later released to generate electricity, and compressed air energy storage (CAES), which is based on storing the excess of energy underground in the form of compressed air [4]. Thermal energy storage (TES) technology involves heating or cooling of a medium (e.g., water, molten salts), allowing the excess thermal energy to be stored and utilized for heating, cooling, and electricity generation applications [5]. Electromagnetic energy storage (EMES) involves two main principles; the first is based on the separation of positive and negative electric charges, using capacitors/supercapacitors, while the second relies on the interactions between electrical and magnetic phenomena, resulting in energy storage in form of magnetic fields generated when direct current flows through a superconducting coil [6]. Moreover, chemical energy storage (CES) refers to the process of storing energy in the form of chemicals, such as gaseous fuels (e.g., hydrogen, ammonia), which could be later released through chemical reactions. Finally, electrochemical energy storage (ECES) involves reversible electrochemical reactions (redox) occurring within electrochemical cells; a prominent example is lithium-ion batteries (LIBs), which currently dominate the market and power applications ranging from small electronic devices to various types of electric vehicles [7].

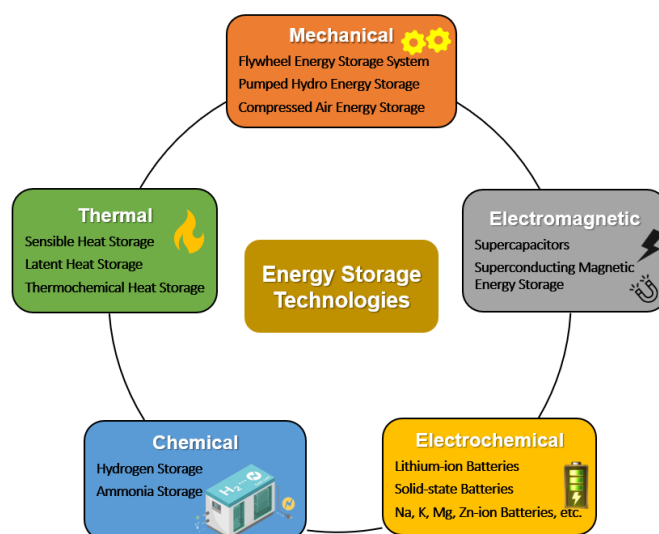


Figure 1. Schematic representation of the classification of energy storage technologies.

Undoubtedly, energy storage technologies play a crucial role in addressing the current challenges by enabling the efficient capture, storage, and supply of energy whenever and wherever it is required. Among them, batteries have emerged as central pillars of modern energy infrastructure. Their versatility, scalability, and compatibility with both small- and large-scale devices make them indispensable for a wide range of technological applications. In recent years, significant research efforts have been directed toward improving their performance in terms of energy density and lifetime, as well as safety and cost. Accordingly, the present review places particular emphasis on batteries, as the most widely adapted energy storage technology, and explores their evolution, performance characteristics, and the most recent advances in the following sections.

1.2. Batteries: From Early Development to Modern Advances

To begin with, any device which converts chemical energy into electrical energy using oxidation–reduction (redox) reactions of its active materials, known as electrodes, is called a battery. Batteries are generally classified into two main categories: i. primary batteries, which are non-rechargeable electrochemical cells, and ii. secondary batteries—rechargeable electrochemical cells in which the redox reactions can be reversed by applying an external electrical current.

The history of battery development began in 1800 when Alessandro Volta (Figure 2a) invented the voltaic pile, which is considered the first true battery. The device consisted of alternating discs of zinc (Zn) and either copper (Cu) or silver (Ag) separated by cloth soaked in saltwater, producing a continuous electric current. The invention of Volta marked a major breakthrough in the study of electricity and laid the foundation for modern electrochemical energy storage systems [8]. In the following years, significant improvements were made in battery technology, including the development of the Daniell cell (Figure 2b) in 1836 by John Frederic Daniell. The Daniell cell, consisting of Zn and Cu electrodes, immersed in zinc sulfate (ZnSO_4) and copper sulfate (CuSO_4) solutions, respectively, with the two electrolytes connected through a salt bridge, provided a more stable and reliable source of electricity, which was used for practical applications of the 19th century, such as telegraph systems. In 1859, Gaston Planté introduced the first rechargeable lead–acid battery (Figure 2c), composed of spiral-wound lead plates, separated by rubber strips, in a vessel of sulfuric acid [9]. A few years later, in 1866, Georges Leclanché used for the first time an oxide (manganese oxide, MnO_2) as one of the electrodes in the Leclanché cell (Figure 2d). A fundamental shift in battery design was achieved in 1899, when Waldemar Jungner used potassium hydroxide (KOH) solution as the electrolyte (Figure 2e), as opposed to acidic electrolytes used until then with nickel (Ni) and cadmium (Cd) electrodes, giving birth to alkaline batteries. Today, lithium (Li)-ion batteries (LIBs) dominate a wide range of applications, ranging from smartphones to electric vehicles. The potential of Li electrodes had already been explored as early as 1913 by Gilbert N. Lewis (Figure 2f) [8]. In 1976 a major breakthrough was achieved with the development of the first rechargeable Li-ion battery by Stanley Whittingham [10]. Subsequent research during the 1980s by John B. Goodenough [11], who introduced lithium cobalt oxide (LiCoO_2) as a high-energy cathode material, and Akira Yoshino [12], who used a carbonaceous anode, further advanced Li-ion technology, ultimately leading to its commercialization by Sony in 1991. Despite their widespread commercialization, LIBs face several challenges including limited resources, high cost, safety risks related to their high toxicity and flammability of their components, as well as environmental concerns associated with mining and recycling processes. Simultaneously, the growing demand for efficient, safe and environmentally sustainable batteries, driven by the global push for cleaner energy, has stimulated intensive research into alternative systems, such as potassium-ion batteries (KIBs), so-

dium-ion batteries (NIBs), magnesium-ion batteries (MIBs), aluminum-ion batteries (AIBs), and zinc-ion batteries (ZIBs) [13].

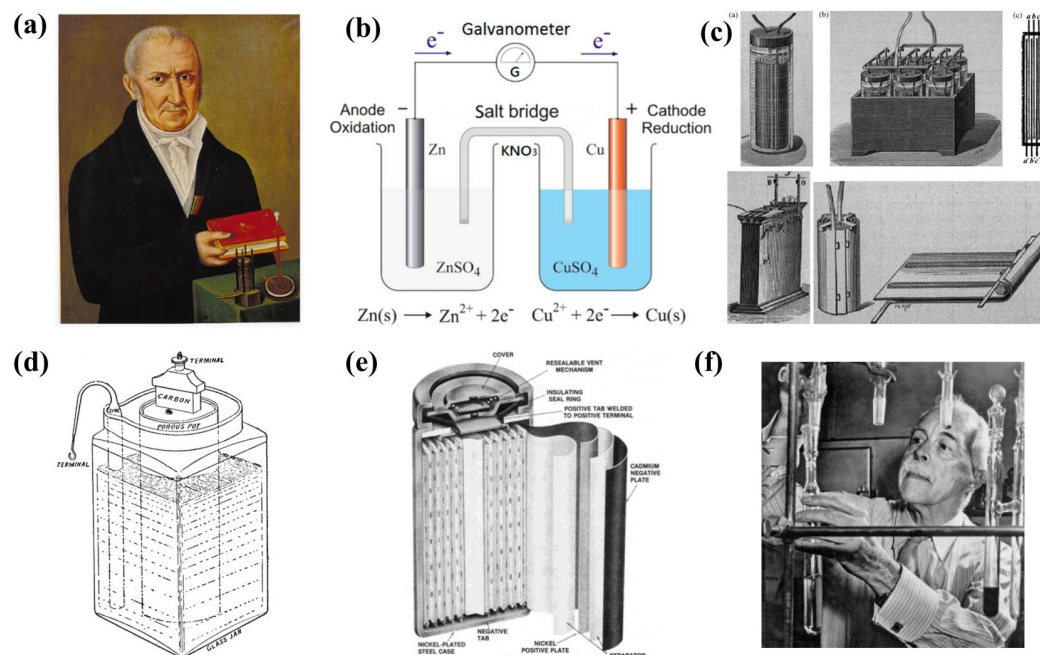


Figure 2. (a) Alessandro Volta, who invented the voltaic pile in 1800. (Adapted with permission by [8]). (b) The Daniel cell developed in 1836. (Adapted with permission by [14]). (c) The first rechargeable battery developed in 1859 by Gaston Planté. (Adapted with permission by [9]). (d) The Leclanché cell (1866) is composed of metal oxide as one of the electrodes. (Adapted with permission by [8]). (e) The utilization of KOH as electrolyte in Ni-Cd batteries was reported for the first time in 1899. (Adapted with permission by [15]). (f) Gilbert N. Lewis investigated the potential of Li electrode in 1913, laying the foundation for the development of modern lithium-based batteries. (Adapted with permission by [8]).

Among the various post-lithium batteries, zinc (Zn)-based systems have attracted particular attention owing to the favorable characteristics of metallic Zn. More specifically, Zn possesses a remarkable theoretical volumetric capacity of $5.855 \text{ mAh}\cdot\text{cm}^{-3}$, which is two times higher than that of Li, low redox potential (-0.76 V vs. standard hydrogen electrode (SHE)), low cost, natural abundance (300 times higher compared to Li), as well as good insensitivity to oxygen and a humid atmosphere [16,17]. ZIBs could be generally classified into: alkaline Zn batteries, where Zn–air batteries, Zn–flow batteries, and aqueous Zn-ion batteries (AZIBs), depending on the electrolyte chemistry, electrochemical reaction mechanism, and cell configuration. Among these systems, AZIBs have recently attracted significant research interest and have been considered as promising alternatives to conventional LIBs, due to their unique properties, such as high intrinsic safety and environmental friendliness. Although the development of AZIBs originated in 1988 when Shoji et al. [18,19] reported the first rechargeable aqueous Zn– MnO_2 battery, using a mild neutral or slightly acidic electrolyte (aqueous ZnSO_4), the research interest in AZIBs has experienced remarkable growth since 2015, driven by the increasing demand for safe, sustainable and cost-effective energy storage technologies. Notably, a basic search on Scopus on the “AZIBs” topic generates a record of more than 8500 papers published during the past decade (2015–2025) (Figure 3), highlighting the growth of research activity and the rapid emergence of AZIBs as a highly competitive technology for electrochemical energy storage.

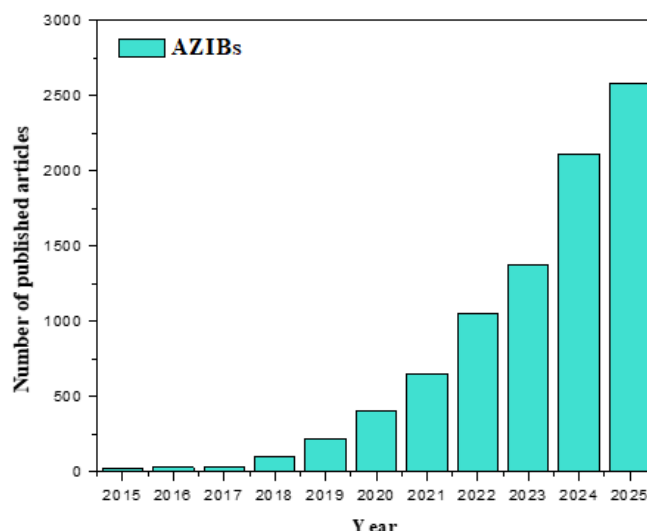


Figure 3. Number of publications in Scopus between 2015 and 2025 on “AZIBs” topic.

1.3. Scope and Structure

AZIBs represent an emerging technology that has not yet been commercialized and remains in the early stages of research and development. Despite their advantages, AZIBs face various challenges which inhibit their practical applications; the intrinsic limitations of cathode materials, including their poor electronic conductivity and structural instability have been considered among the most critical challenges [20]. Therefore, several strategies have been proposed in the literature so as to overcome these drawbacks and develop cathode materials for AZIBs with high efficiency and long-term cycling stability. The aim of this review is to present the most recent advances in cathode materials engineering, with a particular focus on hybrid architectures based on reduced graphene oxide (rGO) (Figure 4). To the best of our knowledge, this is the first review article which systematically and exclusively focuses on the multi-functional role of rGO in cathode engineering of AZIBs. More specifically, emphasis is placed on the synthesis strategies of rGO-based hybrid cathodes, the correlation between material design and electrochemical performance, and the underlying mechanisms by which the rGO integration can effectively mitigate the intrinsic limitations of conventional cathode materials, thereby enhancing the overall electrochemical performance of AZIBs.

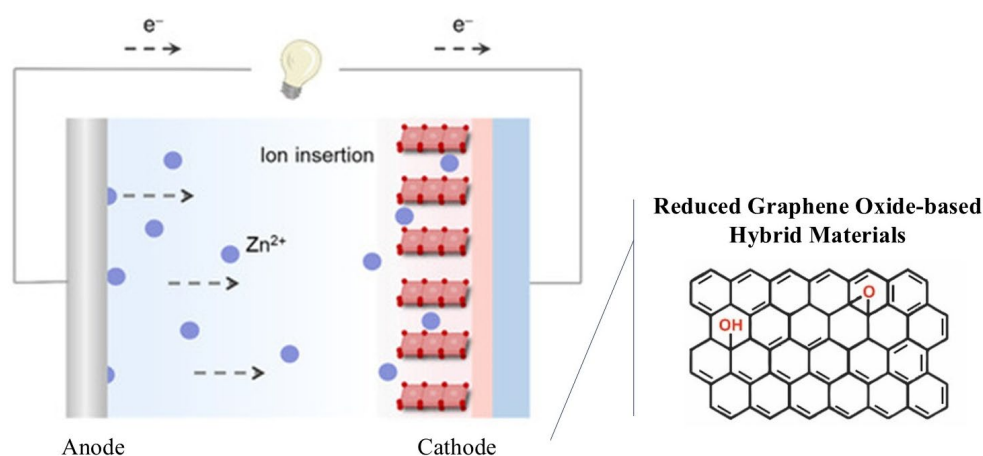


Figure 4. Schematic representation of rGO-based architectures as cathode materials in AZIBs. (Adapted with permission by [21,22]).

Regarding the structure of the present review, it is considered essential to first introduce the fundamentals of AZIB technology, including an overview of the key components—electrodes, electrolyte, and separator—from a materials science perspective, as well as the underlying Zn^{2+} storage and reaction mechanisms. Subsequently, the structural and physicochemical properties of rGO are presented, followed by a comprehensive discussion on the various categories of rGO-based hybrid materials and their application as cathodes in AZIBs. Finally, future perspectives and key challenges in the development of rGO-based cathode materials for next-generation AZIBs are critically discussed.

2. Fundamentals of Aqueous Zinc-Ion Batteries

2.1. Overview of Electrodes, Electrolyte and Separator

Rechargeable AZIBs consist of three fundamental components: i. the electrodes (cathode/anode), ii. the electrolyte, and iii. the separator—each of which plays a critical role in the overall battery performance. From a materials science perspective, the functionality and limitations of AZIBs are intrinsically linked to the physicochemical properties of these components.

To begin with, metallic Zn serves as the anode in AZIBs, undergoing repeated electrochemical plating and stripping of Zn^{2+} ions during cycling. As indicated above, Zn exhibits various advantages such as high theoretical capacity, appropriate redox potential, natural abundance, low cost, environmental friendliness, and non-toxicity. Nevertheless, the Zn anode undergoes a series of side reactions (Figure 5a) caused by active water molecules at the anode–aqueous electrolyte interface [23]. Dendrite formation (Figure 5b) is among the major challenges associated with Zn anodes, which could be attributed to the non-uniform electric field distribution and the inhomogeneous ion concentration on the surface of the anode, leading to internal short circuits, capacity fading, and safety hazards [24]. Hydrogen evolution reaction (HER) is also one of the primary side reactions which degrades the electrochemical performance of AZIBs. HER could be mainly assigned to the thermodynamic instability of the Zn anode within the aqueous electrochemical system, as the redox potential of Zn/Zn^{2+} is more negative than the reduction potential of water (Figure 5c). More specifically, HER is a multi-step process: first the water molecules undergo a weak ionization to generate hydrated protons (H_3O^+), which migrate from the electrolyte to the electrode interface and gain electrons, resulting in the reduction and the formation of adsorbed hydrogen intermediates (H^*), which are eventually released as H_2 gas [25]. Self-corrosion phenomena also occur when Zn is immersed into the aqueous electrolyte, leading to the accumulation of a structurally unstable solid electrolyte interphase (SEI), which further exacerbates corrosion processes [26]. Similarly, surface passivation consumes electrolyte and generates insulating by-products onto the surface of the anode, thereby deteriorating Zn^{2+} transport kinetics and reducing electrochemical efficiency [27, 28]. Consequently, overcoming these interfacial and parasitic side reactions remains a critical prerequisite for the practical application and long-term stability of AZIB systems.

Furthermore, the choice of cathode material plays a critical role in the development of high-performance AZIBs. An ideal cathode should exhibit high specific capacity, fast ion diffusion kinetics, good electronic conductivity, structural stability during repeated cycling, as well as long-term electrochemical durability. In general, cathode materials could be divided into: i. manganese (Mn)-based materials, ii. vanadium (V)-based materials, iii. Prussian blue analogues (PBAs), iv. organic compounds, such as conductive polymers, and v. other materials, including chalcogenides, other metal oxides, etc. (Figure 5d). It is worth mentioning that the pursuit of enhanced electrochemical performance has emphasized the importance of understanding how the structural properties of the cathode affect the overall behavior of the battery (Figure 5e). For instance, tunnel-type architectures facilitate rapid Zn^{2+} transport through well-defined diffusion channels; however, lat-

tice distortion and transition metal dissolution may compromise long-term structural stability and cycling performance. In addition, cathode materials with a layered structure enable Zn^{2+} storage via interlayer intercalation and multi-valent redox activity, but they often suffer from structural collapse and by-product formation during cycling. Despite their excellent ionic conductivity and cycling stability because of their porous 3-D structure, open-framework architectures exhibit low electronic conductivity and low redox site density, leading to restricted overall capacity. Moreover, organic structures offer significant advantages, including tunable redox activity and fast kinetics, yet suffer from poor structural integrity in the aqueous media [29]. Thus, various strategies have been proposed in the literature in order to overcome these drawbacks, including intercalation of pillars [30,31], doping [32] and defect engineering [33], as well as the development of hybrid materials [34].

The electrolyte plays a key role in charge and electron transfer between cathode and anode. Thus, its chemical composition and structure could effectively improve the electrochemical performance of AZIBs. Aqueous electrolytes of AZIBs could be classified into three main categories: i. inorganic salt electrolytes, such as the widely employed zinc sulfate (ZnSO_4), ii. organic salt electrolytes, including zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$) and iii. hybrid electrolytes, combining different mixtures of the aforementioned types. As is known, aqueous electrolytes possess several advantages, such as high ionic conductivity, non-flammability, environmental friendliness, and low cost. Nevertheless, various challenges remain, arising from the complex interactions occurring at the electrode/electrolyte interface, leading to numerous undesired reactions on the Zn anode, as well as cathode dissolution [35,36]. Additionally, it is important to note that the freezing of the aqueous electrolytes at sub-zero temperatures is also a major obstacle for the practical application of AZIBs [37]. Consequently, the rational design of electrolyte systems has been considered crucial for the stability of electrodes and the enhancement of the overall battery performance, under wide temperature conditions. On this basis, various optimization approaches such as pH adjustment, incorporation of additives (Figure 5f), hydrogel formation, etc. have been extensively investigated [38,39].

Finally, the separator is also an essential component of AZIBs, playing the role of a physical barrier between the electrodes, while accommodating the electrolyte and enabling efficient Zn^{2+} ion transport [40]. Although the separator is not electrochemically active in AZIBs, it should satisfy various fundamental structural and physicochemical requirements in order to ensure safe and stable battery operation. More specifically, an ideal separator should exhibit appropriate porosity and homogeneous pore size distribution, so as to promote uniform Zn^{2+} ion migration within the electrolyte, as well as excellent mechanical properties, including high tensile strength and flexibility. Furthermore, the separator should possess superior electrical insulation properties to suppress internal short circuits and self-discharge. Beyond these characteristics, wettability is also essential for sufficient electrolyte uptake and retention. Similarly, chemical stability of the separator is a critical parameter to endure oxidative and reductive conditions and prevent side reactions. In order to fulfill these demanding criteria, various materials have been investigated. Among them, glass fiber (GF) separators have been widely employed in different battery systems due to their unique properties, such as high ionic conductivity, excellent electrolyte wettability, and favorable pore structure [41]. In recent years, non-GF separators (Figure 5g), including natural and synthetic polymers, have also attracted considerable attention because of the micron-level thickness and enhanced mechanical properties [42].

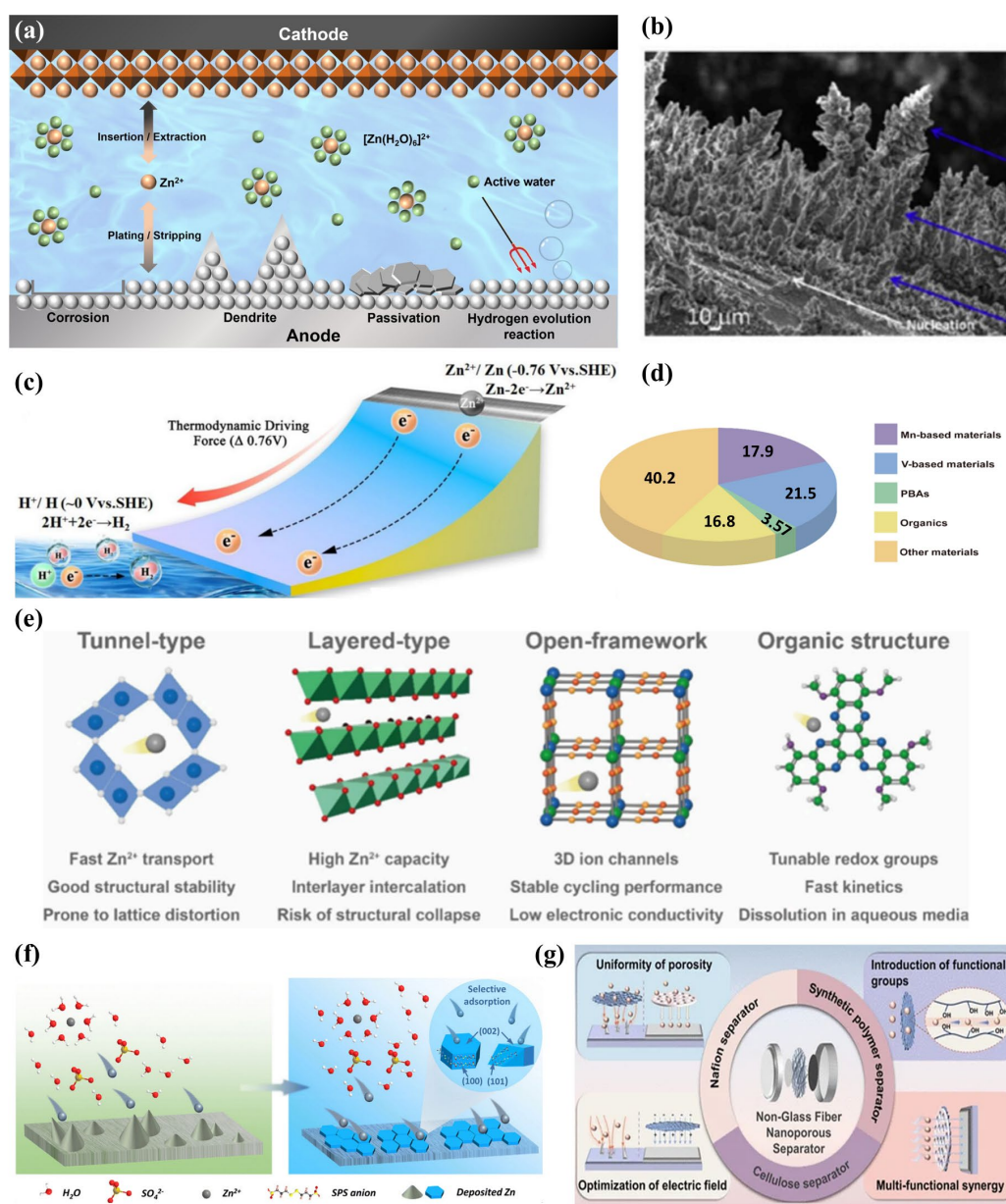
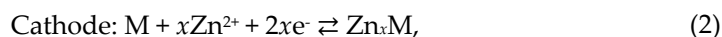


Figure 5. (a) Schematic representation of side reactions occurring on the Zn anode, resulting in the decrease in the overall performance of AZIBs. (Adapted with permission by [28]). (b) SEM image of dendrite formation. (Adapted with permission by [24]). (c) Thermodynamic instability of the Zn anode resulting in HER. (Adapted with permission by [25]). (d) Percentage of publications on AZIB cathode materials, based on data collected from Clarivate Web of Science in April 2025. (e) Schematic illustration of the structure–properties relationships of AZIB cathode materials. (Adapted with permission by [29]). (f) Schematic representation of the incorporation of the sodium 3,3'-dithiodipropionate (SPS) additive into the ZnSO_4 aqueous electrolyte, which effectively mitigates Zn dendritic growth. (Adapted with permission by [39]). (g) Schematic illustration of the recent progress in separator materials for AZIBs. (Adapted with permission by [42]).

2.2. Zn^{2+} Storage and Reaction Mechanisms

Following the discussion of the main components of AZIBs, a clear understanding of the fundamental Zn^{2+} storage and electrochemical reaction mechanisms is of great importance. To begin with, the primary energy storage process in AZIBs relies on the reversible intercalation and deintercalation of Zn^{2+} ions within the lattice of the host material (Figure 6), similar to traditional LIBs. More specifically, during discharging, anodic Zn is

dissolved into the aqueous electrolyte to yield Zn^{2+} ions, which are inserted into the crystal structure of the cathode material. Simultaneously, the cathode material undergoes a reduction process through electron uptake. Upon the subsequent charging process, Zn^{2+} ions, driven by the electric field, are extracted from the cathode, which is oxidized to restore charge neutrality [43,44]. The above process could be described through the following reaction equations:



where M is the cathode material. Nevertheless, variations in cathode structures and electrolyte compositions, as well as interfacial phenomena, result in diverse electrochemistry at the cathode site, affecting the overall battery performance [43,45]. Therefore, the energy storage mechanism of AZIBs is complicated and in some cases controversial.

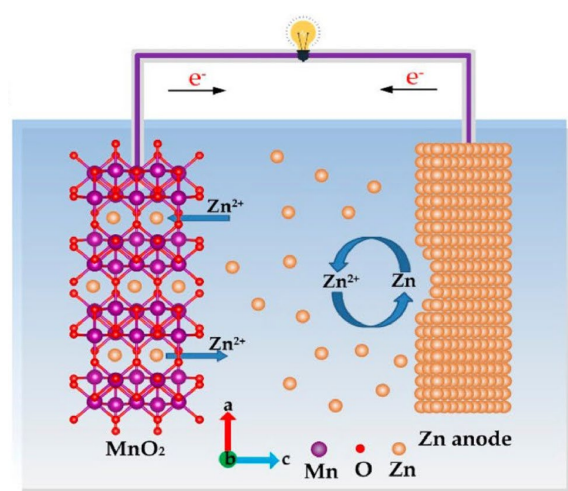


Figure 6. Schematic representation of Zn^{2+} ion intercalation/deintercalation mechanism within the crystal structure of the cathode. (Adapted with permission by [43]).

Beyond the Zn^{2+} insertion/extraction mechanism, the $\text{H}^+/\text{Zn}^{2+}$ co-intercalation mechanism could also take place (Figure 7). Sun et al. [46] confirmed the co-insertion/extraction process of H^+ and Zn^{2+} within the cathode material (MnO_2), via electrochemical and structural analysis. More specifically, the discharge galvanostatic intermittent titration technique (GITT) was performed to study the electrochemical kinetics, providing insights into both charge transfer and ion diffusion processes. The discharge profile of the cathode (Figure 8a) exhibited two distinct voltage plateaus. The former (region I) is associated with a 0.08 V total overvoltage, indicating rapid ion transport and low charge transfer resistance. In contrast, the latter (region II) shows a significantly higher overvoltage of 0.6 V, arising from both large voltage jump and slow ion diffusion within the MnO_2 lattice, despite its equilibrium voltage being only slightly lower than that of region I. The origin of the two voltage plateaus was further clarified by electrochemical impedance spectroscopy (EIS). EIS measurements performed at different states of charge within regions I and II (Figure 8b) revealed that the ohmic resistance is similar across both plateaus. However, the charge transfer resistance and ion diffusion resistance are higher in region II. This could be attributed to the nature of the inserted ions; the smaller H^+ ions dominate insertion in the low overvoltage of region I, enabling faster reaction kinetics, while in region II the insertion of larger Zn^{2+} ions occurs at higher overvoltage, leading to slower diffusion and increased charge-transfer resistance. In addition, the structure of the cathode after discharging was evaluated via XRD analysis and the results (Figure 8c) showed the presence of

MnOOH and ZnMn_2O_4 , confirming the H^+ insertion followed by the subsequent Zn^{2+} insertion. Furthermore, the co-insertion/extraction of Zn^{2+} ions and H_2O molecules has also been reported in various studies, suggesting that the water molecules result in the mitigation of charge repulsion between Zn^{2+} ions and the cathode material [45]. In contrast to the previously reported mechanisms, Zn^{2+} ions may not be inserted into the cathode. The dissociation of H_2O in the electrolyte generates H^+ and OH^- , with H^+ ions inserting first because of their rapid kinetics. Simultaneously, the increased concentration of OH^- in the electrolyte promotes reactions with Zn^{2+} species, forming Zn-based by-products, such as $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$. Compared to other mechanisms, the H^+ insertion/extraction contributes to improved cycling performance [44].

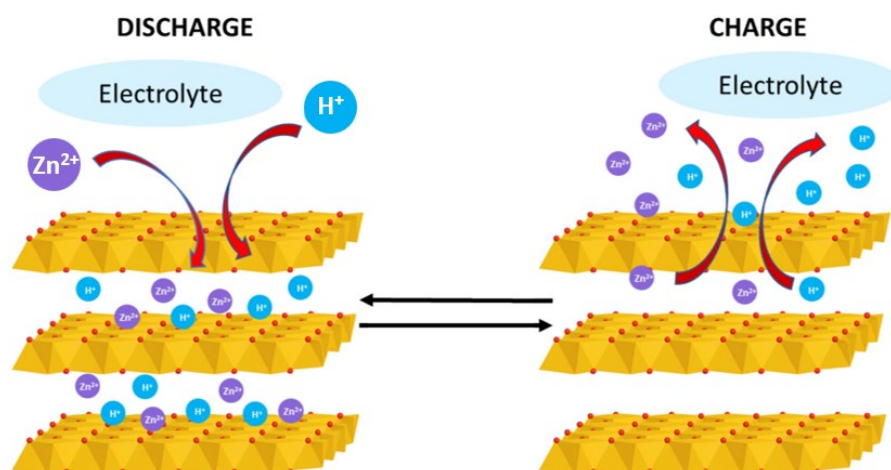


Figure 7. Schematic representation of $\text{H}^+/\text{Zn}^{2+}$ co-intercalation mechanism within the crystal structure of the cathode in AZIBs. (Adapted with permission by [47]).

