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Material Innovations and Storage Mechanisms for High-Performance Zinc-ion Hybrid Capacitors: A Review

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Abstract

With the increasing demand for high-performance energy storage, Zinc-ion Hybrid Capacitors (ZHSCs) have emerged as a promising solution, combining the high power density of supercapacitors with the high energy density of batteries. This review summarizes the recent progress in ZHSCs, focusing on cathode materials (carbon-based and MXenes), electrolyte optimization (aqueous and hydrogel), and anode protection strategies against dendrite growth. While significant achievements have been made, challenges such as low cathode capacity and poor anode stability remain. Future research should focus on interface engineering and advanced electrolyte design to further enhance the electrochemical performance of ZHSCs.

Keywords

Zinc-ion hybrid capacitors, Zinc anode, Interface engineering, Electrolyte optimization, Dendrite inhibition.

1. Introduction

With the prevailing trends of population growth and urbanization across various economic sectors, including transportation, global energy demand has grown exponentially. Energy is an essential prerequisite for human activities. Currently, over 80% of energy consumption relies on the combustion of fossil fuels such as coal, petroleum, and natural gas [1]. This dependence has led to the gradual depletion of non-renewable resources. Furthermore, the combustion of these fossil fuels releases greenhouse gases into the atmosphere, including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), which in turn drive global warming. Simultaneously, the accumulation of greenhouse gases, abnormal climatic patterns, and environmental pollution pose significant threats to human survival [2-5].

Consequently, for the purpose of sustainable development, the primary focus has shifted toward clean, green, and renewable energy resources, such as solar, wind, hydro, tidal, and biomass energy. These resources are both abundant and sustainable. To date, these renewable sources have partially alleviated the pressure of energy shortages [1, 6-10]. According to the International Energy Agency (IEA) report on OECD countries, renewable energy contributed approximately 2,946 TWh to power generation in 2019, making it the second-largest energy source, following natural gas (3,264 TWh) and surpassing coal (2,472 TWh) [11]. However, a major challenge for renewable energy lies in its intermittency and its dependence on weather and climatic constraints. Therefore, there is an urgent need to develop and improve more efficient and cleaner energy storage devices. Meanwhile, with the proliferation and utilization of smart grids and electric vehicles, the demand for energy storage devices with high energy and power densities, exceptional safety, and long cycle life is increasing.

Since the first commercialization of rechargeable lithium-ion batteries in 1990, numerous energy storage systems with superior electrochemical performance—characterized by long

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cycling stability and high energy/power densities—have emerged, including sodium-ion batteries [12, 13], lithium-sulfur batteries [14, 15], aqueous batteries[16, 17], and supercapacitors [18, 19], among others. However, while batteries typically possess extremely high energy density, they often suffer from short cycle life and safety risks resulting from intense redox reactions and dendrite-related complications. Conversely, supercapacitors exhibit higher power density and longer cycle life due to rapid and reversible ion adsorption/desorption at the electrode/electrolyte interface; however, their energy density (5–10 Wh kg^{-1}) is significantly lower than that of batteries, and they are further constrained by high costs, safety risks, and material limitations[20-23]. Since individual batteries and supercapacitors cannot simultaneously satisfy the requirements for both high energy and power densities, hybrid supercapacitors (HSCs) may provide an ideal solution. Composed of a battery-type electrode (offering abundant redox reactions) and a capacitor-type electrode (providing rapid ionic conductivity), HSCs combine the advantages of both batteries and capacitors to meet the requirements of energy storage systems that necessitate high energy density and high power density simultaneously.

1.1. Overview of Zinc-ion Hybrid Capacitors

1.1.1. Energy Storage Mechanisms of Hybrid Capacitors

To understand hybrid supercapacitors, it is essential first to grasp the fundamental concepts of supercapacitors. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are electrochemical devices designed for energy storage. They operate via two primary energy storage mechanisms.

The first is electric double-layer capacitance (EDLC), where the energy storage and release mechanism is based on charge separation at the electrochemical interface formed between the electrode and the electrolyte. EDLCs utilize electrostatic interactions to accumulate energy within the Helmholtz double layer at the electrode-electrolyte interface. The capacitance of an EDLC is based on the potential dependence of the electrostatically stored surface energy at the electrode interface, as illustrated in Figure 1-1 (a) [24]. EDLC-based supercapacitors exhibit exceptionally high power density (1–100 kW kg^{-1}) and long cycle life (>10,000 charge-discharge cycles); however, their energy density remains relatively low (4–10 Wh kg^{-1}) compared to commercial batteries (~100 Wh kg^{-1}).

The second mechanism is pseudocapacitance, in which inorganic materials undergo fast and reversible redox reactions at or near the surface, where charge accumulation is proportional to the potential difference. During charging and discharging, redox reactions occur through chemical bonding, facilitating energy transfer between the electrolyte and the electrode, as shown in Figure 1-1 (b). Another form of pseudocapacitance exists, known as intercalation pseudocapacitance, where charge storage occurs within the bulk of the material rather than just the surface (Figure 1-1 c). Unlike battery-type intercalation (Figure 1-1 d), which is diffusion-limited, the kinetics of intercalation pseudocapacitance are governed by surface-controlled processes, making its behavior capacitive.

