Competitive Rechargeable Zinc Batteries for Energy Storage

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**Abstract**

The continuously increased demand for electrical energy and the associated strong growth in renewable energy necessitates robust, sustainable and cost-effective stationary energy storage solutions. This review paper evaluates zinc-based batteries as viable alternatives to conventional lithium-ion and vanadium redox flow systems for stationary storage applications. Highlighting zinc's accessibility, cost-effectiveness, lower environmental impact, and well-developed recycling infrastructure, this review provides a comprehensive analysis of various zinc battery chemistries, including zinc-metal, zinc-air, and zinc redox flow batteries. The paper provides a historical context of zinc battery development from primary to secondary cells while identifying key challenges, such as low cell voltage, dendrite formation, passivation, and hydrogen evolution. Current advancements in electrode design, including novel three-dimensional architectures, tailored electrolyte formulations, and optimized catalyst development, are discussed in detail. Additionally, a techno-economic analysis compares material costs and operational efficiencies of zinc systems with state-of-the-art alternatives, underscoring their competitive advantage. The interplay between material properties and system performance is also addressed, offering insights into improving cycling stability and energy density. Overall, this review describes the potential to position zinc batteries as promising candidates for large-scale, sustainable energy storage, capable of complementing and potentially replacing existing technologies in an evolving energy landscape.

**Keywords:** zinc-metal, zinc-air, zinc-flow, economics, stationary energy storage

## **1. Introduction**

The growing demand for renewable energy has heightened the need for efficient energy storage solutions. As the reliance on renewable energy sources increases, the integration of robust energy storage systems is essential to stabilize the grid and compensate for periods of low wind and/or low sun.[1,2] While lithium-ion batteries have traditionally dominated this space (with vanadium redox flow batteries being the only flow batteries that have been upscaled to industrial application), alternatives like zinc-based batteries offer substantial promise. Zinc batteries stand out due to zinc’s accessibility, abundance, cost-effectiveness, stability, environmental friendliness, established route of recycling, and inherent safety. When considering the molar mass of material and referring to the amount required to exchange a mole of electrons, though the differences in resource abundance (most widely referred to in tons) between lithium and zinc become small.[3] Currently, zinc is widely utilized in primary alkaline cells for various electronic devices. However, the successful commercialization of secondary cell systems has not yet been realized at an impactful scale. Nevertheless, zinc possesses potential for high energy density applications and benefits from an established recycling infrastructure, positioning it as a viable contender in the pursuit of sustainable energy storage solutions.

Zinc batteries are extensively discussed in literature, indicating their potential in energy storage technology. Several noteworthy reviews have addressed zinc-metal battery materials, including those by Fang et al.,[4] Ming et al.,[5] and Zhang et al.[6] These works explore the underlying chemistry and advancements in materials. Additionally, Konarov et al.[7] and Tang et al.[8] provide insights into current challenges and perspectives of zinc-metal batteries. Secondary zinc-air battery materials and emerging trends have been extensively reviewed by Li et al.,[9] Fu et al.[10] and Leong et al.[11], focusing on issues such as cyclability, reaction kinetics, and bi-functional catalysts. The environmental impacts of zinc-based batteries have been discussed by Iturrondobeitia et al.[12] based on a life cycle assessment. The materials used in zinc redox flow batteries have been extensively studied by Khor et al.,[13] Yuan et al.,[14] and Wang et al.,[15] where the functionality and materials, including challenges and areas for improvement, have been reviewed.

In the context of stationary energy storage systems, total cost of ownership that can be roughly divided into CAPEX (capital expenditures) and OPEX (ongoing costs) are pivotal factors in determining the commercial success of a given technology. A number of techno-economic cost analyses regarding capital costs have been conducted in academic literature. For instance, Gong et al.[16] and Chen et al.[17] calculated the capital costs of zinc-iron redox flow batteries, while Tang et al.[18] calculated the capital costs of a variety of redox flow batteries including ZnBr2. Gourley et al.[19] estimate material and production costs for zinc-metal batteries. However, little attention has been paid in the area of techno-economic analysis for zinc-air batteries.[20] Moreover, many analyses rely on data that do not account for recent changes in political dynamics, market conditions, and technological advancements. Additionally, there is a lack of published studies that enable a direct comparative evaluation of different technologies.

In this review paper, we aim to address this research gap by exploring the following questions:

* What materials and systems are available for various zinc battery technologies?
* Which battery technologies are most likely to succeed in the future?
* How do zinc-based rechargeable energy storage systems economically compare to state-of-the-art storage solutions, such as lithium-ion and vanadium redox flow batteries?
* What potential advantages do zinc-based systems offer over other technologies in terms of abundance, price stability, environmental impact, and recyclability?

A comprehensive overview of zinc battery technologies is provided, and material perspectives are highlighted. On the basis of material perspectives, ecological and market-related factors are analyzed, and explorative techno-economic material cost models are developed for all technologies. This paper aims to address the research gap surrounding zinc batteries, thereby highlighting their position as a viable technology within the broader context of stationary energy storage.

## **2. Basics of Zinc Batteries and Current Developments**

### **2.1. Classification of Zinc Batteries**

Zinc batteries already play an important role in many people's daily lives. For example, universal alkaline primary batteries are commonly used in a wide variety of devices, ranging from children's toys to portable measuring instruments. In the following chapters, we will focus on the chemistry and future potential of zinc-based secondary batteries, as they have substantial potential to contribute to the expanding stationary storage capacity, which is required to accommodate the storage of excess energy from renewable sources.

We begin with a brief historical overview of the development of various types of zinc batteries. Next, we examine different battery types in more detail. In general, zinc-based battery chemistries are classified into four main categories, as illustrated in Figure 1: zinc-ion, zinc-metal, zinc-air, and zinc flow batteries:

* **Zinc-ion batteries** utilize both anode and cathode materials that can reversibly insert and extract Zn²⁺ ions through intercalation mechanisms. Importantly, the anode does not consist of metallic zinc; instead, it features insertion materials where Zn²⁺ (and in case of aqueous systems also often protons) can be reversibly de(inserted).[21–23] These systems typically use conventional aqueous electrolytes and operate in a static configuration. While examples of other anode materials besides zinc are included in the overview on zinc-metal batteries (see Chapter 2.3, Table 1), we believe that using zinc metal as the negative electrode makes the battery types explored in this review particularly promising.
* **Zinc-metal batteries**, on the other hand, employ a metallic zinc anode and a cathode that stores Zn²⁺ ions by (de)insertion.[19,24] During cycling, the anode undergoes a dissolution and deposition process. Like zinc-ion batteries, these systems also operate in a static manner and often incorporate electrode additives to enhance performance and reduce dendrite formation. In the literature, zinc-metal batteries are often referred to as zinc-ion batteries, but this terminology can be misleading, since, as already stated above, zinc-ion batteries do not contain zinc-metal. Therefore, we will use the term "zinc-metal battery" for static systems with a zinc metal anode in accordance with proper nomenclature.
* **Zinc-air batteries** feature a metallic zinc anode combined with an air cathode that facilitates the oxygen reduction and evolution reactions (ORR and OER).[25,26] The reaction occurring at the anode involves the dissolution and deposition of zinc, while the cathode relies on reactions involving oxygen gas. These batteries typically use aqueous electrolytes and can be designed as either static or flow systems,[27] depending on the application requirements. The maximum voltage and capacity of these batteries are determined by the oxygen-consuming compounds at the positive electrode and the zinc metal at the negative electrode. A distinctive feature of zinc-air batteries is their open cell structure, which allows them to use ambient oxygen as the cathode reactant, rather than requiring it to be stored within or near the cell.
* **Zinc flow batteries** consist of a metallic zinc anode and a cathode—usually carbon-based—separated by an ion-conductive membrane. This system features flowing anolyte and catholyte solutions, which are separately stored in tanks and pumped through the reaction chamber which contains the electrodes. The anode reaction involves the dissolution and deposition of zinc, while cathode reactions often include the redox transformations of soluble species, such as metal ions or organic/inorganic compounds.[13,14] The choice of liquid anolyte and catholyte can vary considerably based on the positive counterpart to zinc, which also affects theoretically achievable performance.

The scope of this work is on zinc-based battery chemistries that employ a metallic zinc anode—specifically, **zinc-metal, zinc-air, and zinc flow batteries**. While all three systems share the common feature of utilizing zinc metal at the anode, they differ significantly in terms of cathode design, reaction mechanisms, and system architecture. Therefore, each chemistry is discussed individually in this review to highlight its unique characteristics and operational challenges. Additionally, Chapters 3 and 4 provide an economic analysis and market prospects comparing these options to conventional lithium-ion batteries.

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Figure 1: Illustration on different types of zinc-based batteries. The secondary batteries are distinguished as static and flow systems with zinc-ion and zinc-metal batteries as static systems, zinc flow batteries as flow systems and zinc-air batteries as an intermediate. Zinc-metal, zinc-air and zinc flow systems all share the use of zinc metal as the anode material.

### **2.2. Overview of the Different Types of Zinc Batteries**

An overview of the evolution of zinc batteries, starting with the Volta pile and concluding with state-of-the-art research, is illustrated in Figure 2.

In 1789, Luigi Galvani conducted his experiments on frogs, which are commonly known as the "zombie frog experiments." These experiments laid the foundation for the invention of the electric battery and the subsequent development of the physical investigation of electricity.[28] Alessandro Volta took over the “Galvanic” principle around the year 1800. He used plates of copper and zinc as electrodes. In between he put paperboard soaked with salt solution as an electrolyte. With this setup he invented the first battery and also the first zinc-battery. As oxygen from air takes part in the discharge mechanism of the copper electrode (*via* formation of CuO), this battery can be considered as a first version of a zin-air battery. By stacking several layers on top of each other, a usable voltage was gained. This ’Voltaic’ pile is considered the first battery with continuous current, long before the discovery of the electric generator. In 1802 Ritter basically invented the first rechargeable battery. The “Rittersche Ladungssäule” had a similar assembly compared to a voltaic pile but used only copper disks (i.e. no zinc!). Ritter combined this zero-voltage construction with a Voltaic pile. The Voltaic pile electrolyzed the water of the electrolyte and produced hydrogen and oxygen. The recombination of hydrogen and oxygen led to a discharge current. With this Ritter laid the fundamental groundwork for a rechargeable battery and the working principle of an oxygen-hydrogen fuel cell. This was followed by the Daniell cell in 1836, which was based on a Cu||Zn chemistry and was followed by the Grove cell (Zn|HNO3). The Galvanic Cell of Georges Leclanché and Carl Gassner, called the Leclanché cell or dry cell, with a voltage of 1.5 V consisted of a negative zinc electrode, an ammonium chloride (later also with addition of ZnCl2) containing aqueous solution as electrolyte and a mixture of manganese dioxide and carbon as the positive electrode in 1866. In addition, a carbon rod was used as a positive electrode current collector. In 1878 a zinc-air cell was created by the French engineer Maiché. While the reaction mechanism of the Volta pile from 1800 used already the basic reaction mechanism of a zinc-air battery, this battery was the first energy storage device with a porous carbon air cathode. This Maiché battery, which employed ammonium chloride-based electrolyte, did not get much attention, but it opened the way for the development of other metal-air cells. Due to electrolyte flooding, the low and unstable cell voltage and poor cycle life, the research did not progress much further. Then it took a long while until the first alkaline zinc-air battery, with KOH electrolyte, was invented in 1932 by Heise and Schumacher. Their battery design was a real breakthrough for zinc-air battery technology. In the 1960s, research on hydrogen-oxygen (H2-O2) fuel-cells caught up, which also helped with progressing the improvement of the zinc-air battery, because the gas diffusion electrode was improved by the ongoing research on fuel cells. This allowed stacking of the cells and the use of alkaline electrolytes to increase the energy density to 200 Wh kg⁻1 in the early 1980s. These insights have been used to develop the so-called Zoxy Cells which have been available in various sizes like ZV320, ZV500 and ZV3000 with high capacities.[29] In the 1980s[30] and 1990s[31] , further advancements were made in the development of mechanically and electrically rechargeable zinc electrodes. The early 2000s introduced ionic liquids as alternative electrolytes.[32] In the past decade, there has been a rapid increase in research interest in zinc-based batteries, particularly focused on creating rechargeable (secondary) systems. Recent advancements in this area are summarized in Figure 2, which highlights key developments and contributions from the literature regarding the evolving landscape of zinc batteries.

The turning point for zinc batteries came as Goodenough discovered lithium cobalt oxide (LCO). From 1990 until 2010, research on zinc based systems was less prominent, because of the growing interest in lithium ion batteries (LIB).[33] Because of concerns about the toxicity and flammability of the organic electrolyte in LIB, the heavy reliance on cobalt and other transition metals, as well as other safety concerns and difficulties with respect to recycling of LIBs,[34] research on alternative systems to LIB including zinc batteries has grown notably.

With this shift in focus toward zinc batteries, it is essential to explore their various configurations and the underlying electrochemical processes. An overview of the possible zinc battery configurations—zinc-metal and zinc-air—along with their key electrochemical reactions, is presented in Figure 3. In both zinc-air and zinc-metal cells, zinc undergoes electrochemical oxidation to Zn²⁺ during discharge. In zinc-metal batteries, Zn²⁺ ions migrate to the cathode and integrate into its structure, often through an intercalation process (proton insertion can also occur, either alongside Zn2+ ions or independently, particularly at low pH levels). In contrast, zinc-air batteries utilize oxygen from the surrounding air as the cathode reactant, eliminating the need for oxygen storage within or close to the cathode structure. This unique open-cell feature enhances the energy density of zinc-air cells. During charging Zn2+ de-intercalates from the cathode in the zinc-metal system and is deposited back onto the anode surface, whereas oxygen is produced on the zinc-air cathode while zinc is plated onto the anode.

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Figure : Evolution of zinc chemistry in battery technology. The names marked with \* indicate potentially rechargeable cells. The leaves illustrate the latest advancements in zinc-air,[35–40]zinc-metal,[41–47] and zinc flow[48–50] batteries.

Zinc batteries face several key challenges that impact their performance, reversibility, and longevity. The challenges related to the zinc electrode are common for all zinc-metal-based systems and are shown in Figure 4.[15,26,41] They include dendrite growth, shape change, the formation of a passivation layer, corrosion, hydrogen gas evolution in aqueous electrolytes, and a high dependency on environmental conditions (e.g., dry, humid, cold, hot environments may lead to electrolyte issues unless auxiliary units to control the air access are employed).

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Figure 3: Schematic diagrams of (a) zinc-metal batteries featuring a confined cell structure and (b) zinc-air batteries characterized by an open-cell structure. It is important to note that in aqueous zinc-metal batteries, proton insertion can also occur, either alongside Zn2+ ions or independently, particularly at low pH levels.

Several strategies can be employed to address these challenges, including the use of electrode or electrolyte additives, microstructuring and design of the electrodes or materials, and engineering components from chemicals to cells, as well as optimizing operating parameters. To mitigate dendrite growth and shape change, a variety of strategies are being explored. In addition to modifications on microstructure design,[14,51,52] including the substrate, one effective approach involves incorporating additives in the electrode and electrolyte to promote uniform deposition of Zn2+ ions.[53,54] Additionally, advanced separators or interfacial layers, such as polymer coatings, are being investigated to physically block the propagation of dendrites while still allowing for ion transport.[55,56] Passivation and corrosion, often resulting from parasitic side reactions with the electrolyte, can be addressed through by adding inhibitors to stabilize the zinc surface.[57,58] Hydrogen evolution, a major issue in aqueous systems, can be tackled through electrolyte engineering. This includes not only the use of additives but also modifying the electrolyte content to reduce water activity and lower the overpotential for Zn plating/stripping.[35,59,60]Additionally, optimizing operating conditions can also contribute to these improvements as well.[61,62]

The performance and technical maturity of zinc-based batteries are influenced not only by challenges related to the zinc metal anode but also by limitations of the electrolyte and cathode components. While many of these challenges are specific to particular systems and are not discussed in detail here, a few general ones can be highlighted. On the cathode side, common challenges include slow reaction kinetics, poor chemical stability, unwanted side reactions and leaching of materials over time.[63–65] Similarly, electrolytes face issues such as limited electrochemical stability windows, changes in species concentrations over time, side reactions, sensitivity to environmental conditions, low ionic conductivity, and desolvation penalties at the interface to the electrodes.[14,43,66] These challenges can greatly impact the overall battery performance. Potential solutions for many of these challenges can be found in the approaches mentioned above and also shown in Figure 4.

The following sections summarize the current state of research on three prominent types of zinc batteries: zinc-metal, zinc-air, and zinc flow cell batteries. We delve into the essential components of each battery technology—namely the anode, cathode, and electrolyte—providing an overview of the latest advancements in research. Our findings are summarized in a table or matrix format for clarity. Additionally, at the conclusion of each section, we offer insights into future research directions and potential developments in the field.

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Figure : Major challenges of the zinc-based battery components are displayed on the left side while potential solutions are represented as gears on the right side.

### **2.3 Zinc-Metal Batteries**

Rechargeable zinc-metal batteries (ZMBs) are a class of secondary batteries utilizing a zinc-metal anode, aqueous or sometimes organic electrolytes, and mostly binary transition metal oxides, such as vanadium or manganese compounds, as cathodes (the zinc-air battery as a special case of the zinc-metal battery will be discussed in chapter 2.4). Rechargeable batteries based on manganese oxide at the cathode side and Zn metal at the anode side with an alkaline electrolyte (so-called RAM batteries) have already been patented by Edison in 1901, but were commercialized in the 1970s. However, they are now increasingly being replaced by nickel-zinc batteries, which have a slightly higher cell voltage (1.6 vs. 1.5 V). This type of battery is also cheaper and has a longer service life than the silver-zinc battery, which has also been in commercial production since the 1960s and offers the advantage of very high capacity combined with low volume and weight. The concept of re-chargeable zinc-metal batteries with slightly acidic electrolytes was first introduced by Kang and co-workers [42] in 2011 with a α-MnO2 | 1M ZnSO4 or Zn(NO3)2 in water| Zn cell setup.