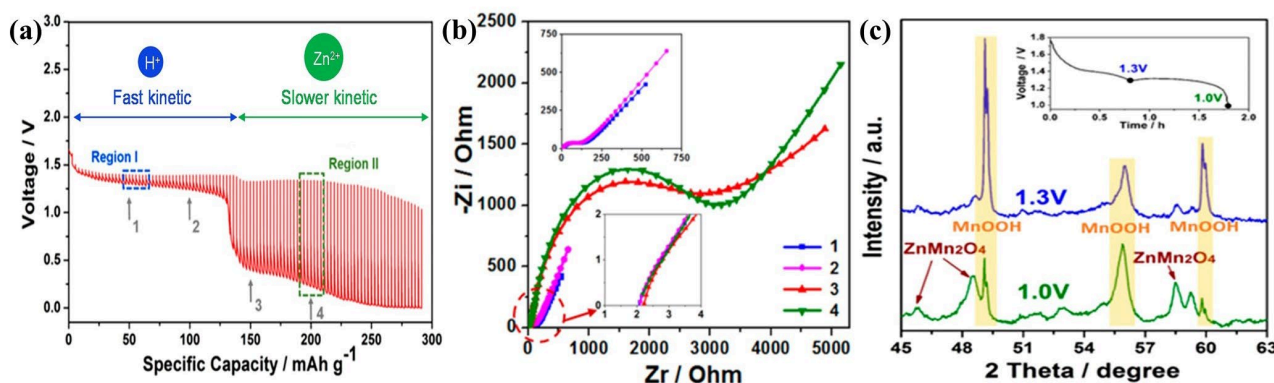


Figure 8. (a) GITT curve illustrating the electrochemical behavior of Zn/MnO₂ battery. (Adapted with permission by [45]). (b) EIS and (c) Ex situ XRD analysis of the cathode at discharge voltages of 1.3 and 1.0 V. (Adapted with permission by [46]).

The conversion reaction mechanism represents a distinct category of charge storage mechanisms in AZIBs, accompanied by chemical transformation during cycling rather than ion insertion into a stable host lattice. In contrast to the intercalation-type mechanism, it could deliver a flat discharge/charge plateau and endow a decent rate capability; thus, it is considered a promising and effective method for the fabrication of high-performance AZIBs [44]. A conversion-type mechanism, relying on protonation/deprotonation (Figure 9), was first presented by Pan et al. [48], where a reaction between H^+ protons and the cathode material (MnO_2) was reported, leading to the formation of a new MnOOH phase,

accompanied by the precipitation/dissolution of zinc hydroxide sulfate. However, it is similar to the H^+ insertion/extraction process that was previously discussed [49].

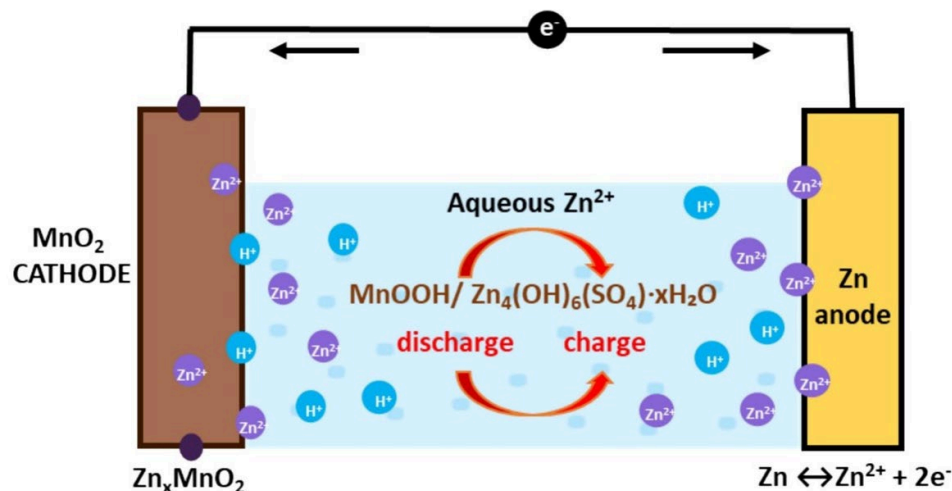
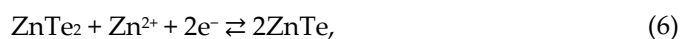


Figure 9. Schematic representation of the conversion mechanism in AZIBs. (Adapted with permission by [47]).

To date, numerous studies on AZIBs have reported the redox-couple conversion mechanism, which could be generally described by the following equation:



where $X = I, Br, S, Se, Te$, etc. and $a = 1$ or 2 [50]. For instance, Chen et al. [51] reported for the first time a ZnTe conversion-type aqueous battery, operating via a two-step solid-to-solid conversion process (Figure 10a). The Zn^{2+} storage mechanism was investigated through ex situ XRD of the cathode material (Te). Upon discharging to 0.61 V, the diffraction peaks of Te were slightly shifted due to Zn^{2+} diffusion. Through the continuous discharge process to 0.56 V, diffraction peaks attributed to zinc ditelluride ($ZnTe_2$) were detected. After being fully discharged to 0.2 V, the characteristic peak of (400) of zinc telluride (ZnTe) is noticed, while no peaks corresponding to $ZnTe_2$ are observed. During the charging process, ZnTe is first converted to $ZnTe_2$ and then to Te. This process could be summarized as below:



Moreover, the voltage response in GITT measurement is presented in Figure 10b. As it is observed, the total overvoltage in region I is larger in comparison with region II. This is attributed to the large voltage jump and slow ion diffusion, suggesting the phase transition. Notably, EIS curves measured at various states of charge within regions I and II (Figure 10c) are consistent within the same region, whereas those from different regions show noticeable differences, primarily in the ohmic resistance. As a result, different compositions are formed during region I and region II, further confirming the conversion reaction mechanism.

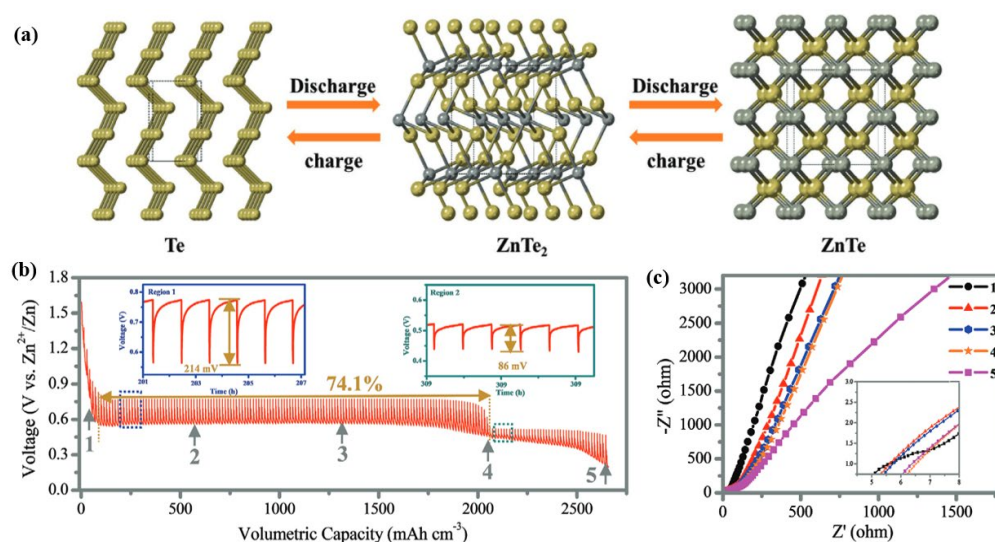
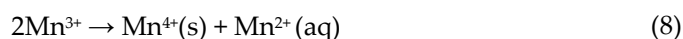


Figure 10. (a) Conversion-type mechanism in ZnTe batteries, forming new phases (ZnTe₂ and ZnTe). (b) GITT curve of ZnTe battery and (c) the corresponding EIS curves at different depths of discharge as indexed by (1–5) arrows in (b). (Adapted with permission by [51]).

In addition to ion intercalation and conversion reaction mechanisms, dissolution/deposition (Figure 11a) is another important mechanism in AZIBs, which was first reported by Lee et al. [52]. As was revealed by XRD analysis, a zinc hydroxide sulfate ($\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 5\text{H}_2\text{O}$) layer was formed on the surface of the cathode material (MnO_2). This was attributed to the formation of Mn^{3+} , which is unstable due to its high-spin electronic configuration ($d^4 = t_{2g}^3 e_g^1$). As a result, it undergoes disproportionation, according to the following equation:



This leads to the increase in Mn^{2+} concentration in the electrolyte, and a gradual rise of pH value, until the precipitation of $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 5\text{H}_2\text{O}$. During charging, the pH value of the electrolyte decreases and Mn^{2+} ions are recombined on the cathode, resulting in the dissolution of $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 5\text{H}_2\text{O}$. Figure 11b shows that, at the end of the discharge, the concentration of Mn^{2+} reaches a maximum, while the concentration of Zn^{2+} is decreased to a minimum. It is also observed that the process is reversible, as the ion concentrations recover their initial values upon charging.

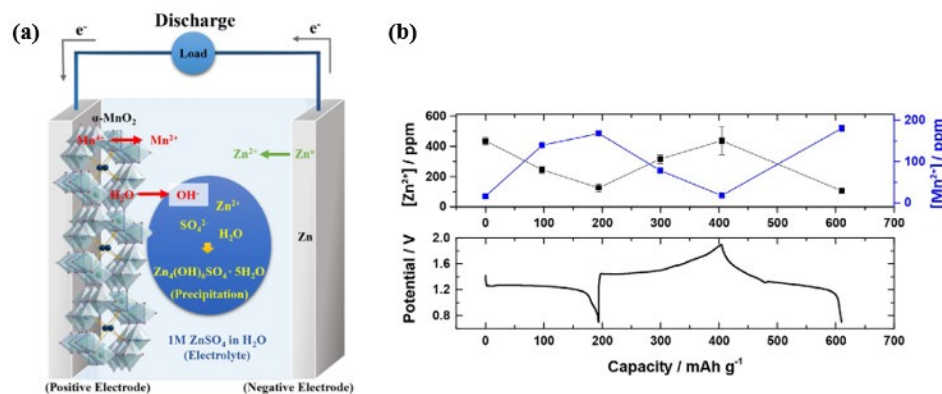


Figure 11. (a) Schematic representation of the dissolution/deposition mechanism in AZIBs. (b) Zn and Mn contents in the electrolyte and discharge–charge curve for the Zn/MnO₂ cell. (Adapted with permission by [52]).

Overall, the coexistence of the aforementioned mechanisms (intercalation, co-insertion, conversion and dissolution/deposition) highlights the complexity of Zn^{2+} storage chemistry in AZIBs and underscores the need for advanced in situ techniques not only to fully elucidate reaction pathways but also to optimize the electrochemical performance of the batteries.

3. Reduced Graphene Oxide (rGO)-Based Hybrid Materials as Cathodes in AZIBs

3.1. The Basics of rGO: Structure and Physicochemical Properties

As discussed earlier, the cathode materials used in AZIBs possess several intrinsic limitations that hinder their electrochemical performance and, consequently, the overall efficiency of the battery. To address these challenges, the development of reduced graphene oxide (rGO)-based cathodes has recently attracted considerable attention. Therefore, prior to the discussion of the latest advances in rGO-based cathodes, it is essential to first introduce the structure and physicochemical characteristics of rGO.

In general, carbon-based nanomaterials, such as zero-dimensional (0-D) fullerenes [53] and carbon dots [54], one-dimensional (1-D) carbon nanotubes [55] and two-dimensional (2-D) graphene [56], as well as its derivatives (graphene oxide and reduced graphene oxide), have garnered significant attention across critical domains, including energy [57,58], environmental science [59,60], and biomedicine [61], due to their unique physicochemical properties. Graphene, a 2-D monoatomic layer of sp^2 carbon atoms arranged in a hexagonal honeycomb lattice structure, is known as the mother of all sp^2 carbon-based nanomaterials, presenting superior mechanical, electronic, optical and thermal properties, as well as chemical inertness and large specific surface area. More specifically, graphene exhibits a Young's modulus of 1 TPa and an intrinsic strength of 130 GPa, making graphene among the strongest materials on Earth. Simultaneously, it possesses exceptional electron mobility at room temperature ($250,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), excellent optical transmittance ($\sim 98\%$) and high thermal conductivity ($5300 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). In addition, due to its sp^2 structure and delocalized π -electrons, graphene exhibits increased resistance toward chemical attack and corrosion. Furthermore, it presents a large theoretical specific surface area of $2630 \text{ m}^2 \cdot \text{g}^{-1}$ [62]. Since its discovery in 2004, graphene has attracted tremendous research interest across a broad range of technological fields. However, the scalability and the high cost of graphene production remain critical concerns, posing significant challenges to its large-scale manufacturing and commercial adoption.

Beyond graphene, graphene oxide (GO) and reduced graphene oxide (rGO) (Figure 12) have also played a key role in recent decades, because of their interesting properties, the cost-effectiveness and scalable production, compared to graphene. GO consists of graphene sheets decorated with abundant oxygen-containing functional groups (e.g., $-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{C}-\text{O}-\text{C}$), located on both the basal plane and sheet edges, which are introduced during graphite oxidation processes, including the widely employed Hummer's method [63]. The introduction of the oxygen-based functionalities disrupts the delocalized π -electron network of graphene, resulting in the increase in structural defects and enhanced hydrophilicity, while decreasing the electrical conductivity. Notably, the reduction of GO towards rGO via thermal or chemical routes [64,65] offers a feasible and low-cost approach for graphene production. More specifically, during the GO reduction process, the carbon hybridization gradually changes from sp^3 to sp^2 , resulting in the partial restoration of the aromatic π -conjugated structure. Therefore, the electronic properties of rGO are significantly improved, compared to GO, while it retains a number of defects, as well as oxygen-based functional groups, which increase its hydrophilicity. Overall, the unique combination of high electrical conductivity (approximately $6300 \text{ S} \cdot \text{cm}^{-1}$) [66], excellent mechanical properties [67], large specific surface area [68], increased hydrophilic

nature [69] and, most notably, its cost-effective and scalable production compared to graphene renders rGO an attractive candidate for numerous technological fields, including energy storage applications.

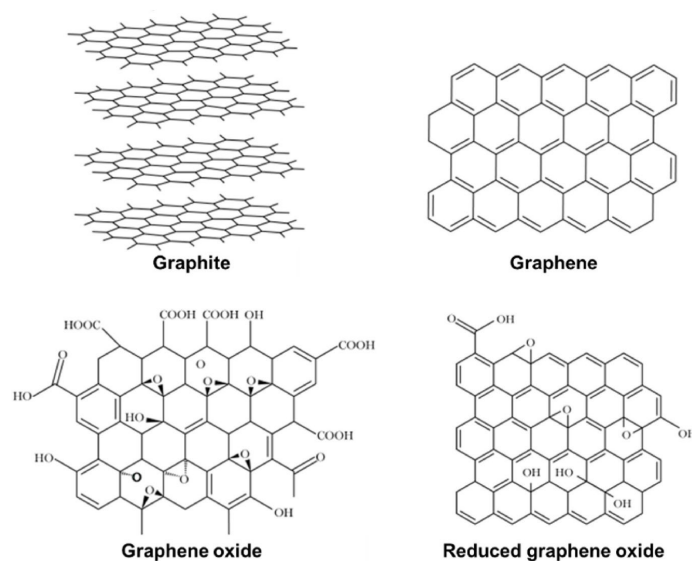


Figure 12. Schematic representation of the bulk graphite, as well as 2-D graphene, GO and rGO. (Adapted with permission by [70]).

3.2. rGO-Manganese Oxides

Manganese oxides (MOs) have been considered among the most promising cathode materials for AZIBs, due to their unique properties, including their various polymorphic structures and versatile oxidation states (+2, +3, +4, +7), as well as low cost and natural abundance [71]. As observed in Figure 13, some of the most common MOs include MnO , MnO_2 , Mn_2O_3 , Mn_3O_4 , Mn_5O_8 and various manganates (M_xMnO_2 , $\text{M}_x\text{Mn}_2\text{O}_4$, $\text{M}_x\text{Mn}_8\text{O}_{16}$, etc.). Among these, MnO_2 was the first to be employed as a cathode material in AZIBs [8], laying the foundation for subsequent research on its derivatives and other MO-based cathodes. In 2011, Xu et al. [72] proposed for the first time the utilization of α - MnO_2 as a cathode; it possesses a $[2 \times 2]$ tunneling structure, where $[\text{MnO}_6]$ octahedra are connected via shared vertices, resulting in a double-chained hollandite-type structure. Due to its large pore structure, which facilitates the diffusion of Zn^{2+} within its framework, α - MnO_2 has been extensively studied as a cathode material in AZIBs. Similarly, various crystalline forms of MnO_2 have attracted significant attention over the years, as evidenced by the increasing number of research articles on this topic (Figure 14). β - MnO_2 has a rutile tetrahedron structure and $[\text{MnO}_6]$ octahedra arranged in a $[1 \times 1]$ tunneling configuration; however, it presents lower specific capacity compared to α - MnO_2 because of its smaller tunneling dimensions. γ - MnO_2 exhibits a $[1 \times 1]$ pyrolusite type and a $[1 \times 2]$ ramsdellite type, while δ - MnO_2 is a layered structure of $[\text{MnO}_6]$ octahedra. ϵ - MnO_2 , an akhtenskite-type structure composed of densely packed $[\text{MnO}_6]$ octahedra, is less favorable for ion transport due to its compact framework. Likewise, λ - MnO_2 , featuring a 3-D spinel $[1 \times 1]$ tunneling structure, also hinders ion transport owing to the limited size of its channels. T- MnO_2 with a $[3 \times 3]$ todorokite-type facilitates rapid ion insertion kinetics, while nsutite-type R- MnO_2 with a $[1 \times 2]$ tunneling configuration composed of $[\text{MnO}_6]$ octahedra arranged in double chains results in a slow dissolution of Mn. Among the different MnO_2 derivatives, α - MnO_2 and δ - MnO_2 are the most promising candidates because of their unique tunnel and layered structure, resulting in enhanced efficiency towards Zn^{2+} storage.

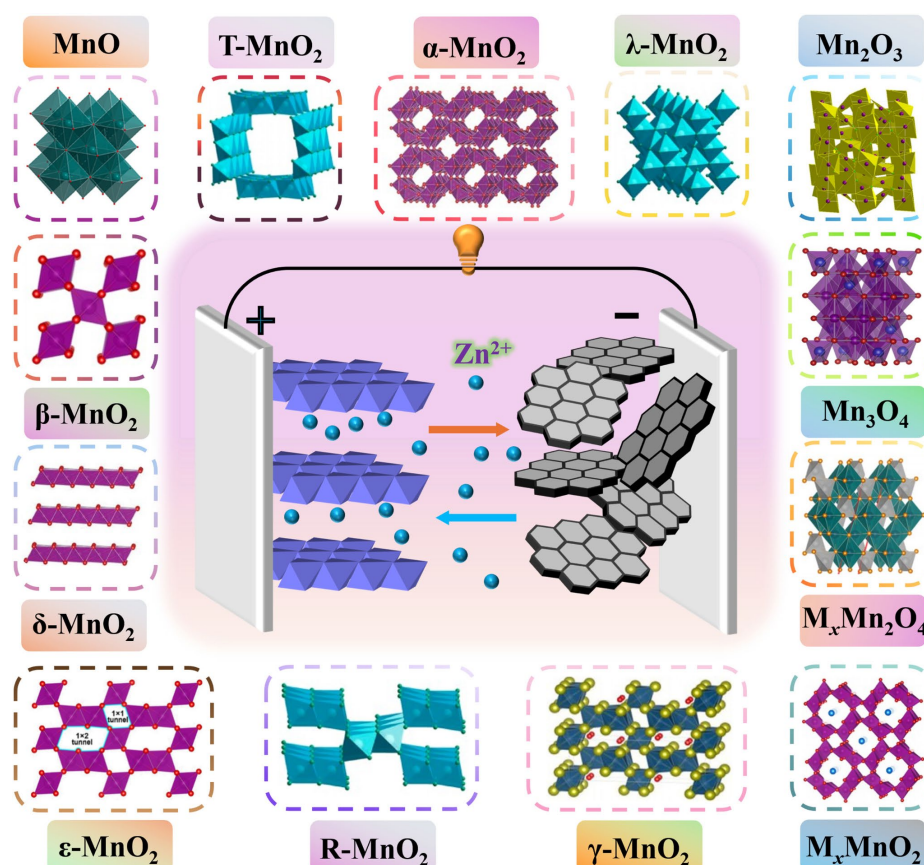


Figure 13. Structure of various manganese-based oxides, which have been considered promising cathode materials for AZIBs. (Adapted with permission by [71]).

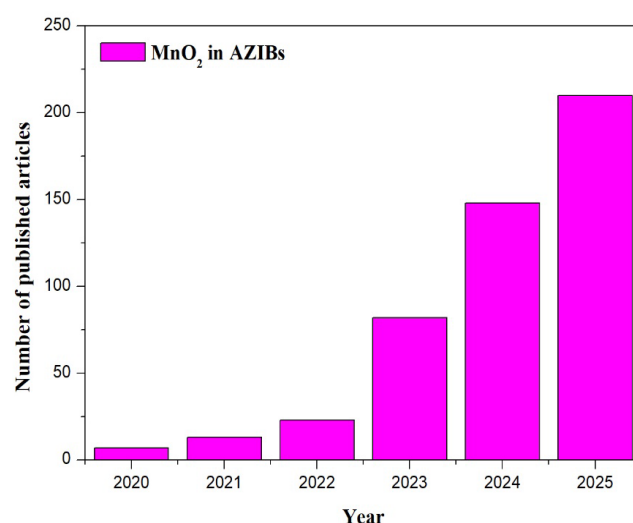


Figure 14. Number of publications in Scopus between 2020 and 2025 related to the topic of MnO_2 in AZIBs.

Although MnO_2 displays significant advantages, such as a wide working voltage window (0.8–1.8 V vs. Zn/Zn^{2+}) and high theoretical capacity ($308 \text{ mAh}\cdot\text{g}^{-1}$), it faces critical challenges including low electrochemical and structural stability, as well as poor electronic conductivity [47,71]. In order to overcome these drawbacks, several strategies have been proposed, such as doping [73,74], vacancy engineering [75] and incorporation of carbon additives [76]. The combination of the different MnO_2 configurations, as well as other MOs with rGO, will be thoroughly discussed herein; Table 1 summarizes the most recent

studies (published since 2023) focused on Mn-based oxides-rGO and their application as cathode materials in AZIBs.

Table 1. Summary of the studies focused on Mn-based oxides-rGO cathode materials in AZIBs (published since 2023).

Cathode Material	Synthesis Method	Specific Storage Capacity	Cycling Stability	Ref.
α -MnO ₂ -rGO	Chemical reduction in the presence of graphitic oxide, followed by annealing (300 °C, 2 h)	164 mAh·g ⁻¹ (at 50 mA·g ⁻¹)	78.68% (300 cycles at 300 mA·g ⁻¹)	[77]
	Hydrothermal treatment (180 °C, 4–8 h)	333 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	94.3% (500 cycles at 500 mA·g ⁻¹)	[78]
MnO ₂ -rGO	Electrodeposition	135.7 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	83.81% (1000 cycles at 200 mA·g ⁻¹)	[79]
δ -MnO ₂ -rGO	In situ oil–water interface reaction under reflux (90 °C, 12 h), followed by annealing (200 °C, 2 h)	331.11 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	97.6% (500 cycles at 100 mA·g ⁻¹)	[80]
δ -K _{0.32} MnO ₂ ·0.15H ₂ O-rGO	Ultrasonication, followed by freeze-drying	373 mAh·g ⁻¹ (at 0.1 C)	99% (120 cycles at 0.1 C)	[81]
ϵ -MnO ₂ -rGO	Wet-chemical redox precipitation	222.0 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	72.6 mAh·g ⁻¹ (3000 cycles at 2.0 A·g ⁻¹)	[82]
Mn-vacancies MnO ₂ -rGO	Self-assembly method by mixing the components prepared in previous steps	305.3 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	88.6% (1000 cycles at 1.0 A·g ⁻¹)	[75]
Sn-doped MnO ₂ -rGO	Hydrothermal synthesis, followed by calcination	352.3 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	108.5 mAh·g ⁻¹ (1000 cycles at 1.0 A·g ⁻¹)	[83]
Υ -doped MnO ₂ -rGO	Hydrothermal synthesis (140 °C, 12 h)	397.5 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	179.2 mAh·g ⁻¹ (2000 cycles at 1.0 A·g ⁻¹)	[84]
Ni-doped KMn ₈ O ₁₆ -rGO	Hydrothermal synthesis (120 °C, 15 h)	417.9 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	88% (1500 cycles at 1.0 A·g ⁻¹)	[85]
Mn ₂ O ₃ -N-doped rGO	Hydrothermal synthesis (180 °C, 12 h)	223.3 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	90% (500 cycles at 500 mA·g ⁻¹)	[86]
Mn ₃ O ₄ -rGO	Chemical reduction	522.3 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	89.3% (800 cycles at 1.0 A·g ⁻¹)	[87]

In a recent study [77], 1-D α -MnO₂ nanowires were successfully formed on the rGO surface via an in situ self-assembly method, and the final hybrid material exhibited a large specific surface area (148 m²·g⁻¹). As shown in Figure 15a, the CV curve at 0.1 mV·s⁻¹ pre-

sented a reduction peak at 1.33 V, corresponding to the Zn^{2+} insertion into the $\alpha\text{-MnO}_2\text{-rGO}$ cathode, accompanied by Mn^{4+} to Mn^{3+} conversion, as well as an oxidation peak at 1.65 V, associated with the extraction of Zn^{2+} ions from the cathode and the reversible Mn^{3+} to Mn^{4+} conversion. Moreover, different scan rates were studied and, as was observed, the diffusion-controlled reactions were prominent at low rates, while the capacitive contribution was notable at higher rates. Furthermore, the charge–discharge curves of the battery at $50 \text{ mA}\cdot\text{g}^{-1}$ are shown in Figure 15b. During the discharge process, two voltage plateaus are observed, leading to a capacity of $164 \text{ mAh}\cdot\text{g}^{-1}$; the former from 1.85 V to 1.26 V could be assigned to the H^+ insertion into the cathode framework, while the latter from 1.26 to 1.0 V indicates the insertion of Zn^{2+} ions. In addition, different current rates (up to $300 \text{ mA}\cdot\text{g}^{-1}$) were applied to evaluate the rate performance of the battery. Notably, the battery presented high-rate capability, demonstrating a capacity of $90 \text{ mAh}\cdot\text{g}^{-1}$ at the highest current rate, which could be attributed to the increase in conductivity and stability of the cathode due to the presence of rGO. Pradhan et al. [78] used a hydrothermal method to synthesize rGO wrapped around $\alpha\text{-MnO}_2$ nanorods (Figure 15c), investigating the effect of the reaction time (4 h, 6 h and 8 h) on the overall performance of the battery. Notably, the hybrid material prepared via hydrothermal treatment for 6 h was identified as the optimal sample, presenting the largest specific surface area. This highlights the importance of reaction parameters in controlling the physicochemical properties of the resulting nanostructure. The electrochemical performance of pristine $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2\text{-rGO}$ samples was evaluated via CV, under the same experimental conditions, and as can be seen in Figure 15d, the sample prepared at 6h exhibited the highest current response. Simultaneously, all the hybrid nanostructures presented improved performance compared to $\alpha\text{-MnO}_2$. Also, it is worth mentioning that the discharge capacities of $\alpha\text{-MnO}_2\text{-rGO-4h}$, $\alpha\text{-MnO}_2\text{-rGO-6h}$, $\alpha\text{-MnO}_2\text{-rGO-8h}$ and $\alpha\text{-MnO}_2$ (at current density of $200 \text{ mA}\cdot\text{g}^{-1}$) are $275.39 \text{ mAh}\cdot\text{g}^{-1}$, $333.26 \text{ mAh}\cdot\text{g}^{-1}$, $297.96 \text{ mAh}\cdot\text{g}^{-1}$, and $187.78 \text{ mAh}\cdot\text{g}^{-1}$, respectively. EIS experiments were also conducted in order to study the impedance behavior. Additionally, the $\alpha\text{-MnO}_2\text{-rGO-6h}$ sample achieved an excellent energy density of $273.32 \text{ Wh}\cdot\text{kg}^{-1}$ at a power density of $0.16 \text{ kW}\cdot\text{kg}^{-1}$ (Figure 15e).