Compared to EDLCs, pseudocapacitors offer higher specific capacitance because redox reactions provide greater charge storage capacity than the electrostatic interactions relied upon by EDLCs. However, due to the high mechanical stress exerted on the electrodes during the faradaic processes of charging and discharging, pseudocapacitors generally exhibit a shorter cycle life than EDLCs and tend to degrade more rapidly over time. Depending on the cell configuration, supercapacitors can be categorized as symmetric (featuring two identical electrode materials) or asymmetric (utilizing two different electrode materials).

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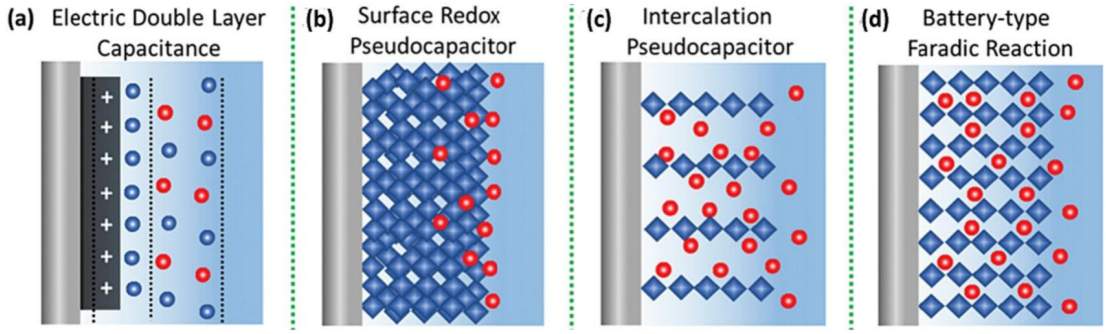

Figure 1-1. Energy storage mechanisms of (a) EDLC, (b) surface redox pseudocapacitor, (c) intercalation pseudocapacitor, and (d) battery-type faradaic reaction [25]

1.1.2. Advantages and Working Mechanisms of Zinc-Ion Hybrid Capacitors

Hybrid ion capacitors (HSCs) are generally named after their shuttle cations, such as lithium-ion capacitors (LICs) [26], sodium-ion capacitors (SICs) [27], and potassium-ion capacitors (PICs) [28]. Various monovalent HSCs have been extensively evaluated, typically utilizing organic solvents that provide wide electrochemical windows [29]. However, organic solvents suffer from inherent flammability and limited ionic conductivity, while the capacity and kinetic mismatch between the cathode and anode also compromise the overall performance of monovalent HSCs. Furthermore, the limited reserves and uneven geographical distribution of lithium sources in the Earth's crust have raised concerns regarding the sustainability of lithium metal [30]. As alternatives, multivalent HSCs based on Zn^{2+}, Mg^{2+}, and Ca^{2+} are gaining increasing attention [31]. These multivalent HSCs utilize less reactive metals as anodes and incorporate aqueous electrolytes with high ionic conductivity, thereby mitigating potential safety concerns and enhancing power output .

Among various hybrid supercapacitors, zinc-ion hybrid supercapacitors (ZHSCs) exhibit numerous unique advantages[32, 33]. For instance, zinc metal is abundant on Earth (approximately 300 times more abundant than lithium) [34] and possesses high theoretical gravimetric and volumetric capacities (820 mAh g^{-1} and 5851 mAh cm^{-3}, respectively) [35] It also features a suitable redox potential (−0.76 V vs. SHE), excellent compatibility with aqueous electrolytes, low toxicity, and ease of material processing and fabrication. As illustrated in the Ragone plot in Figure 1-2, ZHSCs combine the benefits of zinc-ion batteries—such as low cost, environmental friendliness, and the low redox potential of zinc anodes—with the merits of supercapacitors, including fast charge/discharge rates, high power density, and long cycle life, thus demonstrating promising prospects for practical applications.

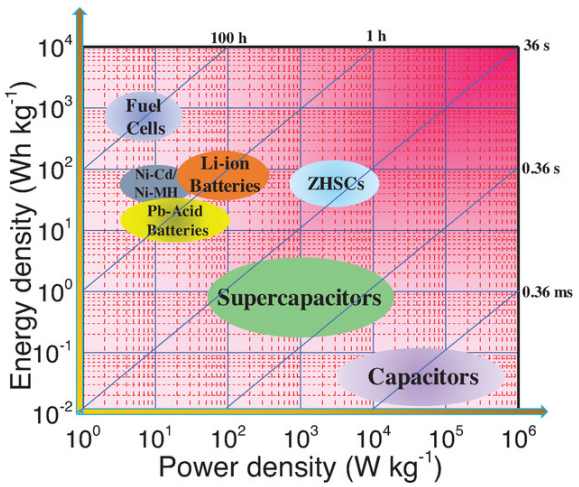

Figure 1-2. Energy density and power density of supercapacitors, batteries, and zinc-ion hybrid supercapacitors.