All these cells have in common that during operation, Zn²+ ions are reversibly shuttled between the electrodes: metallic Zn is oxidized at the anode during discharge, releasing Zn²+ ions into the electrolyte and electrons into the external circuit. At the cathode, these electrons reduce Zn²+ ions, which insert into the host lattice, coupled with the oxidation/reduction of transition metal ions. Charging reverses this process, restoring the original electrode states.[43] . In addition, especially in highly acidic environments, proton transport and (co-)insertion can play a major or even dominant role. In principle, this can also be transferred to zinc- ion batteries, where instead of a zinc-based metallic anode, another insertion/intercalation material is used to host zinc ions and/or protons. However, in this review, we will primarily focus on systems with a zinc metal anode.

Zinc-metal batteries exhibit important potential for reducing the environmental impact associated with battery production and use. The possibility of using a metallic zinc-based anode is particularly favorable concerning sustainability and non-toxicity. This is primarily attributed to the utilization of aqueous electrolytes and the flexibility in cathode material selection. Vanadium-based cathodes, such as vanadium pentoxide (V₂O₅), are popular choices due to their high energy density and excellent cycling stability, as reported in numerous studies and have been excellently reviewed by Ding et al.[44] However, they are less favorable from a sustainability standpoint compared to manganese-based cathodes and Prussian Blue analogues (PBA). These alternatives have been highlighted in recent research, as they offer a more resource-efficient and non-toxic alternative. However, their long term stability and performance is compromised due to Mn dissolution or lower electrochemical potentials of the PBA framework.[67]

The matrix shown in Table 1 provides an overview of different zinc-metal and zinc-ion (with organic or sulfide anodes) cell chemistries sorted by electrolyte ranging from aqueous to solid state electrolytes. A detailed discussion of selected materials is given in the next sections.

Table 1: The matrix provides a structured overview of the various individual aspects of zinc-metal and zinc-ion batteries. Each column and row represent specific characteristics or components of the system, while each cell within the matrix highlights a particular aspect related to these parameters. The matrix summarizes various strategies derived from successful findings in literature. Although most research has been conducted in aqueous media, these strategies can also be adapted for use with other electrolytes, as long as the stability of the materials is carefully considered.

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|  | **Electrolyte** | **Electrolyte Additives** | **Anode** | **Anode Additives** | **Cathode** | **Cathode Additives/ Coatings** |
| **aqueous**  **5<pH<7** | Fluorinated salts[4] | Organic[45,68–70] | Planar with surface textured[71–73] | Interface modifications / surface coatings[74–76] | (doped) Manganese Oxides[77–79] | Conductive Agents[80,81] |
| Inorganic salts[82,83] | 3D Anode[84–90]  (scaffolds/ subsrates) | Vanadium Oxides[91,92] | Binder[78,93] |
| Fluorine-free salts[4,42] | Gelling agents[94–97] | Powder-based[98–100] | Spinels[101,102] | Artificial CEI: |
| Alloy[103–106] | Cobalt Oxides[97] |
| Organic, Zn-free[107] | Artificial SEI[82]: | PBA:[43] |
| Sulfides[108–110] | Organic[111]  Quinone (AQPH) |
| **Aprotic** | (Gel-) Polymer[112] | Salts[112,113] |  |  | Manganese Oxides[114] |  |
| Liquid[115] |  |  | Vanadium Oxides[116] |  |
| Ionic liquids[117,118] |  |  | PBA:[43] |  |
|  |  | Spinels[119] |  |
| **Solid** | Crystalline[120] | | Zn foil[120] |  | Carbon[120] |  |

#### **2.3.1 Anode**

Zinc (Zn) anodes are a vital component of zinc-metal batteries and play a crucial role in determining the battery’s performance. While the anodes are made of Zn-based metal (mostly with additives), various preparation methods and electrode structures exist that can modify their specific properties. Table 1 summarizes different strategies from the literature that aim to enhance the performance of Zn electrodes. While most research to date has focused on aqueous electrolytes, these strategies can also be adapted for other electrolyte systems, provided that the stability of the materials is carefully evaluated.

Most research on ZMBs utilizes planar zinc foils or plates as anodes, primarily due to their commercial availability and user-friendliness. However, these commonly used Zn foils typically have a thickness of >80 µm, resulting in low utilization rates and specific energies, despite the frequently reported high Coulombic efficiencies. In addition to the production related issues,[121] challenges such as limited active surface area, surface defects, corrosion, passivation, non-uniform electric field distribution, and dendrite growth[122] necessitate the exploration of alternative approaches including surface modifications or different types of anode structures.[123,124]

To address the issue of non-uniform Zn deposition on planar Zn surfaces, which can result in dendrite growth, a common approach is to texture the Zn surface to expose specific crystal planes – such as (002) over (001) – that have varying surface energies, surface diffusivities, and chemical stabilities.[71,125] For example, a Zn foil electrode with a (002) texture was prepared through thermal annealing and thus exhibited stable cycling for 3500 h at 2 mA cm-2 in a symmetric cell, while the pristine Zn electrode lasted only for 200 h. A MnO2||Zn (000) full-cell also demonstrated remarkable cycling stability, achieving up to 1000 cycles at a 10C rate with 92.7% capacity retention.[73] The substrate used for texturing the electrode is not limited to Zn foils, as other metal foils can also be used. By applying a direct-current electrodeposition technique, Zhang et al. successfully prepared [0001]-uniaxial oriented Zn anodes with a single (0002) texture. This approach eliminates lattice mismatches and enables ultra-sustainable homoepitaxial growth during cycling.[72] The Zn electrodes exhibited remarkable cycling stability, achieving up to 3500 cycles with a capacity retention of up to 98% at 5 A g-1 in coin cell configuration.

An alternative strategy to enhance the electrochemical performance of ZMBs involves expanding the anode structure into three-dimensional (3D) configurations. This approach effectively increases surface areas, modulates nucleation sites, reduces local current densities and promotes a more uniform electric field distribution.[126,127] 3D anodes can be categorized into two main types: those composed entirely of zinc and those utilizing zinc-free substrate structures. For example, Parker et al. fabricated a 3D zinc sponge electrode and managed to achieve up to 90% depth of discharge (DOD).[85] In a follow up study, Wang et al. demonstrated a prolonged cycle life of MnO2||Zn cells up to 3000 cycles with improved rate performance when utilizing 3D Zn foil electrodes.[86] In order to improve the structural integrity, conductivity, and chemical stability of the Zn electrode even further, substrate structures are employed including carbon-, metal-, or metal-organic framework-based variants.[84] Employing amine-functionalized carbon cloth as the host to prepare a Zn anode via electrodeposition resulted in a remarkable capacity retention of 94% over 6800 cycles.[89] Replacing the host with a 3D printed nickel or copper current collector to fabricate 3D Zn anodes by deposition resulted in impressive cycling stabilities, e.g. up to 1000 cycles at 10 A g-1 along with 80% capacity retention.[88,90] Lately, metal-organic frameworks have also become an emerging substrate due to their unique properties that allow controlling the physical and chemical characteristics of the electrode.[128] Utilizing ZIF-8-500 as a Zn anode substrate, the Zn@ZIF-8-500 electrode could be cycled for many thousands of hours while retaining 72% capacity.[87]

Despite their many attractive properties and numerous reports demonstrating high performance metrics, most 3D electrodes face challenges such as low active material mass loadings or compromised structural integrity during long-term cycling. One potential solution to enhance mass loading involves direct incorporation of zinc powder into the anode mixture instead of relying on plating. This approach also enables the use of composite materials, allowing for the modification of Zn powder properties by tailoring their intrinsic properties.[129,130] Recently, binder-free Zn electrodes were developed by combining commercial Zn powders with a pristine graphene substrate, leading to improved electrochemical performance of MnO2||Zn batteries.[98] Similar performance improvements were also achieved using alternative substrate materials, such as MXene[100] or mixed ionic-electronic conductors[99], with Zn powder serving as the active material.

Alloying represents another promising strategy for fine-tuning the electrochemical behavior of zinc, enabling the modification of its properties.[131] By selecting suitable alloying elements, both the corrosion resistance and cycling properties of the electrode can be improved. For instance, alloying zinc with copper[103] or aluminum[106] has demonstrated remarkably stable cycling performance, achieving up to 40000 cycles or over 2000 h in symmetric cells. Similarly, alloying zinc with bismuth[105] or silver[104] was proven to be effective in regulating the hydrogen evolution overpotential or enhancing the zincophilicity of the surface, also leading to improved cycling behavior. However, many alloying approaches yield planar surfaces, which introduce additional challenges for practical applications. Moreover, structural integrity upon long-term operation is another issue to be improved in order to avoid the collapse of the alloy microstructure. To overcome this limitation, the alloying process should be adapted at particle level. Such a strategy could enable the preparation of 3D electrodes that integrate various substrate materials, resulting in highly promising practical electrodes.

In addition to structural modification strategies for Zn electrodes, improving their electrochemical behavior through interface engineering is also a viable option.[56] This approach can regulate uniform Zn deposition and reduce side reactions by creating a stable interface. There are several methods to modify the interface of the Zn electrode, including surface functionalization or surface protection using anode additives[124] or electrolyte additives[53]. For example, Wang et al. demonstrated that by modifying the Zn anode surface with graphene nanoribbons, they achieved a dendrite-free system capable of operating up to 9000 cycles while maintaining high capacity retention.[75] Similarly, Yang et al. functionalized the Zn metal surface by using nitrogen plasma and thermal treatment, which created numerous active sites extending up to 8.5 µm in depth.[74] Such a bulk-phase reconstructed Zn electrode facilitated uniform Zn deposition, resulting in stable cycling behavior for up to 2000 h at a current density of 5 mA cm-2. Furthermore, Zn surface protection can also be accomplished through 3D printing of a polyvinylidene fluoride (PVDF)-based protection layer (PVDF-MXene), which manipulates the concentration distribution of Zn2+ ions, leading to homogenous deposition.[76] At a current density of 6 mA cm-2, such an anode exhibited excellent stable full-cell operation for up to 15000 cycles. Utilizing such additives to modify the anode surface and anode-electrolyte interface represents a promising complementary strategy. However, the long-term stability of these layers or coatings remains a concern, especially during high rate cycling and deep discharge.

In recent years, there have been efforts to develop zinc metal-free anodes to tackle the challenges associated with Zn-metal anodes.[132] Depending on the choice of material, there are primarily three different types of Zn2+ charge storage mechanisms: conversion,[133,134] intercalation,[109,135] or coordination[107,136]. Among these, batteries employing intercalation-type anodes and cathodes are known as “zinc-ion batteries”. While zinc metal-free anodes offer several advantages, such as good cycling stability, high specific capacities, fast reaction kinetics, they also face some drawbacks. These can include low cycling stabilities, sluggish kinetics, poor conductivity, and limited rate capabilities, depending on the type of material used.

#### **2.3.2 Cathode:**

Unlike the anode, where zinc-metal in some form is almost always the material of choice, there is a plethora of different cathode active materials, all of which have their advantages and disadvantages. For slightly acidic batteries, in particular manganese- or vanadium-based oxides are frequently applied, in part for historical reasons, while for rechargeable alkaline batteries, nickel hydroxide has been successfully commercialized. However, as can be seen in the matrix, work is also being carried out to investigate and optimize Prussian Blue analogues and polyanionic compounds. A few research projects are also looking into iron-[119] or cobalt-based[97] systems. A schematic overview of the reported theoretical electrode potentials and specific capacities can be found in Figure 5.

Even though transporting and inserting Zn2+ would be the preferable reaction for effective ZIB/ZMB, proton insertion is the dominant (e.g. in case of α-MnO2[137]) or even sole reaction, in particular in Zn-ion free electrolytes, neutral and alkaline. Proton co-insertion together with Zn2+ can improve the electrochemical performance of ZIB/ZMB by enabling fast kinetics and additional capacity. For example, in MoS2-based systems, protons reduce electrostatic interactions and accelerate ion diffusion.[138] Proton insertion in VO2 cathodes (along with a reversible deposition of Zn4(OH)6SO4·5H2O on the cathode surface) has also been shown to minimize structural distortion, leading to long cycle life and high rate capability.[139] However, proton insertion also leads to a local change of the pH of the electrolyte, which can strongly impact transition metal dissolution, and lead to hydroxide formation, or gas formation.[140] This leads to issues such as capacity fading, self-discharge, and electrode degradation, which can be at least partly inhibited by active material modification and electrolyte optimization.

Manganese oxides, with tunnel-like structures, layered or 3-dimensional structures are extensively studied due to their high theoretical capacity (between ~300 mAh g-1 for MnO2 materials to up to 755 mAh g–1 for MnO)[46], cost-effectiveness, and reliance on zinc-ion and/or proton intercalation coupled with Mn4+|Mn3+ redox reactions. [141,142] α-MnO2 was actually the first active material to be used in a secondary zinc-metal battery[42] with slightly acidic electrolyte, and manganese oxides have also been part of the commercialized rechargeable alkaline manganese (RAM) batteries, which were first introduced in the 1970s.[143] However, their practical applications are hindered by the dissolution of Mn2+ into the electrolyte and structural degradation caused by volume changes during cycling, which result in capacity fading.[43]

|  |
| --- |
|  |

Figure 5: Schematic overview of specific capacities and electrode potential ranges of different possible cathode materials for zinc-metal and zinc-ion batteries in comparison to lithium iron phosphate .[4,43,130,144,145] Note that the theoretical specific capacity found for Mn-based compounds can be even higher than the shown range.

Apart from manganese systems, nickel zinc batteries (Ni||Zn) have been widely used as rechargeable batteries. Ni||Zn cells typically operate based on electrochemical reactions between a zinc anode and a nickel hydroxide cathode in an alkaline electrolyte, typically potassium hydroxide (KOH). The first Ni||Zn were already patented by Thomas Edison in 1901. However, their widespread adoption was limited due to challenges with cyclic stability and rechargeable system durability. Recent advancements have improved their performance, making them suitable for applications such as telecommunications and reserve power systems.[146] In the 1980s, Ni||Zn batteries were actively developed for electric vehicle applications under the U.S. Department of Energy's Near-Term Electric Vehicle Battery Program. These batteries demonstrated specific energy levels of nearly 70 Wh kg–1 and specific power of 130 W kg–1, though cycle life improvements were still needed at the time.[147] Modern developments have focused on enhancing energy density, cyclic durability, and safety, making Ni||Zn batteries competitive with lithium-ion systems in certain applications.[148]

Another typical cathode material are vanadium oxides, including V2O5 and hydrated vanadium bronzes, which offer higher capacities (~350 mAh g-1) and superior rate performance, enabled by the multi-valence states of vanadium (V5+/V4+/V3+) and their layered or tunneled structures, which facilitate efficient Zn2+ ion and proton diffusion. Despite these advantages, vanadium oxides face challenges related to structural instability under prolonged cycling and relatively high costs, though advances in hydration, defect engineering, and nano-structuring have shown promise in addressing these limitations.[44]

Spinel materials with the general formula ZnM2O4 (M= e.g. Mn, Fe, V, Ni, Co and mixtures thereof)[4,43,119,144,145] are also a promising class of active materials, which – depending on the exact composition – demonstrate high voltages of up to 1.8 V vs. Zn|Zn2+ (e.g. ZnNixMnxCo2-2xO4 with 0.3 M Zn(OTf)2 + 200 ppm 1,4-diazabicyclo[2.2.2]octane in acetonitrile as electrolyte)[149] and specific capacities in a similar range as pure manganese oxides (312 mAh g-1 forZnV2O4).[150] Just as with these, the main problem here is the leaching of the metals on the B-site and the associated low cycling stability of the corresponding cells.

The possible potentials and specific capacities achieved in zinc-metal batteries with oxidic active materials are quite competitive for potential application in commercial storage devices. However, solutions for certain issues still have to be found, especially to suppress gas formation and leaching of metal cations and the associated poor cycling stability in aqueous electrolytes. Both issues can be addressed by optimization of the electrolyte formulation on the one hand, but another well-investigated approach is the formation of an ion conductive layer on top of the positive (cathode electrolyte interphase CEI) or negative (solid electrolyte interphase, SEI) electrode. The concepts and terms SEI[151] and CEI have been used for lithium metal and lithium ion batteries and will be adopted for Zn-based batteries, here. For example, thin layers of phosphate-rich materials like hopeite (Zn3(PO4)2·4H2O) were generated *in situ* on the negative electrode by using phosphate-rich electrolytes like trimethyl/triethyl phosphate or phosphate-rich additives like Zn(H2PO4)2 (cf. Table 1).[82] On the other hand, an artificial CEI or coatings like modified montmorillonite (a natural layered clay mineral)[152] could also be promising, inexpensive and environmentally friendly approaches to protect the positive electrode.