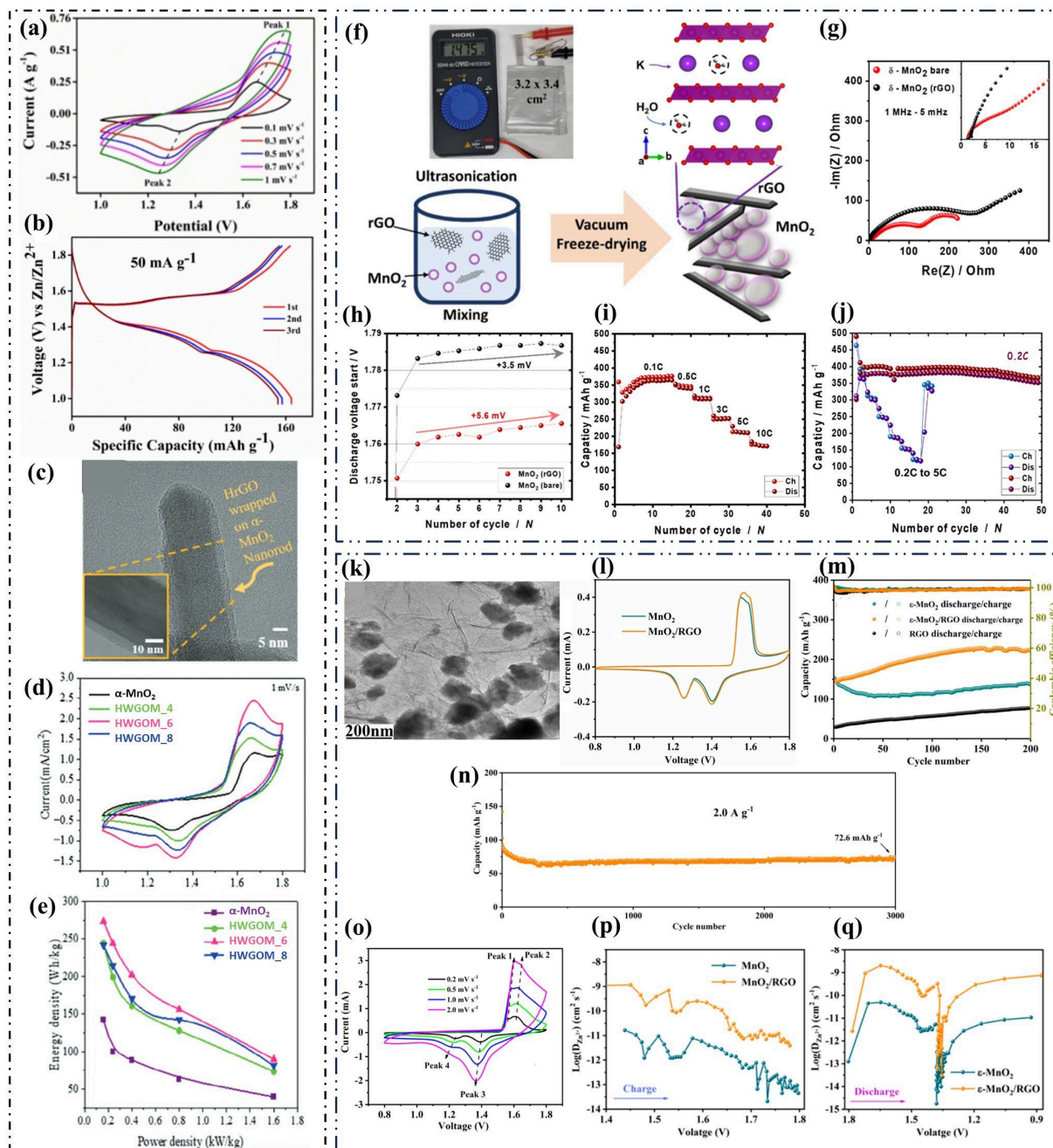


Figure 15. (a) CV curves of a battery based on an α -MnO₂-rGO cathode at different scan rates. (b) Charge/discharge of a battery based on α -MnO₂-rGO cathode at 50 mA g⁻¹. (Adapted with permission by [77]). (c) HR-TEM images of rGO wrapped around α -MnO₂ nanorods. (d) CV curves and (e) energy and power profile of pristine α -MnO₂ and α -MnO₂-rGO hybrid materials prepared for various reaction times. (Adapted with permission by [78]). (f) Synthesis of δ -K_{0.32}MnO₂·0.15H₂O-rGO hybrid material and its utilization in a Zn// δ -K_{0.32}MnO₂·0.15H₂O-rGO Al pouch cell. (g) Electrochemical impedance spectra and (h) discharge voltage start point of both δ -K_{0.32}MnO₂·0.15H₂O and δ -K_{0.32}MnO₂·0.15H₂O-rGO. (i,j) Cyclability and rate capability test results of pristine δ -K_{0.32}MnO₂·0.15H₂O-rGO and δ -K_{0.32}MnO₂·0.15H₂O-rGO. (Adapted with permission by [81]). (k) TEM image of ϵ -MnO₂-rGO. (l) The CV curves of ϵ -MnO₂ and ϵ -MnO₂-rGO. (m) Cycling performance of rGO, ϵ -MnO₂ and ϵ -MnO₂-rGO at 2.0 A g⁻¹. (n) Study of the long-term stability of the ϵ -MnO₂-rGO at 2.0 A g⁻¹. (o) CV curves of ϵ -MnO₂-rGO at incremental scan rates. (p,q) The calculated ion diffusion coefficient of ϵ -MnO₂ and ϵ -MnO₂-rGO in the charging and discharging process, respectively. (Adapted with permission by [82]).

rGO coating on the surface of MnO_2 was investigated by Yang et al. [79] in order to alleviate the Mn^{2+} dissolution and enhance the electronic charge and ion transfer on the surface of the host material. In general, the primary factors responsible for the dissolution of Mn-based cathode materials are the irreversible phase transition induced by Zn^{2+} insertion and the disproportionation of manganese ions driven by the Jahn–Teller effect. During the charging/discharging process, the Mn^{3+} generated disproportionates into Mn^{2+} and Mn^{4+} , resulting in a significant alteration of the $[\text{MnO}_6]$ coordination and consequently deteriorating structural stability. In addition, various by-products are formed at the electrode–electrolyte interface, which further decrease the conductivity of the cathode material. Beyond the Jahn–Teller effect, the repeated Zn^{2+} ion insertion/extraction within the framework of the cathode material contribute to its crystal structure alterations and volumetric changes due to the strong electrostatic interactions among Zn^{2+} and oxygen atoms, as well as formation of irreversible phases, leading to structural instability [71]. The $\text{Zn}/\text{MnO}_2\text{-rGO}$ prepared by Yang et al. [79] obtained a specific capacity of $135.7 \text{ mAh}\cdot\text{g}^{-1}$ at $100 \text{ mA}\cdot\text{g}^{-1}$ and excellent cycling stability, with a capacity retention rate of 83.81% after 1000 cycles at $2.0 \text{ A}\cdot\text{g}^{-1}$. Noteworthy, the highly stable $\text{MnO}_2\text{-rGO}$ was utilized as a cathode material in shape-memory fibrous AZIBs through electrochemical deposition onto the surface of a NiTi shape-memory alloy wire (SMAW), resulting in a composite material with enhanced conductivity, structural stability and mechanical adaptability.

$\delta\text{-MnO}_2$ is a promising cathode material for AZIBs, due to its 2-D layered structure with an interlayer spacing of approximately 0.7 nm, which is theoretically beneficial for the insertion/extraction of charge carriers ($\text{H}^+/\text{Zn}^{2+}$). Nevertheless, its electrochemical performance is limited due to sluggish reaction kinetics, low electronic conductivity, and inferior structural stability [88]. In order to overcome these drawbacks, Liu et al. [80] developed a $\delta\text{-MnO}_2\text{-rGO}$ hybrid material via an in situ oil–water interface reaction. Compared to blending or conventional in situ growth of $\delta\text{-MnO}_2$ onto the rGO surface, this strategy prevents $\delta\text{-MnO}_2$ nanosheet agglomeration, expands interlayer spacing, and forms Mn–O–C bonds between $\delta\text{-MnO}_2$ and rGO. Briefly, a mixture of GO dispersion, KMnO_4 aqueous solution and ethylacetate (EAC), was heated at 90°C for 12 h, followed by annealing at 200°C to obtain the final $\delta\text{-MnO}_2\text{-rGO}$. The electrochemical performance of both pristine $\delta\text{-MnO}_2$ and $\delta\text{-MnO}_2\text{-rGO}$ was evaluated. Notably, the CV curve of $\delta\text{-MnO}_2\text{-rGO}$ exhibited higher peak current density and lower potential of the oxidation peak, compared to $\delta\text{-MnO}_2$, suggesting that the conductive network decreases charge-transfer resistance and enhances electrochemical activity. Moreover, the strong interfacial coupling between rGO and $\delta\text{-MnO}_2$ reduces the activation energy required for Mn^{3+} oxidation, improving the distribution of redox potentials. The capacities of $\delta\text{-MnO}_2$ and $\delta\text{-MnO}_2\text{-rGO}$ electrodes at $200 \text{ mA}\cdot\text{g}^{-1}$ were $324.1 \text{ mAh}\cdot\text{g}^{-1}$ and $329.7 \text{ mAh}\cdot\text{g}^{-1}$, respectively. When the current density was increased to $4.0 \text{ A}\cdot\text{g}^{-1}$, the capacity of $\delta\text{-MnO}_2\text{-rGO}$ was significantly higher ($142.8 \text{ mAh}\cdot\text{g}^{-1}$), compared to pristine $\delta\text{-MnO}_2$ ($119.3 \text{ mAh}\cdot\text{g}^{-1}$). Furthermore, the capacity retention of the $\delta\text{-MnO}_2\text{-rGO}$ electrode is 97.60% after 500 cycles at the current density of $1.0 \text{ A}\cdot\text{g}^{-1}$, whereas the pristine $\delta\text{-MnO}_2$ electrode degrades to 47.45%. It is also worth mentioning the practical application of the $\delta\text{-MnO}_2\text{-rGO}$ cathode material, as it was assembled into a pouch cell, which could power a smartphone, demonstrating a capacity retention of over 74% after 150 cycles. Kinetic analysis showed that the $\delta\text{-MnO}_2\text{-rGO}$ exhibited higher pseudocapacitive contribution than $\delta\text{-MnO}_2$, indicating faster reaction kinetics. EIS results further revealed the significantly lower charge-transfer resistance ($R_{\text{ct}} = 107 \Omega$) of $\delta\text{-MnO}_2\text{-rGO}$, compared to $\delta\text{-MnO}_2$ ($R_{\text{ct}} = 698 \Omega$). This suggests that rGO incorporation effectively promotes electron/ion transfer kinetics.

The pre-intercalation of metal cations into layered $\delta\text{-MnO}_2$ cathodes ($\delta\text{-M}_x\text{MnO}_2$, where M: K, Cu or Li) has emerged as an important strategy for facilitating ion transport and thereby optimizing their electrochemical performance. However, they suffer from ca-

capacity fading and loss of electrical contact, primarily caused by structural degradation during repeated electrochemical cycling. In order to overcome this drawback, Zhanadilov et al. [81] combined $\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}$ with rGO via ultrasonication and freeze-drying processes, resulting in the final $\text{Zn}/\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}\text{-rGO}$ (Figure 15f) with a high capacity of $373\text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C. As is observed in Figure 15g, the resulting impedance of the $\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}\text{-rGO}$ is significantly diminished compared to bare $\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}$ due to the formation of increased conducting pathways. This behavior also justifies the gradual rise of the discharge voltage starting point for the initial 10 cycles, which is shown in Figure 15h. Furthermore, it is worth mentioning that, although the initial capacity of $\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}$ is high, it decays as the current rate increases, suggesting its poor rate capability and sluggish charge-transfer kinetics (Figure 15i). On the other hand, the $\delta\text{-K}_{0.32}\text{MnO}_2\cdot 0.15\text{H}_2\text{O}\text{-rGO}$ hybrid material demonstrates a gradual capacity decrease across a wide range of current densities, maintaining a remarkable capacity even at high rates (Figure 15j). Notably, it retained over 99% for 120 cycles at 0.1 C, 89% for 500 cycles at 5 C and 35% for 2000 cycles at 10C. Overall, the hybrid system exhibits superior rate capability and cycling stability, highlighting the critical role of rGO in optimizing the electrochemical performance of $\delta\text{-MnO}_2$ -based electrodes.

As opposed to $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$, the akhtenskite-structured MnO_2 ($\epsilon\text{-MnO}_2$) has received little attention as cathode material in AZIBs. More specifically, $\epsilon\text{-MnO}_2$ could provide a unique tunnel structure for Zn^{2+} storage; nevertheless, its practical application is limited by inherent drawbacks, such as low electron conductivity, sluggish ion kinetics and structural instability. Recently, Wang et al. [82] reported the successful formation of $\epsilon\text{-MnO}_2$ nanoflowers on the rGO surface (Figure 15k), via a co-precipitation method. As shown in the CV curves (Figure 15l), the $\epsilon\text{-MnO}_2\text{-rGO}$ electrode presented increased current and current integrated area compared to $\epsilon\text{-MnO}_2$, suggesting that the introduction of rGO is beneficial for the electrochemical behavior of the cathode. Notably, the capacity of the $\epsilon\text{-MnO}_2\text{-rGO}$, $\epsilon\text{-MnO}_2$ and rGO is $222.0\text{ mAh}\cdot\text{g}^{-1}$, $136.9\text{ mAh}\cdot\text{g}^{-1}$ and $77.0\text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at $200\text{ mA}\cdot\text{g}^{-1}$, respectively, as observed in Figure 15m. The hybrid material is considered a promising candidate for potential application in AZIBs, as it delivers good stability with a reversible capacity of $72.6\text{ mAh}\cdot\text{g}^{-1}$ within 90 s after 3000 cycles at $2.0\text{ A}\cdot\text{g}^{-1}$ (Figure 15n). Moreover, the current of the $\epsilon\text{-MnO}_2\text{-rGO}$ increases as the scan rate is also increased (Figure 15o), due to the enhanced electrochemical polarization. At this point it is worth mentioning that the correlation between the current and the scan rate could be described through the following equation:

$$\log(i) = b \log(v) + \log(\alpha), \quad (9)$$

where i signifies the peak current, v is the scan rate, α is a constant and b represents the ion-kinetic behavior. The b -value is calculated based on the linear correlation between $\log(i)$ and $\log(v)$; when it is close to 0.5, a diffusion-controlled redox reaction takes place, whereas the reaction has a pseudo-capacitive behavior when the value is close to 1. In addition, the contribution of the diffusion reaction and capacitive process to the current response is calculated based on the following equation:

$$i = k_1 v + k_2 v^{1/2}, \quad (10)$$

where k_1 and k_2 are constants which could be used to differentiate capacitive and diffusion-controlled reactions. Herein, the b -values are 0.72, 0.64, 0.72, and 0.57, for peak 1, peak 2, peak 3 and peak 4, respectively. This indicates that the ion storage of the $\epsilon\text{-MnO}_2\text{-rGO}$ involves both solid-state diffusion and surface capacitive processes. Notably, peak 1 and peak 3 exhibit higher b -values, than peak 2 and peak 4, suggesting that the Zn^{2+} insertion/extraction is predominantly governed by surface capacitive behavior, whereas H^+ insertion/extraction is mainly a diffusion-controlled process. GITT measurements were

conducted to further study the ion diffusion kinetics on both pristine ϵ -MnO₂ and ϵ -MnO₂-rGO. The ion diffusion coefficient (D) could be described by the following equation:

$$D = \frac{4}{\pi t} \left(\frac{m V_M}{M A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2, \quad (11)$$

where: m (g) represents the mass of the electrode, V_M (cm³·mol^{−1}) is the molar volume, M (g·mol^{−1}) the molecular weight, A is the electrode area (cm²), t (s) indicates the relaxation time, and ΔE_t (V), ΔE_s (V) represent the voltage change during current pulse and the steady-state potential change, respectively. The obtained D-values of the ϵ -MnO₂-rGO ranged between 1.15×10^{-9} cm²·s^{−1} and 8.58×10^{-12} cm²·s^{−1} in the charging process (Figure 15p) and from 1.15×10^{-9} cm²·s^{−1} to 3.00×10^{-14} cm²·s^{−1} in the discharging process (Figure 15q). The above values were significantly improved compared to the D-values of ϵ -MnO₂, indicating the faster ion diffusion kinetics for the hybrid material.

The synergistic effects of vacancy engineering and rGO incorporation on the improvement of the AZIB performance have been investigated by Liu et al. [75]. Vacancy engineering, which involves the introduction of atomic-scale defects (Figure 16a), has emerged as an effective approach in order to overcome the intrinsic limitations of Mn-based oxides, including low electron conductivity, sluggish ion kinetics and structural instability. Nevertheless, the localization of excess electrons around Mn-vacancies would lead to strong local electrostatic trapping fields (Figure 16b), impeding the directional flow of electrons and increasing resistance. Therefore, the incorporation of positively charged rGO nanosheets could modulate the localized charge distribution (Figure 16c). In their work, rGO modified with polydimethyl-diallyl ammonium chloride (PDDA) was combined with MnO₂ via a self-assembly method; Mn-vacancies were introduced into the MnO₂ lattice by mechanically shaking K-birnessite MnO₂ in tetramethylammonium hydroxide (TMAOH) aqueous solution for 2 days and ultrasonication for 8 h. The presence of Mn-vacancies was detected by electron energy loss spectroscopy (EELS) and XPS analysis. Briefly, the peak of MnO₂-rGO in the EELS spectrum (Figure 17a) is observed at lower energy, compared to reference MnO₂ (Mn⁴⁺), indicating the lower Mn oxidation state. Moreover, the Mn 2p_{3/2} peak of both Mn-vacancy MnO₂-rGO and Mn-vacancy MnO₂ at approximately 642 eV is shifted toward lower binding energy, in comparison with the commercial MnO₂, indicating a lower average Mn oxidation state than Mn⁴⁺ (Figure 17b). The splitting distance for Mn 3s doublet peaks is higher in the hybrid material, compared to the commercial sample, which further confirms the low oxidation state of Mn (Figure 17c). Furthermore, the electrochemical performance of the Mn-vacancy MnO₂-rGO cathode was evaluated via ex situ XRD analysis, where no significant shift of the diffraction peaks was observed during the charging/discharging process, suggesting the high structural stability of the material. Ex situ SEM and XPS characterization also confirmed the reversible structural evolution of the as-prepared cathode. Regarding the charge storage mechanism, the b -values of Mn-vacancy MnO₂-rGO were higher than those of the Mn-vacancy MnO₂ electrode. This indicates that the as-prepared cathode is dominated by capacitive behavior, enabling the fast Zn²⁺ electrochemical kinetics. The fast ion transport kinetics of the hybrid material were further confirmed via GITT measurements (Figure 17d), where the chemical diffusion coefficient of the Zn²⁺ was in the range of 10^{-11} – 10^{-12} cm²·s^{−1} for the Mn-vacancy MnO₂-rGO and in the range of 10^{-12} – 10^{-14} cm²·s^{−1} for the Mn-vacancy MnO₂. Moreover, Figure 17e presents the Nyquist plots of the electrodes, where the Mn-vacancy MnO₂-rGO electrode exhibits lower ohmic and charge transfer resistance, compared to Mn-vacancy MnO₂. The enhanced conductivity of the electrode is attributed to the rGO presence. Overall, the modification of Mn-vacancy MnO₂ with rGO increased the discharging capacity at 100 mA·g^{−1}, from 195.3 mAh·g^{−1} to 305.3 mAh·g^{−1}. Similarly, the hybrid material exhibited a capacity retention of 88.6% after 1000 cycles at 1.0 A·g^{−1}, whereas MnO₂ achieved 76.8% under the same conditions.

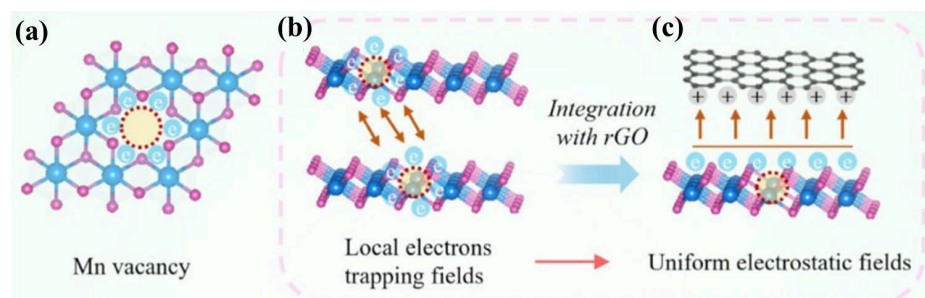


Figure 16. (a) Mn-vacancy engineering. (b) Formation of strong local electrostatic trapping fields. (c) Combination of Mn-vacancy MnO₂ with positively charged rGO. (Adapted with permission by [75]).

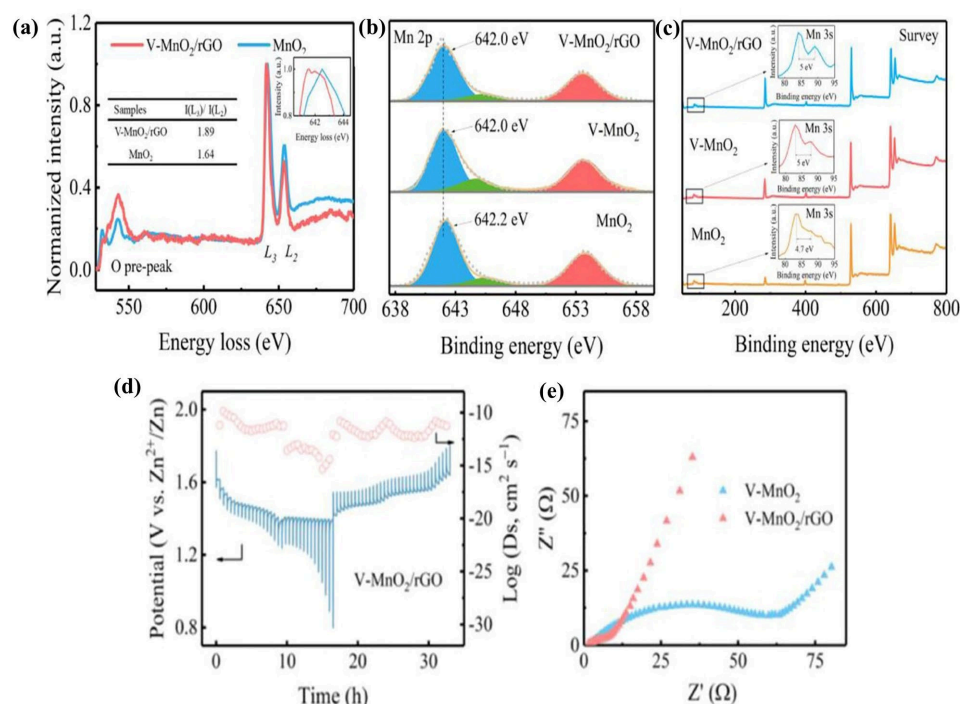


Figure 17. (a) EELS and (b,c) XPS results confirming the presence of Mn-vacancies in the lattice of MnO₂. (d) GITT curve of Mn-vacancy MnO₂-rGO electrode. (e) Nyquist plots of Mn-vacancy MnO₂ and Mn-vacancy MnO₂-rGO electrodes. (Adapted with permission by [75]).

The synergistic effects of MnO₂ doping and rGO incorporation have also been investigated in various research studies [83,84]. Elemental doping is a common strategy to improve electrical conductivity through electron rearrangement, as well as inhibit cathode dissolution and enhance reaction kinetics. Meanwhile, the incorporation of rGO provides a highly conductive network that facilitates rapid electron transport, buffers volume changes during cycling, and increases the active surface area, thereby improving electrochemical kinetics and structural stability. In their study, Chen et al. [83] reported the synthesis of Sn-doped MnO₂-rGO, via a hydrothermal treatment. The as-prepared sample was assembled into a CR2025 coin battery in order to evaluate its electrochemical behavior. As observed in Figure 18a, the Sn-doped MnO₂-rGO exhibits a higher specific capacity of 352.3 mAh·g⁻¹ at 100 mA·g⁻¹ compared to Sn-doped MnO₂, MnO₂-rGO, and MnO₂-rGO, indicating that the presence of both Sn-doping agent and rGO enhance the electrochemical performance of MnO₂. After 1000 cycles the sample can maintain its capacity at 108.5 mAh·g⁻¹. Further study of the kinetic process was also evaluated; therefore, CV curves were obtained at various scan rates (Figure 18b). More specifically, it was observed that the peak of CV gradually widens and is slightly offset, as the scan rate increases from 0.2 mV·s⁻¹ to 1.0 mV·s⁻¹, indicating capacitance behavior. Based on Equations (9) and (10), the

calculated relative contributions of diffusion-controlled and capacitive mechanisms as a function of the scan rate are illustrated in Figure 18c. In a similar study, a Y-doped MnO₂-rGO with excellent structural stability and high electrochemical performance was prepared via the hydrothermal treatment of rGO and metal precursor mixture at 140 °C for 12 h [84]. The integration of Y³⁺ can expand the interlayer spacing of MnO₂, enhance electronic interactions and promote the diffusion of Zn²⁺ ions, while rGO serves as a conductive framework. The as-prepared Y-doped MnO₂-rGO was characterized by XPS analysis, where the results suggested the presence of both Mn³⁺ and Mn⁴⁺. In addition, the oxidation state of manganese could be precisely assessed using the following equation:

$$\text{AOS} = 8.956 - 1.126\Delta E_s, \quad (12)$$

where AOS is the average oxidation state and ΔE_s the polymorphic energy. As was found, the AOS values of pristine β -MnO₂, Y-doped MnO₂ and Y-doped MnO₂-rGO were 3.79, 3.65 and 3.61, respectively. The results indicate that both the Y³⁺ doping and combining with rGO could enhance the concentration of oxygen vacancies, improving the electronic properties of β -MnO₂ and promoting efficient electron transfer. Moreover, in the XPS spectrum of O 1s, a peak attributed to the presence of oxygen vacancies and Mn-O-C bonds could be detected; the former leads to advantageous ion storage and the latter to enhanced interactions among Y-doped MnO₂ and rGO. The formation of these covalent bonds suppresses the Jahn–Teller distortion of MnO₂ during the discharging/charging process. Notably the hybrid material exhibits a high specific capacity of 397.5 mAh·g^{−1} at 100 mA·g^{−1}. rGO can significantly mitigate volume variations of MnO₂ during cycling, resulting in the overall cycling stability of the electrode, while increasing the proportion of pseudocapacitance at different scan rates, compared to Y-doped MnO₂.

A recent study [85] explored the Ni²⁺ doping of a cryptomelane-type KMn₈O₁₆-a 1-D [2 × 2] tunnel structure, which is similar to α -MnO₂, followed by its combination with rGO (Figure 18d). On the one hand, Ni²⁺ was selected as a doping agent because of the absence of Jahn–Teller activity and its atomic radii, which is relatively close to Mn⁴⁺, reducing the likelihood of disrupting the MnO₂ structure. On the other hand, rGO was selected due to its large specific surface area and its high electrical conductivity. The specific capacity of the Ni-doped KMn₈O₁₆-rGO cathode was 417.9 mAh·g^{−1} at 200 mA·g^{−1}, presenting improved performance compared to KMn₈O₁₆ and Ni-doped KMn₈O₁₆, as observed in Figure 18e. The cycling stability was evaluated at 1.0 A·g^{−1} (Figure 18f) and after 1500 cycles the Ni-doped KMn₈O₁₆-rGO cathode showed a reversible capacity of 238 mAh·g^{−1}, whereas KMn₈O₁₆ and Ni-doped KMn₈O₁₆ exhibited 46 mAh·g^{−1} and 122 mAh·g^{−1}, respectively. It is worth mentioning that the feasibility of its practical application was evaluated by assembling a Zn//Ni-doped KMn₈O₁₆-rGO battery into a pouch cell, which was able to power up a 1.5 V digital thermo/hydrometer-cum-clock for 5 days (Figure 18g).

Beyond doping of Mn-based oxides, the strategy of doping rGO has also been investigated in order to further enhance its electrical conductivity. For instance, Yu et al. [86] synthesized a Mn₂O₃-N-doped rGO via a hydrothermal method, resulting in the formation of a cathode with excellent electrical conductivity, a specific capacity of 223.3 mAh·g^{−1} at 100 mA·g^{−1} and enhanced structural properties as over 90% of the initial capacity was retained after 500 cycles.

Finally, spinel Mn₃O₄, presenting a substantial theoretical capacity of 468.5 mAh·g^{−1} and a high operating voltage, is also a promising candidate for AZIBs. However, similar to other Mn-based oxides, it suffers from inadequate conductivity and structural instability and, therefore, rGO integration has been studied by Yang et al. [87]. In this work, Mn₃O₄-rGO samples with different Mn₃O₄:rGO mass ratios were prepared via a chemical reduction method, using hydrazine and ammonia. Notably, the combination of Mn₃O₄ with rGO significantly increased its specific capacity from 199.5 mAh·g^{−1} to 522.3 mAh·g^{−1}

at $100 \text{ mA} \cdot \text{g}^{-1}$. Further evaluation of the cycling stability at $1.0 \text{ A} \cdot \text{g}^{-1}$ for 800 charge–discharge cycles showed that the Mn_3O_4 -rGO exhibited a capacity retention of 89.3%, while the pristine one retained only 40.9% of its initial capacity. The role of rGO in the enhancement of structural stability was assessed via SEM and XRD analysis after 250 cycles at $1.0 \text{ A} \cdot \text{g}^{-1}$. As is observed in Figure 19a,b, the Mn_3O_4 -rGO cathode maintains its initial morphological characteristics with well-dispersed Mn_3O_4 nanoparticles on the rGO nanosheets, indicating its structural stability. On the other hand, the Mn_3O_4 cathode (Figure 19c,d) presents serious aggregation phenomena and structural collapse under the same conditions. Additionally, in the XRD spectra (Figure 19e) it can be observed that the intensity of the characteristic diffraction peaks of Mn_3O_4 is decreased after cycling, suggesting the loss of crystallinity. In contrast, in the XRD spectrum of Mn_3O_4 -rGO the diffraction peaks remain unchanged after cycling.

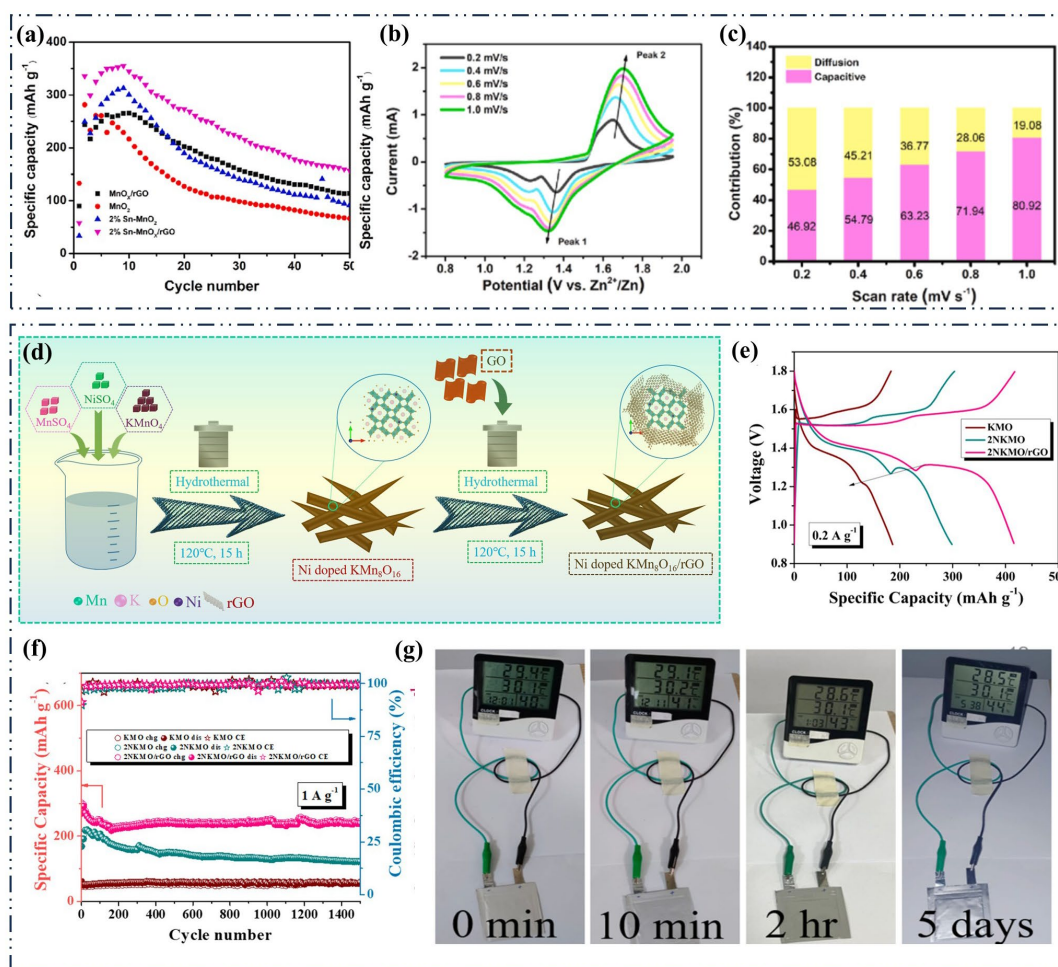


Figure 18. (a) Cycle performance of Sn-doped MnO_2 -rGO, Sn-doped MnO_2 , MnO_2 -rGO, and MnO_2 -rGO. (b) CV curves of Sn-doped MnO_2 -rGO at different scan rates. (c) Contribution rates of diffusion control and capacitance control. (Adapted with permission by [83]). (d) Schematic representation of the Ni-doped KMnO_4 -rGO synthesis process. (e) Rate performance at $200 \text{ mA} \cdot \text{g}^{-1}$ and (f) cycling stability tests of KMnO_4 , Ni-doped KMnO_4 , and Ni-doped KMnO_4 -rGO, respectively. (g) The Zn/Ni-doped KMnO_4 -rGO pouch-cell battery which powers a thermo/hydrometer-cum-clock. (Adapted with permission by [85]).