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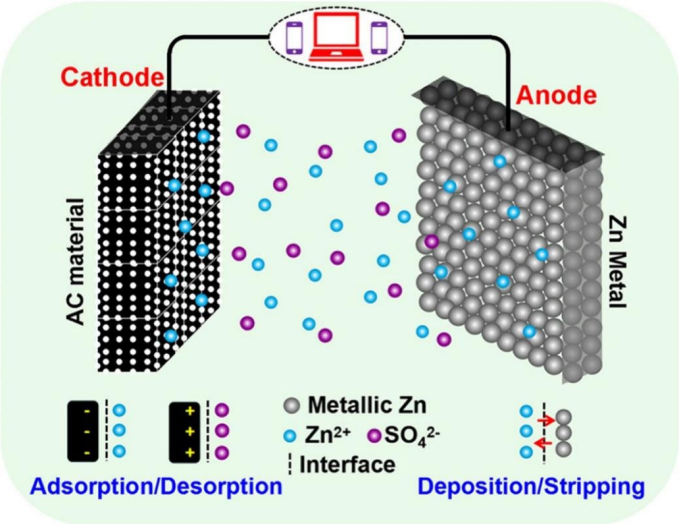

Figure 1-3. Configuration and working mechanism of a typical zinc-ion hybrid capacitor

Typical zinc-ion hybrid supercapacitors (ZHSCs) are composed of components from both zinc-ion batteries and supercapacitors. In these systems, the battery-type anode stores a high capacity of energy through redox reactions, while the electric double-layer capacitive (EDLC) cathode stores energy via electrostatic interactions between the charged electrode surface and the ions in the electrolyte, as illustrated in Figure 1-3. In most ZHSCs, zinc foil is directly employed as the anode, whereas carbon-based materials (e.g., activated carbon, porous carbon, graphene, etc.) are utilized as the cathode. An ion-permeable separator is placed between the anode and the cathode to prevent short circuits. Commonly used liquid electrolytes in ZHSCs are aqueous zinc salt solutions, such as$ZnSO_4$, $ZnCl_2$, $Zn(NO_3)_2$, $Zn(CH_3COO)_2$ and $Zn(CF_3SO_3)_2$. The redox reaction occurring at the zinc anode during the charge-discharge process is a reversible Zn/Zn^{2+} plating/stripping process. During charging, zinc ions in the electrolyte are attracted to the zinc anode, where they acquire electrons and deposit onto the anode surface. Conversely, during discharging, the metallic zinc releases electrons and is converted back into zinc ions [36, 37].

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad (1.1)$$

For carbon-based cathodes, the energy storage mechanism is primarily governed by electric double-layer capacitance (EDLC). During charging, ions and electrons are adsorbed at the electrode-electrolyte interface through electrostatic interactions; during discharging, these ions and electrons desorb from the interface. Since this storage mechanism is predominantly physical, it proceeds at a high rate, enabling high power density and fast charging capabilities.

2. Cathode Materials for Zinc-Ion Hybrid Capacitors

Cathode materials in zinc-ion hybrid capacitors (ZICs) can be categorized into Faradaic pseudocapacitive materials and electric double-layer capacitive (EDLC) materials based on their energy storage mechanisms. In EDLC materials, ions undergo rapid adsorption and desorption: anions from the electrolyte migrate to the material surface to form an electric double layer for energy storage; simultaneously, anion insertion may also occur via Faradaic processes [38]. This mechanism is characterized by extremely fast ion transport kinetics, and the adsorption/desorption process exerts minimal impact on the structural integrity of the electrode material [39]. Consequently, the rapid adsorption/desorption processes within the

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hybrid capacitor endow the device with exceptionally high power density and superior cycling stability.

Research indicates that optimizing the pore size of electrode materials to match the dimensions of electrolyte ions can maximize the utilization of the EDLC electrode space, serving as an effective strategy to enhance volumetric capacitance. To achieve the objective of simultaneously high power and energy density in hybrid capacitors, current research on capacitive materials primarily focuses on nanostructure engineering and elemental doping to increase the electrochemically active surface area (ECSA) [40]. Activated carbon (AC) and other carbon-based materials, characterized by their high specific surface area (SSA) which facilitates rapid charge-discharge processes, have thus become archetypal capacitive materials.

2.1. Carbon -based materials

Taking carbon-based materials as an example, the development of various capacitive electrode materials is fundamentally a process of continuous electrochemical performance optimization. By tuning the pore structure, the grain size can be reduced to the nanoscale, thereby increasing the specific surface area, providing more active sites, shortening ion diffusion paths, and mitigating the stress effects caused by structural changes [41]. Additionally, methods such as atomic defect doping, coating composites, and the development of novel electrode materials can effectively improve electrical conductivity and structural stability, further enhancing electrochemical performance.