Prussian Blue analogs (PBAs), with the general formula Ax*M*1[*M*2(CN)6)]y∙zH2O, are characterized by their open cubic framework,[153] which ideally facilitates rapid Zn2+ ion diffusion and cycling stability.[43] Their hydrated forms (zH2O) make them very suitable for the operation in aqueous electrolytes - but make them less compatible with organic electrolytes.[154] Ax can be vacant or any alkali metal ion, such as Li+, Na+, and K+. M1 and M2 are typically transition metal ions such as Ni, Fe, Cu, Mn, and Zn. These are arranged alternately in a cubic framework and bridged to the CN complex. M1 is directly bonded to the nitrogen atoms of the CN complex, while M2 is directly bound to the carbon atoms of the CN complex. Their local chemical environment, oxidation state and stoichiometric ratio largely determine the electrochemical potential of the material and allow a great extent of flexibility in tuning the materials properties.[153]

PBAs are very well known as innovative and low-cost cathode materials for lithium- and sodium-ion batteries.[153] While the redox behavior of PBAs in the presence of Zn2+ have been explored already in the year 2000,[155] their utilization as cathodes for Zn-ion batteries is a rather new research field that has been explored for about a decade now, yet they have emerged as the most intensively studied material within the class of non-oxidic cathodes for ZMBs.[43] Among them are PBAs with M = Cu and Fe that can accommodate Zn2+ ions at interstitial sites and offer a reversible Zn2+ intercalation and deintercalation through the redox reactions of Fe3+|2+ and Cu3+|2+ at 1.1 and 1.73 V, respectively.[67,156] However, the achieved capacities with 60-80 mAh g-1 remain very low due to limited utilization of redox active sites and restrictions in available Zn2+ sites. Moreover, they undergo irreversible phase transformations during cycling which leads to a rapid capacity fade.[67] On the other hand, Zn₃[Fe(CN)₆]₂·H₂O is a prominent example of a PBA achieving better cycling stabilities, due to structural modification. Here, the absence of alkali metal ions leads to the occupancy of A vacancies with Zn-ions. The material is less prone to undergo phase transitions during charge/discharge and maintains a higher structural integrity – especially with carefully engineered particle morphologies[157], activation of low spin Fe,[156] or subtly modified aqueous electrolytes.[158] With operating at voltages around ~1.6 V, the Zn-based PBAs thus provide moderate energy outputs but are still constrained by a relatively low specific capacity (~60–100 mAh g-1), which limits their energy density compared to manganese and vanadium oxide-based cathodes.[67]

#### **2.3.3 Electrolytes**

##### **2.3.3.1 Liquid Electrolytes**

A special feature of zinc-metal batteries is the possibility of using water as electrolyte solvent. However, this is associated with limitations due to the low thermodynamic electrochemical stability window of 1.23 V. However, in practice, substantial overpotentials are active to kinetically suppress hydrogen and oxygen evolution reactions. This delays water decomposition, effectively widening the stability window to roughly 1.7 V vs. Zn|Zn2+. In addition, limitations are further mitigated by tailoring the redox-reaction at the cathode and the use of additives. Alternatively, these issues can be avoided by employing organic electrolytes that have a wider stability window. The capabilities of cathode materials with voltages well above 1.3 V vs. Zn|Zn2+ (as indicated in Figure 5) can, however, so far mostly be fully exploited with organic electrolytes.

Aqueous electrolytes consist of conductive salts dissolved in water, where KOH is mostly used in alkaline electrolytes, while ZnSO4, Zn(OTf)2 or ZnTFSI are most commonly used in slightly acidic conditions (see also Table 1).[4] In addition, small concentrations of MnSO4 or similar salts are sometimes added as additives because they reduce the leaching of Mn2+ from Mn-based cathode materials.

Although this is in principle an advantage of zinc-metal batteries, the use of water as a solvent poses serious problems: apart from the narrow thermodynamic electrochemical stability window water also limits the temperature range in which the cells can be used. Neutral to slightly acidic pH in addition leads to problems at the electrodes: On the one hand, the Zn metal anode is generally thermodynamically unstable in aqueous solution leading to hydrogen evolution and corrosion. On the other hand, transition metals like Mn2+ can easily be leached from the cathode depending on the pH of the electrolyte, and contact with water can also lead to other unwanted side reactions.

In the context of pH stabilization, proton co-intercalation (insertion of the Zn2+ cation together with its solvation shell) can in some cases lead to a strong local increase in the pH at the cathode, also promoting transition metal leaching,[43] as already discussed in chapter 2.3.2.

The narrow electrochemical stability window of water, side reactions and proton co-intercalation can be avoided at least in part by application of concentrated electrolytes, so called water-in-salt formulations. These electrolytes are characterized by a very low water-to-salt molar ratio, often approaching or even below a 1:1 molar ratio, which means that water molecules are coordinating salt ions rather than existing as free water.[159] This results in a unique solvation environment where water molecules are primarily involved in the hydration shells of ions, leading to a reduction in free water content. The high concentration of salts in these electrolytes also contributes to their enhanced electrochemical stability and wider electrochemical stability window, as the interactions between ions and water molecules are substantially altered compared to conventional aqueous electrolytes, since at least part of the water in the solvation sheath on the Zn2+ ion is replaced by salt anions. At the same time, they suffer from an increased viscosity (~10−1 Pa s compared to ~10-3 Pa s for aqueous electrolytes)[47] and reduced conductivity (~ 10−3 S cm-1) compared to typical aqueous electrolytes (~ 10−1 S cm-1) [47], and they are far more expensive due to the high salt concentration. However, a similar effect on the electrochemical stability window as with water-in-salt formulations can also be achieved by specific electrolyte formulations with lower salt concentrations, for example with an urea-modified electrolyte with 2.9 mol kgsolvent−1 Zn(ClO4)2 and CO(NH2)2. Here, strong intermolecular interactions between added CO(NH2)2 and the solvent H2O decrease the number of free H2O molecules and reduce their activity, effectively suppressing parasitic side reactions and increasing the stability window to 2.6 V vs. Zn|Zn2+.[160]

Compared to aqueous electrolytes, organic electrolytes generally display a much wider electrochemical stability window without additives, do typically not lead to transition metal dissolution, and can generate higher cell voltages even when using the same electrode materials. In addition to the slightly higher price compared to water, the lower solubility of the conducting salt, poorer zinc-metal conductivity, and high de-solvation energy have so far prevented the widespread use of organic electrolytes in zinc-metal batteries.[114] The used salts are basically the same as for aqueous electrolytes. Acetonitrile (sometimes in composition with small amounts of water) and carbonates like e.g. propylene carbonate are most often used as organic ZMB electrolyte solvents. Apart from these well-investigated options, recent studies also show that, for example, trimethyl or triethyl phosphate as the sole solvent or as an additive in aqueous electrolytes can lead to more even stripping/plating and high cycling stability, since the phosphate-rich SEI that forms during cycling substantially reduces dendrite growth at the anode.[161,162] Further examples for cheap, environmentally friendly and abundant additives are sodium citrate, amino acids or ethylene glycol in aqueous electrolytes.[45,68,70] They all help to break the solvation shell of the Zn2+ to mitigate the de-solvation penalty and at the same time support a more even stripping/plating process at the anode by formation of a SEI. In addition to these electrolytes, which are also widely used in lithium-ion batteries, research is also being conducted on other promising electrolyte formulations, such as deep eutectic electrolytes.[163] However, these have in most cases not yet matched the performance of organic or aqueous electrolytes.

##### **2.3.3.2 Solid and Quasi-Solid Electrolytes**

Conventional polymer and gel-type electrolytes, most prominently PEO with or without additional organic solvents, are under investigation for zinc-metal batteries (see Table 1).[114,164,165] Even though these materials are of interest for very specific applications such as flexible cells for wearables, there are still major obstacles to commercial application in terms of ionic conductivity (which is far below 1 mS cm-1) and low cost and manufacturability compared to aqueous electrolytes.

Another way to obtain cheap and environmentally friendly solidified electrolytes and thus to avoid the leakage problem associated with liquid electrolytes is to add gelling agents such as carrageenan or other hydrophilic polymers to aqueous electrolytes to form hydrogels.[166,167] This process was successfully used as early as 1886 by Carl Gassner, who obtained a patent for the manufacture of the first “dry” battery cell with a cell chemistry similar to the Leclanché cell, in which the electrolyte consisted of a paste of ammonium chloride solution in plaster of Paris.[168] Hydrogels can achieve considerably higher conductivities than conventional polymers (e.g. 3.32·10−2 S cm−1 at room temperature for κ-carrageenan with 2 mol L−1 ZnSO4 and 0.1 mol L−1 MnSO4).[94] However, these types of electrolytes suffer from similar problems as their liquid counterparts do (small electrochemical window, gas formation etc.), and in addition can exhibit a lower mechanical stability at increased temperatures, since e.g. carrageenan liquefies at temperatures above 60 °C.

#### **2.3.4 Summary and Outlook of Zinc-Metal Batteries**

Zinc-metal batteries with manganese oxides have already been commercialized in rechargeable alkaline batteries. As shown in Table 2, layered -MnO2, which is cheaper and substantially more environmentally friendly than commonly used V2O5, can also be used to produce cells with slightly acidic pH that show good cycling stability, high specific capacity and much higher average output voltage. By doping with Co or using Co oxides, it would also be possible to increase the cell voltage, albeit at the cost of (partially) losing positive properties such as a favorable price, general availability, and low toxicity. High entropy phases of manganese oxides could also be a feasible future way to prevent dissolution of MnO2 to of Mn2+ in contact with aqueous electrolyte and to additionally ensure high cell voltage and cycling stability.[102,169] Environmentally friendly, non-toxic alternatives for the positive electrode, such as graphite, allow fast charging and discharging of the batteries. However, due to their low specific capacity, they cannot compete with oxide materials.

Compared to typical lithium-ion cells which deliver discharge cell voltages of 3.3-3.8 V and specific energies in the range of 250 to >300 Wh kg-1, and current state of the art sodium-ion cells, which discharge at voltages in the range of 2.0- >3.0 V with specific energies of 100-150 Wh kg-1, rechargeable zinc-metal cells have a substantially lower voltages and specific energies (in the range of 1.0-1.8 V with 50-100 Wh kg-1). However, they can achieve excellent cycling stability, with some systems retaining over 90% capacity after thousands of cycles (see Table 2).[170,171] Together with overall low cost, higher accessibility of zinc compared to lithium with recycling routes for zinc-metal already established,[3] and inherent safety when using aqueous electrolytes, this makes zinc-metal batteries attractive as a potential solution for large-scale stationary storage. Zinc-metal batteries designed for stationary storage based on MnO2| aqueous electrolyte | Zn cell chemistry have recently been commercialized by the Swedish company Enerpoly.[172]

Since the invention of the secondary zinc-metal battery more than 60 years ago, one important topic in research was to find new cathode materials and also the optimization of aqueous electrolytes to suppress unwanted reactions and dendrite formation at the anode. There are very different approaches in the field of cathode materials with regard to doping of the various oxidic materials and corresponding micro-structuring. In the case of aqueous electrolytes, various common salts were investigated, in some cases in combination with SEI-forming additives. However, a comprehensive, basic research-based doping concept to increase the cell voltage and cycling performance while inhibiting transition metal leaching is lacking for several active material groups, such as oxides with a spinel structure.

Aqueous electrolytes are currently superior to organic electrolytes, at least in terms of cost and Zn2+ and proton transport kinetics. In spite of this, future low-cost organic electrolytes which mainly depend on the development of highly soluble, novel conducting salts could solve some fundamental problems of aqueous electrolytes (narrow electrochemical stability window associated with hydrogen and oxygen evolution, transition metal leaching, uneven zinc electrodeposition, and associated dendrite formation).[43] Overall, it is highly likely that aqueous (traditional low concentration electrolytes and water-in-salt) as well as organic electrolyte formulations that are already being intensively investigated in the context of lithium-ion batteries can be adapted and transferred into the zinc-metal battery system. Further optimization of the zinc anode may also result from findings in the field of zinc-air cells, as discussed in the following chapter.

There are several ways to optimize zinc anodes to enhance the battery performance. As illustrated in Table 2, the electrochemical behavior of the cell can be substantially improved, depending on the structure and composition of the zinc electrode. Among the various options, electrodes with a high surface area are more advantageous for reducing local current densities and improving the stripping and plating behavior of the zinc electrode, while also enabling higher discharge rates. However, a larger surface area may also lead to higher activity towards side reactions. This issue can be mitigated, to some extent, through the use of additives in the electrolyte and electrode materials. The typical 3D electrodes discussed in the anode sections often have low zinc mass loading. This limitation can be addressed by incorporating powder mixtures and utilizing 3D current collectors or scaffolds, which not only allow for adjustments in zinc powder content towards alloying or additives but also provide greater flexibility in design.

Table 2: Examples for well-performing zinc-metal batteries with different cell chemistries.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Components** | **Performance Indicator** | | | | | | **REF** | **Comment** |
|  | Cycle number | Coulombic Efficiency | Capacity / mA h g-1 | Current density / C-rate | Mass loading / mg cm-2 | Voltage / V |  |  |
| V2O5 | 3 M Zn(CF3SO3)2 | Zn metal | 4000 | 91.1% | 470 (at 0.2 A g-1) | 5 A g–1 | 2 | 0.72 | Zhang et al.[91] | Good cycling stability, high capacity and mass loadings possible, comparably high C-rates possible, |
| Co-doped -MnO2 | 2 M ZnSO4 + 0.1 M MnSO4 | Zn metal | 100  5000 | ~100%  63% | 500 | 0.3 A g-1  2 A g-1 | 2 | 1.33 | Zhong et al.[78] | Co-doping leads to improved, Co-catalyzed deposition of active Mn compound |
| Co3O4 | 2 M ZnSO4 + 0.2 M CoSO4 | Zn metal | 5000 | 92% | 205 | 0.5 A g-1 | - | 2.2 | Ma et al.[97] | Co-rich Co3O4 nanorods |
| graphite | 1 M Zn(TFSI)2 in acetonitrile | zinc metal | 1000  4000 | 97.3%  82% | 45 | 1 A g‑1 | 10 | 2.2 | Zhang et al.[113] | Fast (dis)charging 39.3 mAh g–1 at 2.0 A g–1; 86.5 Wh kg–1 at 4400 W kg–1, in ∼1 min, but very low capacity |
| ZnHCF | 1 M ZnSO4 + 0.05 M Cs2SO4 in H2O | Zn metal | 300 | 55.9 % | 51 | 0.25 A ⋅ g−1 | 2 | ~1.7 | Pan et al.[158] | Cs as additive in the electrolyte stabilizes the cycling but lowers the capacity |
| NiHCF | 1 M ZnSO4 | Zn metal  NiHCF | 1 M Zn(TFSI)2 + 21 M LiTFSI | Zn metal | 100  1600 | 87%  85 % | 60.0  70 | 0.5 C | 3 | ~1.7 | Li et al.[154] | Comparison of different electrolytes organic vs aqueous vs concentrated (=best) |
| Zn–FeHCF | HCZLE-PAM gel-electrolyte | Zn metal in carbon cloth | 5000 | 82% | 78 | 3 A g−1 | 1.5-2 | ~1.5 V | Yang et al.[156] ) | Activation of the C-coordinated Fe in FeHCF leads to enhanced cycling performance |
| MnO2 | 3 M ZnSO4 + 0.1 M MnSO4 | (002)- Zn metal | 1000 | 99.99% | 83.6 | 10 C | 0.5 | 1.5 | Wang et al.[73] | Good stable cycling, high C-rates, 7000 cycles in symmetric cell |
| *α*- MnO2 | 1 M ZnSO4 + 0.1 M MnSO4 | 3D Zn metal | 3000 | - | ~60 | 2 A g-1 | 1-1.5 | 1.4 | Wang et al.[86] | Improved cycling life but low-capacity retention |
| MnO2 | 3 M ZnSO4 + 0.1 M MnSO4 | Zn-deposited carbon cloth | 6800 | 93.6% | ~100 | 2 A g-1 | 2 | 1.4 | Li et al.[89] | Good cycling life, capacity retention of 94.0% after 6800 cycles |
| PVO | 2 M ZnSO4 |3D Ni-Zn | 1000 | ~99.99 | ~280 | 10 A g-1 | 1 | ~0.8 | Zhang et al.[88] | 80% capacity retention after 1000 cycles under high load, but low voltage yielding only 230 Wh kg‒1 specific energy |
| KzMnO2 | 1 M Zn(OTF)2 + 0.1 M Mn(OTF)2 + 1 mM SDS| ZnxCuy/Zn | ~235  800 | 99.8%  ~99 | 300  210 | 0.2 A g-1  1 A g-1 | 1 | 1.3 | Meng et al.[103] | Specific energy of ~ 430 Wh kg‒1,  symmetric cell with 100C (50 mA cm‒2) cycling up to 40,000 cycles of with energy efficiency of ~ 99.9% |

### **2.4. Zinc-Air Batteries**

The first concept of a primary Zinc-air battery was developed in the 19th century, when the cathode of the Leclanché battery was replaced by a porous air cathode.[173] In the following years, particularly in 1932 and the 1970s, further developments led to commercial applications, especially in low-power telecommunication and medical areas. The conventional ZAB consists of a metallic zinc as the anode material, an electrolyte, a separator, and a porous air cathode. Metal-air batteries have a distinct advantage over conventional batteries due to their open cell structure. This design allows them to achieve high energy densities because the cathode's active material (oxygen) is not stored within the battery but is readily accessible from the surrounding ambient air. During discharge, the metallic Zn anode is oxidized (Zn ⇌ Zn2+ + 2e-), while the O2 from the ambient air is reduced at the air cathode (O2 + 4e- + 2H2O ⇌ 4OH-), as illustrated in Figure 3. These reactions are reversed when the cell is charged. The products of these reactions depend on the composition of the electrolyte. In aqueous electrolytes, the pH and the type of salt play crucial roles in determining the main discharge products, which could be zincate ions, zinc hydroxide, zinc oxide, or Simonkolleite.[35]