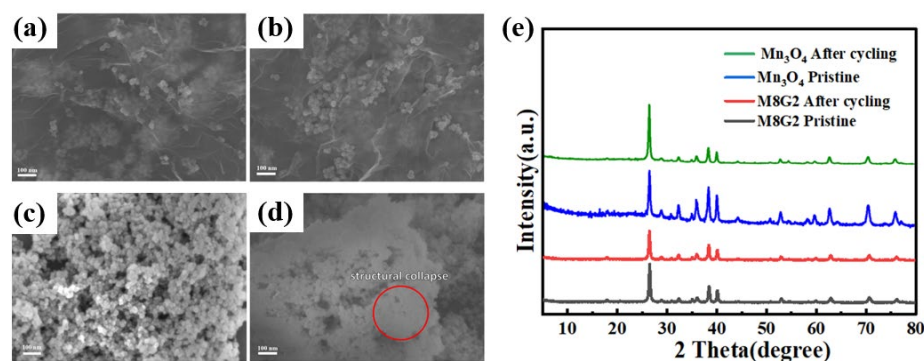


Figure 19. SEM images of (a,b) Mn₃O₄-rGO and (c,d) Mn₃O₄ before and after cycling, respectively. (e) XRD analysis of Mn₃O₄ and Mn₃O₄-rGO before and after cycling. The sample M8G2 indicates the optimum cathode with 8:2 (Mn₃O₄:rGO) mass ratio. (Adapted with permission by [87]).

3.3. rGO-Vanadium Oxides

Vanadium oxides (VOs) are a group of transitional metal oxides, which have been considered among the most promising cathode materials in AZIBs because of their intrinsic characteristics. More specifically, V with various oxidation states (V^{2+} , V^{3+} , V^{4+} , V^{5+}) can coordinate with oxygen to form different types of V-O polyhedrons, as shown in Figure 20a. These polyhedrons could be assembled into VO-based materials with diverse structures. For example, V₂O₅ is a layered structure formed by the corner-sharing of VO₅ square pyramids, whereas VO₂(B) has a tunnel-like architecture formed by the edge-sharing of VO₆ octahedra. Figure 20b illustrates the most commonly employed VO structures as cathode materials, demonstrating their versatility. Notably, more than 300 articles on the utilization of VOs in AZIBs were published during the first half of the current decade, according to Scopus (Figure 21), reflecting the growing scientific interest in exploring the potential application of this class of materials. Beyond structural diversity, VOs exhibit natural abundance and environmental sustainability. During the electrochemical reaction processes, the V-O framework varies based on the oxidation state of V; this variation not only suppresses the crystal structure degradation due to the Zn²⁺ insertion/extraction but also provides additional redox reaction pathways. While VOs are also subject to structural collapse and active species dissolution, these phenomena are less significant than in Mn-based oxides, attributed to their more stable oxidation states and robust structures. In addition, their low electrical conductivity also hinders their application in AZIBs [89–91]. Herein, the most recent studies focused on the combination of VOs with rGO for the development of effective cathode materials in AZIBs (Table 2) will be presented.

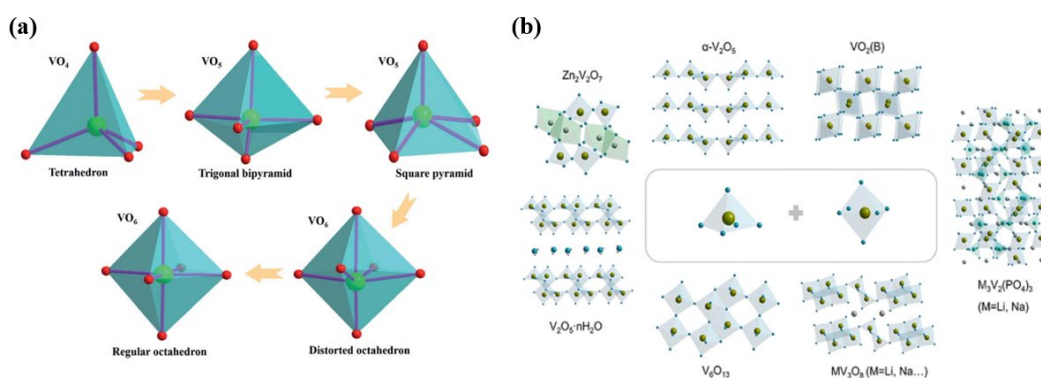


Figure 20. (a) Various V-O polyhedra formed based on the oxidation state of V. (Adapted with permission by [90]). (b) Various vanadium-based oxides (VOs). (Adapted with permission by [89]).

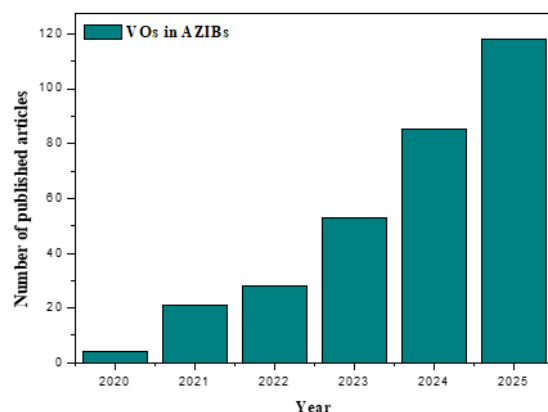


Figure 21. Number of publications in Scopus between 2020 and 2025 related to the topic of VOs in AZIBs.

Table 2. Summary of the studies focused on V-based oxides-rGO cathode materials in AZIBs (published since 2023).

Cathode Material	Synthesis Method	Specific Storage Capacity	Cycling Stability	Ref.
V ₂ O ₅ -rGO	Freeze-drying followed by calcination under argon (400 °C, 2 h)	438.5 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	85.6% (1000 cycles at 2.0 A·g ⁻¹)	[92]
	Laser reduction	276.1 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	98.5% (1000 cycles at 2.0 A·g ⁻¹)	[93]
	Wet spinning	402.5 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	45.5% (4000 cycles at 5.0 A·g ⁻¹)	[94]
	Electrochemical oxidation of MIL-88B(V)-rGO	479.6 mAh·g ⁻¹ (at 50 mA·g ⁻¹)	80.3% (400 cycles at 2.0 A·g ⁻¹)	[95]
V ₂ O ₅ ·nH ₂ O-rGO	Hydrothermal synthesis (180 °C, 12 h)	548 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	83% (100 cycles at 0.1 A·g ⁻¹)	[96]
Mg ²⁺ -doped V ₂ O ₅ -rGO		530 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	89% (5000 cycles at 5.0 A·g ⁻¹)	[97]
Zn _{0.42} V ₂ O _{7.54} -rGO		395 mAh·g ⁻¹ (at 500 mA·g ⁻¹)	28% (from cycle 50 to 2000 at 4.0 A·g ⁻¹)	[98]
Zn _{0.12} Mn _{0.14} V ₂ O _{7.16} -rGO	N ₂ atmosphere (300 °C, 2 h)	291 mAh·g ⁻¹ (at 500 mA·g ⁻¹)	77% (from cycle 50 to 2000 at 4.0 A·g ⁻¹)	
VOOH-rGO	Hydrothermal synthesis (200 °C, 24 h)	330 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	104 mAh·g ⁻¹ (1000 cycles at 2.0 A·g ⁻¹)	[99]
VO ₂ -rGO	Hydrothermal synthesis (180 °C, 12 h), followed by thermal annealing under Ar atmosphere	329.9 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	84% (1000 cycles at 5.0 A·g ⁻¹)	[100]

	(300 °C, 2 h) Hydrothermal synthesis (180 °C, 12 h), followed by thermal annealing under Ar/H ₂ atmosphere (1.000 °C, 2 h)	527 mAh·g ⁻¹ (at 1.0 A·g ⁻¹)	183.4 mAh·g ⁻¹ (30,000 cycles at 20.0 A·g ⁻¹)	[101]
V ₁₀ O ₂₄ ·12H ₂ O- rGO	Hydrothermal synthesis (160 °C, 12 h)	318.65 mAh·g ⁻¹ (at 100 mA·g ⁻¹)	71.37% (1000 cycles at 1.0 A·g ⁻¹)	[102]
NH ₄ V ₄ O ₁₀ -rGO	Hydrothermal synthesis (180 °C, 24 h)	507 mAh·g ⁻¹ (at 200 mA·g ⁻¹)	95% (600 cycles at 5.0 A·g ⁻¹)	[103]

To begin with, vanadium pentoxide (V₂O₅) is among the most studied VO-based cathode materials, due to its relatively straightforward synthesis, environmental friendliness, and high operating voltage. In addition, its layered structure facilitates Zn²⁺ ion intercalation and deintercalation during discharging and charging, respectively [89]. As Zn²⁺ ions are incorporated, V⁵⁺ ions are reduced to V⁴⁺ or V³⁺ in order to maintain the charge balance. The repeated insertion and extraction processes induce structural changes in the lattice (Figure 22), causing its expansion and contraction, which can negatively affect the overall electrochemical performance of the battery. Thus, the modification of V₂O₅ with rGO is considered not only to increase its electrical conductivity but also strengthen the mechanical integrity and stability of the cathode structure.

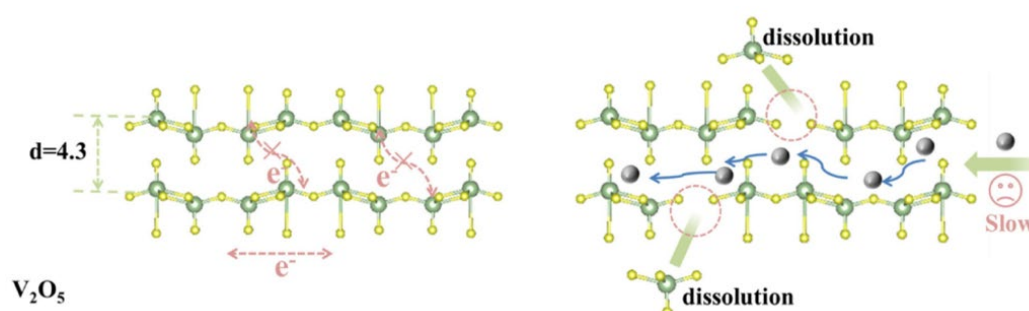


Figure 22. Schematic illustration of V₂O₅ cathode dissolution caused by the intercalation of large Zn²⁺ cations (Adapted with permission by [89]).

Deng et al. [92] synthesized a V₂O₅-rGO hybrid material by a scalable freeze-drying and in situ thermal decomposition–reduction method. More specifically, an aqueous dispersion containing the precursor materials (NH₄VO₃, graphene oxide) and PVP surfactant was transferred into a freeze dryer at −80 °C for 48 h, followed by calcination at 400 °C for 2 h, under argon atmosphere, as observed in Figure 23a. The electrochemical behavior of V₂O₅-rGO as well as pristine V₂O₅ was evaluated via CV at 0.1 mV·s⁻¹ (Figure 23b,c). The pristine V₂O₅ presents two coupled redox peaks located at 1.28/0.90 V and 0.81/0.48 V, corresponding to the Zn²⁺ intercalation/deintercalation. In the case of V₂O₅-rGO cathode, the redox peaks are located at 1.16/0.89 V and 0.80/0.53 V, presenting narrower overpotential compared to V₂O₅, indicating decreased polarization potentials and accelerated electrochemical kinetics. The maximum capacity achieved at 100 mA·g⁻¹ by V₂O₅ and V₂O₅-rGO was 317.7 mAh·g⁻¹ in the 22nd cycle and 438.5 mAh·g⁻¹ in the 8th cycle, respectively. Furthermore, based on EIS analysis, the transfer resistance and internal resistance for V₂O₅-rGO were calculated at 86.6 Ω and 2.2 Ω, respectively. These values were lower than those of V₂O₅ (139.8 Ω and 5.4 Ω), which further confirm the faster reaction kinetics and ion storage kinetics of the V₂O₅-rGO cathode.

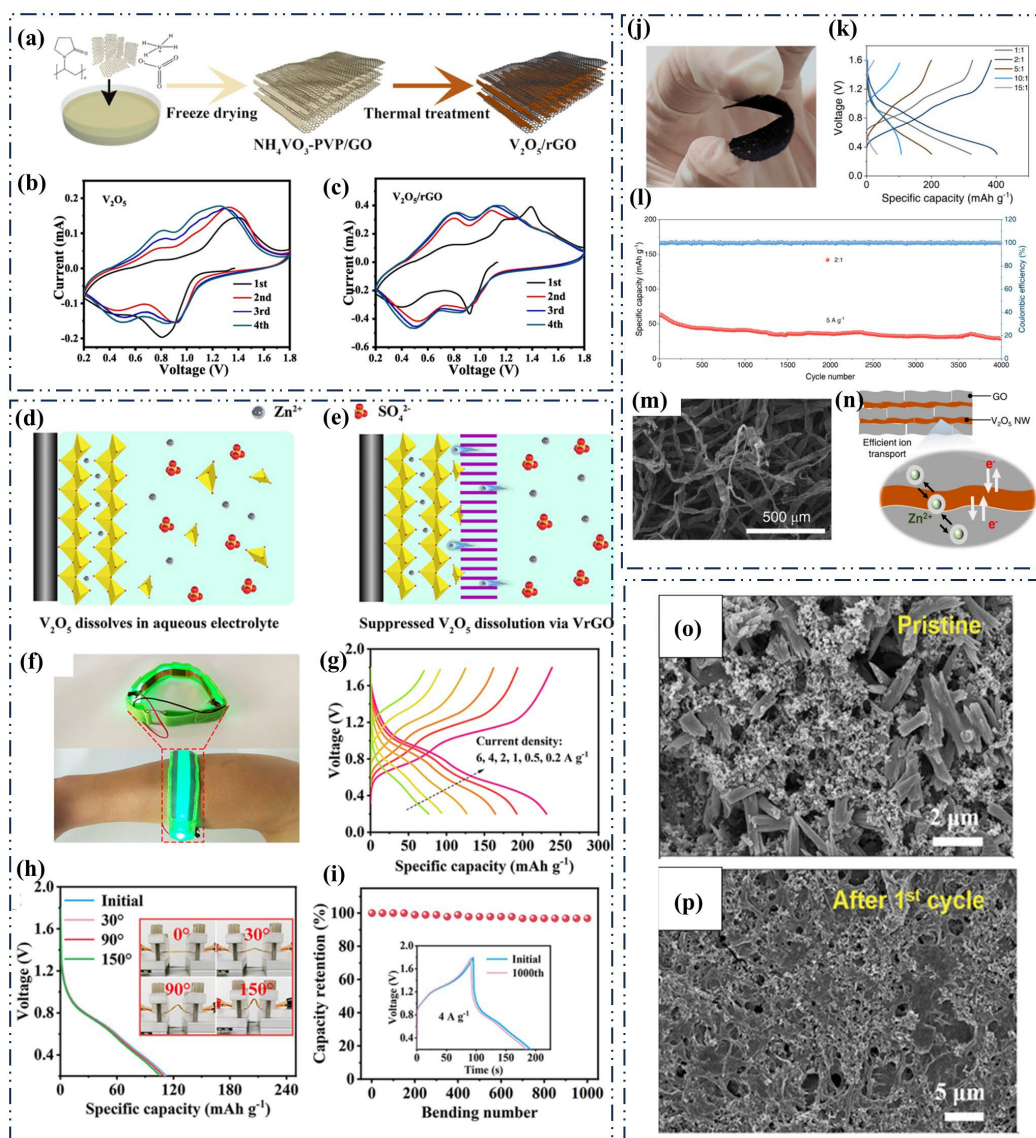


Figure 23. (a) Synthesis procedure of V_2O_5 -rGO hybrid material. CV curves of (b) V_2O_5 and (c) V_2O_5 -rGO at $0.1 \text{ mV}\cdot\text{s}^{-1}$. (Adapted with permission by [92]). (d,e) Schematic representation of cathode dissolution in aqueous electrolyte before and after combination of V_2O_5 with rGO. (f) Digital photograph of three Zn// V_2O_5 -rGO AZIBs connected in series, implanted into the sideband of a sport bracelet. (g,h) GCD curves at different current densities and bending angles, respectively. (i) Capacity retention under bending at 90° . (Adapted with permission by [93]). (j) Digital photograph of a flexible V_2O_5 -rGO cathode. (k) The GCD curves of V_2O_5 -rGO prepared in different ratios, at $0.1 \text{ A}\cdot\text{g}^{-1}$. (l) Cycling test of V_2O_5 -rGO (2:1) sample at $5.0 \text{ A}\cdot\text{g}^{-1}$. (m) SEM image of V_2O_5 -rGO (2:1). (n) Schematic representation of Zn^{2+} and electron transport in the hybrid material. (Adapted with permission by [94]). SEM images of the cathode (o) before and (p) after the first charge/discharge cycle. Due to electrochemical oxidation, the initial MIL-88B(V)-rGO is transformed into V_2O_5 -rGO. (Adapted with permission by [95]).

In another study [93], vertically aligned rGO was deposited onto V_2O_5 via laser reduction. Although the initial specific capacity of Zn// V_2O_5 ($329.8 \text{ mAh}\cdot\text{g}^{-1}$) was higher than Zn// V_2O_5 -rGO ($276.1 \text{ mAh}\cdot\text{g}^{-1}$) at $0.2 \text{ A}\cdot\text{g}^{-1}$, when the current density increased to $6.0 \text{ A}\cdot\text{g}^{-1}$, the corresponding values were $110.0 \text{ mAh}\cdot\text{g}^{-1}$ and $119.2 \text{ mAh}\cdot\text{g}^{-1}$, respectively, suggesting that the latter exhibits higher capacity retention. Notably, when the current density returns back to $0.2 \text{ A}\cdot\text{g}^{-1}$, the capacity of Zn// V_2O_5 -rGO remains at $236.6 \text{ mAh}\cdot\text{g}^{-1}$, while the value of Zn// V_2O_5 is decreased at $218.7 \text{ mAh}\cdot\text{g}^{-1}$. Moreover, after 1000 GCD tests at 2.0

$\text{A}\cdot\text{g}^{-1}$, the capacity retention of $\text{Zn}/\text{V}_2\text{O}_5$ and $\text{Zn}/\text{V}_2\text{O}_5\text{-rGO}$ is 67.3% and 98.5%, respectively. The results indicate that rGO nanosheets can effectively inhibit the dissolution of V_2O_5 and improve the stability of the cathode. They also provide additional ion- and charge-transfer channels, as depicted in Figure 23d,e. It is worth mentioning that in this study a flexible $\text{Zn}/\text{V}_2\text{O}_5\text{-rGO}$ AZIB (Figure 23f) was developed in order to verify the practical application of $\text{V}_2\text{O}_5\text{-rGO}$. The GCD curves at different current densities are presented in Figure 23g. GCD was also performed under various bending angles (from 0° to 150°), presenting similar discharge curves, as shown in Figure 23h. After 1000 bending cycles at 90° the specific capacity of the flexible battery is decreased by only 2%, shown in Figure 23i. The development of a flexible $\text{V}_2\text{O}_5\text{-rGO}$ cathode (Figure 23j) has also been reported by Zheng et al. [94]. As was indicated, V_2O_5 and GO in different ratios (1:1, 2:2, 5:1, 10:1, 15:1, 20:1) were initially mixed into an aqueous solution, followed by the addition of hydrazine, resulting in the reduction of GO. The $\text{V}_2\text{O}_5\text{-rGO}_{(2:1)}$ sample presented the highest capacity ($402.5 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$) (Figure 23k), where two plateau pairs at 0.5V/0.7V and 0.9V/1.1V are observed, assigned to the reversible $\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ conversion, respectively, due to the intercalation of the Zn^{2+} ions. The cycling performance of $\text{V}_2\text{O}_5\text{-rGO}_{(2:1)}$ is presented in Figure 23l, where a specific capacity of $28.8 \text{ mAh}\cdot\text{g}^{-1}$ was achieved after 4000 cycles at $5.0 \text{ A}\cdot\text{g}^{-1}$ (45.5% capacity retention), as well as 100% coulombic efficiency. The increased electrochemical performance could be attributed to the hybrid material morphology (Figure 23m), as V_2O_5 nanowires are closely wrapped by rGO nanosheets, improving the electrochemical kinetics and charge storage capability (Figure 23n).

At this stage, a brief discussion on metal–organic frameworks (MOFs) is warranted before proceeding to the noteworthy study conducted by Jia et al. [95]. In 2025, the Nobel Prize in Chemistry was awarded to Susumu Kitagawa, Richard Robson and Omar M. Yaghi for the development of MOFs; MOFs represent an important class of functional porous materials composed of metal ions or cluster nodes coordinated with organic linkers. Because of the endless combinations of nodes and linkers, MOFs can be produced with a wide range of structure and physicochemical properties. They are well-known for their extremely large specific surface area, adjustable pore size and structural flexibility, which make them ideal for various applications, including gas storage and separation, catalysis, sensing and energy storage [104,105]. However, most MOFs suffer from low electrical conductivity and limited structural stability. As a result, they are often used as precursors to synthesize metal oxides, nitrides, sulfides, phosphides, and carbon-based materials with highly ordered porous structure. Nevertheless, the high-temperature pyrolysis which is typically used in this process can lead to the collapse of the MOF precursor's porous structure. In their work, Jia et al. [95] reported the synthesis of a V-based MOF (MIL-88B(V))-rGO hybrid material (Figure 23o) and the in situ transformation to $\text{V}_2\text{O}_5\text{-rGO}$ (Figure 23p) during the initial charge/discharge cycle, due to electrochemical oxidation. The resulting amorphous V_2O_5 exhibits more channels and active sites for Zn^{2+} ions, compared to MIL-88B(V) nanorods, resulting in high specific capacity. Simultaneously, the rGO nanosheets provide continuous pathways for electron transport and ion diffusion, thereby enhancing redox reactions and pseudocapacitance. Based on the electrochemical studies, the novel $\text{V}_2\text{O}_5\text{-rGO}$ cathode presented an extremely high specific capacity of $479.6 \text{ mAh}\cdot\text{g}^{-1}$ at $50 \text{ mA}\cdot\text{g}^{-1}$, a superior rate capability of $263.6 \text{ mAh}\cdot\text{g}^{-1}$ at $5000 \text{ mA}\cdot\text{g}^{-1}$, as well as good cycling stability with a capacity retention of 80.3% after 400 cycles at $2000 \text{ mA}\cdot\text{g}^{-1}$.

Several studies have shown that the modification of V_2O_5 structure through the incorporation of guest species or molecules acting as “pillars” can expand the interlayer spacing, thereby enhancing Zn^{2+} diffusion, while others have highlighted the importance of exposing additional active oxygen sites within the structure. Sun et al. [96] followed an approach of introducing rGO between $\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$ layers, resulting in the expansion of the interlayer spacing up to 2 nm, as well as the increase in the oxygen active sites. The as-

prepared $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -rGO hybrid material exhibited outstanding electrochemical performance, achieving a specific capacity of $548 \text{ mAh} \cdot \text{g}^{-1}$ at $0.1 \text{ A} \cdot \text{g}^{-1}$ and 83% capacity retention after 100 cycles. Furthermore, density functional theory (DFT) calculations were also conducted. Firstly, the interlayer distance of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ layers increased from $9.10 \text{ \AA}$ to $11.52 \text{ \AA}$, after the introduction of rGO nanosheets. Additionally, in the vanadium oxide, Zn^{2+} coordinates with three oxygen atoms, occupying sites from both the upper and lower layers. By contrast, in $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -rGO, Zn^{2+} only coordinates with three oxygen atoms on a single layer of VO. This difference exposes more active oxygen sites in the hybrid material for Zn^{2+} ion accommodation, enabling them to be stored on both the upper and lower VO layers. Simultaneously, the incorporation of rGO introduces additional active oxygen sites, which further enhance the Zn^{2+} storage capacity of the cathode. As shown in Figure 24, $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -rGO exhibits a lower diffusion barrier (0.52 eV) than $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (0.74 eV), indicating improved ion mobility. Moreover, the hybrid material provides two additional diffusion pathways on the upper and lower sides of the rGO. The side lacking oxygen-containing groups shows an even lower barrier (0.35 eV), further promoting diffusion kinetics.

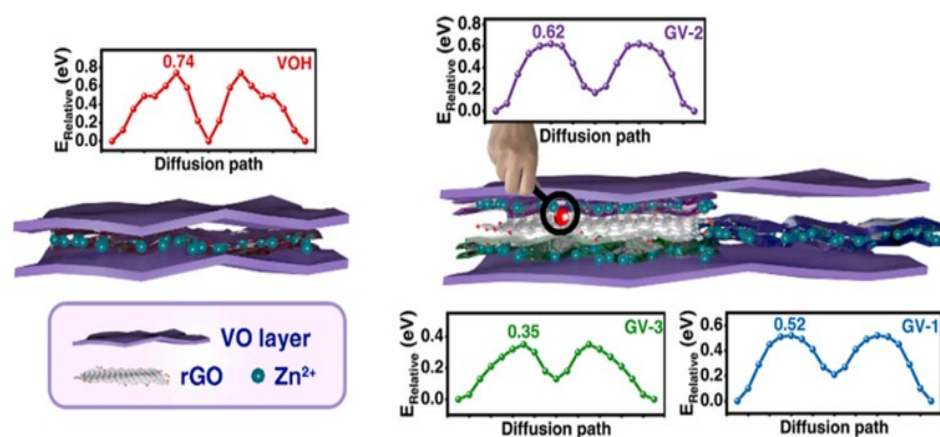


Figure 24. The Zn^{2+} diffusion barriers at $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -rGO (blue, red, grey, and white spheres represent V, O, C, and H atoms, respectively). (Adapted with permission by [96]).

Luo et al. [97] reported the combination of Mg^{2+} - V_2O_5 with rGO via a hydrothermal treatment. The presence of rGO enhances the electron transfer and reduces the dissolution of the cathode in the electrolyte, while Mg^{2+} ions play the role of the “pillars”, increasing the interlayer spacing of the V_2O_5 . The as-prepared cathode material exhibited a remarkable specific capacity of $530 \text{ mAh} \cdot \text{g}^{-1}$ at $0.1 \text{ A} \cdot \text{g}^{-1}$ and an excellent cycle performance, achieving 89% capacity retention for 5000 cycles at $5.0 \text{ A} \cdot \text{g}^{-1}$. In their work, Muthukumar et al. [98] developed a V_2O_5 -rGO via a co-precipitation method, using divalent metal ions (e.g., Zn^{2+} , Mn^{2+}) to form strong bonds between the two components. Simultaneously, a portion of metal ions are inserted into the structure of V_2O_5 nanoribbons, enhancing the Zn^{2+} ion storage. More specifically, when only Zn^{2+} ions were present during the co-precipitation process, the $\text{Zn}_{0.42}\text{V}_2\text{O}_{7.54}$ -rGO cathode exhibited a maximum specific capacity of $395 \text{ mAh} \cdot \text{g}^{-1}$ at $0.5 \text{ A} \cdot \text{g}^{-1}$, but only 28% of its capacity was retained from cycle 50 to cycle 2000 at $4.0 \text{ A} \cdot \text{g}^{-1}$. When both Zn^{2+} and Mn^{2+} ions were present during the synthesis procedure, the final $\text{Zn}_{0.12}\text{Mn}_{0.14}\text{V}_2\text{O}_{7.16}$ -rGO cathode exhibited lower specific capacity ($291 \text{ mAh} \cdot \text{g}^{-1}$ at $0.5 \text{ A} \cdot \text{g}^{-1}$), but its capacity retention was significantly increased to 77%. The increased capacity of the $\text{Zn}_{0.42}\text{V}_2\text{O}_{7.54}$ -rGO may be attributed to the reversible insertion/extraction of the pre-inserted Zn^{2+} , which are weakly bound to the V_2O_5 framework. On the other hand, the Mn^{2+} ions in the $\text{Zn}_{0.12}\text{Mn}_{0.14}\text{V}_2\text{O}_{7.16}$ -rGOs are strongly anchored onto the V_2O_5 and remain inactive during charging/discharging. As a result, they occupy potential Zn^{2+} sites, reducing the overall capacity. However, the strong binding of manganese ions

to both V_2O_5 and rGO enhances structural stability and facilitates faster electron transport, ultimately leading to improved capacity retention of the cathode.

Furthermore, VOOH has been considered a suitable cathode for Zn^{2+} storage due to its layered structure, while its good compatibility with aqueous electrolytes arises from the presence of hydroxyl ($-\text{OH}$) groups, which improve the interfacial properties and facilitate ion transport. Recently, a VOOH-rGO hybrid material was synthesized via a hydrothermal method and employed as a cathode material in AZIBs [99]. The resulting 3-D VOOH-rGO network effectively accommodates volume changes during charging/discharging, while providing efficient pathways for both ion diffusion and electron transport. The CV curves of the initial cycles of the VOOH-rGO are presented in Figure 25a. In the first cycle, the two pairs of redox peaks at 0.53/0.67 V and 0.9/1.0 V suggest the Zn^{2+} intercalation/deintercalation and the $\text{V}^{4+}/\text{V}^{3+}$ redox transition. Additionally, the distinct oxidation peak at 1.14 V and the anodic peak at 1.0 V merged into a broader oxidation peak in the subsequent cycles, suggesting that VOOH may gradually undergo a phase transition, leading to the formation of $\text{V}_{10}\text{O}_{24}\cdot n\text{H}_2\text{O}$ during prolonged charge/discharge. The rate capability of VOOH-rGO cathode is presented in Figure 25b, revealing its excellent performance with only a slight reduction in specific capacity observed across different current densities. The average capacity value of VOOH-rGO was $330 \text{ mAh}\cdot\text{g}^{-1}$, $292 \text{ mAh}\cdot\text{g}^{-1}$, $256 \text{ mAh}\cdot\text{g}^{-1}$, $224 \text{ mAh}\cdot\text{g}^{-1}$, $188 \text{ mAh}\cdot\text{g}^{-1}$ and $131 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$, $0.5 \text{ A}\cdot\text{g}^{-1}$, $1.0 \text{ A}\cdot\text{g}^{-1}$, $2.0 \text{ A}\cdot\text{g}^{-1}$, $3.0 \text{ A}\cdot\text{g}^{-1}$ and $5.0 \text{ A}\cdot\text{g}^{-1}$, respectively. Notably, the capacity of VOOH-rGO was $275 \text{ mAh}\cdot\text{g}^{-1}$, when the current density was restored to $0.5 \text{ A}\cdot\text{g}^{-1}$, indicating its good reversibility. The charge/discharge profiles of VOOH-rGO up to 2800 cycles are presented in Figure 25c, while the cyclic performance at $1.0 \text{ A}\cdot\text{g}^{-1}$ is depicted in Figure 25d, exhibiting a specific capacity of $189 \text{ mAh}\cdot\text{g}^{-1}$ after 280 cycles. Moreover, the long-term cycling stability of VOOH-rGO at $2.0 \text{ A}\cdot\text{g}^{-1}$ is shown in Figure 25e, where after 1000 cycles the specific capacity of the electrode was $104 \text{ mAh}\cdot\text{g}^{-1}$.