2.1.1. Based Carbon materials

Activated carbon (AC) is a widely reported cathode material; however, its primary drawback is poor ion diffusion and transport capabilities due to its microporous nature and limited wettability. He [42] proposed a surface engineering strategy for AC with a mesoporous structure. Through the dehydrogenation of polyvinylpyrrolidone (PVP), the material exhibited improved wettability and an extended cycling life, delivering a high specific capacity of 176 mAh g^{-1} at a current density of 0.5 A g^{-1}. It also demonstrated excellent high-rate performance (72 mAh g^{-1} at 10 A g^{-1}) and robust ultra-fast long-term cycling stability, maintaining 78% capacity after over 40,000 cycles. Carbon nanotubes (CNTs) have garnered significant research interest due to their high electrical conductivity, superior mechanical strength, large specific surface area, excellent chemical stability, low resistivity, and low mass density [43]. However, the manufacturing cost of CNTs remains high due to the high temperatures required for synthesis and the complex processes involved in controlling their morphology, diameter, length, and number of walls [44].

Yan et al. prepared thin-walled carbon nanotubes (TCNTs) and employed various oxidizing agents for oxidative modification to obtain hydroxyl (-OH)-rich TCNTs . Among these, TCNT-H_2O_2 exhibited the best electrochemical performance, achieving a specific capacitance of 118.1 F g^{-1} at 1 A g^{-1}, a significant improvement over the 55 F g^{-1} of pristine TCNTs under the same conditions. This proves that the presence of -OH groups can significantly enhance the specific capacity of the electrode. The assembled TCNT-H_2O_2||$ZnSO_4$||Zn foil aqueous zinc-ion hybrid supercapacitor (ZHSC) maintained 100% capacity after 10,000 cycles at 5 A g^{-1}, delivering a maximum energy density of 80 Wh kg^{-1} and a maximum power density of 4 kW kg^{-1}. Li et al. synthesized and compared pristine CNTs (p-CNTs), hydroxylated CNTs (h-CNTs), and carboxylated CNTs (c-CNTs). They found that h-CNTs contain more oxygen-containing functional groups than c-CNTs, enabling higher Zn^{2+} adsorption and better hydrophilicity, which resulted in a higher specific capacity [45]. The introduction of polyaniline (PANI) not only enhanced the redox-based energy storage capacity of the cathode but also increased its mechanical strength. By using an h-CNT/PANI nanocomposite as the cathode, the assembled ZHSC achieved a specific capacity of 97 mAh g^{-1} at a current density of 0.1 A g^{-1} with a Coulombic efficiency of 100%.

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As a sustainable carbon material, biomass-derived carbon offers multiple advantages, including environmental friendliness, cost-effectiveness, and excellent electrochemical performance. Its precursors are sourced from a wide range of materials—including sweet potato [46], rice husk [47], waste sponge [48], shrimp shells, osmanthus [49], and sod , all of which serve as viable sources for biochar. The utilization of these materials not only mitigates reliance on fossil fuels and reduces carbon emissions but also facilitates waste valorization. Furthermore, during the carbonization process, biomass can spontaneously undergo heteroatom doping (such as nitrogen, oxygen, and sulfur) and develop hierarchical porous structures. These characteristics synergistically enhance electrical conductivity, ion transport efficiency, and pseudocapacitive contributions, allowing the material to exhibit high specific capacity and superior rate performance in energy storage devices. Consequently, it represents a highly promising green electrode material.

Lignin is an organic compound found in plant cell walls and stands as one of the most significant structural polymers in plants. Lignosulfonates, a byproduct of the papermaking industry, generate inorganic salts during pyrolysis; these salts can serve as templates for the preparation of porous carbon (PC), thereby reducing costs. Liu et al.[50] synthesized PC using activated zinc-ligand lignin as a precursor. The condensation of phenolic lignin with tetrafluoroterephthalonitrile yields a more densely interconnected three-dimensional (3D) network. During pyrolysis, zinc and the potassium elements from KOH react with the oxygen species within the lignin. The resulting salt particles act as self-templates, facilitating the formation of hierarchical macropores.

Since the discovery of graphene in 2004, it has garnered significant attention due to its exceptional properties, including a remarkable room-temperature electron mobility exceeding 2,000 $cm^2\ V^{-1}\ s^{-1}$, an estimated Young's modulus of 0.5–1.0 TPa, a stiffness of 300–400 $N\ m^{-1}$, a fracture strength of approximately 42 $N\ m^{-1}$, and a high theoretical specific surface area of 2,630 $m^2\ g^{-1}$. Owing to its high electrical conductivity, large surface area, and high theoretical electric double-layer capacitance (EDLC), graphene is widely utilized in energy storage devices such as batteries and supercapacitors. Li et al. [51] synthesized vertically aligned graphene (VGN) arrays on high-surface-area activated carbon fibers via plasma-enhanced chemical vapor deposition (PECVD), followed by activation to obtain activated vertical graphene (A-VGN) with optimized pore structures and surface chemical states. The vertically aligned structure effectively exposes electrochemically active sites and enables rapid ion transport within the electrode, allowing A-VGN to exhibit superior performance in electrochemical evaluations. The ZHSC (zinc-ion hybrid supercapacitor) based on the A-VGN cathode retained 97.4% of its initial capacity after 10,000 charge/discharge cycles at 5 $A\ g^{-1}$. Although vertically aligned graphene prevents restacking (agglomeration) and enhances the overall performance of ZHSCs, further optimizations can be implemented. For instance, using reduced graphene oxide (rGO)—which possesses higher hydrophilicity than pristine graphene—can facilitate greater KOH absorption during the activation process, thereby achieving a higher specific surface area.