The performance of the ZABs mainly depends on two reactants: oxygen at the cathode and Zn at the anode. Considering the unlimited amount of O2 in the atmosphere, the performance of ZABs is heavily dependent on properties of the Zn electrode. Most of the studies on ZABs typically utilize the Zn anode in various forms, such as powder-based, foil, foam etc.[26,174] The most common aqueous electrolyte for secondary ZABs is the conventional alkaline electrolyte due to its high ionic conductivity, high solubility of Zn salts, and high electrochemical reversibility of Zn.[35] There is also a growing interest in neutral electrolytes due to their advantages, such as more homogenous Zn deposition behavior and reduced carbonate formation.[175] At the air cathode, bifunctional catalysts capable of facilitating both oxygen reduction and evolution reactions are required. Thus, current research mainly focuses on developing highly stable and active electrocatalyst in combination with electrode engineering.[36] The complex nature of the reactions and reaction zones at the air cathode remains one of the major factors that limit the efficient cell operation.[37]

Table 3: The matrix provides a structured overview of the various individual aspects of zinc-air batteries. Each column and row represent specific characteristics or components of the system, while each cell within the matrix highlights a particular aspect related to these parameters. The matrix summarizes various strategies derived from successful findings in literature. Although most research has been conducted in aqueous media, these strategies can also be adapted for use with other electrolytes, as long as the stability of the materials is carefully considered.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Electrolyte** | **Electrolyte Additives** | **Anode** | **Anode Additives** | **Cathode catalyst** |
| **Alkaline**  **pH>13** | **6M KOH** | **Organic compounds**[35,176–180] | **Planar surface**[181–183] | **Metal oxide**[184–186] | **Noble metal based**[187–191] |
| **Inorganic compounds**[192,193] | **3D structures**[194–197] | **Conductive agents**[198] | **Non-noble metal based**[190,199] |
|  | **Powder**[200–202]  - |  | **Carbon matrix with embedded non-noble metal catalyst**[38,203,204] |
| **Surfactants**[205,206] | **Alloy**[39,40,131,207,208] | **Coatings**[54,209] | **Layered double hydroxide based**[191,210] |
|  |  |  | **Metal chalcogenides**[211,212] |
| **Gel** | **Polymer**[195,213–215] |  | **Mostly planar Zn** |  |  |
| **Others** | **Crosslinked PVA/PAA in 6 M KOH**[216]**.** |  | **Powder** |  |  |
| **(near)-neutral**  **5<pH<10** | **NaCl/NH4Cl**[177,178,217–220] |  | **Planar Zn** |  |  |
|  |  |  |
| **Others**[39,221] |  |  |
|  |  |  |

#### **2.4.1 Anode**

Zinc anodes are essential to the operation of zinc-air batteries, directly impacting their performance, efficiency and longevity. Despite the success of primary zinc-air batteries, the commercialization of secondary Zn-air batteries has been limited primarily due to their short cycle life. Over the past decades, most of the research focused on addressing several key issues related to zinc anodes, including surface passivation, dendrite formation, shape change, corrosion, and hydrogen evolution.[26] Optimization of the electrode structure through various design and fabrication methods, along with surface modifications, has proven to be one of the most effective strategies to enhance the electrochemical behavior of the anodes, leading to improvements in performance and reductions in degradation.[54] Table 3 summarizes the most common strategies related to anodes. While most of the research has been conducted in aqueous alkaline media, the same strategies can also be applied to other types of electrolytes. However, the compatibility of the additives and materials should be taken into account.

Unlike the current research on zinc-metal batteries, there are only a limited number of studies exploring the use of flat zinc (Zn) metal surfaces in zinc-air batteries. Most of these studies focused on developing catalysts for the air cathode. For instance, when a polished zinc plate or foil is used as the anode, zinc-air batteries can achieve good cycling performance for up to 400 cycles at moderate currents.[181–183] However, the practical application of zinc anodes with flat surfaces is hindered by limited utilization efficiencies, restrictions on the actually utilized active surface area, and constraints related to additive usage.

Current developments on the anode focus on tailored designs for highly conductive and high surface-area 3D structures that are made entirely of Zn or fabricated either by powder pressing or by electrodepositing zinc onto 2D or 3D substrates. For example, when a 3D Zinc sponge was used as the anode in a silver-zinc battery, it yielded high specific energies and volumetric capacities (based on Zn) for up to 100 cycles.[194] In a subsequent study, a 3D printing method was employed to create 3D Zn electrodes consisting of 90% Zn and 10% carbon based conductive agents, resulting in stable cycling up to 350 cycles with relatively high capacities.[195] 3D Zn electrode designs made through electrodeposition allow for the selection of various substrate materials, such as 2D meshes, 3D metal foams, or carbon-based materials. By using pulsed electrodeposition of zinc on copper foam, Yan et al. extended the cycle life of Zn electrodes to 10,000 cycles while maintaining high specific capacities.[196] There is also the option to tailor the properties of the substrate by applying coatings, such as a tin coating,[197] to improve its electrochemical behavior. However, utilizing such 3D structures poses potential challenges, including the high reactivity of zinc in aqueous electrolytes, relatively low mass loadings, and it raises concerns regarding structural integrity during long-term operation.

One alternative approach involves using powder-based materials that are compressed onto conductive substrates. This method enhances mass loadings and allows for the incorporation of electrode additives that can improve the electrochemical performance of electrodes. Zinc[200] or zinc oxide[201] powders are commonly used to fabricate electrodes. These anodes have demonstrated stable cycling for several hundred cycles while maintaining high specific capacities. This method even allows for the preparation of anodes for flexible zinc-air batteries, achieving relatively high performance.[202] However, challenges remain mostly regarding the structural integrity of the electrodes after many cycles.

Zinc anode alloying is another emerging strategy for enhancing the corrosion resistance and cycling performance of zinc-air batteries. Various metals, such as aluminum (Al), bismuth (Bi), indium (In), and lead (Pb), can be added to the zinc matrix to modify its electrochemical properties.[131,207] For instance, Peng et al. developed Zn-Sn alloys using a powder sintering method, which showed improved cycling stability compared to pure zinc.[39] Similarly, other studies with alloys consisting of nickel and indium[208] or ytterbium and cerium[40] exhibited a substantial reduction in zinc dendrite formation.

In addition to various fabrication methods for zinc anodes, incorporating electrode additives is a promising approach to enhance the performance of zinc electrodes. This enhancement primarily focuses on improving electrical conductivity, reducing corrosion, and lowering overpotentials.[222] Additives can be classified into several categories: metals and metal (hydro-)oxides, conductive agents, organic additives, and coating layers. For example, Al2O3[184] or Bi2O3[185] have been shown to positively affect hydrogen evolution overpotentials. Additionally, Ca(OH)2 can be used as an additive to prevent the diffusion of zincate ions, which helps minimize dendritic growth.[186] The introduction of Super P has also been effective in improving conductivity, leading to enhanced electrochemical performance of the battery.[198] Alternatively, applying a coating layer—either at the particle level or on the electrode surface—can modify the deposition process and address passivation issues.[54] Despite the positive effects of these additives, each type has its limitations, ranging from environmental impacts to costs. Therefore, careful attention must be given when selecting additives.

#### **2.4.2 Electrolyte**

A suitable electrolyte should have a high ionic conductivity (>10-4 S cm-1) and low electronic conductivity (<10-10 S cm-1), a high electrochemical stability window, be of low cost and ensure safety. In the context of zinc-air batteries, typically alkaline electrolytes are studied.[122] Some disadvantages are the corrosion of zinc, the evaporation of the electrolyte, the limited temperature window, creep, seepage, and leakage and a low thermodynamic stability. Aqueous electrolytes are the most used electrolyte in zinc-air batteries (ZAB), because of their low cost, sustainability, high ionic conductivity, and compatibility with the zinc electrode. Current ZABs are based on concentrated alkaline liquid electrolytes, with high ionic conductivity, but suffer from leakage, evaporation, and carbonate precipitation due to the semi-open design of these systems. The use of an aqueous electrolyte like KOH with a concentration of 6M is most common. The challenge of the electrolyte is the composition change of the electrolyte due to reacting with CO2. In 2022 an electrolyte was developed, which consisted of 6 M KOH and 0.2 M Zn(Ac)2. This electrolyte improved cycling and zinc utilization. This concept was further developed by Wei et al.[223]. By using zinc-peroxide instead of the Zn(OH)2 reaction path, high cycle life and zinc utilization could be achieved. An acidic aqueous electrolyte, i.e., zinc trifluoromethanesulfonate (Zn(OTF)2 1M) was used. This system ran for over 500 h without exchanging the zinc anode. However, when using aqueous electrolytes the ZAB still faces the problem of hydrogen evolution and the formation of zinc dendrites on the zinc surface. This is also the main issue, when using a pure alkaline electrolyte as shown in the matrix below.[216]

Using gel type electrolytes is a promising concept to prevent leakage and the reaction with CO2 from the air. Such electrolytes are prepared by mixing KOH and hydroponics gels.[224] Such gels could be used as electrolytes in ZABs, but such electrolytes are not very stable and do not hinder the formation of dendrites on the zinc electrode. But the concept was improved by using different polymers and gels. For example, the use of agarose in highly concentrated KOH was very beneficial.[213] By also using Zn paste, the ZAB could be cycled up to 300 times. Even more cycles could be achieved when the gel was made of poly(vinyl alcohol) and bacterial cellulose. In this gel not only KOH was used, but also zinc acetate, and the cycle number could be increased to 650 cycles.[214] This is the reason for research shifting to gel, polymer, and all solid-state electrolytes. With the development of hybrid electrolytes, polyacrylamide (PAM) polymers have been used in zinc-air batteries.[225] The usage of polymer electrolytes has some advantages like high conductivity, water absorption/water retention and mechanical strength, therefore becoming one of the most used gel polymers for ZABs.[226] Polyacrylic acid (PAA) can also be used as a polymer for gel polymer electrolytes. This polymer shows a much better interface contact to the electrode surfaces, because of the softness of the material.[227] In addition, PVA, PEG with salts for polyethylene glycol or even polyethylene oxide (PEO) can also be used. In current research low-cost environmentally friendly gel polymers, such as agar gel, have been developed for solid-state electrolytes.[216,228]

Zinc-air batteries using chloride-based (near-)neutral electrolytes with a pH around 7 have gained attention due to their advantages, including reduced corrosion of zinc, decreased dendrite formation, and the absence of carbonization in the electrolytes.[35] These batteries demonstrate exceptional cycling stability and maintain acceptable charge and discharge voltages at relatively low applied currents.[177,217] The improved stability is attributed to reduced carbon corrosion in the air cathode and less carbonation in batteries with neutral electrolytes. Issues related to the potential formation of a passivation layer on the zinc surface can be addressed by using electrolyte additives.[178] Additionally, the performance of zinc-air batteries with neutral electrolytes at high applied currents can be enhanced by incorporating more active catalysts and fine-tuning the properties of the neutral electrolyte.

Another approach is to shift the research towards non-aqueous electrolytes. They offer the benefit of having a higher operating voltage without the presence of parasitic hydrogen evolution. One of the main drawbacks of using non-aqueous electrolytes is the high volatility and therefore the risk of drying out the cell.[35] To overcome this issue, ionic liquids as molten salts have been studied.[229] They have several advantages over organic electrolytes, which allow for enhanced reaction kinetics at higher temperatures without any loss of electrolyte.[230] These electrolytes can suppress the corrosion of zinc, e.g., when 1-ethyl-3-methylimidazolium dicyanamide(emin)(dca) ionic liquid is used.[231] Such a cell has the potential to be used in a secondary battery. However, Xu et al. observed high overpotentials with ionic liquids.[232]

It is also possible to use additives to improve the electrolyte and the overall battery performance. Here the main goal is to overcome anode limitations. In this respect many different additives have been used, i.e. conductive organic or inorganic additives and surfactants.[35,177,178,217,218,221,233,234] As mentioned above, the common aim is to overcome anode limitations, thus increasing the reversibility. For zinc-based batteries, applying alkaline electrolytes is one of the most common strategies to reduce the high solubility of zinc in the strongly alkaline electrolyte. The pursuit of an extended cycle life has enabled this technology to, for example, adjust the alkalinity and ionic strength of the electrolyte, thus reducing zinc solubility as well as minimizing shape change and dendrite formation (i.e., cycle life) of the system. Here many different approaches have been investigated. Some of them have been listed in Table 3.

In addition it was found that ionic liquids were too viscous to effectively wet the gas-diffusion electrode, giving rise to a quick voltage decay in the zinc–air battery during discharge.[235] Using pure 1-butyl-3-methylimidazolium dicyanamide ([BMIM][dca]) as the electrolyte, a discharge current density of 0.2 mA cm−2 at 0.8 V was obtained. So far, the performance of zinc-air batteries using KOH as the electrolyte has not yet been matched when applying any aprotic electrolyte instead.

#### **2.4.3 Cathode**

The round trip efficiency of rechargeable zinc-air cells is poor compared to many other battery technologies, as relatively high overpotentials are required to drive the respective electrochemical charge and discharge reactions that occur on the air electrode side.[236] It is critical to further develop catalyst materials that effectively facilitate the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charging cycles:

O2 + 4e- + 2H2O ↔ 4OH-

The electrode features an active layer, a gas diffusion layer, and a current collector.[36] Typical catalyst layers consist of carbon particles onto which the catalyst nanoparticles are dispersed. The gas diffusion layer exhibits a relatively high porosity for facile mass transfer of gaseous reactant and product species. The current collector typically consists of expanded metal, mesh, or foam made of stainless steel or nickel. Cohesion of the layers is provided by a binding polymer, predominantly polytetrafluoroethylene (PTFE), which also acts as a hydrophobic agent to enable adequate gaseous reactant transport to the active sites and prevent flooding of the electrode. At present, there is no alternative that is competitive with PTFE in terms of its efficacy and stability, but it is an important research topic. The ORR requires a three-phase boundary, i.e., access to the active catalyst sites for oxygen must be provided in conjunction with adequate electronic (catalyst and support) and ionic (electrolyte) conductivity. The generated oxygen must be readily removed from the electrode. Thus, the requirements for the incorporation of a hydrophobic agent are fundamentally different for ORR and OER catalysts, and the respective electrode structures, which poses a design challenge for electrode development. Agglomeration or detachment of catalyst particles and thus loss of active surface area hamper the long-term performance of rechargeable zinc-air batteries. Irreversible oxidation of active components leads to higher overpotentials during the charge-discharge process, which can be adverse to the extent of cell failure.[237]

Carbon does have certain limitations with respect to chemical and electrochemical stability. High anodic potentials lead to carbon corrosion, which is often exacerbated by the catalyst.[238] The oxygen gas bubbles can cause mechanical stress leading to detachment. This problem can be circumvented by applying a carbon-free metal oxide-based charge electrode in addition to, but spatially separated from, an ORR gas diffusion electrode, both working in conjunction with the zinc anode at the expense of increased complexity and lower energy density.

In principle, separate individual high-performing catalysts can be employed for the ORR and OER, respectively. With respect to the ORR, platinum is the unsurpassed benchmark catalyst in terms of activity. Silver exhibits certain kinetic parameters matching those obtained with platinum at higher hydroxide concentrations, albeit without approaching the ORR activity of platinum at practically relevant current densities.[239,240] Iridium oxide, ruthenium oxide, or mixtures thereof are well-known oxygen evolution catalysts, in particular as anode catalysts in PEM electrolysis cells with high performance and stability.[241,242] Noble metals combined with, e.g., transition metals allow electrode fabrication with a lower cost penalty.[187,243] Further, purely non-noble metal-based materials represent a viable alternative. For instance, nickel exhibited decent OER performance compared to iridum.[244]

It is desirable to utilize bifunctional catalyst materials, which facilitate both the charge and discharge reactions. Such catalyst compositions consist of noble metals, transition metals, metallic (oxide) nanoparticles, layered double hydroxides, metal chalcogenides or combinations thereof. To enable high activity through fine dispersion of the catalyst particles, carbonaceous materials with high surface areas act as a catalyst support. An Fe3Pt intermetallic nano-alloy supported by Ni3FeN exhibited high ORR performance with a half-wave potential of 0.93 V vs. RHE.[187] A noble-metal free variant, i.e., cobalt oxide supported on nitrogen-doped mesoporous carbon, also exhibited a high half-wave potential of 0.91 V vs. RHE and an OER overpotential of 0.27 V vs. RHE at 10 mA cm-2, which is close to 0.24 V vs. RHE obtained with IrCo supported on nitrogen-doped carbon nanotubes.[189] Other cobalt containing catalyst compositions without any noble metals also yielded reduced overpotentials for charge and discharge and substantially extended cycle life compared to combined Ir and Pt.[190,191] Cobalt is a common element in many of the best performing catalysts[38,211], but it is also a key material for lithium-ion batteries, and therefore, there are some concerns with respect to cost, sustainability, and human rights violations. The support material or the catalyst itself is often doped, e.g., with nitrogen, to further boost performance.