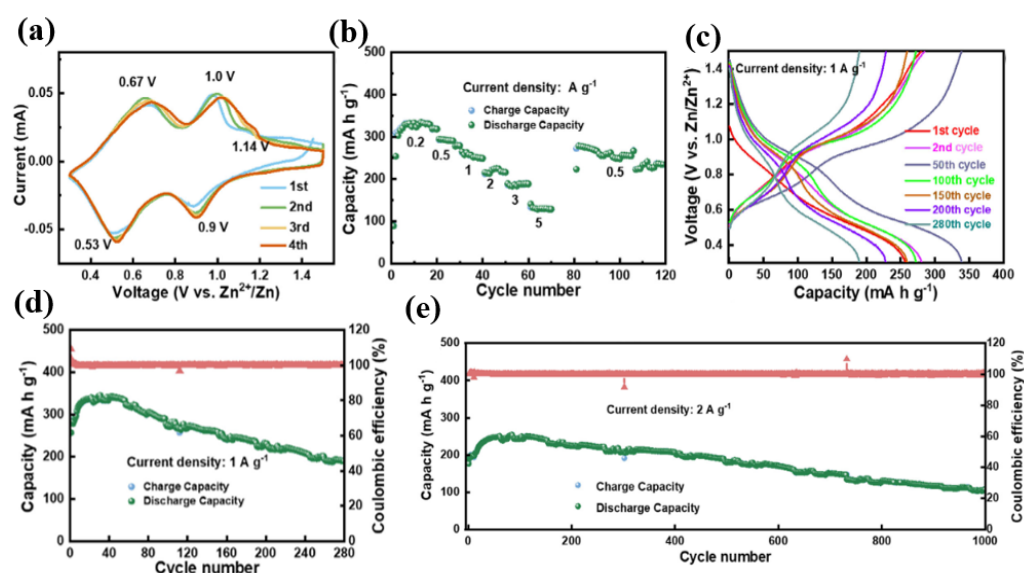


Figure 25. (a) CV curves of VOOH-rGO at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. (b) Rate capability of VOOH-rGO at various current densities. (c) Charge/discharge profiles of VOOH-rGO at $1.0 \text{ A}\cdot\text{g}^{-1}$. (d) The cycling performance of VOOH-rGO at $1.0 \text{ A}\cdot\text{g}^{-1}$. (e) Long-term cycling performance of VOOH-rGO at $2.0 \text{ A}\cdot\text{g}^{-1}$. (Adapted with permission by [99]).

Vanadium dioxide (VO_2) is another promising cathode material due to its high theoretical capacity ($646 \text{ mAh}\cdot\text{g}^{-1}$). Li et al. [100] reported the hydrothermal synthesis of a VO_2 -rGO hybrid material with superior conductivity. The tunnel-structured VO_2 -rGO cathode

material underwent a phase transition after the first charging process at 1.6 V, leading to the formation of laminated $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ -rGO (T-VO₂-rGO), which offers better Zn²⁺ ion storage and diffusion. According to the Nyquist plots, T-VO₂-rGO also exhibits lower charge-transfer resistance ($R_{\text{ct}} = 123 \, \Omega$), compared to pristine VO₂ ($R_{\text{ct}} = 279 \, \Omega$). In order to further study the reaction kinetics, the CV curves of T-VO₂-rGO at different scan rates were obtained and the results suggested a multi-step Zn²⁺ intercalation/deintercalation process with two pairs of redox peaks. Based on Equation (9), which describes the battery-capacitive behavior, the calculated *b*-values for peaks 1, 2, 3, and 4 were 0.51, 0.89, 0.72, and 0.55, respectively. These results indicate that the electrode exhibits a combination of capacitive and diffusion-controlled processes. It is also worth noting the crucial role of rGO in enhancing the structural stability of T-VO₂-rGO, resulting in a capacity retention of 84% after 1000 cycles at 5.0 A·g^{−1}, compared to only 51% achieved by VO₂ under the same conditions. Another study [101] reported the hydrothermal synthesis of a VO₂-rGO hybrid material presenting ultra-high specific capacity of 527 mAh·g^{−1} at 1.0 A·g^{−1} and ultra-long stability of 183.4 mAh·g^{−1} at 20.0 A·g^{−1} after 30,000 cycles. As was revealed by ex situ XRD and XPS analysis, beyond the typical H⁺/Zn²⁺ co-intercalation/deintercalation process during charging/discharging, the cathode underwent a phase transition from amorphous VO₂ to V₂O₃ (Figure 26).

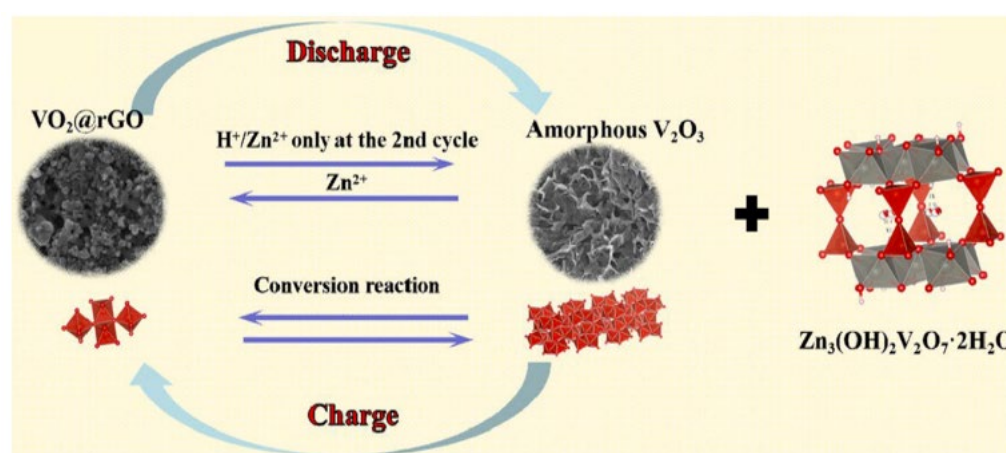


Figure 26. Schematic representation of the zinc storage mechanism of the Zn//VO₂-rGO battery. (Adapted with permission by [101]).

The combination of other VO_s with rGO has also been studied, including V₁₀O₂₄·12H₂O-rGO [102] and NH₄V₄H₁₀-rGO [103] hybrid materials. V₁₀O₂₄·12H₂O is a mixed-valence vanadium oxide, containing both V⁵⁺ and V⁴⁺ species. As a result, it exhibits higher electronic conductivity and superior cyclic performance compared to single-valence VO_s, such as V₂O₅. However, it faces structural degradation and dissolution during the charging/discharging process. In their work, Giri et al. [102] synthesized a V₁₀O₂₄·12H₂O-rGO hybrid material via a hydrothermal method (160 °C, 12 h) and evaluated its electrochemical performance. As demonstrated, the specific capacity of V₁₀O₂₄·12H₂O-rGO (318.65 mAh·g^{−1} at 0.1 A·g^{−1}) was significantly higher than pristine V₁₀O₂₄·12H₂O (222.47 mAh·g^{−1} at 0.1 A·g^{−1}) (Figure 27a). Furthermore, the capacity retention of a V₁₀O₂₄·12H₂O-rGO cathode was 71.37%, while V₁₀O₂₄·12H₂O achieved only 30.39% after 1000 cycles at 1.0 A·g^{−1} (Figure 27b). In the study of Lin et al. [103], density functional theory (DFT) calculations (Figure 27c–f) were initially employed to predict that incorporating rGO into NH₄V₄H₁₀ would expand the interlayer spacing and weaken electrostatic interactions, thereby facilitating Zn²⁺ ion diffusion within the framework of the cathode. Subsequently, NH₄V₄H₁₀ and NH₄V₄H₁₀-rGO were synthesized via a hydrothermal method (Figure 27g). The electrochemical tests validated the theoretical predictions,

as the $\text{NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$ demonstrated a specific capacity of $507 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$, which was higher than the specific capacity of $\text{NH}_4\text{V}_4\text{H}_{10}$ ($464 \text{ mAh}\cdot\text{g}^{-1}$). Additionally, $\text{NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$ retained 95% of its initial specific capacity ($388 \text{ mAh}\cdot\text{g}^{-1}$ at $5.0 \text{ A}\cdot\text{g}^{-1}$) after 600 cycles (Figure 27h). In contrast, $\text{NH}_4\text{V}_4\text{H}_{10}$ presented lower capacity retention under the same conditions. The above study shows that integrating rGO with $\text{NH}_4\text{V}_4\text{H}_{10}$ is an effective way to create high-capacity, long-life cathodes for AZIBs, validating theoretical predictions with experimental performance.

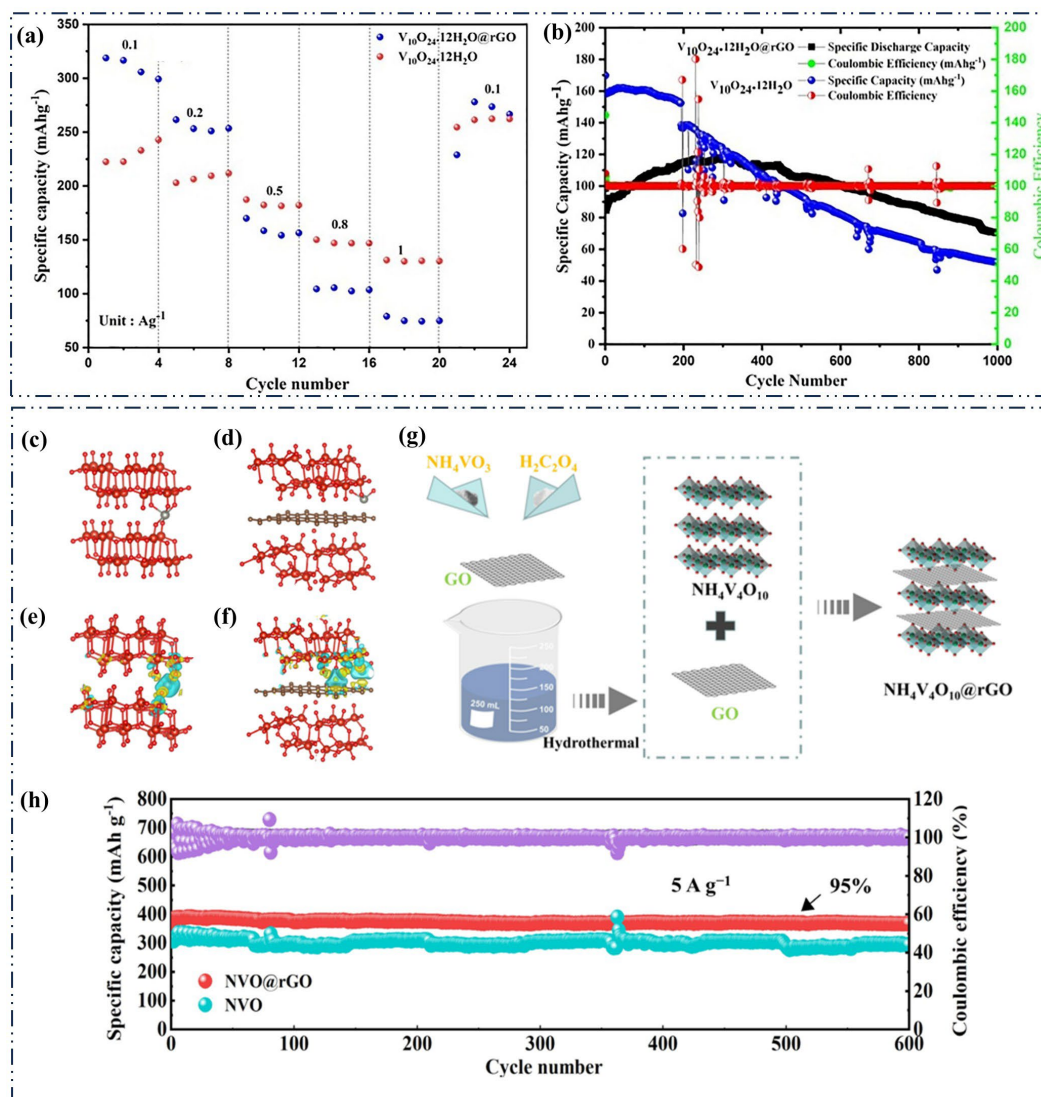


Figure 27. (a) Rate performance of $\text{V}_{10}\text{O}_{24}\cdot 12\text{H}_2\text{O}$ and $\text{V}_{10}\text{O}_{24}\cdot 12\text{H}_2\text{O}\text{-rGO}$ at different current densities. (b) Cycling performance of $\text{V}_{10}\text{O}_{24}\cdot 12\text{H}_2\text{O}$ and $\text{V}_{10}\text{O}_{24}\cdot 12\text{H}_2\text{O}\text{-rGO}$ at $1.0 \text{ A}\cdot\text{g}^{-1}$. (Adapted with permission by [102]). Optimized structure of (c) $\text{Zn-NH}_4\text{V}_4\text{H}_{10}$ and (d) $\text{Zn-NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$. Charge density difference between (e) $\text{Zn-NH}_4\text{V}_4\text{H}_{10}$ and (f) $\text{Zn-NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$. (g) Schematic representation of $\text{NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$ synthesis procedure. (h) Cycling performance of $\text{NH}_4\text{V}_4\text{H}_{10}$ and $\text{NH}_4\text{V}_4\text{H}_{10}\text{-rGO}$ at current density of $5.0 \text{ A}\cdot\text{g}^{-1}$. (Adapted with permission by [103]).

3.4. rGO-Prussian Blue Analogues

Prussian blue is a ferric hexacyanoferrate ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), where Fe atoms connected to N could be replaced and interstitially modified with Cr, Zn, Mn, Co, Ni, Cu, and other elements to produce a series of metallic hexacyanoferrates (MHCFs), with a similar composition and crystal structure. MHCFs are also known as Prussian blue analogues (PBAs) (Figure 28), which are typically represented by the general formula $\text{A}_2\text{M}_\text{A}\text{M}_\text{B}(\text{CN})_6$ ($\text{A} = \text{Li}^+, \text{Na}^+, \text{K}^+$, zeolite water; $\text{M}_\text{A} = \text{Fe}, \text{Ni}, \text{Mn}, \text{V}, \text{Mo}, \text{Cu}, \text{Co}, \text{Zn}$; $\text{M}_\text{B} = \text{Fe}, \text{Co}, \text{Cr}, \text{Ru}$). PBAs are considered a promising class of cathode materials in AZIBs due to their facile synthesis process, environmentally friendly characteristics, large insertion sites and ion channels, enabling rapid reaction kinetics, as well as working voltage of up to 1.5–1.8 V (vs. Zn^{2+}/Zn) [106].

The utilization of PBAs as cathode material in AZIBs was firstly reported in 2014 by Zhang et al. [107], investigating the role of $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (ZnHCF) (Figure 29). Since then, numerous studies have explored the application of PBAs in AZIBs; however, several challenges persist, including their limited energy density and structural instability during cycling. In order to overcome these limitations, PBAs have been combined with rGO, as discussed in the present section. Recently, Hu et al. [108] developed a vanadium–zinc diphasic PBA (ZnVHCF)-rGO hybrid material with excellent storage performance. ZnHCF shows low capacity because of the electrochemical inactivity of Zn. More specifically, Zn^{2+} does not participate in redox reactions; instead, only the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple is electrochemically active, leading to a single charge/discharge plateau associated with Fe-based electron transfer. Therefore, a diphasic PBA is proposed in order to overcome this issue. ZnVHCF exhibits multi-electron transfer during redox reactions, enhancing the specific capacity of ZnHCF from $62.4 \text{ mAh}\cdot\text{g}^{-1}$ to $96.7 \text{ mAh}\cdot\text{g}^{-1}$ at a current of $0.1 \text{ A}\cdot\text{g}^{-1}$. However, its electrochemical stability in an aqueous environment is relatively poor. Thus, its combination with rGO could protect the material from direct contact with water molecules and delay its dissolution process, as well as increase the electrical conductivity. Consequently, the ZnVHCF-rGO achieved enhanced electrochemical performance, reaching a specific capacity of $152.3 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$. Based on XPS analysis, it was observed that, during discharging, accompanied by Zn^{2+} insertion, V^{5+} and V^{4+} are reduced to lower oxidation states to maintain charge balance. Notably, during charging the V^{3+} peak disappears, while V^{5+} and V^{4+} are dominant. Similarly, the Fe^{2+} signal increases during discharging, whereas the Fe^{3+} signal becomes more pronounced during charging. Herein, it is worth noting that, to the best of our knowledge, the study by Hu et al. [108] remains the only reported work published since 2023. Notably, PBAs-rGO hybrid materials have been recently explored as cathodes in other energy storage applications, including sodium-ion batteries (SIBs) [109,110] and hybrid supercapacitors [111].

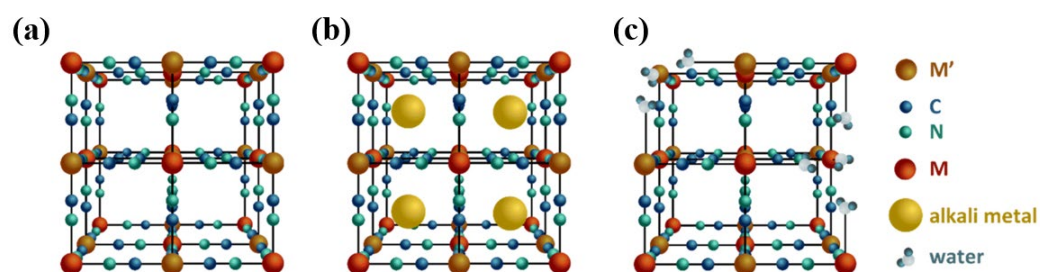


Figure 28. Schematic illustrations of (a) the theoretical lattice of PBAs, (b) defect-free lattice of PBAs with alkali ions and (c) PBA lattice with defects (water molecules in defect sites). (Adapted with permission by [112]).

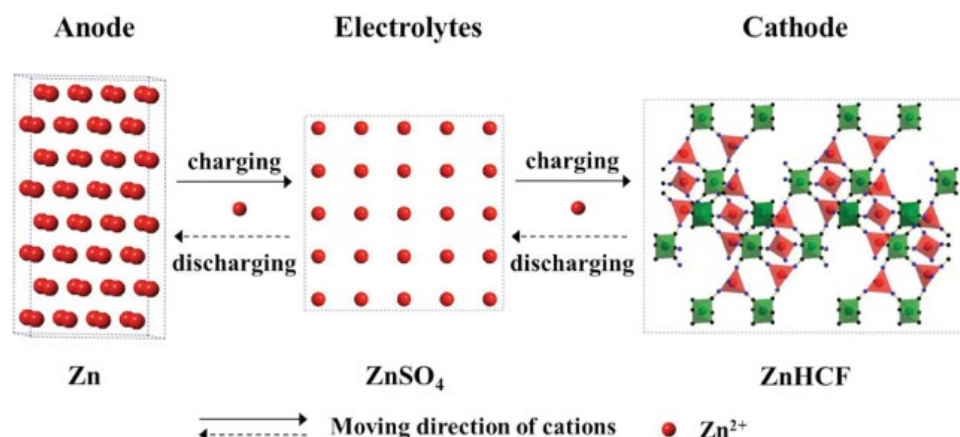


Figure 29. Schematic illustrations of AZIBs based on ZnHCF cathode. (Adapted with permission by [107]).

3.5. rGO-Conductive Polymers

Conductive polymers (CPs), including polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), are considered a promising class of organic materials for electrochemical energy storage systems, such as supercapacitors and rechargeable batteries. This is attributed to their unique π -conjugated backbones, enabling high charge carrier mobility, tunable electrical conductivity, inherent mechanical flexibility and ease of fabrication. Nevertheless, their practical application in AZIBs is often limited by several factors, such as insufficient active surface area, volume changes during cycling, etc. [113–115]. To address these challenges, the integration of CPs with rGO has emerged as an effective strategy to enhance their electrochemical performance. To the best of our knowledge, since 2023 only two studies have reported the combination of CPs with rGO for utilization as cathode materials in AZIBs; these cases are discussed in the present section, whereas ternary CPs/rGO-based hybrid materials have also been explored and will be addressed later.

Among CPs, PANI has attracted significant attention as a cathode material in AZIBs because of its high theoretical capacity ($294 \text{ mAh}\cdot\text{g}^{-1}$) [116], multiple redox states, fast redox kinetics, low cost and eco-friendliness. However, it suffers from a small specific surface area and a tendency to aggregate. Recently, Liu et al. [117] reported the fabrication of a PANI-rGO aerogel cathode with remarkable specific capacity and excellent rate performance. As is presented in Figure 30a, deprotonated PANI was initially added into N-methyl-2-pyrrolidone (NMP), forming a homogeneous dispersion, followed by the addition of GO aqueous dispersion and sodium ascorbate. Subsequently, the mixture was heated at 95°C for 3 h and, after it was dialyzed in DI water for 24 h, a lyophilization process occurred for 48 h. Notably, the PANI-rGO aerogel exhibited an increased specific surface area of $189.55 \text{ m}^2\cdot\text{g}^{-1}$. In addition, a maximum specific discharge capacity of $200 \text{ mAh}\cdot\text{g}^{-1}$ ($0.5 \text{ A}\cdot\text{g}^{-1}$) and a rate performance of $135 \text{ mAh}\cdot\text{g}^{-1}$ ($10.0 \text{ A}\cdot\text{g}^{-1}$) were achieved. As depicted in Figure 30b,c PANI-rGO//Zn presented a superior rate capability, compared to PANI//Zn battery. The excellent performance of the cathode is attributed to its unique structure, which enables the polymeric chains to achieve high contact with both electrolyte and the conductive rGO network, as well as the π - π stacking interactions between PANI and rGO, providing effective channels for rapid electron transport.

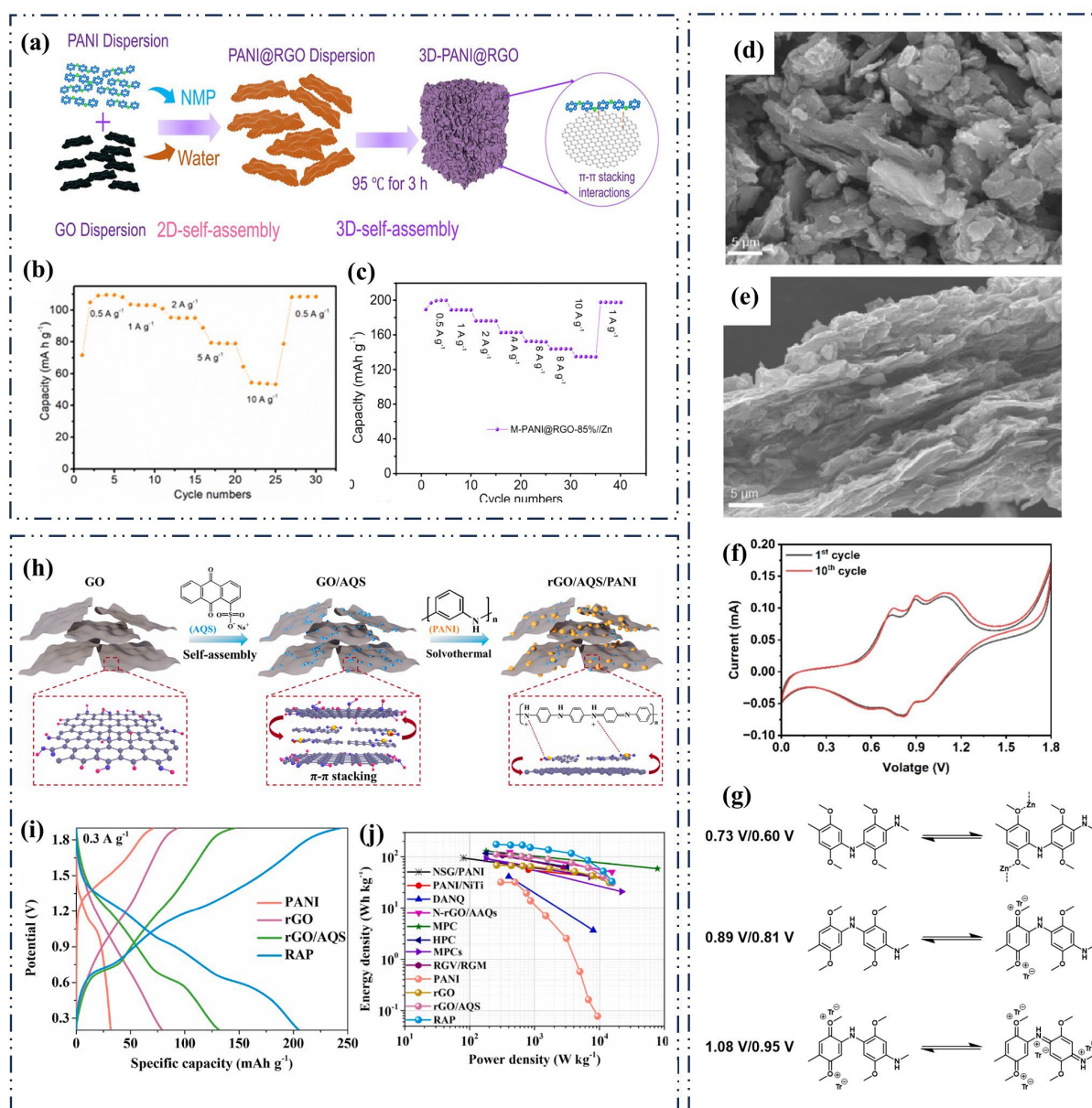


Figure 30. (a) Schematic representation of the fabrication process of the 3-D PANI-rGO aerogel. (b,c) The rate capability of PANI//Zn and PANI-rGO//Zn batteries, respectively. (Adapted with permission by [117]). (d,e) FE-SEM images of polyAHQDME-rGO. (f) CV test of polyAHQDME-rGO at 0.1 mV/s. (g) Reaction mechanism at the positions of each redox peak. (Adapted with permission by [118]). (h) Schematic representation of the preparation of rGO-AQS-PANI. (i) The galvanostatic charge-discharge (GCD) curves of PANI, rGO, rGO-AQS and rGO-AQS-PANI (RAP). (j) Ragone plots of PANI, rGO, rGO-AQS, RAP and other PANI-based cathode composites reported in the literature. (Adopted with permission by [119]).

In their work, Zhang et al. [118] suggested the utilization of a hybrid polymer with heterozygous structural characteristics of a PANI backbone and quinone functional groups, named poly-amino-hydroquinone-dimethylether (polyAHQDME), so as to enhance the capacity of the PANI. The polyAHQDME was subsequently grafted onto the rGO surface via an in situ technique in order to enhance its electrical conductivity. The as-prepared polymer-rGO hybrid material exhibited various channels in its structure, as revealed by FE-SEM images (Figure 30d,e). Furthermore, the electrochemical performance of the Zn//polyAHQDME-rGO battery was evaluated using a coin cell assembled with a polyAHQDME-rGO cathode, a Zn anode, and a porous glass fiber separator in

$\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte. It is interesting to note that CV tests at a scan rate of 0.1 mV/s (Figure 30f) revealed three pairs of redox peaks at 0.73 V/0.60 V, 0.89 V/0.81 V, and 1.08 V/0.95 V, respectively, which can be attributed to the reversible redox reactions of the PANI backbone and the methylated quinones (Figure 30g). Furthermore, the specific capacity of the device was calculated at 242.8, 206.5, 188.8, 173.5, 156.3, 128.0, and 83.8 $\text{mAh}\cdot\text{g}^{-1}$, for current densities of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 A/g, respectively. Notably, the battery achieved a capacity of 236.1 $\text{mAh}\cdot\text{g}^{-1}$ when the current density returned to 0.2 A·g^{−1}, indicating increased electrochemical stability. On the other hand, both rGO and non-polymerized AHQDME-rGO samples yielded inferior capacity and rate capability.

Finally, it is worth highlighting the application of PANI-rGO in Zn-ion capacitors (ZICs). While batteries offer high energy density, they are typically limited by low power performance and poor rate capability. In contrast, supercapacitors exhibit high power density and excellent cycling stability, yet suffer from low energy density. By combining the advantages of both systems, hybrid ion capacitors have been developed to achieve high energy, as well as high power characteristics, attracting significant attention in recent years. Hu et al. [119] reported the decoration of 1-anthraquinonesulfonic acid sodium salt (AQS)-modified rGO with PANI, as shown in Figure 30h. When combined, rGO establishes a stable 3-D conductive framework that accommodates the volumetric changes of PANI, thereby alleviating mechanical stress and improving structural integrity during repeated cycling. At the same time, PANI chains, which are uniformly distributed onto and between rGO layers, inhibit restacking, regulate pore size distribution, and enhance the availability of electrochemically active sites. Furthermore, AQS contributes additional redox-active sites through reversible benzoquinone/phenol conversion and supplies H⁺/Zn²⁺ ions for PANI doping, thereby alleviating irreversible deprotonation and enhancing the structural and electrochemical stability of PANI. As a result, the final ZIC achieved higher specific capacity (205.1 $\text{mAh}\cdot\text{g}^{-1}$) and superior energy density (175 $\text{Wh}\cdot\text{kg}^{-1}$) (Figure 30i,j), as well as excellent cycling stability (86.2% capacity retention over 10,000 cycles), compared to rGO, PANI and rGO/AQS counterparts.

3.6. rGO-Transition Metal Chalcogenides

Transition metal chalcogenides (TMCs) are a unique class of nanomaterials formed by the combination of transition metals (e.g., Mn, V, Mo, etc.) and chalcogen elements (S, Se, Te). In recent years, 2-D TMCs have attracted significant scientific interest due to their tunable electrical properties (varying from semiconducting to metallic), layered structure (Figure 31), in which the interlayers are bound together by weak van der Waals interactions, and large specific surface area. As a result, they provide abundant active sites and efficient pathways for both electron and ion transport, which make them promising cathode materials in AZIBs [120]. Beyond the 2-D layered TMCs, 1-D TMCs nanorods (NRs) and 0-D TMCs nanoparticles (NPs) have also been explored as cathodes in AZIBs. Herein, the most recent studies on the combination of 2-D, 1-D and 0-D TMCs with rGO will be discussed.

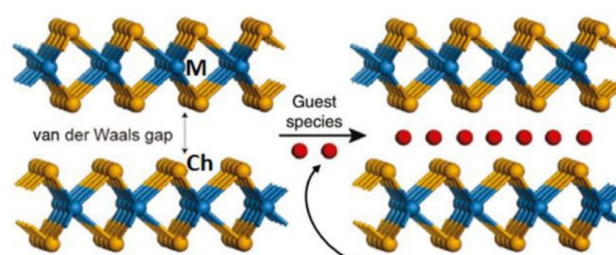


Figure 31. The layered structure of 2-D TMCs. (Adapted with permission by [121]).