Carbon-based materials with tunable pore sizes, high specific surface areas, and favorable surface morphologies generally hold immense potential for energy storage devices. However, they often fail to achieve high theoretical performance in terms of energy density and specific capacity, as their energy storage mechanism is primarily capacitive, which constitutes a bottleneck for ZHSC performance. Consequently, non-carbon-based materials, known as pseudocapacitive materials, have attracted significant research interest because they can deliver much higher capacitance compared to electric double-layer capacitance. Furthermore, some pseudocapacitive materials provide a combination of both pseudocapacitance and EDLC, thereby further enhancing the performance of ZHSCs.

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2.1.2. MXene materials

MXenes have emerged as a rising star in the fields of energy storage and materials science owing to their exceptional properties. As a class of two-dimensional (2D) nanomaterials, MXenes possess remarkable electrical conductivity and unique chemical characteristics—specifically their tunable interlayer spacing—enabling a wide range of applications from energy storage to biosensors [52]. While exhibiting extraordinary mechanical strength, MXenes also inherit distinct chemical attributes derived from their nature as transition metal carbides or nitrides.

Maughan et al. synthesized pillared Ti_3C_2MXene in situ by incorporating surfactant pillars into the electrolyte. This material, which maintains a stable interlayer spacing, was employed as a cathode for zinc-ion hybrid supercapacitors (ZHSCs), achieving high specific capacity [54]. To fabricate the MXene electrode, the prepared MXene, carbon black, and polyvinylidene fluoride (PVDF) were mixed in a mass ratio of 75:15:10, using N-methyl-2-pyrrolidone (NMP) as the solvent to form a slurry, which was then coated onto a 0.1 mm thick titanium foil. The ZHSC was assembled by punching the MXene and zinc electrodes into 16 mm diameter discs and placing them within CR2032 coin cells, utilizing 0.1 M $ZnSO_4$ as the electrolyte and glass fiber as the separator.

The pillared MXene exhibited an initial discharge capacity of 189 mAh g^{-1}, significantly outperforming the untreated MXene (mAh g^{-}) and the pre-pillared samples (105 mAh g^{-1}). The pillaring treatment allows the MXene to expose more active sites to the electrolyte, facilitating the formation of a solid electrolyte interphase (SEI) film and the trapping of zinc ions. Furthermore, the ZHSC demonstrated a high capacity retention of 96% after 1000 cycles at a current density of 0.2 A g^{-1}, with a Coulombic efficiency approaching 100%. Although MXene-based electrodes show great potential as cathode materials, current understanding is still insufficient to fully optimize their performance in energy storage applications. Therefore, further research is required to comprehensively elucidate their storage mechanisms and reaction kinetics.

2.2. Electrolyte

n Zinc-ion Hybrid Supercapacitors (ZHSCs), the electrolyte is as critical a component as the electrode. An ideal electrolyte must satisfy several essential requirements: high ionic conductivity, excellent chemical stability, a wide electrochemical stability window, ion compatibility, and the ability to suppress the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER). The most commonly utilized electrolytes for ZHSCs are aqueous zinc-based solutions, such as $(ZnNO_3)_2$, $ZnSO_4$, $Zn(CH_3COO)_2$, $Zn(CF_3SO_3)_2$.

Due to its low cost, superior stability, and high ionic conductivity, $ZnSO_4$ is employed in the majority of ZHSCs. However, certain issues—such as significant performance degradation at low temperatures and side reactions like zinc dendrite growth—can increase interfacial charge transfer resistance, which is detrimental to rate performance [53]. During device operation, by-products are generated on the zinc surface after repeated stripping/plating cycles, which significantly impacts performance. The formation of by-products in common electrolytes is summarized below:

$ZnSO_4$[54]:

$$Zn + H_2O \rightarrow Zn^{2+} + H_2 + 2OH^- \quad (1.2)$$

$$4Zn^{2+} + 6OH^- + SO_4^{2-} + 5H_2O \rightarrow Zn_4(OH_6)SO_4 \bullet 5H_2O \quad (1.3)$$

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$Zn(CF_3SO_3)_2$[55]:
Cathode:

$$H_2O \leftrightarrow H^+ + OH^- \tag{1.4}$$

$$PSCA600 + CF_3SO_3^- \leftrightarrow CF_3SO_3^- \| PSCA600 \tag{1.5}$$

$$C - OH + Zn^{2+} + e^- \leftrightarrow C \cdots O \cdots Zn + H^+ \tag{1.6}$$

$$2Zn^{2+} + 4OH^- + 2Zn(CF_3SO_3)_2 + 3H_2O \leftrightarrow [Zn(CF_3SO_3)_2Zn(OH)_2] \bullet 3H_2O \tag{1.7}$$