#### **2.4.4 Summary and Outlook of Zinc-Air Batteries**

Zinc-air batteries, along with iron-air batteries[245], play a notable role among the various metal-air battery technologies due to their rechargeability and the use of abundant active materials. In comparison to conventional Li-ion batteries, Zn-air batteries can achieve up to twice the practical specific energy and volumetric energy density at the cell level, reaching energy densities of up to 500 Wh kg-1 and volumetric energy densities of up to 1400 Wh L-1.[54,246] However, one of the critical challenges is to maintain this high performance during long-term secondary battery operation, where zinc-air batteries currently fall short due to challenges related to the anode, the electrolyte, and the cathode.[25] Nevertheless, the current developments and the right combination of materials may lead to specific energies of up to 450 Wh kg-1 at the system level.[247]

Table 4: Examples of high-performing zinc-air batteries featuring various cell chemistries.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Components** | **Performance Indicator** | | | | | | **REF** | **Comment** |
|  | Cycle number | Coulombic Efficiency | Capacity | DoD | Current density/c-rate | Mass loading |  |  |
| Fe3Pt/Ni3FeN | 6 M KOH + 0.2 M ZnCl2 | Znplate | 240 | 56.3 % |  |  | 10 mA cm-2 | 0.12 mg cm-2 | Cui et al.[187] | Higher efficieny compared to Pt/Ir catalyst |
| N-doped Co3O4 | 6 M KOH + 0.2 M Zn acetate | Znfoil | 1200 | 58 % |  |  | 5 mA cm-2 | NA | Wang et al.[190] | Improved charge and discharge voltage and extended cycle life compared to Pt/Ir catalyst |
| CoMn LDH/N,P-doped graphene |6 M KOH + 0.2 M Zn acetate | Znplate | 432 | 60 % |  |  | 5 mA cm-2 | NA | Zhang et al.[191] | Superior charge and discharge voltage and extended cycle life compared to Pt/IrO2 catalyst |
| CF@SnFeNC | 6M KOH+0.2M Zn(Ac)2+S ZnO | F-Ni27Fe10  LDH | 5220 h |  | 800 mAh cm-2 | 88.1% | 10 mA cm-2 |  | Zhong et al.[197] | Three-electrode full-cell. Excellent cycling at high DOD. |
| MnO2 | 45% KOH | ZnO paste | 1000 |  | 192 mAh mLanode -1 | 15% | 6.5 mA cm-2 |  | Turney et al.[200] | Long-term cycling without use of Pb or Hg |
| 3D ZnCu foam | 8 M KOH + 0.5 M ZnO | Zn | 10000 |  |  | 100% | 250 mA cm-2 |  | Yan et al.[196] | Robust 3D electrode with no dendrite, 620 mA h g−1 after 9000 cycles in Zn/Ni battery. |
| Co3O4@Ni foam | BG-PVA in 6 M KOH + 0.2 M Zn Acetate | Zn foil | 650 | 100% | 80 mA cm-2 |  |  |  | Zhao et al.[214] | Flexible soild state Zn cell |
| MnO2@C | 5 M NH4Cl + 35 g L-1 ZnCl2 | Zn foil | 500 | 98,5% | 168 mA cm-2 |  | 13.8 mA cm2 |  | Sumboja et al.[177] | Near neutral electrolyte |

Table 4 provides a few examples of high performing cells obtained from the literature on zinc-air batteries. It is important to note that comparing the performance of zinc-air batteries or zinc-anodes across different published studies is quite challenging due to variations in experimental conditions and the partial lack of reported experimental parameters.[246] The following works include some comparison tables focusing on anode performance and/or full-cell performance: Turney et al.[200], Yang et al.[54], Stock et al.[246].

The research on zinc-air batteries, especially within the last few decades, mostly focused on the bifunctional air electrode. The works described in references[187,190,191] in the table above focused on the development of high performing bifunctional cathode catalysts. These are high surface nanostructured materials with tailored compositions to enable both the charge and discharge reactions at low overpotentials, which translates into high efficiency. All featured catalyst compositions outperform pure noble metal-based catalysts, both in terms of activity and cycling stability. As cobalt is a critical material for lithium-ion battery technologies and is also quite expensive compared to other transition metals, the amount of cobalt should be reduced, or alternative elements should be implemented, if possible. Both the OER and the ORR performance can be improved by taking advantage of catalyst-support interactions, which favorably alter the local electron density.[248] Since moving away from alkaline electrolytes towards near neutral electrolytes offers certain advantages, e.g., reduced leakage and electrode seepage, it is important to ensure that future catalyst development will be focused on testing materials under such conditions. For the vast majority of secondary zinc-air cells studied in the literature, the cycling time was fairly short, and typically the current density was 10 mA cm-2 or lower for full cell testing, which is impractical regarding applications in the field. Further, there is a lack of post-test and post-mortem analytical data, which would be beneficial for an in-depth understanding of degradation mechanisms.[36] These issues should be addressed in future work. Accelerated stress tests and deep discharge cycles should be investigated systematically as well.

The advancements on the anode side have been relatively limited compared to those with respect to the air cathode. Most research focused on addressing the primary challenges of shape change, dendrite growth, corrosion, and passivation by optimizing the electrode structure, as discussed in section 2.4.1. Among various options, a promising approach is to use a 3D anode structure made from Zn and ZnO powder due to its high surface area. This method offers flexibility in adjusting electrode properties, including particle size and the selection of electrode additives. Additionally, it facilitates the scale-up of the electrode size to meet practical requirements, especially for large-scale applications. Challenges associated with high surface areas, such as corrosion and hydrogen evolution, can be mitigated by incorporating additives within the electrode. It is important to remember that the issues related to the anode cannot be solved with a single solution alone. Instead, a synergistic approach that combines the use of electrode additives, surface coatings, and adjustments to electrolyte properties is necessary.

Traditionally the electrolyte for zinc-air batteries is an aqueous alkaline electrolyte with KOH. This does not lead to stable cycling of the battery, due to leakage, evaporation and hydrogen evaluation. Therefore, tailoring of the electrolyte is necessary. Here a combination with additives seems to be a promising way to go forward.[249] In particular working with electrolytes with near or light acidic conditions are a good alternative for the pure KOH electrolytes used before in a ZAB.[223] Here we still see the formation of hydrogen at higher currents. But stable cycling and long-term stability of the metal anode is achieved. Also, it has been shown that pure aprotic electrolytes suffer from the same disadvantages as lithium-air cells. To address these issues, gel polymer electrolytes (GPE) have been proposed as a suitable alternative for use in zinc-air batteries. GPEs are less prone to leakage, pose no chemical exposure hazards, and help prevent short circuits.[213] These electrolytes exhibit a good cycle life, and because they incorporate liquid components, they can offer improved performance. Additionally, the materials used in GPEs can be environmentally friendly, making them a viable alternative to traditional liquid electrolytes in ZAB applications. It is generally reported that aqueous electrolytes are safer than organic electrolytes due to their non-volatility; however potential hydrogen evolution during charging requires special attention, particularly for large-scale applications.

As shown in some examples in Table 4, individual experiments may demonstrate extremely high cycling numbers or capacities, even under high current loads. However, these values are not easily comparable to the performance of state-of-the-art batteries at cell level. This indicates that there is considerable room for improvement for zinc-air batteries to achieve performance metrics that are suitable for real-world applications. It is also important to note that, despite their long history, global efforts to develop zinc-air batteries—comprising both academic and industrial initiatives—are at a smaller scale than those focused on conventional Li-ion batteries. Therefore, comparisons with Li-based batteries may not be entirely appropriate. Rather than positioning zinc-air batteries as competitors with Li-ion, the focus should be on developing them for specific applications where they can offer complementary solutions.[250]

### **2.5 Zinc-Based Redox Flow** **Batteries**

Zinc-based redox flow batteries (Zinc-RFBs) differ from conventional redox flow systems by utilizing a solid zinc anode, where energy is stored through the reversible electrodeposition and dissolution of metallic zinc. While electrodeposition also occurs in some zinc-metal and zinc-air batteries, zinc RFBs uniquely integrate this process within a flow system, making them inherently hybrid redox flow batteries, see Figure 6. Zinc-RFBs have since evolved through various chemistries. The following sections outline their historical development, key chemistries, and electrochemical principles.

The historical development of zinc-based redox flow batteries can be traced back to the late 19th century. Zinc-based redox flow batteries always feature a solid zinc anode. Consequently, zinc redox flow cells, in contrast to all-liquid redox flow cells, store charge within the conversion cell via electrodeposition of metallic zinc on the current collector.[251] Therefore, zinc-based redox flow cells are inherently hybrid redox flow cells. A schematic representation is shown in Figure 6 below.

The first zinc-bromine cells were developed in the 1870s, marking the beginning of zinc-based RFB technology.[252] Over the decades, various zinc-based cells were explored by coupling zinc metal with suitable catholytes, including zinc-halide, -manganese, -iron, -nickel, -lead, -cerium, -ferrocene and -organic (2,2,6,6-tetramethylpiperidinyloxyl (TEMPO)- or quinone-based) systems.[15] Similar to regular zinc batteries, these cells can be divided into those with neutral or acidic anolyte with (φ= -0.76 vs. SHE) at the negative electrode, and cells with a basic anolyte with the half-cell reaction (φ= -1.22 vs. SHE).

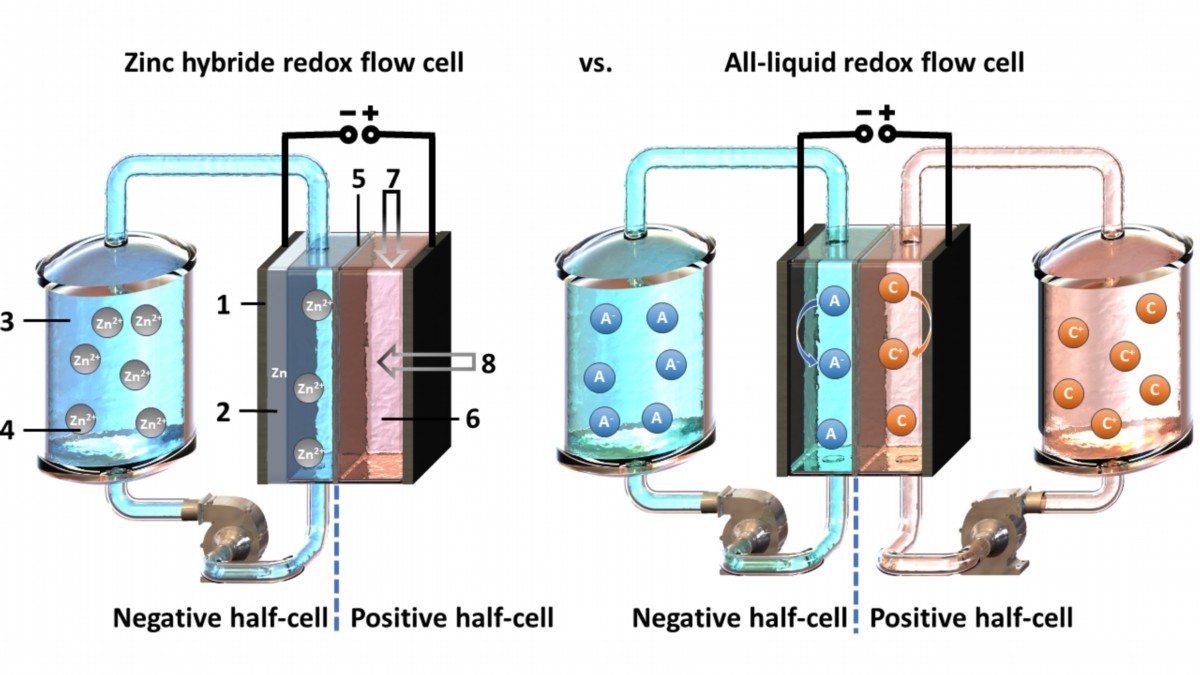


Figure 6: Comparison of zinc hybrid redox flow cell setup (left) and general all-liquid redox flow cell setup (right): During the charging process, zinc ions (Zn²⁺), stored as zinc salt solutions in the reservoir (3), are electrochemically deposited onto the current collector (1) as metallic zinc (2). The negative half-cell is physically separated from the positive half-cell by a membrane (5). In addition to standard liquid-liquid redox conversion processes, the positive half-cell (6) may function as a gas redox conversion chamber (7) or as a hybrid solid-liquid conversion system utilizing an active material (8).

The zinc-bromine flow battery gained attention due to high energy density, and high cell voltage.[253] So far, the Br2||Zn flow battery, which works with a pH neutral anolyte, is the only grid-scale zinc-based RFB that reached a commercially relevant level.[254] The system delivers a high output voltage of 1.85 V, a theoretical capacity of 335 mAh gBr‑1, and a theoretical energy density of 440 Wh kg-1, but also suffers from several drawbacks that severely limit the applicability:[13,253] First, the system’s high operating voltage and low electrolyte pH of 1–3.5 result in a competing water-splitting reaction, which drastically reduces the Coulombic efficiency (CE) of the device. Second, bromine gas generated during charging is volatile, corrosive, and toxic, posing health and environmental hazards and increasing the costs associated with maintenance and sealing (the same is true for the related Cl2||Zn system). Third, the oxidation of Br⁻ during charging produces soluble polybromide anions (e.g., Br₃⁻, Br₅⁻), which can diffuse to the zinc anode (“crosstalk”), causing self-discharge and zinc dendrite formation. Finally, the practical current density of Br2||Zn RFBs is typically limited to less than 20 mA cm⁻² due to the slow kinetics and complex mechanisms of the Br₂|Br⁻ conversion reaction, resulting in a relatively low practical energy density of 60–75 Wh kg⁻¹. Another disadvantage is the high corrosiveness of elemental bromine, which makes it necessary to use special materials and stainless-steel alloys for the conversion cells as well as for the pumps and tanks. Together with special cell designs to increase tightness and safety, this represents a cost and maintenance factor.

The zinc-cerium flow battery, introduced in 2005, is notable for its high open-circuit cell potential, exceeding 2.4 V at full charge. It contains a cation exchange membrane to separate both conversion chambers.[255] In another approach, a dual-membrane configuration was used.[256] This configuration effectively minimizes RAS crossover through the inclusion of a third chamber and supports a pronounced pH gradient between the anolyte and catholyte. This gradient can enhance the cell voltage. The redox reactions occurring in the anolyte and catholyte compartments are given by the following equations:

This system demonstrates an exceptionally high cell voltage of 3.08 V, a voltage efficiency of 91%, and a Coulombic efficiency of 98% at a current density of 5 mA cm-². However, the incorporation of two ion-selective membranes, a third electrolyte chamber, and a pronounced pH gradient between the two half-cells—employing NaOH and HClO4 as electrolyte components for the negative and positive half-cells, respectively—increases costs and introduces substantial safety concerns, particularly in large-scale stationary energy storage systems.

Recent advancements in zinc-based RFB have focused on addressing additional challenges, such as hydrogen evolution, zinc dendrite formation, and the stability of catholytes. These issues can be mainly tackled through the development of new electrode materials, membrane technologies, and electrolyte formulations.[15] In parallel with these advancements, the incorporation of organic electrolytes in zinc-based redox flow batteries (Zn-RFBs) has drawn increasing attention. Unlike conventional aqueous systems, organic electrolytes offer an expanded electrochemical stability window exceeding 2 V, enabling higher energy densities and improving long-term stability.[257] Notably, organic redox-active molecules provide greater chemical versatility, allowing for precise molecular tuning to enhance the redox potential, the solubility, and the electrochemical resilience. This tunability not only mitigates common degradation pathways observed in aqueous Zn-RFBs, such as dendritic zinc deposition and hydrogen evolution, but also facilitates the development of novel charge-storage mechanisms that afford optimized energy efficiency and cycling performance.[258,259]

Moreover, the use of organic electrolytes in Zn-RFBs reduces the reliance on highly corrosive and pH-sensitive environments, thereby enhancing the compatibility of system components and prolonging operational lifetimes as well enabling mostly cheap and widely available polymer-based materials like polypropylene for the whole redox flow setup, which makes the installation of organic-based redox flow cells more affordable. Furthermore, organic redox flow cells offer a more sustainable and environmentally friendly alternative, as they eliminate the reliance on scarce and environmentally hazardous transition metals like vanadium, cobalt or nickel, reduce the carbon footprint of battery production, and enable more efficient recycling pathways, thereby contributing to a greener energy storage landscape.[260] However, the environmental benefit of organic systems depends critically on the choice of solvent. The use of volatile and flammable solvents such as acetonitrile has raised concerns about safety and sustainability, particularly in flow applications. Recent studies have addressed this challenge by introducing non-flammable, low-toxicity alternatives like propylene carbonate (PC), which offer suitable electrochemical properties and significantly lower vapor pressure. For example, PC has been shown to improve iodine redox kinetics and suppress parasitic film formation in I2||Zn systems, while enabling membrane-free cell designs with Coulombic efficiencies exceeding 90%.[261] This highlights that the “green” classification of organic Zn-RFBs is not intrinsic, but rather dependent on electrolyte formulation and system design.

#### **2.5.1 Anode**

The anode is one of the critical component that influences the efficiency, safety, and cycling stability of zinc‐based redox flow batteries by ensuring uniform and reversible zinc deposition. Drawing upon techniques developed in zinc‐ion battery research, typical anode materials include high-purity zinc foils or sheets, sintered zinc granules, and composite electrodes that integrate porous carbon substrates—such as carbon felts, carbon papers, or even 3D printed scaffolds—with dispersed zinc particles and engineered surface coatings. In addition to the choice of material, the microstructural and interfacial properties of the anode surface play a key role in guiding zinc nucleation and growth under flow conditions. Recent modeling efforts have shown that the interplay between surface topology and flow-induced ion transport critically influences the zinc plating behavior. For instance, Mushtaq et al. demonstrated that under flow conditions, the electric field distribution and ion flux at the electrode surface can be shaped by microstructural features of the anode.[262] Their multiscale simulations suggest that smoother or engineered surfaces help homogenizing the local ion concentration and reducing tip-enhancing field gradients, thereby suppressing the formation of high-energy crystallographic orientations, such as (100) and (101), which are commonly linked to dendritic growth. These insights underline the importance of surface engineering strategies, not only for morphology control but also for stabilizing the zinc deposition in hybrid flow battery environments.