To begin with, molybdenum disulfide (MoS_2) has emerged as a compelling cathode candidate because of its lamellar structure, adjustable interlayer spacing for Zn^{2+} ion diffusion, and high theoretical capacity ($335 \text{ mAh}\cdot\text{g}^{-1}$). Despite its advantageous properties, practical implementation of MoS_2 cathodes faces critical challenges, such as inherently low conductivity, and undesirable side reactions in aqueous electrolytes, leading to decreased capacity retention and cycle life [122]. MoS_2 exists in two commonly observed crystalline phases: the 2H phase, which exhibits semiconducting properties, and the 1T phase, which displays metallic behavior. Although 2H MoS_2 is structurally stable, the small interlayer spacing and inactive basal plane decrease its electrochemical performance. On the other hand, 1T MoS_2 with larger interlayer spacing and improved electronic conductivity is beneficial for both ion and electron transfer; however, it is metastable in nature. Despite the promising characteristics, the electrochemical performance of MoS_2 -based AZIBs remains significantly below the level required for practical applications. Jia et al. [123] investigated the combination of 1T-2H phase mixed MoS_2 with rGO, via a hydrothermal treatment (180°C , 24 h). The resulting flower-like hybrid material (Figure 32a) exhibits an expanded interlayer distance from $7.0 \text{ \AA}$ to $9.6 \text{ \AA}$, a high proportion of the 1T phase, and enhanced hydrophilicity, all of which promote Zn^{2+} ion diffusion, charge transfer, and electrolyte penetration. The incorporation of rGO into the MoS_2 framework not only enlarges the interlayer spacing but also triggers a phase transition. More specifically, based on the XPS analysis, the 1T phase percentage in 1T-2H MoS_2 -rGO is 74.5%, which is higher than the 65.9% observed in 1T-2H MoS_2 . The CV curves at $1 \text{ mV}\cdot\text{s}^{-1}$ and GCD profiles at $0.2 \text{ A}\cdot\text{g}^{-1}$ of bulk 2H MoS_2 , 1T-2H MoS_2 and 1T-2H MoS_2 -rGO cathodes are presented in Figure 32b and Figure 32c, respectively. As is observed, the CV area of bulk 2H MoS_2 is very small, indicating its poor Zn^{2+} storage capability. This is attributed to the limited interlayer spacing and dominant 2H phase. In contrast, both 1T-2H MoS_2 and 1T-2H MoS_2 -rGO exhibit larger CV area, with the latter cathode material delivering the highest specific capacity. The results are further confirmed by GCD. The specific capacity of bulk 2H MoS_2 , 1T-2H MoS_2 and 1T-2H MoS_2 -rGO at $0.2 \text{ A}\cdot\text{g}^{-1}$ is calculated at $2.9 \text{ mAh}\cdot\text{g}^{-1}$, $203.1 \text{ mAh}\cdot\text{g}^{-1}$ and $294.6 \text{ mAh}\cdot\text{g}^{-1}$, respectively. In addition, the long-term cycling stability of 1T-2H MoS_2 -rGO cathode is improved, compared to 1T-2H MoS_2 . Specifically, the capacity retention of the hybrid material is 96.8% after 1600 cycles at $3 \text{ A}\cdot\text{g}^{-1}$, while the 1T-2H MoS_2 cathode shows 86.2% retention under the same conditions. In Figure 32d the Zn^{2+} ion storage within the bulk 2H MoS_2 , 1T-2H MoS_2 and 1T-2H MoS_2 -rGO is illustrated. The narrow interlayer spacing ($6.2 \text{ \AA}$), poor hydrophilicity, and low electrical conductivity of bulk 2H MoS_2 limit Zn^{2+} diffusion, resulting in poor storage performance. The 1T-2H MoS_2 cathode shows improved capacity and rate capability due to its expanded interlayer spacing ($7.0 \text{ \AA}$) and enhanced electronic conductivity. Further improvement is achieved by 1T-2H MoS_2 -rGO heterostructure, where intercalated rGO increases the spacing to $9.6 \text{ \AA}$, reduces Zn^{2+} diffusion resistance, and improves electrolyte infiltration through enhanced hydrophilicity due to oxygen-containing groups. Additionally, rGO incorporation promotes the increase in the metallic 1T phase content, further enhancing electrical conductivity and enabling ultrafast charge transfer. In another recent study [124], 1T MoS_2 -rGO hybrid material was prepared via a hydrothermal method (150°C , 24 h), as shown in Figure 32e and further tested to evaluate its electrochemical behavior. The specific capacity of 1T MoS_2 and 1T MoS_2 -rGO at $0.1 \text{ A}\cdot\text{g}^{-1}$ was calculated at $216 \text{ mAh}\cdot\text{g}^{-1}$ and $304 \text{ mAh}\cdot\text{g}^{-1}$, respectively, indicating that rGO improves the performance of the cathode. Moreover, the capacity retention of 1T MoS_2 -rGO (81%) is increased compared to 1T MoS_2 (45%) after 1000 cycles at $1 \text{ A}\cdot\text{g}^{-1}$. The results suggest that rGO increases the metallic 1T phase content, while inhibiting the transformation of the metastable 1T MoS_2 into the semiconducting 2H MoS_2 . Furthermore, the reaction kinetics of the 1T MoS_2 -rGO hybrid material were evaluated, and the results revealed that the charge storage process is dominated by surface capacitive

behavior. As is observed in Figure 32f,g, the 1T MoS₂-rGO exhibits higher capacitance contribution than 1T MoS₂.

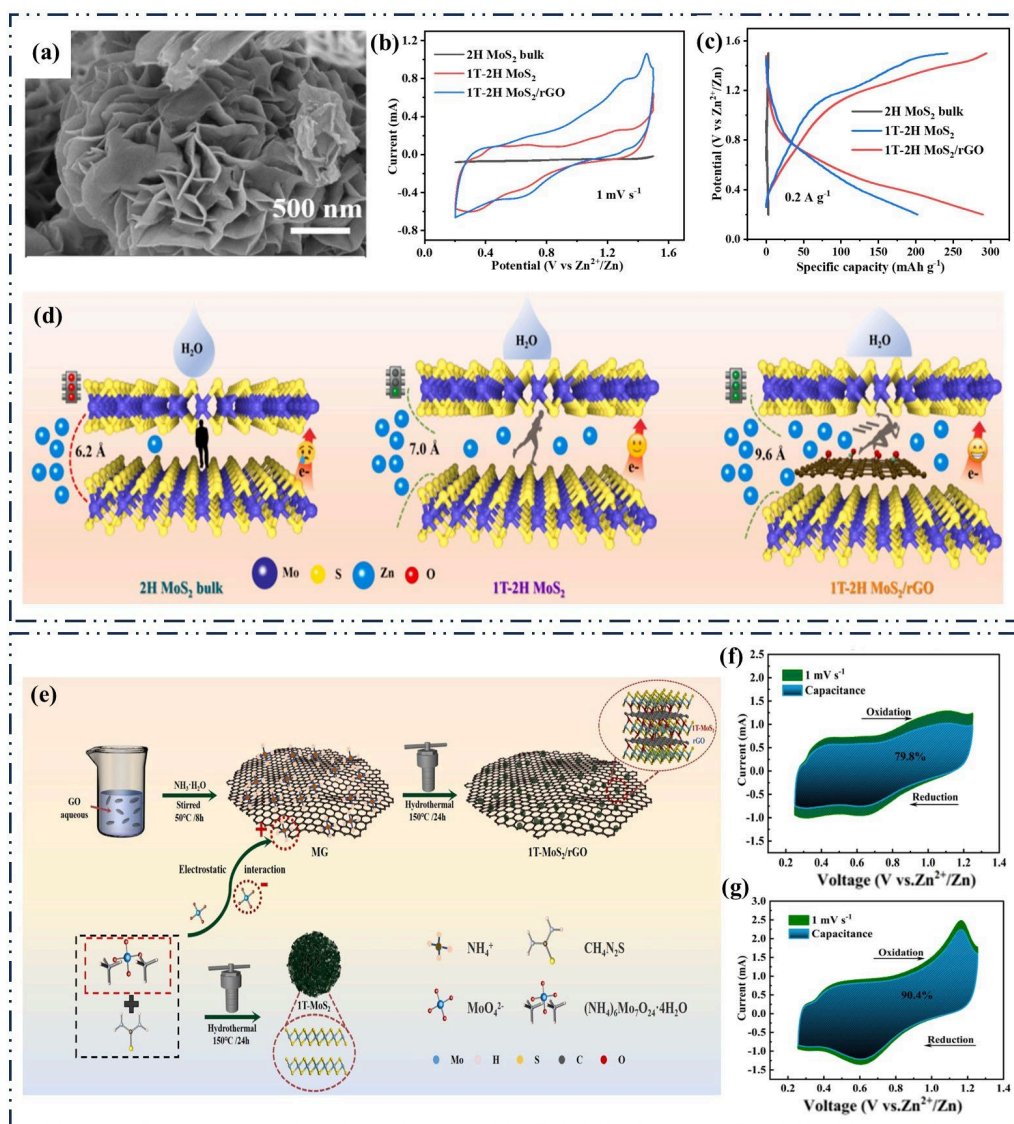


Figure 32. (a) SEM image of the 1T-2H MoS₂-rGO hybrid material. (b) CV curves and (c) GCD profiles of the bulk 2H MoS₂, 1T-2H MoS₂, and 1T-2H MoS₂-rGO cathodes. (d) Schematic illustration of the Zn²⁺ storage within the framework of the bulk 2H MoS₂, 1T-2H MoS₂, and 1T-2H MoS₂-rGO cathodes. (Adapted with permission by [123]). (e) Schematic representation of the 1T MoS₂-rGO synthesis process. (f,g) Capacitance contribution of 1T MoS₂ and 1T MoS₂-rGO at 1 mV s⁻¹ and different scan rates, respectively. (Adapted with permission by [124]).

Vanadium sulfides (V_xS_y) are also a category of TMCs which have sparked interest as high-performance cathode materials in AZIBs. Compared to VO₂ that were previously mentioned, V_xS_y exhibit lower electrostatic attraction with Zn²⁺, facilitating their faster diffusion within the cathode. Ju et al. [125] synthesized different types of V_xS_y-rGO hybrid materials and explored their electrochemical performance. More specifically, a three-step process was followed for the synthesis of V₅S₈-rGO and V₆S₈-rGO (Figure 33a). Briefly, a VO₂-rGO sample was initially prepared via a hydrothermal route (270 °C, 12 h), followed by a sulfidation process using chemical vapor deposition (CVD) to produce V₂S₈-rGO. The V₂S₈-rGO sample was further annealed under Ag/H₂ gas at 350 °C for 2 h and 12 h to obtain V₅S₈-rGO and V₆S₈-rGO, respectively. rGO prevents the agglomeration of V_xS_y nanorods

and improves electrical conductivity. All the V_xS_8 ($x = 2, 5, 6$)-rGO hybrid materials were characterized and tested as cathodes in AZIBs. Notably, the specific surface area of V_5S_8 -rGO ($50.4 \text{ m}^2\cdot\text{g}^{-1}$) and V_6S_8 -rGO ($47.4 \text{ m}^2\cdot\text{g}^{-1}$) were increased compared to V_2S_8 -rGO ($5.4 \text{ m}^2\cdot\text{g}^{-1}$), which is advantageous for increasing the contact area between the cathode and the electrolyte, contributing to higher charging/discharging capacity. Indeed, the V_5S_8 -rGO and V_6S_8 -rGO electrodes exhibited higher initial capacities and rate capabilities than the V_2S_8 -rGO electrode. Nevertheless, they present poorer structural robustness over cycling (70% after 700 cycles at $5 \text{ A}\cdot\text{g}^{-1}$), as opposed to V_2S_8 -rGO (99%), which may be attributed to the crystalline-to-amorphous transitions of their structure (Figure 33b).

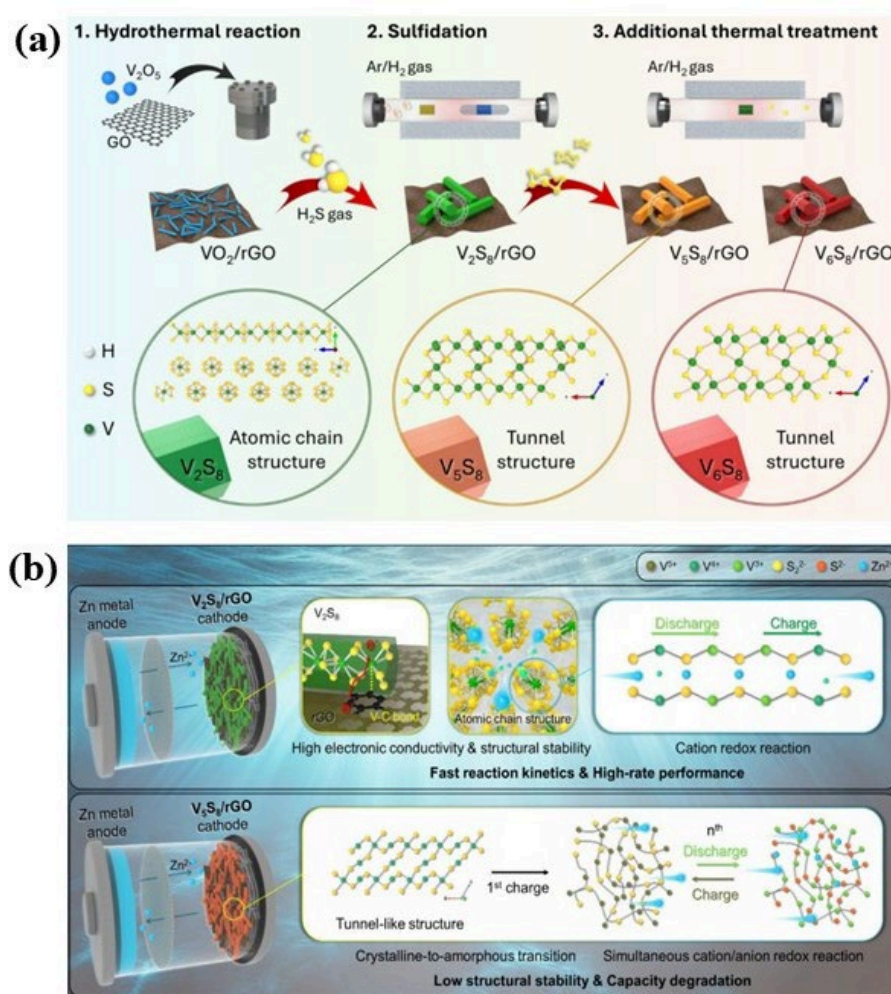


Figure 33. Schematic representation of (a) V_2S_8 -rGO, V_5S_8 -rGO and V_6S_8 -rGO synthesis procedure and (b) Zn^{2+} storage mechanism. (Adapted with permission by [125]).

Manganese chalcogenides, such as manganese selenide (MnSe), with high specific capacity and lower direct bandgap (1.2 eV), compared to the previously discussed manganese oxides, also hold great promise for applications in AZIBs. Nevertheless, they are susceptible to dissolution in the aqueous electrolyte, which not only degrades battery performance but also poses significant environmental concerns. Recently, Feng et al. [126] synthesized a MnSe-rGO hybrid material (Figure 34a) via a hydrothermal method, followed by annealing, where rGO serves as a conductive framework to anchor MnSe and enhance the structural stability and reversibility of the cathode. As shown in HR-TEM images (Figure 34b–d), MnSe NPs with an average diameter of around 40 nm are encapsulated within an rGO shell and these core-shell structures are homogeneously distributed onto the rGO surface. The specific capacity achieved by MnSe at 0.2 C was 172.5

$\text{mAh}\cdot\text{g}^{-1}$, while MnSe-rGO delivered an enhanced capacity of $236.7 \text{ mAh}\cdot\text{g}^{-1}$, which reached $310.3 \text{ mAh}\cdot\text{g}^{-1}$, after 12 cycles. The increase in the capacity is attributed to the continuous phase transition; the Mn-Se is a weaker bond compared to Mn-O and kinetically favors the conversion reaction (Figure 34e). Moreover, the cycling performance of the MnSe-rGO electrode was also improved. At this point it is worth mentioning that, after 150 charge/discharge cycles, XPS analysis of the Zn anode was conducted. As was revealed, there were no visible peaks attributed to Mn or Se, suggesting that rGO prevented the ion migration towards the anode, thus mitigating its passivation. Also, optical images of the separator after 150 cycles of MnSe and MnSe-rGO cathodes can be observed in Figure 34f,g. In the Zn//MnSe-rGO battery the separator maintains its initial white color, whereas the discoloration in the Zn//MnSe is attributed to MnSe decomposition, leading to separator contamination.

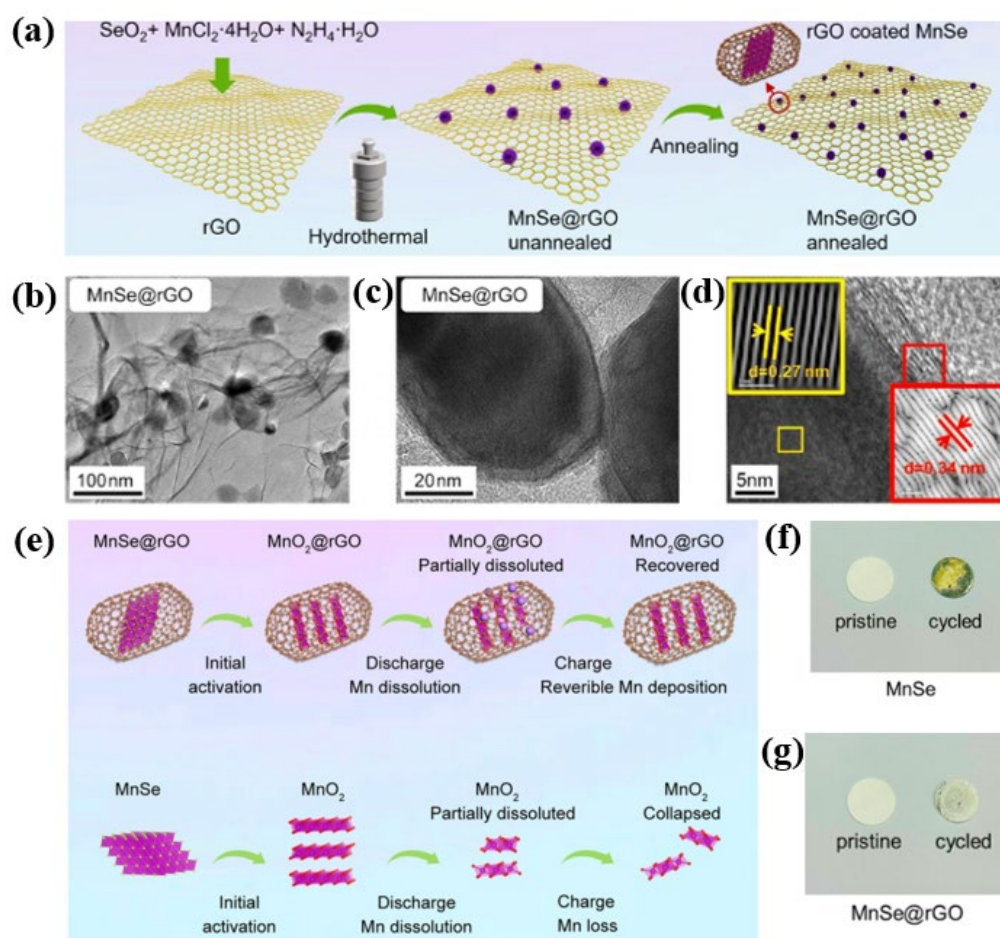


Figure 34. (a) Schematic representation of the MnSe-rGO hybrid material. (b–d) HR-TEM images of the MnSe-rGO hybrid material. (e) Schematic representation of the MnSe dissolution. (f,g) Optical images of the separator after 150 charge/discharge cycles of Zn//MnSe and Zn//MnSe-rGO, respectively. (Adapted with permission by [126]).

3.7. rGO–Other Materials

In addition to the studied combinations of rGO with MOs, VOs, PBAs, CPs and TMCs, increasing attention has been directed toward its integration with a broader range of materials. These include, but are not limited to, metal oxides, metal phosphates, metal nitrides, as well as other emerging inorganic or organic frameworks. Such hybrid systems highlight the versatility of rGO as a conductive matrix, structural stabilizer, and interfacial mediator. It is evident that the presence of rGO enhances electrical conductivity, mitigates

structural degradation during cycling, and facilitates ion transport, ultimately improving the overall electrochemical performance of AZIBs. The most recent advances in these novel rGO-based hybrid materials are summarized in the present section.

3.7.1. rGO–Metal Oxides/Metal Phosphates/Metal Nitrides

Beyond manganese and vanadium oxides, various metal oxides have been proposed as cathode materials in AZIBs. Among them, the polyanionic manganese vanadate (MnVO), consisting of interconnected VO_6 octahedral chains with Mn^{2+} located among the oxygen sheets, has been considered as a promising candidate due to the multiple accessible oxidation states of Mn and V, which enable high capacity. However, the low electrical conductivity of MnVO results in poor electrochemical performance. Therefore, Liu et al. [127] synthesized a MnV_2O_6 -N-doped rGO hybrid material via a co-precipitation method, followed by calcination, where N-doped rGO plays the role of the conductive framework, which inhibits volume changes of MnV_2O_6 nanorods and accelerates ion and electron diffusion, thereby enhancing the overall AZIB performance. Based on the electrochemical characterization, the MnV_2O_6 -N-doped rGO hybrid material delivers a discharge capacity of $331.1 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$ after 100 cycles, whereas only $211.7 \text{ mAh}\cdot\text{g}^{-1}$ is achieved by MnV_2O_6 . In a similar study [128], a $\text{MnV}_6\text{O}_{13}$ -rGO hybrid material was prepared via a hydrothermal method and applied as cathode material in AZIBs. In the CV curves of $\text{MnV}_6\text{O}_{13}$ -rGO (Figure 35a) at $0.2 \text{ mV}\cdot\text{s}^{-1}$, two pairs of redox peaks at $1.1/0.95 \text{ V}$ and $0.7/0.58 \text{ V}$ are observed, attributed to the valence changes of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$, respectively. As shown, the CV curves overlapped after five cycles, suggesting a $\text{MnV}_6\text{O}_{13}$ -rGO cathode with stable cycling performance. GCD profiles and rate performance of pristine $\text{MnV}_6\text{O}_{13}$ and $\text{MnV}_6\text{O}_{13}$ -rGO hybrid materials, containing different amounts of rGO, are presented in Figure 35b and Figure 35c, respectively. Based on the above results, there is an optimum rGO concentration in $\text{MnV}_6\text{O}_{13}$ -rGO hybrid material, where a maximum capacity of $360.3 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$ is achieved. Furthermore, the optimum hybrid material delivers enhanced cycling stability at $1 \text{ A}\cdot\text{g}^{-1}$, compared to all samples, as shown in Figure 35d, as well as after 10,000 cycles at $20 \text{ A}\cdot\text{g}^{-1}$ (Figure 35e).

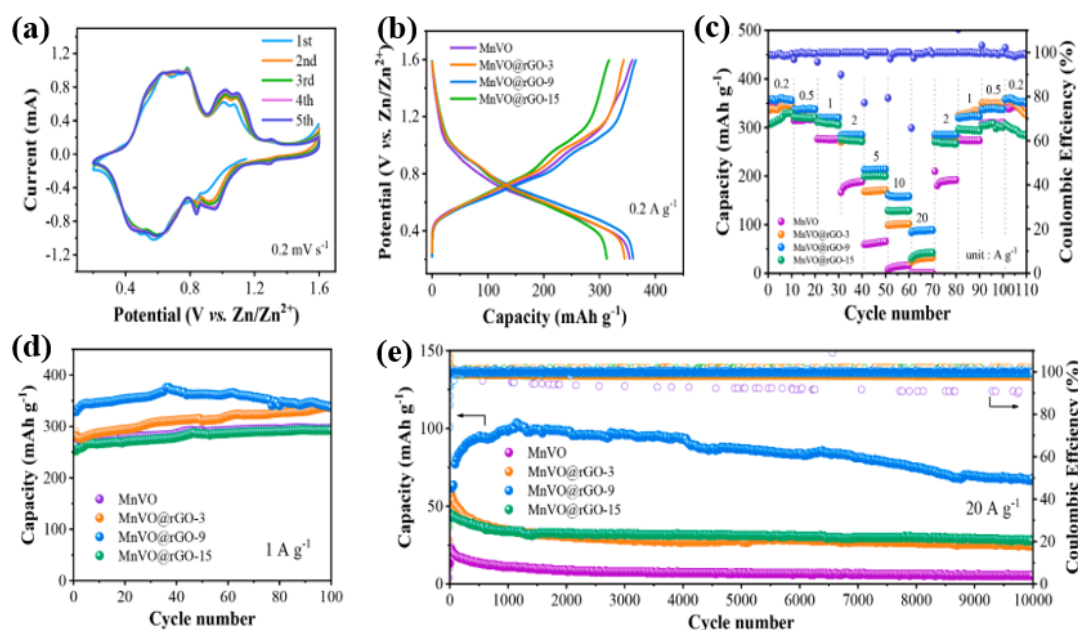


Figure 35. (a) CV curves of $\text{MnV}_6\text{O}_{13}$ -rGO at $0.2 \text{ mV}\cdot\text{s}^{-1}$. (b) GCD profiles, (c) rate performance, (d,e) cycling performance (at $1 \text{ A}\cdot\text{g}^{-1}$ and $20 \text{ A}\cdot\text{g}^{-1}$) of pristine $\text{MnV}_6\text{O}_{13}$ and $\text{MnV}_6\text{O}_{13}$ -rGO hybrid materials, containing different amounts of rGO. (Adapted with permission by [128]).

Vanadium phosphates (VPs) are another class of polyanionic materials with interesting properties, such as large ion diffusion channels, that have recently attracted significant attention in the field of energy. In their work, Zhou et al. [129] reported the fabrication of a NaVPO_4F -rGO electrode via a hydrothermal method and a post-calcination process. NaVPO_4F delivers high theoretical capacity ($143 \text{ mAh}\cdot\text{g}^{-1}$), while the introduction of F results in the increase in its operating voltage. However, the wide band gap of NaVPO_4F decreases the electronic conductivity, which could be mitigated by rGO incorporation. As a result, the as-prepared NaVPO_4F -rGO cathode exhibited a capacity of $143.1 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C after 50 cycles, surpassing the capacity of pristine NaVPO_4F ($91.1 \text{ mAh}\cdot\text{g}^{-1}$). Furthermore, the long-term cycling performance of both NaVPO_4F -rGO and NaVPO_4F samples at 30 C for 4000 cycles was investigated. As was observed, the hybrid material presented enhanced performance compared to NaVPO_4F , with an extremely low capacity decline (0.0098%) per cycle. In a similar study conducted by Huang et al. [130], a $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -rGO hybrid material was synthesized via microwave-assisted hydrothermal treatment (130°C , 1 h), followed by calcination (600°C , 7 h) (Figure 36a), resulting in the homogeneous deposition of NaVPO_4F nanoparticles on the rGO surface (Figure 36b). The electrochemical performance of $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ and $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -rGO containing different rGO amounts was investigated. As is observed in GCD curves (Figure 36c), the optimum $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -rGO sample delivered higher specific capacity than that of $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$, as well as superior rate performance (Figure 36d).

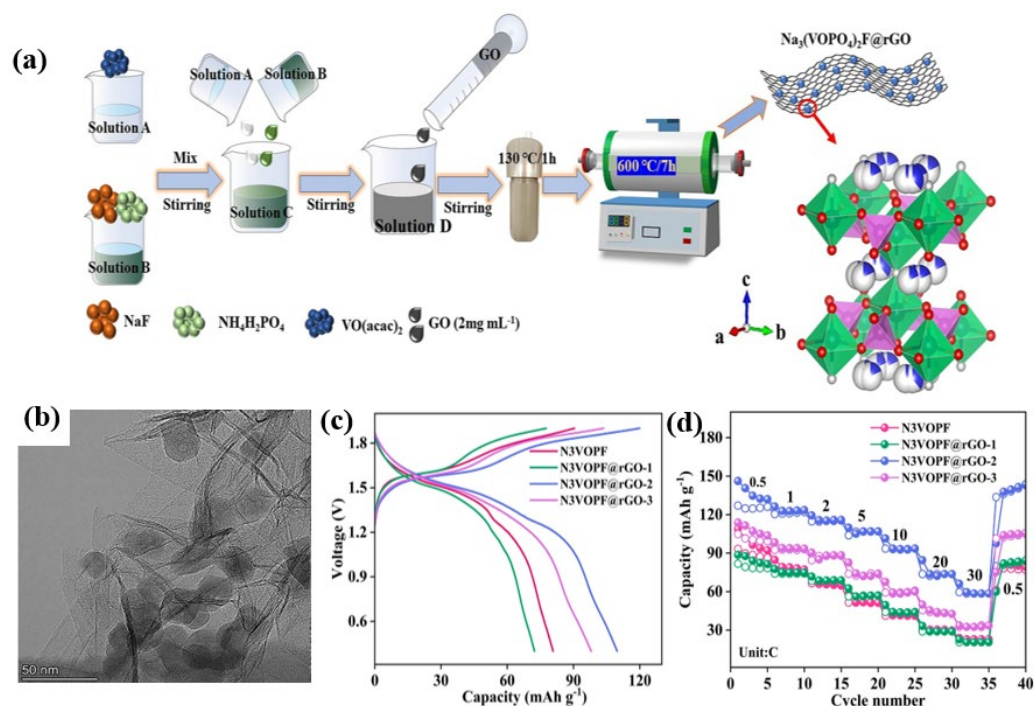


Figure 36. (a) Schematic representation of the synthesis process and (b) HR-TEM image of $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -rGO hybrid material, respectively. (c) GCD curves and (d) rate performance of pristine $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ and $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ -rGO containing different amounts of rGO, respectively. (Adapted with permission by [130]).

Oxygen-free compounds, such as metal nitrides (MNs), have higher electrical conductivity and specific capacity. Among them, vanadium nitride (VN) is one of the most suitable cathodes for AZIBs because of its superior theoretical capacity, good chemical stability, low cost and resource abundance. Nevertheless, Zn^{2+} diffusion and migration are hindered because of its rocksalt-type structure. Therefore, modification of VN is needed for practical applications. On this basis, Ma et al. [131] reported the combination of VN

with N-doped rGO, via a facile solid-phase sintering method, forming a porous hybrid material with increased specific surface area, compared to pristine VN (Figure 37a). The fabricated VN-N-doped rGO cathode delivered a superior reversible capacity of 529.8 mAh·g⁻¹ at 0.05 A·g⁻¹, an excellent long-cycle stability (261.6 mAh·g⁻¹ after 1000 cycles at 8 A·g⁻¹) and a good rate capability, higher than that of a VN electrode (Figure 37b), confirming that the presence of N-doped rGO improves the overall electrochemical performance. The electrochemical reaction mechanism was further investigated by ex situ XRD. As shown in Figure 37c–e, during the initial discharge, the majority of the VN is converted into Zn₃(OH)₂V₂O₇(H₂O)₂, while the Zn²⁺ ions are inserted into its interlayer structure. This results in a slight shift of the (002) diffraction peak toward lower 2θ values, suggesting the expansion of the interlayer spacing. Moreover, during the initial charge process, the extraction of Zn²⁺ ions results in the shift of the (002) diffraction peak of Zn₃(OH)₂V₂O₇(H₂O)₂ back to higher 2θ values, while VN is completely transformed into Zn₃(OH)₂V₂O₇(H₂O)₂, and no reverse conversion occurs during charging, demonstrating the irreversibility of this phase transformation. Subsequently, in the second discharging/charge process (Figure 37f–h) the Zn₃(OH)₂V₂O₇(H₂O)₂ structure remains stable and the interlayer spacing associated with the (002) plane exhibits reversible changes. At this point, it is worth mentioning that, in this work, 3-D printing technology was also employed to fabricate a high-mass-loading VN-N-doped rGO cathode. The 3-D printed electrode composed of two layers exhibited a specific capacity of 390 mAh·g⁻¹ at 0.05 A·g⁻¹ and a capacity retention of approximately 89% after 30 cycles at 0.05 A·g⁻¹, indicating its great potential as high-mass-loading electrodes for AZIBs.