Researchers have found a close correlation between electrolyte concentration and the efficiency of zinc (Zn) plating and stripping. When 1 M conventional electrolytes are used in Zn-Ti asymmetric cells, they exhibit low initial Coulombic efficiency (CE) (55–65%), indicating poor reversibility of Zn plating/stripping. As the electrolyte concentration increases to 3 M, the CE of all zinc-based electrolytes rises to 90%. Among them, $Zn(CF_3SO_3)_2$ shows the best performance, achieving CEs of 96.8% and 97% at concentrations of 3 M and 4 M, respectively [56]. Yang et al. discovered that $Zn(ClO_4)_2$ is a more cost-effective and superior electrolyte compared to commonly used liquid electrolytes [57]. In comparison with $ZnSO_4$ and $Zn(CF_3SO_3)_2$ using the same anodes and cathodes, $Zn(ClO_4)_2$ exhibits a larger Cyclic Voltammetry (CV) curve area and longer discharge times, indicating higher specific capacity and energy density.

Electrolyte additives are considered an effective strategy to promote uniform Zn-ion migration and deposition, suppress dendrite formation, and inhibit the hydrogen evolution reaction (HER). The synergistic effects of cations or anions introduced via additives can endow Zinc-ion Hybrid Supercapacitors (ZHSCs) with excellent electrochemical performance. For instance, adding Na_2SO_4 to $ZnSO_4$ can restrict the growth of Zn dendrites in ZHSCs while enhancing electrochemical performance [58]. This is attributed to Na^+, which possess a high redox potential (in terms of stability), anchoring to dendrite sites via the local electric field. This creates an electrostatic shielding effect that repels Zn^{2+} from these sites, thereby suppressing Zn dendrite growth and achieving uniform Zn deposition. The addition of organic compounds to the electrolyte can regulate ion and current distribution to prevent dendrite formation [59]。. For example, the introduction of polyethylene glycol (PEG) expands the Zn surface polarization and reduces the local current density, which slows down the deposition rate of Zn^{2+} ions, thereby modulating the deposition and diffusion of zinc [60]. Additionally, sodium dodecyl benzene sulfonate (SDBS), an inexpensive surfactant, has been introduced as an electrolyte additive in MnO_2||Zn batteries. It has been proven that the introduction of SDBS enhances the adsorption capacity on the Zn (100) crystal plane. This prevents preferential Zn deposition on the (002) plane. Such a change in crystal growth orientation transforms the zinc anode surface from disordered dendrites to uniform deposition, thus inhibiting dendrite growth. Furthermore, the introduction of SDBS improves the interfacial wettability between the aqueous electrolyte and

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the Zn anode, promoting uniform Zn deposition. SDBS can also adsorb onto the Zn surface to form a passivation layer, protecting the zinc from corrosion [61].

Compared to aqueous electrolytes, hydrogel electrolytes effectively satisfy the criteria for elasticity, self-healing, leak prevention, and inhibition of dendrite formation, which significantly enhances the overall lifespan and safety of zinc-ion hybrid supercapacitor (ZHSC) devices. Hydrogel electrolytes can be endowed with functional attributes such as high ionic conductivity, self-healing capability, and flexibility through various structural strategies, including the generation of polyionic chains and the incorporation of non-covalent cross-linking. Fu et al. developed a flexible hydrogel polymer electrolyte for flexible ZHSCs based on a poly (acrylic acid)/sulfobetaine methacrylate (PAA-co-PSBMA) copolymer and rod-like cellulose nanocrystals (CNCs), which demonstrated exceptional performance even at low temperatures[62]. Furthermore, the addition of 7.5 M $ZnCl_2$ to the hydrogel resulted in a "water-in-salt" electrolyte. This electrolyte offers a widened electrochemical potential window, leading to higher energy density and mitigating the adverse effects of low temperatures due to the strong electrostatic interactions between ions and water molecules. The synthesized hydrogel exhibited a high ionic conductivity of 15.6 mS cm^{-1}, an excellent adhesion strength of 98 kPa, and maintained high mechanical strength even at -60°C. At room temperature, the assembled ZHSC demonstrated a broad potential window of 0 to 2.2 V, achieving a high specific capacity of 253 mAh g^{-1}, an energy density of 253 Wh kg^{-1}, and a maximum power density of 27.5 kW kg^{-1}, while retaining 95.6% of its initial capacity after 100,000 cycles at 5 A g^{-1}. Despite the superior electrochemical performance, flexibility, and low-temperature characteristics of the fabricated ZHSC, the synthesis of the hydrogel involves complex procedures and expensive materials. These factors, coupled with the requirements for specialized skills and equipment, pose significant challenges for large-scale production.