For instance, in an alkaline Fe||Zn cell,[263] a zinc plate operating in a NaOH + ZnO electrolyte undergoes the reversible conversion of zincate species (Zn(OH)₄²⁻) to metallic zinc (Zn⁰). This reaction not only provides a broad voltage window—as indicated by the standard potentials of approximately 0.76 V for Zn|Zn²⁺ and –1.24 V for Zn|[Zn(OH)₄]²⁻ versus the standard hydrogen electrode (SHE)—but also impacts overall cell efficiency. However, the use of thick (>80 µm) planar foils often limits the active surface area, leading to non-uniform current distribution and dendritic growth that can degrade performance over time.

To mitigate these challenges, researchers have employed advanced surface texturing techniques to preferentially expose crystallographic planes such as (002) over (001), which exhibit lower nucleation overpotentials and higher zinc affinity.[264] Such texturing promotes more uniform zinc deposition and reduces the risk of dendrite formation. Additionally, composite electrode designs that directly incorporate zinc powder into porous matrices have been developed, thereby increasing the effective active surface area and enabling higher mass loadings. These approaches also benefit from the inclusion of tailored additives that modify the electrode–electrolyte interface, further suppressing dendrite formation and enhancing plating/stripping reversibility.

In Ce||Zn systems,[256] innovative strategies, such as the use of cadmium-plated copper substrates under alkaline conditions, have been implemented to overcome the challenges imposed by high pH gradients. These substrates help to achieve a more homogeneous zinc deposition while mitigating corrosion and uneven growth. Moreover, emerging strategies involving three-dimensional (3D) architectures—such as sintered zinc sponges, amine-functionalized carbon cloth, or 3D printed nickel/copper current collectors—demonstrate promising improvements by reducing local current densities and ensuring robust mechanical integrity during cycling.[265]

Collectively, these advanced materials and structural modifications are essential for attaining stable, high-efficiency zinc deposition, ultimately enhancing the performance and durability of zinc‐based redox flow batteries for large‐scale energy storage applications.

#### **2.5.2 Cathode**

The cathode influences mainly the overall performance and efficiency of zinc‐based redox flow cells by “catalyzing” the redox reactions of the catholyte. A wide range of materials is employed to fabricate high-performance cathodes, including carbon‐based electrodes (such as carbon felt, carbon paper, and graphite), metal‐based catalysts, and conductive polymers. The ideal cathode material must exhibit high electrochemical activity, excellent electrical conductivity, robust chemical stability in the selected electrolyte, and resistance to parasitic side reactions, as illustrated in the performance-related tables. Highly porous carbon materials—such as carbon felts and graphene‐based structures—are particularly attractive due to their large active surface area, tunable surface chemistry, and superior mass transport properties. For instance, in an alkaline Br₂||Zn cell reported by Thamizhselvan et al.,[266] carbon felt facilitates the necessary reaction 3 Br⁻ ⇔ Br₃⁻ to achieve at high cell voltage of 2.34 V with current densities between 20 and 120 mA cm⁻², maintaining an energy efficiency of about 55% over 500 cycles. In contrast, Ni||Zn systems, as demonstrated by Cheng et al.,[267] utilize a Pt/C‐coated gas diffusion layer that supports a sintered Ni(OH)₂/NiOOH catalyst, thereby enabling the reaction 2 Ni(OH)₂ + 2 OH⁻ ⇔ 2 NiOOH + 2 H₂O + 2e⁻ without the need for a physical separator. This approach enhances ion transport and minimizes voltage losses.

For Zn–organic systems, cathodes based on a Ti₄O₇/Ketjenblack catalyst deposited on carbon felt have been successfully paired with a dual electrolyte configuration (using H₂SO₄ and NaCl) to achieve very high current densities (up to 200 mA cm⁻²) and cycle numbers exceeding 2000, although the overall energy density is somewhat limited by the molecular weight of the organic redox-active species.[268]

Moreover, transition metal oxides, such as MnO₂ and Co₃O₄, as well as Prussian Blue analogs (PBAs), have shown promising redox activity when coupled with inorganic catholytes like FeCl₂, ZnBr₂, or ZnI₂. In alkaline systems, nickel-based catalysts may further enhance the catalytic activity and long-term stability, while in neutral electrolytes, functionalized carbon materials balance cost-effectiveness with high electrochemical performance. Additionally, the use of organic redox-active species (RAS) enables tailoring of catholyte properties by modifying functional groups, which helps to optimize solubility, minimize crossover, and adjust the redox potential to enhance the volumetric energy density. A fundamental approach in molecular design relies on basic principles of organic chemistry. For example, electron-withdrawing and electron-donating groups are commonly used to modulate the redox potential via inductive (-*I*EFFECT and -*I*EFFECT) and mesomeric effects,[269] thereby adjusting the operational voltage window to match the zinc redox couple. Long alkyl chains or PEG linkers are often introduced to increase the molecular flexibility and reduce crystal packing tendencies, which enhances solubility by disrupting regular intermolecular interactions. Additionally, concepts from hard and soft acid–base (HSAB) theory[270] are applied to improve the solubility and compatibility with the electrolyte environment—for instance, by matching soft donor groups on the RAS with the Zn²⁺ coordination environment in organic or aqueous media.

Typical examples of functional group modifications include the introduction of ionic substituents, such as sulfonate (–SO₃⁻), phosphonate (–PO₃²⁻), or quaternary ammonium (–NR₄⁺) groups to improve the water solubility and electrostatic repulsion, thereby reducing crossover through porous membranes. Electron-withdrawing groups like cyano (–CN), trifluoromethyl (–CF₃), or nitro (–NO₂) increase redox potentials via inductive effects, making the molecules suitable for high-voltage catholytes in combination with Zn anodes. Conversely, electron-donating groups (e.g., –OH, –NH₂, –OMe) can shift redox potentials cathodically, which may help in stabilizing reduced states or avoiding the HER. In sterically sensitive systems, bulky alkyl chains or PEG linkers are introduced to suppress π–π stacking and radical–radical interactions, enhancing the chemical and electrochemical stability over extended cycling. While the redox activity resides in the core structure (e.g., viologen, quinone, ferrocene, or TEMPO), these peripheral modifications enable molecular-level tuning of performance parameters, such as solubility, redox reversibility, diffusion, and stability across a range of pH conditions. Overall, the cathode material selection is highly dependent on the electrolyte composition and targeted operating conditions, with each material class—whether carbon-based, metal oxide-based, or organic—offering unique advantages in terms of voltage output, stability, and cost-effectiveness.

Table 5: Different types of RFB sorted by anolyte pH.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Type of RFB** | **Cathode** | **Catholyte** | **Cathode Reaction** | **Separator** | **Anode** | **Anolyte** | **Anode reaction** | **REF** |
| **Alkaline**  **pH>7** | Fe||Zn | Carbon felt | Na4Fe(CN)6 + K4Fe(CN)6 in water | Fe(CN)64−⇔Fe(CN)63− + e- | Nafion (Na+) | Zinc plate | NaOH +  ZnO | Zn(OH)42 ⇔  Zn0s + 4OH‑ | Wang et al.[263] |
| Br2||Zn | Carbon felt | ZnBr2 | 3 Br- ⇔ Br3- | Nafion-117 | Carbon felt | NaOH +  ZnO | Thamizhselvan et al.[266] |
| Ni||Zn | Pt/C coated gas diffusion layer | sintered Ni(OH)2/NiOOH | 2 Ni(OH)2 + 2 OH− ↔ 2 NiOOH + 2 H2O + 2e− | No separator | Zinc plate | ZnO + KOH | Cheng et al.[267] |
| Zn-air | O2 | CoIIITiPA + NaOH | cobalt triisopropanolamine-mediated ORR reaction | anion-exchange membrane (Sustainion X37-50) | Granules of 90 wt % Zn 5 wt % carbon black, 5 wt % of PVDF | DHPS + NaOH | Zhang et al.[265] |
| Mn||Zn | Carbon felt | MnSO4 + H2SO4 + NiSO4 | MnO2 + 4H++ 2e− ⇔ Mn2+ + 2H2O | Selective membrane | porous Zn @ carbon-felt | NaOH +  ZnO | Chao et al.[271] |
| Ce||Zn | Pt, Au or Ti on C. | Ce(ClO4)3 |  | AEM: Fumasep® FAA  CEM: Nafion® 1135 | Cadmium plated Copper, | NaOH +  ZnO | Gu et al.[256] |
| Zn-Organic | Ti4O7/ Ketjenblack catalyst on carbon felt | H2SO4 (Catholyte)  NaCl (middle electrolyte in dual membrane setup) |  | AEM: Selemion DSV®  CEM: Nafion® 117 | Carbon felt | NaOH +  ZnO | Park et al.[268] |
| **Neutral** | Fe||Zn | Carbon felt | FeCl2 | Fe2+ ⇔ Fe3+ | polybenzimidazole (PBI) porous mem-  brane | Carbon felt | ZnBr2 | Zn2+⇔ Zn | Xie et al.[272] |
| I2||Zn | Carbon felt | ZnI2/NH4I | 3 I- ⇔ I3- | CEM:  Nafion® 117 | Carbon felt | ZnI2 | Mousavi et al.[273,274] |
| Br2||Zn | Thermally treated carbon felts | ZnBr2 | 3 Br- ⇔ Br3- | CEM:  Nafion® 212 | Thermally treated carbon felts | ZnBr2 | Wu et al.[264], Shin et al.[275],  Mahmood et al.[276] |
| Zn-polymer | graphite felt/carbon paper | PolyTEMPO |  | Dealysis membrane Spectra/Por® 6 | Zinc plate | ZnCl2 | Schubert et al.[277] |
| Zn-organic |  | R-TEMPO |  | Zinc plate |  |  |
| Zn-organic | Carbon felt | Zn[Fc(SPr)2] | [Fc(SPr)2]2- ⇔ [Fc(SPr)2] | Nafion® 212 | Carbon felt | Zn[Fc(SPr)2] | Luo et al.[278] |
| **Acidic**  **pH7** | Fe||Zn | Carbon felt | FeCl2 | Fe2+ ⇔ Fe3+ + e- | CEM:  HZ115 ion exchange membrane | Zinc foil | ZnSO4 | Zn2+⇔ Zn | Xie et al.[279] |
| PbO2||Zn | lead dioxide paste from  (Yuasa NP 1.2-6) | PbSO4 |  | microglass fiber separators | carbon polymer electrode TF6 bipolar, SGL Carbon | ZnSO4 | Leung et al.[280] |
| Ce||Zn | Carbon felt | Ce(CH3SO3)3 |  | CEM:  Nafion® 1135 | Carbon-Polymer composite | Zn(CH3SO3)3 | Walsh et al.[255] |
| Zn-organic | Carbon felt | TEMPOL |  | CEM: Nafion® or AEM:  SELEMION | Zinc foil | ZnAc2 | Orita et al.[281] |

#### **2.5.3 Electrolytes**

The electrolyte formulation is fundamental in regulating the cell voltage, zinc deposition behavior, and overall cycling stability in zinc‐based redox flow batteries. In aqueous systems, salts, such as ZnSO₄ or ZnCl₂, are typically dissolved in water with the pH adjusted to alkaline, neutral, or mildly acidic conditions to suit different redox chemistries. For example, in an alkaline Br₂||Zn cell,[266] an electrolyte composed of NaOH and ZnO facilitates the formation of zincate complexes (Zn(OH)₄²⁻), which are critical for efficient zinc plating. This formulation yields a cell voltage of 2.34 V and an energy density of 125.43 Wh L⁻¹. In contrast, alkaline Ce||Zn cells operating under similar conditions can reach cell voltages as high as 3.08 V,[256] although these systems require a double ion exchange membrane setup that increases cost and slows ion transfer kinetics. Aqueous I₂||Zn systems[273] have demonstrated exceptional cycle numbers (>2500 cycles) and high energy density (137 Wh L⁻¹) at moderate current densities (~10 mA cm⁻²), yet challenges, such as high material costs, iodine-related environmental concerns, and self-discharge persist.

Alternatively, organic electrolytes based on solvents like acetonitrile or propylene carbonate offer a broader electrochemical stability window—with oxidative limits up to approximately 3.6 V vs. Zn|Zn²⁺—and enable operation at high current densities (up to 200 mA cm⁻² as reported for Zn–organic cells by Luo et al.[278] However, the lower solubility of zinc salts in organic media often restricts the volumetric energy density. To address these limitations, tailored additives, such as trimethyl phosphate and sodium citrate, are incorporated to improve ion transport, modify the solvation environment of Zn²⁺, and suppress dendritic growth. Recent studies by Shoaib et al.[282] and Yuan et al.[283] have demonstrated that these additives can enhance both the ionic conductivity and the chemical stability of zincate species, leading to improved cell performance. Furthermore, the integration of ionic liquids as co‐solvents or additives has emerged as a promising strategy to extend the electrochemical window and stabilize the electrode–electrolyte interface.[284] These approaches collectively contribute to the optimization of electrolyte formulations, a key step toward advancing the practical deployment of zinc‐based redox flow batteries for large‐scale energy storage.

Note: In polymer- and organic-based redox flow battery systems, ZnCl₂ is typically used as a supporting electrolyte or Zn²⁺ source and does not participate in redox reactions in contrast to the ZnBr2 /Br2 system. Since these systems operate at voltages well below the Cl⁻/Cl₂ redox potential (~1.36 V vs SHE), the evolution of chlorine gas is not expected.[277] This is in contrast with traditional Cl₂||Zn batteries, in which Cl₂ gas formation is a deliberate part of the charge/discharge process.[285]

In ZnI₂-based systems, elemental iodine (I₂) formation and precipitation can occur at high states of charge, potentially leading to passivation effects and reduced cycling stability. However, recent studies, including a comprehensive review by Fan et al.,[286] emphasize that iodine volatility is not a dominant issue under standard operating conditions. Instead, the formation of I₂ films and low iodide utilization are the primary challenges. These are being addressed through electrolyte formulation strategies, including the use of Br⁻, Cl⁻, and SCN⁻ as complexing agents to stabilize iodine species in solution.[286]

#### **2.5.4 Summary and Outlook of Zinc-Based Flow Batteries**

As mentioned above in chapter 2.3.4, lithium-ion batteries typically deliver cell voltages between 3.6 V and 4.2 V and energy densities in the range of 150–250 Wh kg⁻¹. However, they often face challenges related to limited cycle life, safety concerns, and scalability issues for large-scale grid storage. In contrast, zinc-based redox flow batteries (RFBs) offer very long cycle lives, modular scalability, lower costs, and improved environmental sustainability—thanks to zinc’s abundance, accessibility, and established recycling routes. Among the promising zinc-flow chemistries, several systems have demonstrated outstanding performance. For example, aqueous Br₂||Zn cells achieve a respectable energy density of about 125 Wh L⁻¹, making them attractive for high-power applications despite challenges, such as corrosion and toxicity. In aqueous Ce||Zn cells, the highest reported cell voltage of 3.08 V and an energy efficiency of 90% stand out, although these systems achieve extremely low cycle numbers, as well as expensive and complex membrane systems. Additionally, aqueous I₂||Zn systems demonstrate exceptional longevity with cycle numbers exceeding 2500 at moderate current densities, though high material costs and environmental issues related to iodine remain as concerns as well as self-discharge. Organic Zn-based RFBs, exemplified by Zn–organic cells, show robust cycling performance over 2000–3000 cycles and support very high current densities (up to 200 mA cm⁻²), albeit with modest energy density (~20 Wh L⁻¹) due to the inherent molecular mass of the redox-active species. A summary of the above-mentioned outstanding zinc-based redox flow chemistries can be found in Table 6.

Table 6: Examples of high-performing zinc-flow batteries featuring various cell chemistries.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Cell type** | **Components** | **Performance Indicator** | | | | | **REF** | **Comment** |
|  |  | Cycle number | Energy Efficiency / % | Capacity / Wh L-1 | Cell voltage / V | Current density/  mA cm-² | Mahmood et al.[276]  Wang et al.[287] 2024  Leung et al.[288]  Cremoncini et al.[289]  Emmel et al.[290] |  |
| aqueous | Br₂||Zn | 500 | 55 | 125.43 | 2.34 | 20-120 | Thamizhselvan et al.[266] | Very high current densities, partially commercialized, corrosion, toxicity and environmental hazards are challenges. |
| aqueous | Ce||Zn | 5 | 90 | 41.72 | 3.08 | 5 | Gu et al.[256] | Highest known cell voltage for aqueous RFBs, high safety risk due to very strong pH gradient, double ion exchange membrane system is very expensive, membrane transfer kinetics therefore very slow. |
| aqueous | I₂||Zn | >2500 | 80 | 137 | 1.37 | 10 | Mousavi et al.[273] | Extremely high lifespan/number of cycles, high energy density but low current densities during charging/discharging, high material costs (I2, ion exchange membrane), potentially hazardous to the environment. |
| organic | Zn-Organic | >2000  >3000 | 81.5 | 20.2 | 1.13 | 200 | Luo et al.[278] | Organic Zn-based RFBs are highly versatile, compatible with all cell types (alkaline, neutral, acidic), and support a bipolar setup. They enable high current densities and cycle numbers, though their molecular mass limits energy density to a medium level. |

Overall, organic electrolytes eliminate the need for scarce transition metals like nickel and cobalt and allow tunable redox properties for improved cycling stability. However, their higher synthesis costs can offset zinc’s cost advantage, making economic feasibility a key factor. While organic-based systems may increase material costs, they offer long-term benefits such as reduced reliance on critical raw materials, extended lifespan, improved power density, and lower environmental and disposal costs. Aqueous zinc-RFBs remain the more cost-effective option, but organic-based systems present a scalable and sustainable alternative for next-generation energy storage, balancing economic and environmental considerations.