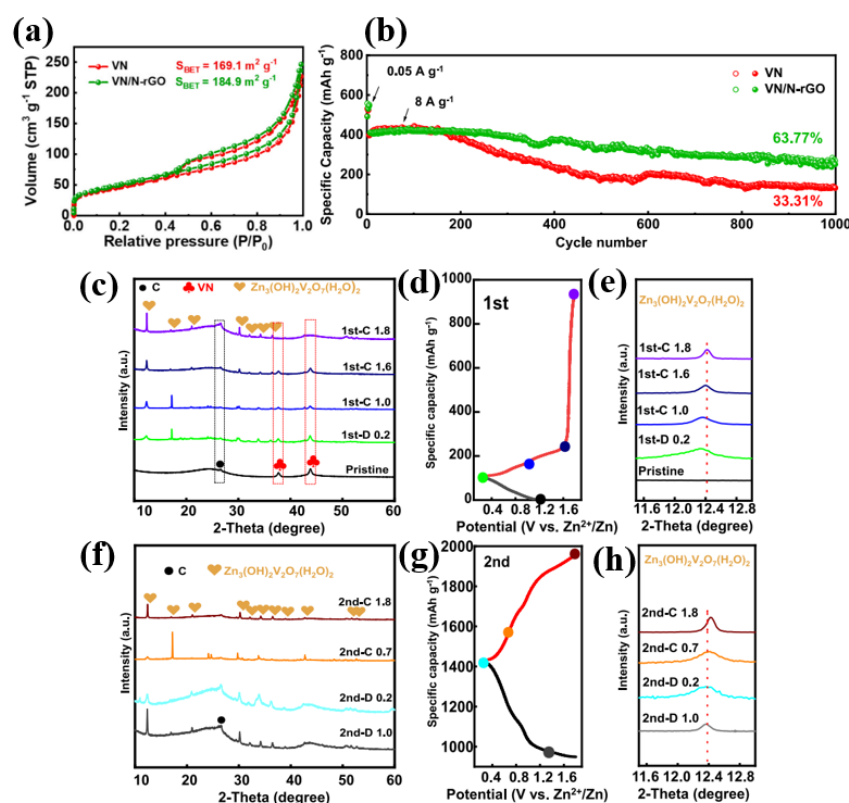


Figure 37. (a) N₂ adsorption/desorption isotherms of VN and VN-N-doped rGO samples. (b) The long-term cycling performance VN and VN-N-doped rGO cathodes at 8 A·g⁻¹. (c,e) Ex situ XRD spectra of VN-N-doped rGO during the first discharge/charge process and (d) the corresponding first discharge/charge curves. (f,h) Ex situ XRD spectra of VN-N-doped rGO during the second discharge/charge cycle and (g) the corresponding second discharge/charge curves. (Adapted with permission by [131]).

3.7.2. rGO–Organic Frameworks

Organic frameworks, particularly covalent organic frameworks (COFs) and MOFs, have emerged as promising cathode materials for AZIBs, owing to their highly ordered and porous architectures. These materials offer abundant and tunable redox-active sites, enabling efficient and reversible Zn^{2+} ion storage. Additionally, the well-defined channels facilitate rapid ion diffusion, while the structural versatility allows precise control over functionality at the molecular level. Nevertheless, their relatively low intrinsic electrical conductivity remains a key limitation, often addressed via several strategies, including their combination with conductive materials, such as rGO. Furthermore, the rGO substrate can suppress their hydrolysis, enhancing their structural stability [132]. Therefore, organic framework–rGO hybrid materials provide a promising solution for the development of advanced AZIB cathodes with enhanced electrochemical performance.

Yi et al. [132] synthesized a COF based on hexaazatrinaphthalene, containing C=O and C=N groups that increase the density of redox-active sites and optimize the electronic distribution within the framework, followed by rGO integration via π – π interactions. The electrochemical performance of the COF-rGO hybrid material (Figure 38a) was investigated. The CV curves of the initial five cycles are presented in Figure 38b, where two pairs of redox peaks are observed at 0.87/0.74 V and 0.60/0.45 V, indicating the multi-step reversible redox reaction of the COF-rGO. Moreover, based on the GCD curves (Figure 38c), the COF-rGO cathode exhibited a high capacity of $331 \text{ mAh}\cdot\text{g}^{-1}$ and a high plateau voltage of 0.66 V at a current density of $0.1 \text{ A}\cdot\text{g}^{-1}$. On the other hand, COF only delivers a capacity of $255 \text{ mAh}\cdot\text{g}^{-1}$ and an average discharge voltage of 0.58 V, under the same conditions. Notably, the COF-rGO achieved a superior capacity retention rate of 90.33% after 20,000 cycles at $10 \text{ A}\cdot\text{g}^{-1}$ (Figure 38d). As is known, the charge storage performance of AZIBs is strongly influenced by the nature of the charge carriers. While Zn^{2+} ions suffer from sluggish kinetics due to their large size and multi-valency, H^+ ions exhibit faster diffusion, lower mass, and more favorable coordination with common organic functional groups such as C=N and C=O. Quantitative analysis revealed that H^+ ions contribute dominantly to the charge storage process in both COF and COF-rGO electrodes. More specifically, the H^+ contribution to the total capacity in COF and COF-rGO accounts for 78.13% and 85.85%, respectively, suggesting that C=O present in both COF and rGO structures play the role of H^+ receptors. Proton-dominated storage significantly improves reaction kinetics and rate performance; however, excessive H^+ participation may lead to stability issues, highlighting the importance of a balanced $\text{Zn}^{2+}/\text{H}^+$ storage mechanism for optimal electrochemical performance.

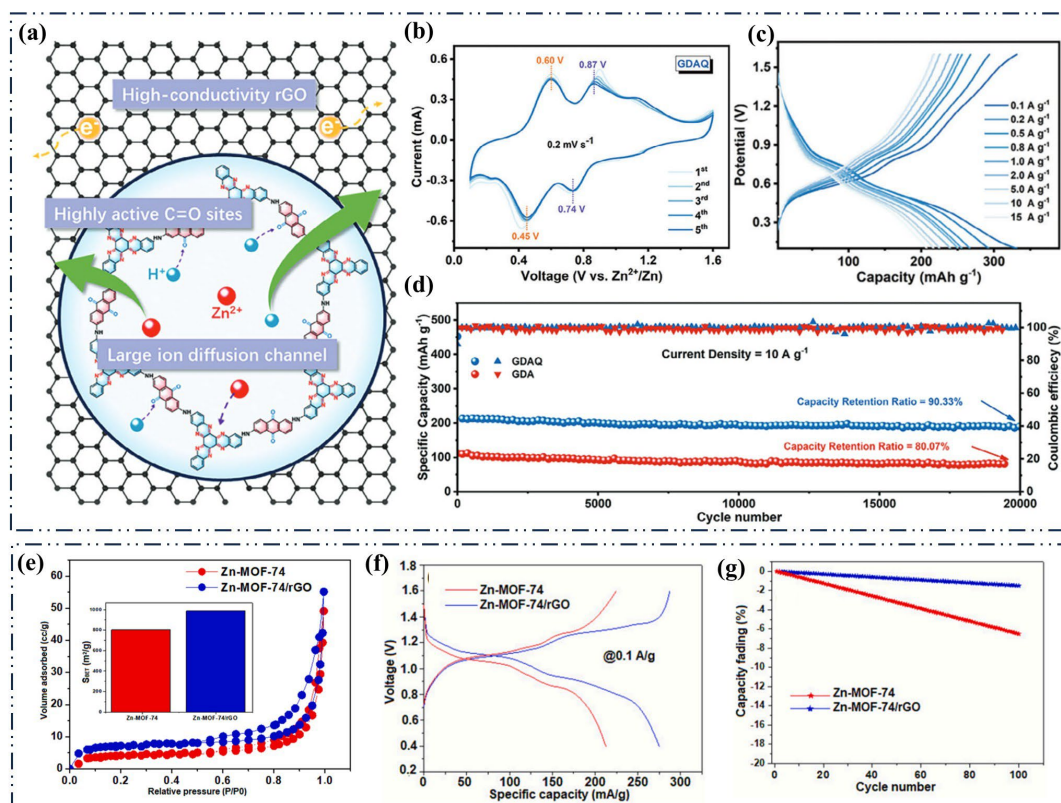


Figure 38. (a) Schematic representation of the COF-rGO hybrid material. (b) CV curves of COF-rGO at a scanning rate of $0.2 \text{ mV} \cdot \text{s}^{-1}$. (c) GCD curves of COF-rGO at current density ranging from 0.1 to $15 \text{ A} \cdot \text{g}^{-1}$. (d) The cycling stability of COF-rGO at a current density of $10 \text{ A} \cdot \text{g}^{-1}$. (Adapted with permission by [132]). (e) N_2 adsorption–desorption isotherms of Zn-MOF-74 and Zn-MOF-74-rGO. The calculated specific surface areas of the samples are $750 \text{ m}^2 \cdot \text{g}^{-1}$ and $950 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. (f) GCD curves at $0.1 \text{ A} \cdot \text{g}^{-1}$ and (g) capacity fading of the two samples, respectively. (Adapted with permission by [133]).

In a recent study [133], a metal-based organic framework (Zn-MOF-74) composed of Zn^{2+} nodes coordinated with 2,5-dihydroxyterephthalic acid linkers was synthesized via a solvothermal method. The material is characterized by 1-D open channels and metal sites that can facilitate efficient Zn^{2+} ion transfer. In order to enhance its electronic conductivity, Zn-MOF-74 was formed in situ in the presence of rGO via solvothermal treatment (120°C , 24 h). The as-prepared Zn-MOF-74-rGO hybrid material presented a superior specific surface area of $950 \text{ m}^2 \cdot \text{g}^{-1}$ (Figure 38e), as well as enhanced electrochemical performance. As is observed in Figure 38f, the Zn-MOF-74-rGO exhibited improved specific capacity, compared to Zn-MOF-74. This is attributed to the enhanced electrical conductivity, as well as charge-transfer kinetics provided by rGO. It is also interesting to note that, while the Zn-MOF-74 cathode exhibits a continuous decline in capacity (Figure 38g), the Zn-MOF-74-rGO demonstrates significantly improved cycling stability, maintaining a high-capacity retention after 100 cycles at $0.1 \text{ A} \cdot \text{g}^{-1}$, with a fading rate under 2% . This enhanced performance indicates that the incorporation of rGO effectively improves structural stability and facilitates charge transport, thereby boosting the overall electrochemical performance of the battery.

3.8. rGO-Based Ternary/Quaternary Hybrid Materials

Up to this point, the significance of hybrid materials has been widely acknowledged, emphasizing the enhanced properties that arise from the synergistic combination of two individual components. The tremendous progress in materials science and technology has

led to the development of novel structures, often involving more than two constituents. These advanced multi-component systems exhibit improved and synergistic functionalities, underscoring the growing potential of modern materials design [134]. In the final section of the present review article, rGO-based ternary or quaternary hybrid materials employed as cathodes in AZIBs will be presented, highlighting their design strategies, synergistic effects, and potential for high-performance energy storage. Table 3 summarizes the most recent studies (published since 2023) focused on rGO-based ternary/quaternary hybrid materials and their application in AZIBs.

Table 3. Summary of the studies focused on rGO-based ternary/quaternary hybrid materials as cathodes in AZIBs (published since 2023).

Cathode Material	Synthesis Method	Specific Storage Capacity	Cycling Stability	Ref.
rGO-Polypyrrole-ZnMn ₂ O ₄	Hydrothermal method (180 °C, 6 h), followed by in situ polymerization	295.3 mAh·g ⁻¹ (at 0.1 A·g ⁻¹)	88.7% (900 cycles at 1.0 A·g ⁻¹)	[135]
rGO-Polyaniline-V ₂ O ₅	Mixing under ambient conditions	560.5 mAh·g ⁻¹ (at 0.1 A·g ⁻¹)	81% (1000 cycles at 2.0 A·g ⁻¹)	[136]
rGO-Polydopamine-Zn ₃ V ₃ O ₈	Ultrasonication of GO and polydopamine-Zn ₃ V ₃ O ₈ , followed by thermal treatment (600 °C, 2 h) in Ar atmosphere	300 mAh·g ⁻¹ (at 0.15 A·g ⁻¹)	93.1% (1000 cycles at 5.0 A·g ⁻¹)	[137]
rGO-Cellulose-NH ₄ V ₄ O ₁₀	Hydrothermal method (180 °C, 3 h)	388 mAh·g ⁻¹ (at 0.2 A·g ⁻¹)	144 mAh·g ⁻¹ (1000 cycles at 5.0 A·g ⁻¹)	[138]
rGO-V ₂ O ₃ -Single-Walled Carbon Nanohorns	Freeze-drying, followed by calcination	422 mAh·g ⁻¹ (at 0.2 A·g ⁻¹)	238 mAh·g ⁻¹ (1000 cycles at 5.0 A·g ⁻¹)	[139]
rGO-Hollow Carbon Spheres-MnO ₂	Hydrothermal method (180 °C, 3 h), followed by in situ synthesis of MnO ₂ in ambient conditions	405 mAh·g ⁻¹ (at 0.2 A·g ⁻¹)	93% (4000 cycles at 3.0 A·g ⁻¹)	[140]
rGO-Carbon NPs-MnO	Thermal annealing of Mn-MOF-GO (500 °C, 2 h) in H ₂ /Ar atmosphere	318.7 mAh·g ⁻¹ (at 0.2 A·g ⁻¹)	85.1% (1200 cycles at 2.0 A·g ⁻¹)	[141]
rGO-CNTs-Graphene-PQPD	In situ polymerization, followed by ultrasonication and hydrothermal treatment (50 °C, 2 h)	120.7 mAh·g ⁻¹ (at 0.1 A·g ⁻¹)	82.6% (2000 cycles at 1.0 A·g ⁻¹)	[142]

To begin with, the combination of rGO with both conductive polymers and MOs or VO_s represents one of the most widely adapted strategies in the literature. Several studies are discussed herein to elucidate the role of each component. In the study of Gao et al. [135], a ternary hybrid material consisting of polypyrrole-coated ZnMn₂O₄ nanoparticles anchored onto rGO was prepared via a two-step process. Briefly, the ZnMn₂O₄-rGO sample was first synthesized under hydrothermal treatment (180 °C, 6 h), followed by in situ

polymerization, resulting in the fabrication of the final ZnMn_2O_4 -rGO-PPy hybrid material. ZnMn_2O_4 is the first reported spinel-like cathode material with Zn^{2+} storage potential [143] and, therefore, it has attracted the interest of researchers. However, there are several limitations which hinder its practical application. The combination of ZnMn_2O_4 with rGO and PPy significantly improved its electrical conductivity (from 4.78×10^{-2} to $3.89 \times 10^3 \text{ S}\cdot\text{m}^{-1}$) and prevented its dissolution and structural distortion during the electrochemical cycle. Based on the electrochemical characterization of ZnMn_2O_4 , ZnMn_2O_4 -PPy and ZnMn_2O_4 -rGO-PPy, the discharge capacity at $0.1 \text{ A}\cdot\text{g}^{-1}$ was $124.4 \text{ mAh}\cdot\text{g}^{-1}$, $247.6 \text{ mAh}\cdot\text{g}^{-1}$ and $295.3 \text{ mAh}\cdot\text{g}^{-1}$, respectively, clearly demonstrating the synergistic effect of rGO and PPy in enhancing the electrochemical performance of the ZnMn_2O_4 cathode. In another study [136], a ternary hybrid material was synthesized, combining the advantageous characteristics of V_2O_5 , polyaniline and rGO. The high theoretical capacity of V_2O_5 , the pre-intercalation of polyaniline, leading to the expansion of the V_2O_5 interlayer spacing and $\text{Zn}^{2+}/\text{H}^+$ co-insertion facilitation, as well as the high electrical conductivity and mechanical strength of rGO, resulted in the fabrication of a novel cathode material with enhanced electrochemical performance. More specifically, the PANI- V_2O_5 -rGO cathode delivered a specific capacity of $560.5 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$ and 81% capacity retention after 1000 cycles at $2.0 \text{ A}\cdot\text{g}^{-1}$. Furthermore, Kam et al. [137] investigated the synthesis of polydopamine(PD)- $\text{Zn}_3\text{V}_3\text{O}_8$ -rGO hybrid material, following a three-step process: i. $\text{Zn}_3\text{V}_3\text{O}_8$ preparation via sol-gel method, ii. $\text{Zn}_3\text{V}_3\text{O}_8$ -PD synthesis by in situ polymerization and iii. $\text{Zn}_3\text{V}_3\text{O}_8$ -PD-rGO fabrication by mixing PD- $\text{Zn}_3\text{V}_3\text{O}_8$ and GO under ultrasonication, followed by thermal treatment in an Ar atmosphere. Herein, $\text{Zn}_3\text{V}_3\text{O}_8$ —a Zn-rich vanadium oxide—was utilized as cathode material in an anode-free AZIB. The presence of rGO improves not only the electrical conductivity but also the hydrophobicity of the $\text{Zn}_3\text{V}_3\text{O}_8$ cathode (Figure 39a), thereby mitigating undesirable side reactions with the electrolyte. Simultaneously, the hydrophobicity of the cathode promotes the desolvation of the Zn^{2+} , enhancing the introduction of the ions into its framework. Furthermore, the addition of PD as a surface modifier aims to decrease aggregation phenomena among rGO nanosheets. The as-prepared $\text{Zn}_3\text{V}_3\text{O}_8$ -PD-rGO cathode exhibited a high reversible capacity of $242.7 \text{ mAh}\cdot\text{g}^{-1}$ at $5.0 \text{ A}\cdot\text{g}^{-1}$ after 1000 cycles, corresponding to a capacity retention of 93.1%, whereas pristine $\text{Zn}_3\text{V}_3\text{O}_8$ maintained only 67.85% under the same conditions. Finally, Xu et al. [138] reported the synergistic boosting of the electrochemical performance of $\text{NH}_4\text{V}_4\text{O}_{10}$ -rGO-cellulose hybrid material (Figure 39b). In their study, $\text{NH}_4\text{V}_4\text{O}_{10}$ was selected as a promising cathode for AZIBs due to its adjustable layered structure and significant specific capacity. Moreover, the introduction of rGO increased the electrical conductivity, the specific surface area and the electron transfer, while the presence of cellulose-based nanofibers, with excellent chemical stability, improved rGO dispersion and contributed to the formation of a porous framework, facilitating ion transport. The hybrid material was synthesized via the hydrothermal treatment (180°C , 3 h) of $\text{NH}_4\text{V}_4\text{O}_{10}$ and GO-cellulose dispersion. The as-prepared $\text{NH}_4\text{V}_4\text{O}_{10}$ -rGO-cellulose exhibited 3 times higher capacity ($344 \text{ mAh}\cdot\text{g}^{-1}$) than $\text{NH}_4\text{V}_4\text{O}_{10}$ at $1 \text{ A}\cdot\text{g}^{-1}$.

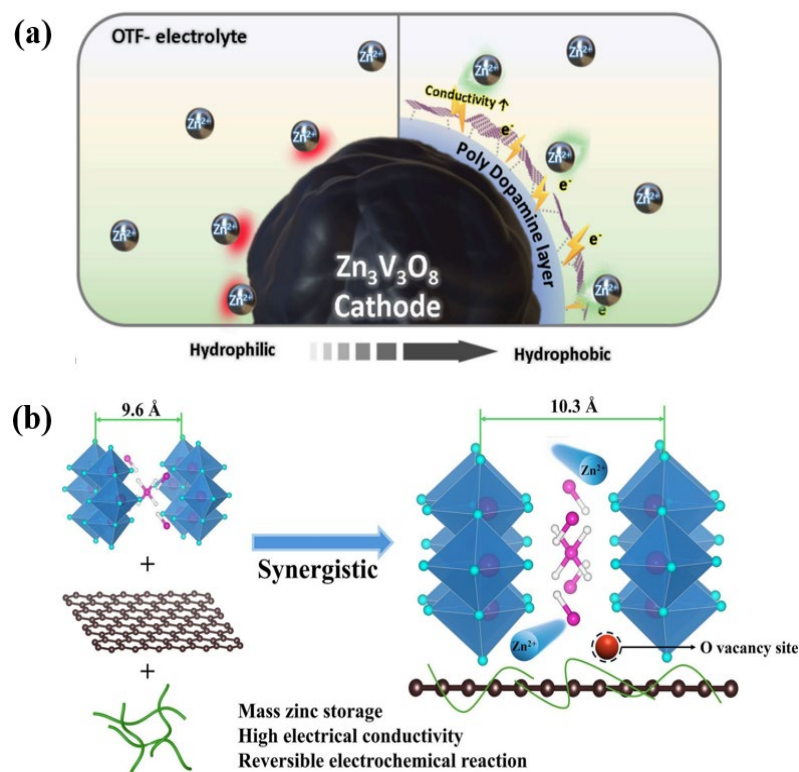


Figure 39. Schematic illustration of (a) Zn²⁺ ion intercalation/deintercalation in the Zn₃V₃O₈ and Zn₃V₃O₈-PD-rGO cathode materials, respectively (Adapted with permission by [137]). (b) Schematic illustration of the combinations of NH₄V₄O₁₀ with rGO and cellulose towards the formation of a high-performance cathode. (Adapted with permission by [138]).

The combination of traditional cathode materials with more than one carbon-based nanomaterial, so as to further enhance the overall performance of AZIBs, has also been addressed in various research studies. In this context, Hong et al. [139] synthesized a multi-dimensional hybrid material, consisting of V₂O₃ nanosheets and single-walled carbon nanohorns (SWCNHs) crosslinked together and wrapped by rGO (Figure 40a,b). While rGO supports the V₂O₃ structure, SWCNHs prevent V₂O₃ nanosheet stacking and provide 3-D ion transport channels. The hierarchical structure integrated with SWCNHs and rGO enhances electronic conductivity, while reinforcing the structural stability of the cathode. The discharge capacity achieved by V₂O₃, V₂O₃-rGO, and V₂O₃-rGO-SWCNHs at 0.2 A·g⁻¹ was 382 mAh·g⁻¹, 389 mAh·g⁻¹ and 422 mAh·g⁻¹, respectively. In Figure 40c, the rate capability of the above electrodes is presented, where the best performance is achieved by the ternary hybrid material, exhibiting a high capacity of 467, 421, 382, 360, 335, and 300 mAh·g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A·g⁻¹, respectively. Notably, the capacity can be recovered to 383 mAh·g⁻¹ (capacity retention of 90%) when the current is back to 0.2 A·g⁻¹. Moreover, the long-term cycling performance after 1000 cycles at 5.0 A·g⁻¹ is shown in Figure 40d, where the V₂O₃-rGO-SWCNHs achieved a capacity of 283 mAh·g⁻¹ which is significantly improved compared to V₂O₃ (163 mAh·g⁻¹) and V₂O₃-rGO (195 mAh·g⁻¹).

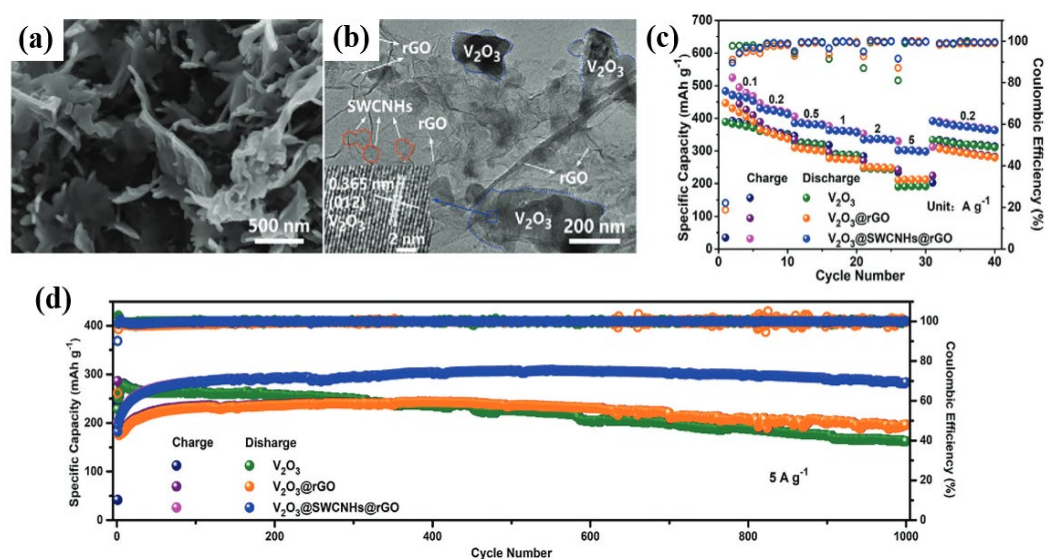


Figure 40. Combination of V_2O_3 with different carbon-based nanomaterials. (a) SEM and (b) TEM images of V_2O_3 -rGO-SWCNHs. (c) Rate capability and (d) long-term cycling of pristine V_2O_3 , V_2O_3 -rGO and V_2O_3 -rGO-SWCNHs. (Adapted with permission by [139]).

Another interesting architecture has been developed by Ding et al. [140], involving the in situ growth of hollow carbon spheres (HCSs) on rGO. This design forms a well-organized network of interconnected channels that function as efficient “highways” for electrolyte transport. Subsequently, MnO_2 nanoparticles are uniformly distributed throughout this structure, acting as numerous “service stations” that offer abundant active sites for ion storage along these transport routes. The process followed for the synthesis of the final rGO-HCS- MnO_2 is shown in Figure 41a. The as-prepared rGO-HCS- MnO_2 exhibited remarkable electrochemical performance, achieving a specific capacity of $405 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$. In contrast, HCS- MnO_2 and rGO- MnO_2 presented decreased values ($225.81 \text{ mAh}\cdot\text{g}^{-1}$ and $172.28 \text{ mAh}\cdot\text{g}^{-1}$, respectively) under the same conditions. In addition, rGO-HCS- MnO_2 presented excellent cycling stability with a capacity retention rate of 93% even after 4,000 cycles at $3.0 \text{ A}\cdot\text{g}^{-1}$. It is also interesting to note that the diffusion coefficients of Zn^{2+} ions (Figure 41b,c) calculated from GITT were found to be in the ranges of 10^{-8} – 10^{-11} for rGO-HCS- MnO_2 , 10^{-9} – 10^{-11} for HCS- MnO_2 and 10^{-9} – 10^{-12} for rGO- MnO_2 . The results indicate that the 3-D framework of rGO-HCS- MnO_2 enhances the diffusion kinetics. Zhang et al. [141] reported the fabrication of MnO-carbon-rGO by directly anchoring Mn-based MOFs onto reduced rGO sheets, followed by thermal treatment under H_2/Ar atmosphere (Figure 42a). When employed as a cathode for AZIBs (Figure 42b), the presence of rGO facilitates the formation of smaller, well-dispersed nanoparticles rather than larger aggregates. Meanwhile, MnO NPs encapsulated within a carbon layer and anchored onto rGO not only suppress manganese dissolution but also enhance electrical conductivity. As a result, the MnO-carbon-rGO cathode exhibited excellent electrochemical performance, including strong cycling stability (85.1% capacity retention after 1200 cycles at $2.0 \text{ A}\cdot\text{g}^{-1}$) and impressive rate capability ($318.7 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ A}\cdot\text{g}^{-1}$).

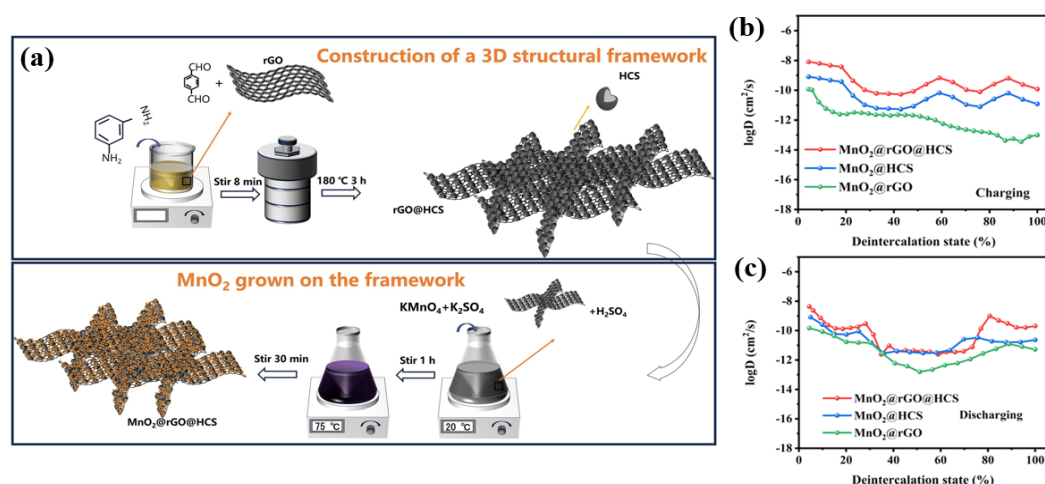


Figure 41. (a) Schematic representation of the synthesis process of rGO-HCS-MnO₂. (b,c) Charging and discharging ion diffusion coefficient of rGO-MnO₂, HCS-MnO₂ and rGO-HCS-MnO₂, respectively. (Adapted with permission by [140]).

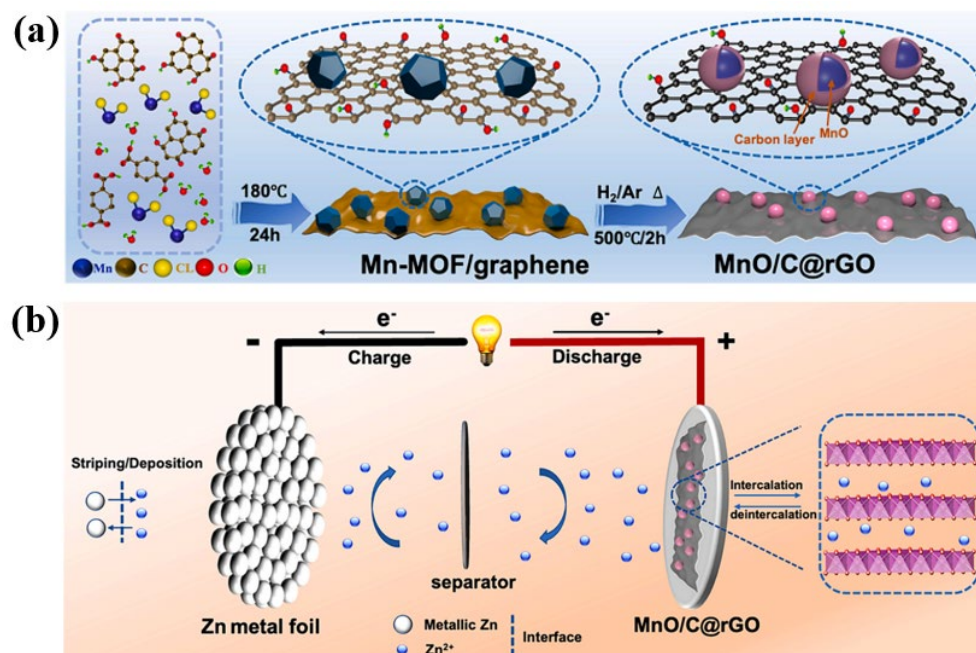


Figure 42. Schematic representation of (a) the synthesis process of MnO-Carbon-rGO and (b) the Zn²⁺ storage mechanism when used as a cathode material in AZIBs. (Adapted with permission by [141]).