2.3. Research Progress in Anode Materials

Zinc metal possesses immense potential as a widely utilized alternative to lithium metal in energy storage devices, owing to its high theoretical gravimetric and volumetric capacities (820 mAh g^{-1} and 5855 mAh cm^{-3}, respectively), low reduction potential relative to the standard hydrogen electrode (SHE, −0.76 V), and high elemental abundance in the Earth's crust (Table 1.1). Most researchers directly employ zinc foil or polished zinc foil (sanded to remove the surface oxide layer) as the anode material, favored for its low cost, robust mechanical strength, excellent flexibility, and widespread availability. However, when zinc is utilized as an anode for zinc-ion hybrid supercapacitors (ZHSCs), persistent challenges such as dendrite growth, corrosion, and the hydrogen evolution reaction (HER) frequently arise. These issues inevitably lead to suboptimal electrochemical performance in ZHSCs.

Table 1-1. Ionic radii, theoretical capacities (gravimetric and volumetric), redox potentials, and crustal abundances of various metals.

Metal	Ionic Radius (Å)	Theoretical Capacity (mAh g^{-1})	Volumetric Capacity (mAh cm^{-3})	Redox Potential (VS.SHE)	Elemental Abundance (%)
Lithium	0.76	3860	2061	-3.04	0.0017
Sodium	1.02	1166	1129	-2.71	2.3
Potassium	1.38	685	610	-2.92	1.7
Magnesium	0.72	2206	3834	-2.36	2.9
Zinc	0.75	820	5855	-0.76	0.0079
Calcium	1.00	1337	2072	-2.84	5.0
Aluminum	0.53	2980	8046	-1.68	8.2

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The formation of zinc dendrites is ascribed to the inhomogeneous distribution of the electric field and electrolyte ions on the zinc anode surface. Following dendrite growth, a sequence of parasitic side reactions is triggered:

(1) The enlarged specific surface area of the zinc anode accelerates the hydrogen evolution reaction (HER); (2) As protons are consumed by the HER within the electrolyte, the concentration of hydroxyl ions increases; (3) The generated hydroxyl ions react with the zinc anode, initiating the zinc corrosion process; (4) During corrosion, zinc hydroxide species accumulate on the surface of the zinc anode.

The aforementioned byproducts reduce the electrical conductivity of the anode, increase polarization, and further intensify the non-uniformity of the electric field, thereby exacerbating dendrite propagation. The corresponding side reaction equations are as follows[63]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1.8)$$

$$4Zn^{2+} + 6OH^- + SO_4^{2-} \rightarrow Zn_4SO_4(OH_6) \quad (1.9)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \quad (1.10)$$

To address these issues, extensive research has been conducted. Inspired by the solid electrolyte interphase (SEI) layer in lithium-ion batteries, researchers have constructed artificial interphase layers on zinc anodes to protect the zinc from direct contact with the electrolyte, thereby mitigating dendrite formation and suppressing side reactions [64]. For instance, carbon materials have been utilized as protective coatings. As illustrated in Figures 1-4 (a, b), mesoporous carbon hollow spheres (MCHS) were synthesized to function as both the capacitor-type cathode and a protective layer for bare zinc [67]. When applied to the anode, the introduction of the MCHS layer reduces the interfacial resistance between the electrolyte and the zinc anode, maintains a uniform charge distribution, and provides efficient electron transport pathways to hinder the growth of zinc dendrites (Figure 1-4 c). ZHSCs with the MCHS coating achieved over 550 cycles, exhibiting significantly better cycling stability than those using bare zinc anodes.

Scanning electron microscopy (SEM) was employed to observe the surface of the MCHS coating after cycling. Prior to cycling, the surface of the bare zinc foil was dense, smooth, and flat. However, after 100 stripping/plating cycles, several spikes appeared on the surface of the bare zinc foil, indicating severe dendrite issues. In contrast, the surface of the MCHS-coated zinc foil remained smooth and porous after cycling, with no obvious spikes. When the MCHS coating was removed using low-power ultrasonication, the underlying zinc foil surface remained uniform with only minor protrusions. The morphology of the MCHS remained almost identical to its original structure. These findings demonstrate that the aforementioned coating technology can effectively inhibit and regulate dendrite growth, thereby enhancing electrochemical performance.