## **3. Economic Aspects of Zinc Batteries**

### **3.1 Background**

While the consideration of materials and technology is important, ecological and economic factors also play a crucial role in assessing the long-term viability of any technology. In this context, the availability of resources must be evaluated. According to recent studies, the zinc content in the earth's crust is estimated at 198 trillion tons up to a depth of 5 kilometers. Assuming that mining at a depth of 5 km is technically feasible, the extractable global zinc resources are calculated at 63 billion tons.[291] Worldwide, approximately 247 million tons of zinc are currently in use.[292] The annual demand for zinc is 20 million tons, with 12.8 million tons supplied by mining and 7.6 million tons from recycling pre- and post-consumer scrap.[292] Based on the present rate of demand, it can be projected that the extractable zinc reserves will be sufficient to sustain supply for more than 5,000 years.[292] In contrast, the global lithium resources are projected to be 105 million tons, while current global reserves are estimated at only 28 million tons.[293] However, despite the double electron exchange, the high molar mass and low potential of zinc vs. SHE means that significantly more zinc is required to achieve the same energy as with lithium. This substantially reduces the difference between reserves and resources in the context of energy storage. Furthermore, zinc resources are widely distributed, making the supply less vulnerable to geopolitical instability.[3] . In contrast, more than 96% of lithium production comes from Australia, Chile, China and Argentina.[3] Due to the high availability of zinc and the rising global demand for lithium, the market price of zinc is expected to be less volatile than that of lithium.

The price volatility of lithium precursors has been a major issue for the lithium-ion battery industry, affecting cell costs and market stability. Lithium carbonate and lithium hydroxide are important precursors for lithium-ion batteries. Market prices are dependent on a variety of influencing factors, such as supply chain constraints, geopolitical factors and an uneven supply/demand balance from the rapidly growing electric vehicle sector. Figure 7 (Raw Material Price) shows that spot prices for lithium carbonate rose sharply in 2022, reaching $68 kg-1. This resulted from a supply deficit due to EV ramp-up, which was reflected in delayed deliveries, irrational purchasing behavior and inventory build-up to protect against rising prices. After 2022, prices collapsed again, with the main drivers being Chinese overcapacity, Chinese macro policies in the form of government subsidies and a slowing EV market. Thus, it is unclear if and at what level lithium prices will settle in the long term. Similarly, volatile price movements can be seen to a lesser extent for cobalt and nickel, both of which serve as precursors for NMC (lithium nickel manganese cobalt oxide), which is used as a cathode material in lithium-ion batteries. The situation is similar for vanadium pentoxide for redox flow systems, where a price jump of 300% can be observed in 2018 (cf. Fig. 7).

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Figure 7: Development of precursor material cost since 2010; Source: U.S. Geological Survey, Mineral commodity summaries 2012-2024[293] (Note: Nickel, Cobalt and Zinc are metal prices and need further processing for use as battery precursor material).

In contrast, zinc and manganese dioxide, essential components for zinc-based battery technologies, exhibit relatively low and stable pricing, currently at $3.49 and $2.11 per kilogram (see Fig. 7). The global abundance of zinc and manganese, coupled with their less complex extraction processes, contribute to their price stability. This disparity offers a compelling advantage for zinc battery technologies, suggesting a potential shift or diversification in the energy storage industry. Manufacturers may increasingly explore alternatives that provide more predictable cost structures while maintaining performance, particularly in stationary energy storage applications.[294]

Assuming that future rechargeable zinc-based batteries will be primarily utilized for stationary energy storage, the potential market for zinc batteries has increased in recent years and further growth is expected. Between 2023 and 2031, the global market for stationary energy storage systems is projected to nearly double, increasing from 256.49 billion USD to 506.5 billion USD. During this period, the European market for stationary energy storage systems is also predicted to double, maintaining a relatively constant share of approximately 14% of the global market (cf. Fig. 8).[295,296]

Due to the growing market, zinc-based battery technologies are increasingly supported to advance sustainable energy storage solutions. Within Europe, the program Horizon Europe provides funding for a wide range of innovative energy storage projects, including research into zinc-based batteries for applications in grid storage and renewable energy integration.[297] On a national level, the Swedish Energy Agency supports the Enerpoly Production Innovation Center (EPIC), which aims to scale up the production of sustainable zinc-metal batteries. The project is expected to begin production in a mega-factory in Stockholm in 2025, with the intention to increase capacity progressively over time.[172]

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Figure 8: Forecast of the market size for stationary energy storage in Europe in billions of USD with the compound annual growth rate (CAGR). (Source: Statista 2024[295], CAGR own calculations).

### **3.2 Cost Analysis**

One of the key factors that needs to be considered when assessing the potential success of a technology is its cost, especially when considering global market penetration. This is also true for the zinc batteries discussed in this work. For further consideration, economic analyses must be carried out to be able to make assessments with respect to economic viability. There are several cost factors that can influence the economic viability of different battery systems. These include material costs, production costs, operating costs and disposal costs. In the early phases of LIB research, often only material costs were considered[298,299] or production costs were modeled in a highly simplified way.[300,301] It was argued that materials account for a high share of the total costs. In addition, the available data on large-scale production was probably limited at that time. For zinc batteries, it is expected that material will account for a smaller share of the total cost than it does for LIBs, although the exact share is still unclear. However, the data on the production of secondary and primary cells is similarly limited. Therefore, a similar approach is taken in this work. After the initial look at the economic benefits in Chapter 2, this chapter will take an in-depth look at the material cost of zinc batteries. Although production, operation, and disposal are excluded, leaving some aspects unaddressed, focusing on material costs still permits an initial evaluation of the technologies.

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Figure 9: Detailed material costs of the zinc-metal batteries in comparison to a NMC811 and an LFP cell (see supplementary information S1 for input data).

Lithium-ion batteries currently represent the state-of-the-art for metal-ion batteries. To compare the material costs of ZMBs, the material costs of NMC811 and LFP (lithium iron phosphate) batteries were also calculated. A promising candidate for ZMB is a manganese dioxide cathode paired with a zinc-metal anode. While current β-MnO2 has a capacity of about 258 mAh g-1,[24] δ-MnO2 has the potential for capacities of up to 500 mAh g-1.[78] For this reason, Figure 9 presents both β-MnO2 as the current material and δ-MnO2 as a potential future material. The material cost for the β-MnO2 cell at $48 kWh-1 is slightly lower than that of the NMC811 reference cell at $49 kWh-1, but higher than the LFP material cost at $37 kWh-1. In contrast, the material costs for the δ -MnO2 cell are lower at around $24 kWh-1. A cost comparison reveals the clear advantage of using MnO2 as the cathode active material (CAM), which offers excellent performance parameters while being inexpensive. The cost of δ-MnO2 at $4.8 kWh-1 is half that of LFP at $12.45 kWh-1 and several times lower than NMC811 at $31.4 kWh-1. The costs for cathode binders for zinc are higher than for lithium, given the assumption of a 10% mass fraction of PVdF here, compared to 5% for lithium batteries. On the other hand, the electrolyte for ZMBs is cheaper, using aqueous 3M ZnSO4 instead of the more expensive LiPF6 in organic solvents in LIBs. The thickness of the Zn anode is a practical constraint. According to Gourley et al.[19], zinc foils thinner than 50 µm are currently difficult to obtain, resulting in a substantial oversizing of the anode. Here it is assumed that zinc foils with 10 µm can be produced and fully utilized in the cell. To quantify this effect, an δ-MnO2 battery was modeled with zinc powder as the anode, as there are no restrictions on foil thickness. This approach would make the battery $2.3 kWh-1 more expensive. Overall, zinc-metal batteries still have lower material costs, estimated at $80 kWh-1 by Gourley et al.[19] It is therefore expected that zinc-metal batteries will have a cost advantage, even over low-cost LFP cells in the future.

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Figure 10: Detailed material costs of the modeled zinc air battery (see S2 for input data).

In the current research landscape, little attention is paid to the cost modeling of zinc-air batteries and metal-air batteries. Given the absence of a model to analyze the costs of ZABs, this work developed a simplified material cost model. This model is based on a single-layer 10x10 cm zinc-air cell, where a bill of materials is calculated using geometric factors, and the material costs are determined based on the mass. This results in a 37 Wh cell and material costs of $12.7 kWh-1 (see Fig. 10). The porous anode, with a thickness of 1 mm, consists of zinc particles, binder, conductive carbon, and zinc oxide with a ratio of 86:2:2:10. The assumed electrolyte reservoir thickness is 1 mm. On the cathode side, a nickel-iron-cobalt catalyst supported by a carbon matrix was modeled. In addition, a current collector made of nickel-steel mesh and a gas diffusion layer made of carbon cloth are included. The cell is encased in a 0.8 mm thick steel casing, which accounts for most of the cell's weight. One of the most important cost factors is the anode material zinc at $3.59 kWh-1. Another major cost factor is the nickel-iron-cobalt catalyst, which is based on expensive metals with volatile prices (see Chapter 3.1). However, only small quantities are required, with mass loadings of 0.5 to 2 mg cm-², to facilitate the ORR and OER. Consequently, the catalyst accounts for a relatively small share, despite its higher input price. It can be concluded that, in principle, a high theoretical cell energy can be achieved with a low material input. This suggests that the material costs per kWh of cell energy are low. However, as described in Chapter 2.3, the theoretical performance of zinc-air batteries may not directly translate to practical real-world applications, particularly during long-term operation where capacity retention is problematic. This could lead to higher costs of practical zinc-air batteries.

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Figure 11: Detailed material cost analysis of the Br2||Zn and all vanadium redox flow battery (see S3 for data).

A techno-economic model by Tang et al. was adapted to analyze and compare redox flow battery technologies (see supporting information S3).[18] Figure 11 shows that materials for Br2||Zn batteries are slightly more expensive at $191 kWh-1 than vanadium batteries at $162 kWh-1. Both technologies share common materials, such as bipolar plates, graphite felt electrodes, PVC frame, and anionic selective membranes. However, the energy per stack, the functional unit of a redox flow battery, differs between all vanadium and Br2||Zn batteries. Therefore, approximately 33 stacks are required for vanadium, but 58 stacks are required for Br2||Zn to achieve the target energy. As a result, identical cost items for the Br2||Zn battery are higher, as more membrane material is needed to provide the same energy in kWh. Another difference is the active material, with vanadium pentoxide being more expensive at $20.4 kg-1 than zinc bromide at $2.3 kg-1. This is partially offset by the need for a sequestration agent for the Br2||Zn system, with material costs of $28 kg-1 reported by Tang et al. making this one of the largest cost factors. It is assumed here that the costs for such organic materials can be reduced by a factor of five in the future through economies of scale and more mature technology, resulting in costs of about $5 kg-1 for the sequestering agent (see S3 for further information). In this model, the vanadium battery still has a small cost advantage over the zinc-bromine battery. However, this advantage is smaller than the $435 kWh-1 figure reported by Tang et al. for Br2||Zn.[18] Additionally, it is questionable whether this advantage compensates for the criticality of vanadium as a raw material and its volatile price development. When considering the material costs of zinc redox flow batteries alone, further development is needed to achieve cost advantage. A potential avenue for exploration is the development of organic materials as a substitute for bromine. This would eliminate the need for a sequestering agent and, importantly, allow the anion-selective membrane to be replaced by a simple porous membrane, removing the largest cost factor (cf. chapter 2.4). Furthermore, the requirements for corrosion protection are less stringent for organic materials than for vanadium and Br2||Zn batteries, likely to result in lower production and maintenance costs. However, the material cost for organic materials could be too high to enable cost-efficient commercialization, which should be investigated in future studies.

When the three battery technologies are compared, it is immediately apparent that zinc-bromine redox flow batteries have the highest material costs per kWh at $191 kWh-1 (see Fig. 12). Zinc-metal batteries follow with costs of $48 kWh-1 for the β-MnO2 cell and $24.4 kWh-1 for the δ‑MnO2 cell. The zinc-air battery is the most cost-effective, especially with material costs of $12.7 kWh-1, implying a high potential for providing low-cost electrochemical energy storage for stationary applications.

Within the metal battery technology group, ZMBs offer a cost advantage over state-of-the-art LIBs. In addition, LIBs are industrially scaled and highly developed, so ZMBs may be able to benefit from economies of scale and knowledge transfer, which is not the case for secondary metal-air batteries, which still face challenges with short cycle-life.[302,303] This could lead to ZMBs becoming established in stationary energy storage applications in the near future.

Of the technologies examined, the zinc-bromine battery is the most expensive. However, as redox flow batteries generally have long lifespans, high cycling stability, and are easily scalable, they could prove advantageous for stationary storage in the long term, whereby the advantage of zinc-bromine in terms of raw material criticality and price volatility can be exploited. Therefore, it is likely that these technologies will coexist as complementary solutions rather than one prevailing over the others.

While material costs provide valuable insights, they do not account for factors like cycle life and thus longevity, efficiency losses, and recyclability, highlighting the need for comprehensive evaluations when comparing different technologies. Material cost analysis can be used to identify trends for specific technologies, but it is of limited value for cross-technology analysis.

By considering technology roadmaps for zinc batteries, the results of this study can be contextualized. According to the Fraunhofer ISI Alternative Battery Technology Roadmap 2030+ by Thielmann et al. (2023), current lab-scale ZMB coin cells have gravimetric energy densities of 30-60 Wh kg-1, which are expected to reach 50-120 Wh kg-1 in larger future cells.[20] The ZMBs considered in this work surpass these projections, achieving 128 Wh kg-1 for the β-MnO2||Zn pouch cell and 253 Wh kg-1 for the δ‑MnO2 cell. Thielmann et al. (2023) report theoretical capacities for zinc and MnO2 that are consistent with those used in this study.[20] However, in the absence of specific information on the sources or methods for the energy density calculations, it is difficult to determine the cause of this discrepancy between this work and Thielmann et al. It is hypothesized that the much lower practical capacities assumed by Thielmann et al. could explain this difference, possibly due to reduced energy efficiency or parasitic reactions within the cell. Results from this study are comparable to the work of Innocenti et al. who modeled a MnO2||Zn cell with an energy density of 189 Wh kg-1.[3]

In terms of projected costs, Thielmann et al. estimate the total costs, including production, at €80 kg-1 in 2025, dropping to €40 kWh-1 or less in the future.[20] Using the 77% share of material costs in total costs found by Duffner et al.[304] for LIBs, the results of this study can be extrapolated to determine total costs, including production, for a better comparison. Converted to Euros, the total costs are €57 kWh-1 for the β-MnO2 cell and €29 kWh-1 for the δ‑MnO2 cell, which is about 25-30% lower than in Thielmann et al.[20] and 30-60% lower than the $72 kWh-1 estimated by Innocenti et al.[3]

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Figure 12: Material cost comparison of all modeled batteries.

For zinc-air batteries, energy densities between 100 and 300 Wh kg-1 were reported by Thielmann et al.[20] The zinc-air cell modeled in this work is in this range at 181 Wh kg-1. The cell casing assumed in the material cost calculations accounts for a large proportion of the total weight of the zinc-air cell. Therefore, a high potential for optimization is expected here, which will have an effect on the energy density in the future. The energy density of 181 Wh kg-1 given in this work is therefore stated as the energy density that can be achieved in the short term, while the upper end of 300 Wh kg-1 by Thielmann et al. is stated as the energy density that can be achieved in the long term.

The chemical cost of storage is reported by Armstrong et al. at $6  kWh-1,[305] which is consistent with the material costs of the full cell calculated in this work at $12.7 kWh-1. Short-term manufacturing costs were reported by Thielmann et al. to be between 100 and 150 $ kWh-1, but it is unclear whether these are full costs or production costs only. Long-term costs were reported to be lower than $10 kWh-1, which is taken from a highly simplified material cost estimate by Toussaint et al.[20,306] Since no further data is available, the cost of $150 kWh-1 by Thielmann et al., which was quoted from an expert interview, is given as the short-term achievable cost, and the material costs of $12.7 kWh-1 from this work as the long-term goal.

### **3.3 Life Cycle Assessment**

A life cycle assessment (LCA) is a valuable tool for evaluating and comparing the environmental impact of various technologies. It encompasses diverse impact categories, from resource consumption to water pollution. Nonetheless, a thorough analysis of all 18 categories exceeds the scope of this study, which is why only the global warming potential (GWP), one of the most critical categories concerning climate change, is examined here. Lifecycle inventories from literature and the Ecoinvent 3.11 database were utilized for this purpose (see supporting information S4). The results are presented in kilograms of CO2 equivalents per kWh, as different gases have varying effects on global warming, and standardization based on battery capacity allows for comparison between battery types.

Figure 13 displays the GWP of the batteries studied. A comparison of the two LIB reference cells with the ZMB and ZAB cells indicates a substantially higher GWP in the former. The primary contributors are the CAM, particularly in the NMC 811 cell, and most notably graphite. The high GWP of graphite (47.7 kg CO₂‑eq. kg‑1) is attributed to the high temperatures needed for its production, resulting in unfavorable outcomes. In contrast, the ZMBs range from 28.8 to 42.5 kg CO2‑eq. per kWh, from δ‑MnO2 to β‑MnO2. The zinc metal anodes and manganese oxide cathodes perform better compared to their lithium counterparts, leaving the cathode binders as one of the main emitters. Here, PVdF at 61.6 kg CO2‑eq. per kg is used at a high mass fraction of 10% for the manganese dioxide cathode. Therefore, substituting with a different binder could further enhance the GWP of ZMBs.

The main drivers for the ZAB are the NFC 111 catalyst and the gas diffusion layer. However, due to the ZAB's high energy and energy density, comparatively few materials are needed, resulting in a low GWP. Similar to the costs, however, it remains questionable whether theoretical energies can be achieved over a higher number of cycles, which would significantly affect the CO2 footprint. The largest factor is the steel housing, accounting for 16.3 kg CO2-eq. per kWh. For the packaging container, a wall thickness of 0.8 mm used for prismatic cells was assumed, meaning the housing accounts for two-thirds of the total weight of the cell, skewing the result of the LCA. It can be assumed that, in large-scale industrial production, optimizing the housing would reduce this impact.