A quaternary hybrid material based on carbon-based nanomaterials has been recently proposed by Zhou et al. [142] as a binder-free cathode for AZIBs. As is observed in Figure 43a, poly(benzoquinone-phenylenediamine) (PQPDA) was coated on the surface of graphene nanosheets by in situ polymerization, forming a 2-D PQPDA-GNS structure, which was then added into a GO-CNT suspension, under sonication. After filtration, the obtained film could be easily peeled off and treated under solvothermal conditions in order to reduce GO. Figure 43b presents the cross-section SEM image of PQPDA-GNS-CNT-rGO, which exhibits a layered and loose structure that facilitates the ion transport across the film. Based on the charge/discharge curves of the Zn//PQPDA-GNS-CNT-rGO battery at various current densities (Figure 43c), the specific capacity was calculated to be 120.7, 103.8, 97.6, 87.9, 79.8 and 75.8 mAh·g⁻¹ at 0.1, 0.2, 0.3, 0.5, 0.8 and 1.0 A·g⁻¹, respectively. When the current was reverted to 0.1 A·g⁻¹, the battery exhibited a high specific capacity of 112.6 mAh·g⁻¹ (Figure 43d). The present study demonstrates remarkable technological

advancements including the absence of insulating binders, such as PVDF and PTFE, which enables the active material PQPDA to be directly integrated with conductive substrates, thereby reducing interfacial resistance, paving the way for the development of high-performance cathodes.

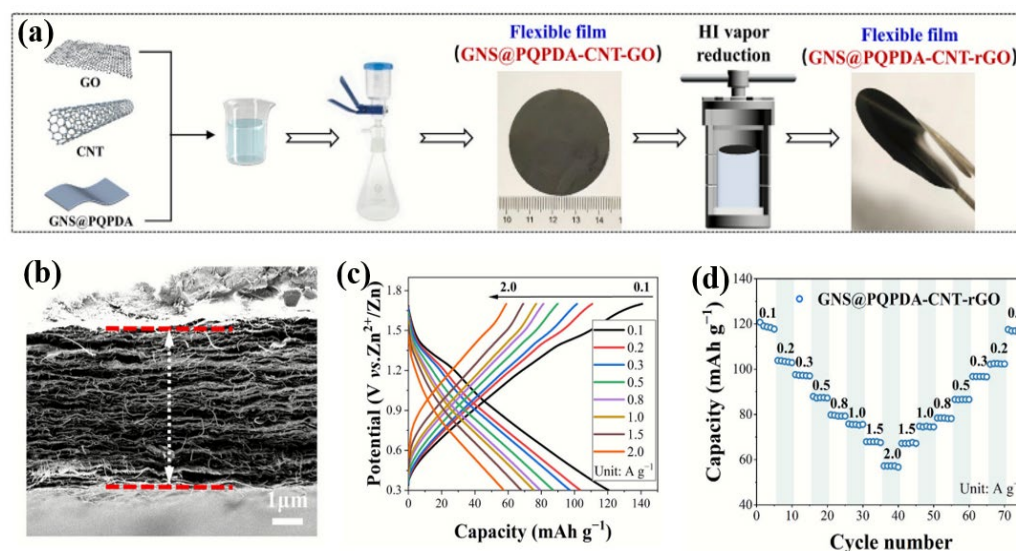


Figure 43. (a) Schematic representation of the preparation of the PQPDA-GNS-CNT-rGO film. (b) Cross-section SEM image of the PQPDA-GNS-CNT-rGO film. (c) Charge/Discharge curves and (d) rate performance of the Zn//PQPDA-GNS-CNT-rGO battery at various current densities. (Adapted with permission by [142]).

4. Comparative Analysis and Critical Discussion

Following the discussion of individual studies, the integration of rGO into cathode architectures represents a milestone in the development of high-performance AZIBs. As described in the preceding sections, rGO can effectively mitigate the electronic bottlenecks, buffer the severe volume fluctuations during cycling, and suppress active mass dissolution across different materials categories. Herein, a critical comparison among the various rGO-based cathodes is presented to elucidate their underlying structural and physicochemical properties and identify the key factors governing electrochemical performance.

To begin with, manganese oxides, with polymorphic structure and versatile oxidation states, have been considered among the most promising cathode materials for AZIBs due to their unique properties. Among these, MnO₂ stands out as one of the most extensively investigated and prominent cathodes owing to its wide working voltage window and high theoretical capacity. Nevertheless, its practical implementation remains hindered by several intrinsic limitations, including low electrical conductivity and structural instability, which is mainly attributed to the irreversible phase transition during repeated Zn²⁺ insertion/extraction processes and the disproportionation of manganese ions driven by the Jahn–Teller effect. In order to overcome these drawbacks, several studies [77–82] have investigated the combination of MnO₂, exhibiting different dimensional characteristics, such as 1-D tunnel-type [77,78], 2-D layered structures [80,81] and 3-D nanoflowers [82], with rGO. It is worth mentioning that, although rGO consistently improves the overall electrochemical performance of MnO₂-based cathodes, its dominant contribution depends strongly on the structural characteristics of the host MnO₂ polymorph. For instance, α-MnO₂ nanorods facilitate Zn²⁺ diffusion owing to their characteristic 2 × 2 tunnel structure but suffer from low intrinsic electrical conductivity and structural instability during repeated cycling. Consequently, their integration with rGO [77,78] provides a conductive and mechanically robust framework that enhances electron transport and buffers volume

changes. The layered architecture of δ -MnO₂ provides large interlayer spacing (~ 0.7 nm), facilitating rapid ion diffusion and proton-assisted charge storage, thereby contributing to its enhanced reversible capacity. The combination of δ -MnO₂ with rGO [80,81] further enhances the electrochemical performance by establishing efficient electron transport and improved interfacial charge-transfer kinetics between δ -MnO₂ layers. Compared to the tunneled and layered polymorphs, the ε -MnO₂ nanoflower-based morphology offers abundant electrochemically active sites; however, it is susceptible to particle agglomeration, which can adversely affect its electrochemical performance. Based on the reported studies, it was found that rGO could effectively hinder the agglomeration phenomena of ε -MnO₂, ensuring homogeneous electrolyte penetration and continuous electron transport pathways, while preserving structural integrity during prolonged cycling [82]. In addition, the synergistic effects of rGO incorporation and vacancy engineering [75] or/and doping strategy [83–85] on the electrochemical properties of MO-based cathodes have also been investigated. As is known, the introduction of Mn-vacancies modifies the local coordination environment and generates additional electrochemically active sites, thereby facilitating ion adsorption and shortening the diffusion pathways. Nevertheless, the charge localization around Mn-vacancies may lead to strong electrostatic trapping fields, inhibiting the directional flow of electrons and increasing structural instability. On this basis, the combinations of vacancy-engineered MnO₂ with positively functionalized rGO [75] redistributes the localized charges and generates more uniform internal electric fields across the heterointerface, indicating enhanced rate capability and structural stability under prolonged cycling. A similar synergistic principle is observed in metal-doped MOs-rGO cathodes [83–85], taking into consideration that the contribution of the doping agent strongly depends on its ionic radius, valence state, coordination chemistry, and interaction with the Mn-O framework. Beyond vacancy or/and doping engineering of MOs, the modification of carbon framework through N-doping of rGO [86] has also emerged as an effective strategy to further increase its electrical conductivity, introduce additional defect sites and polar functional groups, and enhance its interactions with MOs nanoparticles. At this point it is important to note that, unlike other studies that employ a predefined rGO content, Yang et al. [87] investigated the optimization of the Mn₃O₄:rGO mass ratio, demonstrating that the electrochemical performance depends on rGO loading. Notably, the optimum composition (8:2) resulted in the homogeneous dispersion of Mn₃O₄ onto rGO nanosheets, whereas insufficient rGO loading failed to establish an effective conductive network and excessive rGO loading promoted nanosheet π - π restacking, increasing the electrochemically inactive mass. Overall, the most promising design strategy of MOs-rGO cathodes is not simply to increase the rGO content but to develop heterojunctions in which the crystal structure of manganese oxide, defect chemistry, and conductive framework will be simultaneously optimized.

Furthermore, vanadium oxides, including V₂O₅, constitute another extensively investigated family of cathodes for AZIBs due to their unique layered structures and high theoretical capacity. Similar to MOs, they are prone to structural collapse and dissolution; however, these phenomena are less significant due to their more stable oxidation states and robust structures. In addition, their low electrical conductivity also hinders their application in AZIBs. Several studies focused on the combination of V₂O₅ with rGO [92–95] investigate critical parameters such as the morphology and rGO loading. For instance, both Deng et al. [92] and Zhong et al. [93] synthesized V₂O₅-rGO hybrid materials with distinct morphological architectures. The former employed ultrathin V₂O₅ nanosheet arrays uniformly decorated on rGO, while the latter developed vertically aligned rGO on-to-V₂O₅ substrate. Although direct comparison between the two cathodes is complicated due to their differences in synthesis method, electrode architecture, mass loading, and electrochemical testing conditions, both systems exhibited remarkable electrochemical

performance. The enhanced properties of the ultrathin V_2O_5 nanosheet arrays-rGO [92] are mainly attributed to the thickness of V_2O_5 nanosheets (20–30 nm), which shortens Zn^{2+} diffusion pathways and increases the number of accessible redox sites, while rGO enhances not only the electrical conductivity but also the hydrophobicity of the electrode, thereby suppressing dissolution. In contrast, the vertically aligned rGO [93] enables electron and ion transport, while acting as a protective barrier against V_2O_5 structural degradation. Moreover, the study of Jia et al. [95] represents one of the most unconventional synthesis strategies of V_2O_5 -rGO structure, utilizing MOFs as a precursor of V_2O_5 . Notably, the as-prepared amorphous hybrid material exhibited a large number of channels and active sites for Zn^{2+} , with rGO providing continuous pathways for both electron and ion diffusion. The effect of rGO loading (~5–50 wt%) in the electrochemical properties of V_2O_5 -rGO was investigated by Zheng et al. [94], identifying an optimum rGO content of ~30 wt%, where the lowest charge-transfer resistance and the fastest ion transport kinetics were achieved. As a consequence, the electrochemical performance is governed by an appropriate balance between electronic conductivity and active-material utilization. Further studies [96–98,102] have also explored simultaneous rGO incorporation and VO structure modification through guest molecules or species acting as “pillars” so as to increase the interlayer spacing and enhance Zn^{2+} diffusion. Beyond V_2O_5 , several other VOs have attracted scientific interest, such as VOOH, due to its high theoretical capacity and relatively stable framework. Nevertheless, its practical application is still restricted by sluggish reaction kinetics and insufficient electrical conductivity. To address these limitations, the development of a VOOH-rGO heterojunction [99] results in spontaneous interfacial charge redistribution, accelerating electron transport and facilitating Zn^{2+} diffusion. Particular emphasis should be placed on the studies focused on VO_2 -rGO cathodes for AZIBs [100,101]. As opposed to conventional approaches that aim to preserve the crystal structure of the cathode, the aforementioned studies proposed the electrochemically induced phase transformation as a strategy to overcome the intrinsic limitations of VO_2 , including sluggish Zn^{2+} diffusion and poor electronic conductivity; however, different design principles are followed. More specifically, Li et al. [100] promoted the irreversible transformation of tunneled VO_2 into a layered $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ structure with increased interlayer spacing, enabling ion storage and extending the operating voltage window, whereas Wu et al. [101] tailored the charging cut-off voltage to induce the in situ transition of VO_2 to amorphous V_2O_3 , with a defect-rich framework, isotropic ion diffusion pathways and reduced Zn^{2+} migration barriers. In both cases, the incorporation of rGO played a critical role by providing a continuous conductive network, promoting charge-transfer kinetics, and maintaining structural integrity throughout the phase evolution. Collectively, these studies highlight that the superior electrochemical performance of the cathode material relies on the synergistic integration of multiple structural design strategies rather than on a single modification approach.

Prussian blue analogues represent an important category of cathode materials for AZIBs, combining various advantages such as environmental friendliness, rapid reaction kinetics and a working voltage of up to 1.8 V (vs. Zn^{2+}/Zn). However, their limited energy density and structural instability during cycling inhibit their practical application. To the best of our knowledge, the study of Hu et al. [108] combining PBAs, and more specifically ZnVHCF , with rGO remains the only reported work published since 2023. As the authors indicated, rGO could effectively prevent the dissolution of the cathode, by enhancing its hydrophobicity and simultaneously increase electrical conductivity. Notably, the list of promising cathodes is not exhaustive, and many other materials have demonstrated significant potential. Among these, conductive polymers with π -conjugated backbones, mechanical flexibility and ease of fabrication have been considered as promising candidates for AZIBs. Nevertheless, their practical application is limited by several factors, such as

insufficient active surface area and volume changes during cycling. On this basis, the studies conducted by Liu et al. [117] and Zhang et al. [118] highlight two complementary directions for the development of polymer-based AZIB cathodes. The former is focused on microstructural engineering via a π - π -stacking-assisted self-assembly method for the homogeneous dispersion of PANI on rGO, so as to overcome aggregation phenomena, resulting in a highly porous architecture with enhanced conductivity and rapid ion transport. On the other hand, the latter involves molecular engineering, achieved by incorporating quinone redox centers into a conductive polyaniline backbone, followed by covalent grafting onto rGO. Although both strategies improve the overall battery performance, molecular engineering results in greater improvements in specific capacity and cycling durability, whereas microstructural engineering offers a simple and scalable route for enhancing the electron transport in polymers. Consequently, future research may benefit from integrating both approaches to combine optimized electrode architectures with intrinsically high capacity.

Transition metal chalcogenides have also attracted significant attention because of their tunable electrical properties. Among them, a characteristic example is MoS₂, which exists in two crystalline phases: 2H with semiconducting properties and 1T metastable phase with metallic behavior. Recently, the combination of MoS₂ with rGO was explored [123,124] in order to enhance its electrochemical performance and it was found that rGO enlarges the interlayer spacing of MoS₂, improving ion transport kinetics, while it promotes the formation of a conductive 1T phase [123]. Specifically, the work of Peng et al. [124] achieved the stabilization of 1T-rich MoS₂ through the formation of strong covalent bonds (C-S and C-O-Mo) among rGO and MoS₂. Although in both cases the electrochemical performance of MoS₂-rGO is increased, compared to pristine MoS₂, it is worth mentioning that electron-injection engineering could simultaneously stabilize the active phase and modify the electronic structure. Beyond MoS₂, similar synergistic effects of rGO have also been demonstrated in other TMCs employed as AZIB cathodes [125,126]. For instance, Feng et al. [126] reported the development of MnSe-rGO core-shell structures, with enhanced electronic conductivity and structural integrity. Additionally, these structures suppress both Mn dissolution and Se loss during cycling, preserving the active material, mitigating Zn anode corrosion, and minimizing the release of environmentally hazardous species. Ju et al. [125] investigated a series of vanadium sulfide-rGO hybrid materials (V₂S₈-rGO, V₅S₈-rGO and V₆S₈-rGO), revealing that rGO prevents particle agglomeration, improves electronic conductivity and facilitates the electrochemical activation process required for reversible Zn-ion storage. Moreover, the study highlighted that the electrochemical behavior depends on the crystal structure of V_xS_y, with the V₂S₈-rGO sample exhibiting remarkable structural stability, compared to V₅S₈-rGO and V₆S₈-rGO, that underwent activation-induced structural evolution, while maintaining high-rate capability. Consequently, these studies demonstrate that, although the role of rGO varies according to the host TMCs, its contribution extends beyond improving conductivity, encompassing structural stabilization, regulation of phase evolution, suppression of active species dissolution and optimization of Zn-ion storage kinetics.

Increasing attention has been directed toward rGO integration with a broader range of materials, including metal oxides, metal phosphates, metal nitrides and organic frameworks. Such hybrid systems highlight the versatility of rGO as a conductive matrix, structural stabilizer, and interfacial mediator. Recent studies on manganese-vanadate-based cathodes [127,128] further demonstrate the multi-functional role of rGO. While Liu et al. [128] primarily exploited rGO to develop a continuous conductive network, increasing the intrinsically low electronic conductivity of MnV₆O₁₃ and accelerating charge transport, a more recent approach [127] employed N-doped rGO wrapped around MnV₂O₆ nanorods to simultaneously regulate ion diffusion, stabilize the electrode/electrolyte interface,

mitigate volume variations, and promote reversible multi-valent redox reactions. In both studies the optimization of rGO content has emerged as a critical design parameter, and as was observed, an intermediate rGO loading provides the best electrochemical performance. The results suggest that the optimum rGO content should be carefully balanced to ensure the formation of an efficient conductive network, while preserving a sufficient proportion of electrochemically active material. Furthermore, the combination of rGO with vanadium-phosphate-based cathodes [129,130] has also been investigated as a strategy to enhance their electrochemical properties. Rather than focusing solely on conductivity enhancement of the NaVPO_4F , Zhou et al. [129] employed rGO to regulate particle morphology and develop uniformly distributed nanorectangular blocks wrapped in rGO nanosheets. This architecture promotes faster Zn^{2+} diffusion, decreases charge-transfer resistance, and improves the structural stability of the electrode during prolonged cycling. Similarly, Huang et al. [130] combined $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ with rGO to overcome its intrinsically low electronic conductivity and mitigate agglomeration phenomena of the nanoparticles. In their study, rGO content optimization (~3.5–9 wt%) took place, with an intermediate loading (~5 wt%) providing the best balance between electronic conductivity and active-material utilization. Although oxygen-free compounds, such as metal nitrides, exhibit higher electrical conductivity, several challenges hinder their practical application, including slow Zn^{2+} diffusion kinetics and limited cycling stability. To address these issues, Ma et al. [131] combined VN with N-doped rGO, forming a porous architecture, in which uniformly distributed VN nanoparticles were embedded within a conductive N-doped rGO framework. Besides facilitating electron transport, the incorporation of pyridinic, pyrrolic, and graphitic nitrogen species enhanced the electrode/electrolyte interfacial contact and accelerated ion transport. Finally, organic frameworks have also been considered as a promising solution for the development of advanced cathodes for AZIBs, due to their highly ordered and porous structure and abundant and tunable redox-active sites. However, their low electronic conductivity continues to be a major obstacle to their practical implementation. As was indicated by different studies [132,133], the incorporation of rGO into porous frameworks provides a continuous conductive network that accelerates electron transport, prevents dense stacking, and enhances the accessibility of electrochemically active sites, thereby improving charge storage kinetics and cycling stability.

There is no doubt that the tremendous progress in materials science and engineering has led to the development of multi-component systems, exhibiting enhanced properties and synergistic functionalities. More and more studies are focusing on the synthesis of rGO-based ternary or quaternary hybrid materials for cathodes in AZIBs [135–142], underscoring the growing potential of modern materials design. For instance, in MO-based systems [135,140,141] rGO has been combined with conductive polymers, carbon coatings, or hollow carbon spheres to further enhance electron transport, restrict particle growth, mitigate cathode dissolution, and promote interconnected ion-diffusion pathways. Furthermore, the electrochemical performance of VO-based cathodes has been further improved by combining rGO with complementary components, including polymers [136,137], cellulose nanofibers [138] and carbon nanohorns [139], due to enhanced lattice stability, enlarged interlayer pathways enabling ion diffusion, and mitigation of rGO nanosheet restacking. Notably, in organic quinone-polymer electrodes, rGO served as a structural matrix for the fabrication of binder-free, self-standing films, while CNTs provided channels for rapid ion diffusion and minimized interfacial resistance [142].

To sum up, the literature reveals the multi-functional role of rGO. Initially employed to overcome the low electrical conductivity of conventional cathodes, rGO has progressively evolved into a versatile component capable of controlling particle morphology, interfacial chemistry, and phase evolution, while enhancing the structural stability of the electrode. Additionally, it should be emphasized that, among all the reported design strat-

egies of rGO-based cathodes, the identification of a single universally superior approach remains challenging, since the electrochemical performance of AZIBs is highly influenced by differences in crystal structure, synthesis methods, electrode formulation, electrolyte composition, electrochemical testing conditions, etc. Notably, some of the highest values of specific storage capacity were reported when rGO incorporation was synergistically combined with structural engineering strategies, such as heteroatom doping [84,85,97] or guest species introduction, acting as structural “pillars” [96]. Nevertheless, direct comparison of the reported electrochemical results should be treated with caution, since specific storage capacity was evaluated using different cathode material, electrolyte, current density, mass loading, and electrode configuration.

Beyond the presented experimental evidence, density functional theory (DFT) calculations conducted by several studies [96,99,101,103,123,124,126] have provided fundamental insights into the multi-functional role of rGO in AZIB cathodes. For instance, DFT calculations were performed on pristine $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and rGO-intercalated $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ models to elucidate the atomic-scale role of rGO in Zn^{2+} storage, by evaluating changes in interlayer spacing, Zn^{2+} coordination environment, and diffusion energy barriers [96]. The results showed that rGO increased the interlayer spacing, while altering the Zn^{2+} coordination environment, enabling the metal cations to interact with oxygen atoms from a single VO layer rather than bridging adjacent layers. This configuration preserved additional oxygen active sites on the opposite layer, giving rise to a double-sided Zn^{2+} storage mechanism. Furthermore, the reduced Zn^{2+} diffusion energy barriers indicated accelerated ion transport kinetics, explaining the enhanced electrochemical performance of the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -rGO cathode. Complementary insights were provided by Zhao et al. [99] investigating the electronic structure of the VOOH-rGO heterojunction. Notably, density of states (DOS) analysis revealed an increase in electronic density near the Fermi level after rGO integration, suggesting enhanced electronic conductivity. Furthermore, work function and charge density difference calculations demonstrated spontaneous electron transfer from rGO to VOOH, leading to interfacial charge redistribution and the formation of a built-in electric field. This electronic modulation tuned the d-band center of V and strengthened Zn^{2+} adsorption at the heterointerface, thereby facilitating charge transfer and improving the electrochemical reaction kinetics. Similar computational approaches were adopted in other VOs-rGO-based cathodes [101,103]; however, different mechanisms were identified. In the VO_2 -rGO system [101], DFT highlights the advantages of the amorphous structure, revealing favorable Zn^{2+} adsorption, lower diffusion energy barriers and increased density of electronic states near the Fermi level, whereas in the $\text{NH}_4\text{V}_4\text{O}_{10}$ -rGO [103] DFT calculations demonstrated that rGO not only increases the interlayer spacing but also weakened the electrostatic interactions between Zn^{2+} ions and the host lattice, thereby facilitating ion insertion and diffusion. Moreover, computational analysis has also revealed the role of rGO in transition-metal chalcogenide cathodes [123,124,126]. DFT analysis of vertically stacked MoS_2 -rGO [123], showed that the presence of rGO reduced the Zn^{2+} diffusion barrier and narrowed the band gap of MoS_2 , thus accelerating both ion diffusion and charge transfer, whereas in the case of rich-1T- MoS_2 -rGO [124], hydroxyl functional groups of rGO acted as electron donors, inducing the 4d-orbital reorganization of Mo and increasing the energy barrier for the 1T-to-2H phase transition. An interesting approach on MnSe -rGO [126], involving adsorption-energy calculations performed on pristine, defective, and Se-doped rGO, demonstrated that hetero-doped rGO exhibits strong affinity toward dissolved Mn^{3+} and Se^{2-} species, thereby suppressing elemental dissolution and associated side reactions. In conclusion, DFT calculations provide compelling atomic-scale evidence for the experimentally observed enhancements in electrical conductivity, reaction kinetics, structural stability, and long-term cycling performance of rGO-based cathodes.

Finally, a critical comparison of rGO with other conductive additives used in AZIB cathode engineering, such as CNTs, conductive polymers and the emerging 2-D MXenes, is essential to better assess its advantages. Although CNTs generally exhibit higher intrinsic electrical conductivity than rGO, the latter offers several additional advantages owing to its 2-D structure and the presence of oxygen-containing functional groups on its basal planes and edges, providing larger interfacial contact area and increased interactions with the host material. Thus, rGO not only facilitates conductive pathways but also regulates heterointerfacial chemistry, inhibits nanoparticle agglomeration phenomena, increases the interlayer spacing of layered cathodes, and enhances the structural stability. In addition, conductive polymers contribute to charge storage mechanisms through their intrinsic redox activity and pseudocapacitive behavior; however, they suffer from volumetric swelling, gradual degradation during repeated cycling processes, and limited long-term electrochemical stability. On the other hand, rGO exhibits superior chemical, electrochemical, and structural stability, while avoiding the volumetric changes and gradual degradation associated with repeated charging/discharging cycles. Recently, 2-D MXenes, a family of transition metal carbides, nitrides, and carbonitrides, have emerged as a promising class of conductive additives in AZIB cathodes due to their unique structural and physicochemical properties. Nevertheless, MXenes are susceptible to oxidation in aqueous environments which decreases their long-term stability. In contrast, rGO offers superior chemical stability, enabling high electrochemical performance under prolonged cycling conditions. Overall, conductive additives should be regarded as complementary rather than competing materials, as each offers distinct physicochemical characteristics that could be exploited according to the requirements of the cathode system.

5. Conclusions and Future Perspectives

AZIBs have emerged as among the most promising post-lithium energy storage technologies due to their excellent safety profile, environmental benignity, cost-effectiveness and high resource abundance. Nevertheless, the practical implementation of AZIBs remains hindered by several intrinsic challenges. Among these, the conventional cathode materials remain the major bottleneck due to their poor electronic conductivity, sluggish reaction kinetics, structural degradation during cycling and dissolution. To address these issues, the scientific community has explored various mitigation strategies, including the combination of cathode materials with carbon-based nanomaterials, such as rGO, with exceptional physicochemical properties.

This review has presented a comprehensive overview of the most recent advances (since 2023) regarding the development of next-generation AZIBs employing rGO-based architectures as cathode materials. Particular emphasis was placed on the role of rGO in addressing the fundamental challenges associated with conventional cathode materials. Owing to its high electrical conductivity, large specific surface area, mechanical robustness, and favorable interfacial properties, rGO has proven to be an effective platform for constructing advanced hybrid architectures with enhanced electrochemical performance. Based on the literature, the combination of manganese-based oxides, vanadium-based oxides, Prussian blue analogues, conductive polymers, chalcogenides, and other compounds with rGO has resulted in the development of advanced cathode materials with improved electron transport, Zn^{2+} ion diffusion, as well as high structural stability after numerous discharging/charging cycles. In addition, synergistic strategies combining rGO with elemental doping, defect engineering, interlayer expansion and ternary or quaternary heterostructure design have also enabled remarkable enhancements in specific capacity, rate capability and long-term cycling performance. Overall, the incorporation of rGO provides a highly effective approach to overcome the inherent limitations of cathode materials in AZIBs. From a materials-design perspective, several universal principles could be pro-

posed for the rational design and development of next-generation rGO-based cathodes, based on the collective findings of the reviewed literature. Firstly, it is important to highlight the multi-functional role of rGO, acting not only as a conductive framework but also as a structural scaffold and interfacial regulator. Moreover, intimate and robust interactions between rGO and the host material are essential to maximize charge-transfer kinetics, while maintaining structural stability during prolonged cycling. These interactions could be further enhanced through complementary strategies, such as heteroatom doping and defect engineering. Furthermore, controlling the morphology of both the active material and the rGO framework is of great importance to suppress nanoparticle agglomeration and rGO nanosheet restacking, thereby enabling homogeneous electrolyte penetration, continuous electron transport, and improved accessibility of the electrochemically active sites. In addition, the optimization of rGO content is crucial, as insufficient loading fails to establish an effective conductive network, whereas excessive loading increases the electrochemically inactive mass and reduces the overall active-material utilization.

Although significant progress has been achieved during the past few years in the development of rGO-based cathodes for AZIBs, various critical challenges remain and should be addressed to bridge laboratory-scale research and real-world energy storage applications. First and foremost, further research is required to fully understand the complex Zn^{2+} storage mechanisms in AZIBs. The coexistence of intercalation, co-insertion, conversion, and dissolution/deposition storage mechanisms complicates the identification of the dominant charge storage process and highlights the complexity of AZIB electrochemistry. Therefore, advanced in situ characterization techniques should be employed to elucidate reaction pathways and structural evolution during cycling. Operando XRD, Raman, XPS, and EELS characterization techniques could also provide real-time insights into the role of rGO during battery operation, by monitoring structural evolution, phase transitions, and interfacial charge-transfer procedures, thereby clarifying the mechanisms through which rGO regulates electron transport, stabilizes the structural properties of the cathode, modifies the cathode/electrolyte interface throughout cycling, etc. Thus, such studies are expected to provide a deeper understanding of the multi-functional role of rGO and guide the rational design of high-performance AZIB cathodes. Furthermore, great attention should be devoted to the rational design of the rGO–cathode material interface; although rGO improves the electronic conductivity and structural stability of the conventional cathodes, the fundamental mechanisms governing charge transfer, ion diffusion, and interfacial interactions remain insufficiently understood. Thus, computational approaches, including density functional theory (DFT) calculations and machine learning (ML), could provide valuable insights into interface engineering and cathode materials optimization. Moreover, the effect of the intrinsic physicochemical characteristics of rGO on the electrochemical properties of the hybrid cathodes remains among the most significant research gaps in the current literature. Specifically, the reduction degree of rGO is a critical parameter since it determines both the restoration of the π -conjugated structure and the retention of oxygen-containing functional groups. Achieving an appropriate balance between these two factors results in rGO with high conductivity and enhanced interfacial interactions with the cathode. Thus, the reduction degree could influence electron transport, charge-transfer kinetics, functionalization of nanoparticles onto the rGO surface, electrolyte wettability, and long-term structural stability. Similarly, the number of rGO layers, defect density and specific surface area are also critical parameters that should be systematically optimized across a series of rGO-based cathodes so as to evaluate their individual and synergistic contributions to the electrochemical performance of rGO-based cathodes. Additionally, systematic studies are required to establish a quantitative correlation between the rGO content and key electrochemical metrics, including specific storage capacity, rate capability, and gravimetric energy density. Since the available literature

encompasses a broad range of synthesis approaches for rGO, cathode materials, and rGO-based hybrid materials, systematic comparisons remain challenging, preventing a comprehensive assessment of the influence of rGO loading on battery performance. Thus, future studies should adopt standardized synthesis and characterization protocols, while systematically investigating the effect of rGO loading on the electrochemical properties, under comparable experimental conditions. Such efforts will enable the identification of the optimum rGO concentration for specific cathode materials, thereby facilitating scale-up and commercialization of high-performance rGO-based AZIB cathodes. Beyond the aforementioned challenges associated with the cathode optimization, several critical issues related to the intrinsic properties of rGO remain unresolved, hindering the commercialization of rGO-based AZIBs. In particular, synthesis of rGO with controlled structural and physicochemical properties remains a major challenge as the variations in synthesis conditions may lead to significant differences in defects density, number of layers, and the concentration of oxygen-containing surface functional groups. Such variability compromises the reproducibility of rGO-based cathodes and hinders the establishment of reliable structure–electrochemical performance correlation. Moreover, future research should also be extended to zinc anode, electrolyte and separator optimization, in order to support a more holistic strategy for the development of durable, high-performance and commercially viable AZIBs. In addition, the scalability and economic feasibility of rGO-based cathodes must be considered. Numerous reported synthesis routes involve complex and high-cost procedures, long reaction times and multiple steps, which may hinder their scale-up to industrial production. Consequently, the development of sustainable, low-cost, and large-scale fabrication methods remains a key research priority. It is also worth mentioning that the evaluation of next-generation AZIBs under practical operating conditions, such as high mass loading, lean electrolyte configurations, flexible device architectures and pouch-cell formats, remains an important direction for future research. Undoubtedly, the rapid progress of materials science and engineering, advanced characterization techniques, computational tools, as well as scalable manufacturing approaches are expected to play a pivotal role in the design and optimization of rGO-based cathodes, ultimately accelerating the development of safe, sustainable, high-performance, and commercially viable AZIBs.

Looking forward, future studies are expected to shift from materials optimization to the rational design of integrated rGO-based cathodes with enhanced electrochemical properties. Simultaneously, the integration of operando characterization techniques, computational modeling, and data-driven materials design is anticipated to establish predictive structure–property correlations, paving the way for the development of high-performance and commercially viable AZIB technologies.

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