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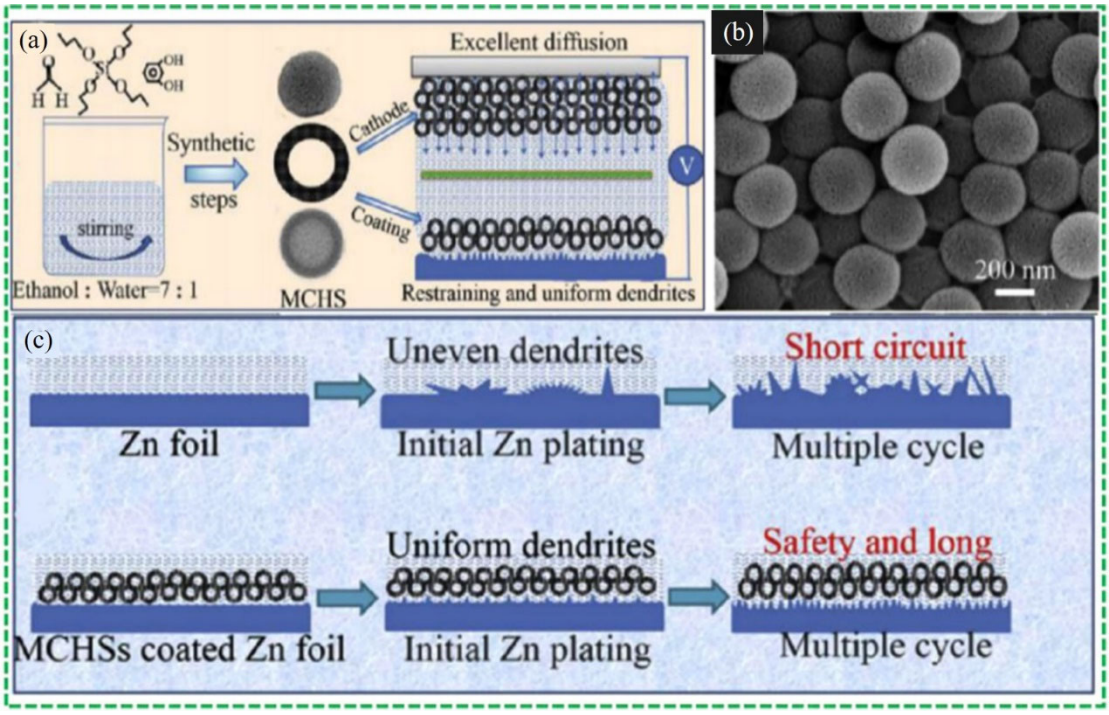

Figure 1-4. (a) Synthesis method; (b) SEM images; and (c) dendrite suppression mechanism of the MCHS coating.

Meanwhile, various metal oxides have also been employed as protective layers for zinc anodes, such as TiO_2[65], HfO_2[66], ZnO[67], Nb_2O_5[68], Al_2O_3[69] and ZrO_2[70]. Li et al. developed a rutile nano- TiO_2 protective layer to suppress the formation of Zn dendrites. In symmetric cells, the Zn anode protected by the TiO_2 coating exhibited a reduced voltage hysteresis (50 mV at 0.4 mA cm^{-2}). Additionally, in Zn-MnO_2 full cells, the configuration with the TiO_2-coated anode also demonstrated superior cycling stability. While the uncoated Zn- MnO_2 full cell maintained a discharge capacity of only 27.69 mAh g^{-1} after 500 cycles, the Zn@ TiO_2-MnO_2 full cell achieved a much higher capacity of 89.14 mAh g^{-1}. This enhanced electrochemical performance can be attributed to the improved wettability provided by the TiO_2 coating, uniform Zn^{2+} deposition, and the mitigation of Zn dendrites.

Furthermore, Liu et al. utilized an atomic layer deposition (ALD) process to fabricate a ZrO_2 coating, which enabled uniform Zn deposition, reduced the Zn^{2+} nucleation overpotential, and effectively inhibited side reactions on the zinc anode, thereby promoting reversible Zn^{2+} plating/stripping. Consequently, the Zn anode with a 40 nm ZrO_2 coating exhibited an outstanding cycle life. Moreover, the ZrO_2 coating contributed to excellent cycling performance in Zn- MnO_2 batteries, achieving a durable lifespan of over 2,500 cycles at a 10 C rate. Despite the effectiveness of metal oxides in suppressing Zn dendrites, challenges such as limited surface area, suboptimal electrolyte wettability, and the inherent rigidity of these protective layers still affect the long-term cycling stability of the batteries.

3. Conclusion and Outlook

3.1. Conclusion

In summary, Zinc-ion Hybrid Capacitors (ZHSCs) have demonstrated great potential as a next-generation energy storage technology by bridging the gap between high-energy batteries and high-power supercapacitors. This review has highlighted the fundamental storage mechanisms, including EDLC and pseudocapacitance, and discussed the recent advancements in cathode materials (such as carbon-based materials and MXenes), electrolyte optimization, and anode

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protection strategies. Specifically, surface engineering of the zinc anode and the use of functional additives have proven effective in suppressing dendrite growth and hydrogen evolution, thereby significantly extending the cycle life of ZHSCs.

3.2. Outlook

Despite the significant progress, several challenges must be addressed to realize the full potential of ZHSCs for practical applications:

Enhancing Cathode Capacity: While carbon-based cathodes offer excellent stability, their limited specific capacity remains a bottleneck. Future research should focus on developing novel pseudocapacitive materials or hybrid structures that balance high capacity with fast kinetics.

Anode Interfacial Stability: Zinc dendrites and side reactions (HER and corrosion) are still the primary causes of device failure. Advanced coating layers with high ionic conductivity and uniform electric field distribution are needed to achieve long-term stability under high current densities.

Electrolyte Engineering: Expanding the electrochemical stability window of aqueous electrolytes is crucial for increasing the energy density. Exploring "water-in-salt" electrolytes, deep eutectic solvents, or multi-functional hydrogels could be promising directions.

Practical Performance Evaluation: Most current studies are based on coin cells. Future work should transition toward pouch cells and evaluate performance under extreme conditions, such as low temperatures, high mass loading, and self-discharge rates, to meet industrial requirements.

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