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Figure : Global warming potential of the analyzed technologies in kg CO2-equivalents per kWh of battery storage.

Among all the technologies examined, the Br2||Zn redox flow battery performed worst, with 145.8 kg CO2‑eq. per kWh. A major contributor is the graphite-containing bipolar plates. Due to the lower energy per cell stack in Br2||Zn batteries compared to vanadium batteries, more bipolar plates are needed, increasing the GWP. At 54.5 kg CO2‑eq. per kWh, the results of this study are similar to those of the analysis by He et al.[307] The second important contributor is the sequestration agent, where Shin et al.[275] suggest using N-ethylpyridinium bromide, which has an impact of 8.69 kg CO2‑eq. per kg (see Table S 4.4). However, Figure 13 only considers the environmental impact of the battery materials. Therefore, when considering the entire service life of a battery, the redox flow battery's performance will improve due to its high cycle life.

In summary, static zinc batteries exhibit a better GWP than comparable lithium technologies, with the potential for further improvement. Although zinc redox flow batteries currently have a higher GWP, their long lifespan could offset the difference.

### **3.4 Recycling**

The recycling of zinc from pre- and post-consumer scrap currently amounts to 7.6 million tonnes per year and is expected to increase by approximately between 9.3 and 14.3 million tonnes by 2050.[308] To better assess the potential of zinc-based batteries, the recycling process is evaluated in comparison to current state-of-the-art battery technologies.

Recent research highlights the advantages of zinc battery recycling over lithium-ion batteries, which face challenges, such as toxic solvents and complex cathode materials. These factors contribute to higher costs, increased complexity, and a greater environmental impact during the recycling process.[12] In contrast, zinc-based batteries can utilize aqueous electrolytes that do not contain toxic substances, making them potentially more suitable for recycling. Therefore, one advantage is the potential to efficiently recover metallic zinc from used batteries, achieving efficiencies of up to 99% through methods such as evaporation and controlled oxidation, without compromising battery performance.[309] Similarly, cathode materials can be recovered cost-effectively through thermal treatment methods with high resource recovery rates.[310] The salts used in zinc-based batteries can also be easily separated and recycled through membrane distillation combined with crystallization, further enhancing the sustainability of the recycling process.[311] However, the glass fiber and Nafion® separators or membranes often utilized in ZMBs are likely more challenging to recycle. Furthermore, recycling, particularly for Zn-air batteries, may be economically unattractive due to the low value of the raw materials used.[20]

An additional benefit of zinc-based batteries is their high compatibility with established recycling processes. Specifically, zinc-based batteries can be integrated into current pyro- and hydrometallurgical recycling processes that have been established for primary zinc-carbon and alkaline batteries.[19,310] Research in this field is currently in its infancy, but it can be assumed that minor adjustments to the current recycling process for primary zinc batteries will be necessary. It can therefore be assumed that the effort required for the recycling of zinc based batteries is likely to be lower than for LIBs.[20]

In comparison, the purification steps required for regenerating the electrolyte of an end-of-life redox flow battery are currently unknown, making an assessment difficult at this time. However, it can be assumed that the recycling process is generally feasible.[312] It can also be assumed here that the existing zinc recycling capacities represent an advantage over vanadium. If the perspective is to switch to zinc-organic materials, it is questionable to what extent the organic compounds can be recycled. The recovery of the battery cell or stack is more complex, but since no rare or critical materials are involved, it is less substantial. The components, such as tanks and tubes, can be recycled using standard methods for polymers and metals.[20]

## **4. Areas of Application and Market Prospects**

Currently, the only commercially available zinc-based battery technology is zinc-air in the form of primary cells. These batteries are ideal for applications that require long-term storage and operate at low current densities. Typical uses include medical devices, such as hearing aid batteries, barricade flashlights, fence controls, and emergency phones, particularly in areas without access to power lines.[313] Common forms of these batteries include cylindrical, prismatic, and button cells. Standardized large storage cells consist of models like the AR40 and 5AR40 (7 V, 85 Ah), as well as the 6AS4 and 6AS6 (5.1 V, 130 Ah).[313] Since these batteries are only available as primary cells, current research is focused on improving cyclability and energy densities to develop viable secondary (rechargeable) cells.

Zinc-metal battery technology represents the cell system that is clearly advanced in terms of secondary cell operation. Ongoing research efforts aim to create a resource-efficient electrolyte that can also help in controlling the dendrite growth on the anode. The high-capacity cathode intercalation materials and processing technologies from lithium-ion research can be applied here. As a result, the market entry for zinc-metal batteries is expected soon at relevant scales for stationary and industrial applications.

The main advantages of zinc-metal technology compared to lithium-ion include affordable raw-materials and established recycling routes. This will lead to reduced costs per kilo watt-hour (kWh) of the cells, which is crucial for stationary storage. By improving cycle life with newly developed electrolyte additives, the application of zinc-metal technology in stationary energy storage is anticipated to increase substantially. The current state of research and development, along with the perceived future potential, is illustrated in Figure 14.

The next anticipated advancement in market entry is the zinc-air secondary cell technology. Similarly to the zinc-metal system, research on the zinc anode primarily focuses on controlling dendrite growth. However, a notable research effort in recent years has been directed towards moving the technology beyond the conventional primary cells that use alkaline electrolytes. This involves developing new bifunctional cathodes. Combining the efficiencies of the newly explored near-neutral battery systems with more stable air electrodes can help to bring this technology to market. It is evident that scaling both existing and new developments is essential for the future advancement of this technology, particularly for stationary storage and aviation applications, to meet projected goals.

The following Figure 15 outlines the commonly discussed applications for zinc-air batteries and addresses open research questions. These include developing strategies to prevent dendrite growth and the need for stable bifunctional catalysts and gas diffusion electrodes. The power density of these batteries is heavily influenced by the air electrode, which appears to be a bottleneck for high-power applications. Therefore, these cells are primarily anticipated to be used in stationary energy storage.

The limitations of zinc-air battery technology primarily stem from zinc corrosion, solubility of zinc ion species in alkaline environments, and electrolyte issues e.g. dry out due to environmental conditions. To address this issue, many researchers have explored the use of pumped electrolyte cells, which can help controlling corrosion and prevent the unwanted segregation of zinc species. The development of zinc-redox flow batteries is a promising next step for these pumped alkaline zinc-air systems. This type of battery separates the storage volume from the power density.

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Figure 14: Roadmap for implementation of zinc-metal batteries.

In contrast to conventional intercalation or conversion cells, the power density of pumped redox flow batteries does not scale with the stored energy as the energy is stored in different oxidation states of ions diluted within the electrolyte. This characteristic makes flow batteries particularly advantageous for applications where the size of the battery is less critical, such as stationary storage and marine vessels. Currently, most flow batteries rely on vanadium, which poses challenges due to its high toxicity and cost.

In contrast, the next generation of flow batteries based on zinc can adapt advancements from zinc-metal and zinc-air technologies for anode development. Additionally, the recycling processes for these batteries can be integrated into existing infrastructures. Zinc-based redox flow technology is a promising solution for coupling storage with renewable energy production that is dependent on external factors such as sun and wind. Such battery systems offer better long-term storage capabilities than lithium-ion batteries. However, they cannot be easily adapted to fast transient operating modes, which makes them ideal candidates for storing wind energy during periods of low wind, as an example. Figure 16 presents the current developments and application directions for zinc flow batteries.

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Figure 15: Roadmap for the development of zinc-air batteries.

In summary, zinc-based batteries offer several advantages due to the low material costs and non-toxic nature of zinc and many of their components. These factors are expected to support the implementation of these battery technologies in the near future. The primary application for these batteries appears to be stationary energy storage, where the price per stored kWh will ultimately determine which technology will be adopted. Zinc-based batteries, particularly in the forms of zinc-metal, zinc-air, and zinc redox flow technologies, are well-suited for stationary energy storage. The global market for these applications is projected to nearly double between 2023 and 2031, leading to an increased demand for cost-effective and stable energy storage solutions (see Chapter 3.1). The European market is expected to follow a similar growth trajectory, maintaining a substantial share of the global market.[295,296]

To meet the increasing demand for stationary energy storage through electrochemical solutions, a substantial need for battery materials will arise. Relying solely on LIBs and vanadium redox flow batteries may lead to supply shortages and increased price volatility, ultimately hindering progress. Additionally, focusing on these technologies exclusively could deplete economically viable lithium reserves over the long term. Moreover, a substantial amount of material will accumulate after the decommissioning of stationary storage units, creating a need for recycling as part of a circular economy. Currently, the recycling capacity for lithium and vanadium at this scale does not exist and would have to be developed from scratch. In contrast, zinc battery technologies may help address these challenges because global zinc reserves are considerably more accessible, reducing the risk of future supply shortages and price volatilities. Furthermore, an established recycling system for zinc used in primary batteries already exists and could be expanded in the future. The outlook for zinc-based battery technologies is promising due to their cost advantages, resource accessibility, and simpler recyclability compared to lithium-ion and vanadium redox flow batteries.

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Figure 16: Roadmap for the development of zinc redox flow batteries.

The variety of battery technologies underpins their diverse applications in stationary storage systems, with specific uses especially within the renewable energy sector. LIBs are primarily geared towards short- and mid-term energy storage for residential or industrial applications, but they can also be integrated into the grid, which can be applied to zinc-metal and zinc-air batteries. These technologies are effective in compensating for fluctuations in electricity generation from renewable sources and in addressing variations in industrial electricity prices. Typical applications include energy storage systems paired with photovoltaic (PV) systems in single-family and multi-family homes, with capacities ranging from 1 to 20 kWh, and industrial storage systems with capacities between approximately 50 kWh and 25 MWh. Their rapid response capabilities make them ideal for applications such as demand support, power oscillation damping, wind power gradient reduction, and frequency regulation.[1] Conversely, redox flow batteries, including zinc-bromine are more suited for long-term energy storage applications. Although they require a similar amount of floor space as lithium-ion batteries, they are particularly well-suited for off-peak storage solutions due to their high discharge capacity, good scalability, and excellent lifespan.[314] They are also effective for time-shifted energy storage, voltage sag mitigation, and rapid demand support, given their long discharge times. This distinct separation in application profiles highlights the complementary nature of these technologies in addressing various energy storage needs within the market. As demand for both short-term and long-term storage solutions grows, these technologies present promising prospects.[1,20]

## **5. Conclusions**

In this work, we addressed four central questions outlined in the introduction, focusing on how zinc-based battery technologies are poised to play a pivotal role in the future of stationary energy storage systems. These technologies offer promising alternatives to conventional lithium-ion and vanadium redox flow technologies. We reviewed the historical development, current state of research, and future potential of three zinc battery chemistries: zinc-metal (ZMB), zinc-air (ZAB), and zinc redox flow batteries (ZFB). Each system has unique advantages and technical challenges, and they are at different technology readiness levels, suggesting a staggered but complementary deployment path within the stationary energy sector.

Rechargeable zinc-metal batteries are the most mature among the three systems and are expected to enter large-scale markets in the near future. Their success will critically depend on two key research directions: the development of high-capacity, stable cathode materials (e.g., doped manganese oxides, spinels, or Prussian Blue analogues) and the optimization of electrolyte formulations to improve interfacial stability, minimize dendrite growth, and suppress hydrogen evolution. Innovations such as hydrogel-based quasi-solid electrolytes or novel high-solubility conducting salts may prove transformative. Importantly, most manufacturing processes can be adapted from lithium-ion production infrastructure, facilitating market integration.

Zinc-air batteries, while capable of delivering high theoretical energy densities, require substantial advancements to become truly rechargeable and cycle-stable. Future efforts should prioritize the development of bifunctional, non-noble-metal catalysts with high ORR/OER activity and durability, as well as cathode architectures that ensure optimal gas diffusion and catalyst utilization. On the anode side, moderate surface structuring and the use of synergistic additives for both electrodes and electrolytes will be critical to mitigate passivation, corrosion, and shape change. Although aqueous electrolytes offer intrinsic safety benefits, hydrogen evolution and carbonation pose challenges for long-term operation. Transitioning to near-neutral or hybrid electrolytes—possibly combined with solid-state or gel-based approaches—could enable stable, safe, and efficient systems. However, achieving a fully integrated and scalable cell design remains an open challenge and a prerequisite for commercialization.

Zinc redox flow batteries (ZRFBs), while less developed in comparison, hold significant promise due to their decoupled power and energy scalability. Their further development will benefit from insights gained in ZMB and ZAB research, particularly regarding zinc electrode stabilization and interfacial control. In the short term, improving membrane selectivity, electrolyte compatibility, and the structural integrity of zinc deposition layers will be essential. In the medium-to-long term, organic or hybrid organic-zinc redox couples offer a compelling route to higher voltage systems, improved temperature stability, and reduced material costs. Achieving high solubility and redox reversibility of organic molecules, alongside robust membrane technologies, will be key to realizing these goals.

Table : The perspectives on the zinc batteries in terms of short term, medium/long-term and vision.

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| **System** | **Short term** | **Medium/long term** | **Vision** | **Field of application** |
| ZMB | ~130 Wh kg-1  $48 kWh-1 | Stability of electrodes and electrolytes, cathode materials with higher capacity | ~250 Wh kg-1  with improved power densities and cycling stability,  $24 kWh-1 | Stationary storage, industrial backup systems, smart city, renewable grid support |
| ZAB | ~180 Wh kg-1  ~$150 kWh-1a, [20] | Stability of electrodes and bifunctional catalyst | ~450 Wh kg-1[247] while maintaining high cycling stability, $12 kWh-1 | Stationary storage, industrial backup systems |
| ZFB | 50-125 Wh L-1  $435 kWh-1[18] | Stability of electrodes and electrolyte, modular flow cell system | 80-190 Wh L-1, with regards to organic redox flow cells with higher cell voltage,  $191 kWh-1 | Off-peak storage for renewables, rapid demand support, stationary storage |
| a: Potentially including both material and production cost. | | | |  |

Across all three systems (see Table 7), extending the cycle life and achieving high energy efficiency remain overarching challenges. Future research must systematically address degradation mechanisms—including the dissolution of transition metals, dendritic growth, and parasitic side reactions—through targeted material design, interface engineering, and electrolyte optimization. A deeper understanding of these failure modes, especially under practical operating conditions, will enable the development of mitigation strategies essential for long-term durability. However, to our knowledge, there are currently no standardized testing protocols available for the comparable assessment of stationary cells under real-life conditions. This lack of standardized testing poses additional challenges when translating new laboratory developments to industrial applications.

Beyond their technical features, zinc batteries present significant economic and ecological advantages, partly due to the accessibility and price stability of zinc resources. Firstly, the accessibility of zinc resources and the stability of their prices are crucial factors. Conversely, lithium is in high demand and has experienced supply shortages in the past, resulting in price volatility. Similar issues affect other materials that are essential for state-of-the-art battery systems, including nickel, cobalt and vanadium. The accessibility of zinc, along with the consistency of its costs and prices, makes it a sustainable resource for long-term technological applications, particularly in battery production. Furthermore, zinc flow and zinc-air batteries require only minimal amounts of scarce raw materials, whereas intercalation chemistries (such as lithium-ion) necessitate larger quantities. The sustainability and availability of the materials used in zinc metal batteries have been thoroughly investigated, as these factors are key to successful implementation.

In terms of cost implications, zinc-based batteries have notable advantages. The material costs associated with zinc-metal batteries are lower on a per kilowatt-hour basis compared to their lithium-ion counterparts. In particular, zinc-air batteries stand out due to their overall potential for low material costs, positioning them as potentially cost-effective options for electrochemical energy storage. However, the practical feasibility of transferring the theoretically modeled zinc-air battery with the assumed specifications into real world application remains questionable, particularly with regard to lifespan and cyclability. This is due to the aforementioned issues and limitations that need to be addressed, which may have cost implications. Zinc redox flow batteries are even more expensive than their already quite costly vanadium counterparts, but have advantages in terms of lower price volatility and the hopes for cost savings with organic materials in the future.

Regarding environmental impact, the ZMBs and the ZAM outperform their lithium counterparts with a substantially lower global warming potential. While the ZRFB exhibits a higher GWP, this may be offset by its potentially longer cycle life. Recyclability is another area where zinc-based batteries excel. Their use of non-toxic aqueous electrolytes allows for simpler and less environmentally impactful recycling processes. They integrate easily into the existing recycling infrastructure, supporting the transition to closed-loop systems. The growing market for stationary energy storage enhances the appeal of a diverse battery technology space including zinc-based batteries, supported by funding and development projects, indicating their potential role in sustainable energy solutions.

In conclusion, while each zinc battery chemistry exhibits unique strengths and application niches, their shared advantages—such as material abundance, low toxicity, and established recyclability—position them as highly attractive candidates for sustainable, large-scale energy storage. A coordinated research effort that integrates material innovation with system-level engineering and techno-economic analysis will be critical to unlock their full potential in future energy infrastructures.

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**TOC-(Text 50-60 words):**

Growing energy demands and the associated increase of renewable energy production require robust, sustainable, and cost-effective energy storage, in particular for large scale stationary applications. This review evaluates zinc-based batteries as alternatives to lithium-ion and vanadium redox flow systems by emphasizing zinc’s accessibility, affordability, reduced environmental impact, and recycling advantages. Diverse chemistries, advanced electrode designs, and techno-economic analyses underscore zinc batteries’ promise for sustainable energy storage.

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