

CHAPTER 5

RECHARGEABLE ZINC BATTERIES FOR GRID STORAGE

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Abstract

Rechargeable alkaline zinc batteries are a promising technology for large-scale stationary energy storage due to their high theoretical energy density similar to lithium-ion batteries, as well as their use of abundant and inexpensive raw materials that could push costs below \$100/kWh. However, the poor reversibility of zinc anodes in alkaline electrolytes poses a formidable challenge to commercial viability, and certain cathodes for zinc battery chemistries suffer similar poor reversibility. The development of zinc batteries for the electric grid market is still in its infancy, with only two companies having deployed such systems to date and several other young companies having demonstrated proof of concepts. In addition, while zinc batteries are often touted as being inherently safe because of their environmentally benign active materials and nonflammable aqueous electrolyte, there are few detailed studies on their safety aspects and behavior under abuse conditions. This chapter discusses the principles behind the leading zinc battery technologies, their current implementation in grid markets, the specific challenges to reversibility, possible safety concerns, and recent developments by companies and their collaborators to improve the performance of zinc batteries to enable a practical cost-effective, long-duration storage technology.

Key Terms

alkaline, batteries, depth of discharge (DoD), gas diffusion layer (GDL), potassium hydroxide (KOH), zinc (Zn), zinc-air (Zn-air), zinc-manganese oxide (Zn-MnO₂), zinc-nickel (Zn-Ni), zinc oxide (ZnO), zincate

1. Introduction

1.1. Background

Battery systems comprise a small but rapidly growing segment of global stationary energy storage. As of mid-2017, batteries made up 1.1% or 1.9 GW of installed storage power capacity worldwide, with this share expected to grow at least 17-fold by 2030[1]. Among specific chemistries, lithium-ion, sodium-ion, and lead-acid systems are the leaders, comprising 59% (~1.1 GW), 8% (0.15 GW), and 3% (0.06 GW), respectively, of global operational electrochemical storage as of mid-2017[1]. These types of batteries are discussed in Chapter 3: Lithium Ion Batteries, Chapter 4: Sodium-Based Battery Technologies, and Chapter 2: Lead-Acid and Advanced Lead-Acid Battery Technologies, respectively. Lithium-ion batteries offer the best combination of energy density, power density and cycle life (up to 500 Wh/L, 300 W/kg, and 10,000 cycles respectively) [2, 3]. However, they have significant drawbacks from cost, safety, and environmental standpoints. The minimum energy installation cost of lithium-ion systems is around \$200/kWh and is unlikely to fall below that level.[1, 4]. Furthermore, they use toxic, flammable organic electrolytes that pose a safety hazard in the event of overcharge, thermal runaway, or physical shock which necessitate safety and thermal management components that add to cost [1, 3].

Sodium-ion systems on the electric grid are mainly of sodium-sulfur chemistry that uses molten electrode materials. Thus, they also pose a flammability risk, require high operational temperatures

of 250–350°C, offer little cost advantage over lithium-ion systems, and are limited to ~300 Wh/L [1]. Lead-acid batteries are the most mature and inexpensive rechargeable battery technology, with costs as low as \$50/kWh, but they suffer from poor cycle life (up to 2,500), low energy density (50–100 Wh/L) and toxicity of lead, which is a problem in developing countries where the batteries are often recycled without proper protective measures [1, 5].

The ideal battery system for grid storage should have high energy density, long cycle life, low cost, and low-risk components. Ideally, its cost should be below \$100/kWh and its energy density above 250 Wh/L to be competitive for grid storage applications. From the latter two standpoints, aqueous battery chemistries using earth-abundant, minimally processed materials are attractive options. In particular, alkaline battery chemistries with zinc electrodes, such as zinc–manganese oxide (Zn–MnO₂), zinc–nickel (Zn–Ni), and zinc–air (Zn–air), are already being developed (or are in serious consideration) for grid storage applications. Zinc is the twenty-third most abundant element in the earth’s crust and is fourth among metals in terms of worldwide production, which stood at 13 million tons in 2018 with a price of \$1.19 per pound [6]. Additionally, zinc batteries benefit from a long-established supply chain and market in small-scale consumer devices. Zn–MnO₂ forms the underlying chemistry of disposable “alkaline” batteries, which are used in numerous household items and make up 80% of manufactured batteries in the United States, with a capital cost as low as \$10–65/kWh [7]. Zn–air batteries have long been used in hearing aids due to their high energy density and flat discharge profile. Zn–Ni batteries are a fairly common rechargeable system well-suited to high-voltage, high-drain applications such as digital cameras. The practical energy density of zinc battery chemistries can be quite high as well, up to 150 Wh/kg or 400 Wh/L for Zn–MnO₂ and up to 440 Wh/kg or 1,670 Wh/L for Zn–air [8–11]. These values are on par with or exceed commercial lithium-ion batteries today, with the caveat that Zn–MnO₂ and Zn–air batteries have only been widely commercialized in primary (non-rechargeable) form.

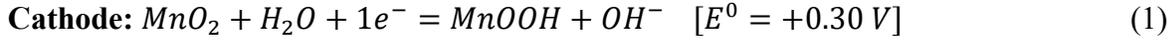
This chapter focuses on alkaline zinc battery systems. Zinc–bromine flow batteries, a different aqueous zinc battery technology being investigated for grid storage applications, are covered in Chapter 6: Redox Flow Batteries.

1.2. Technology Overview

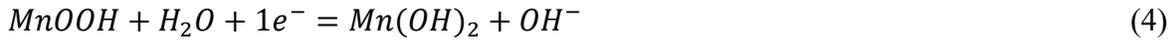
1.2.1. Zn–MnO₂ Batteries

Zn–MnO₂ batteries were first introduced as primary dry cells in 1952 and patented by Marsal, Kordesch, and Urry in 1960 [12, 13]. They have since become one of the most commercially successful battery technologies and are ubiquitous in everyday electronics. Furthermore, they are more environmentally friendly than other types of batteries, even being EPA-certified for landfill disposal in the United States [14]. Off-the-shelf disposable Zn–MnO₂ batteries have an energy density up to 150 Wh/kg or 400 Wh/L [8, 9].

This battery has zinc as the negative electrode (or anode, which is oxidized during discharge) and manganese dioxide (MnO₂) as the positive electrode (or cathode, which is reduced during discharge). Traditionally, a form of MnO₂ called electrolytic manganese dioxide (EMD) is used. The alkaline electrolyte is a solution of potassium hydroxide (KOH), which in commercial “dry” cells is mixed with zinc powder into a paste-like substance in the anode compartment. Additionally, carbon powder is typically added to MnO₂ in the cathode to increase conductivity. The nominal half-reactions at each electrode and overall reaction of the cell during discharge are:



A further reduction step to $\text{Mn}(\text{OH})_2$ is possible at the cathode upon deeper discharge:



This system is schematically illustrated in Figure 1. In principle, the reverse reactions occur during charge. Eq. 1 and Eq. 4 are called the “first-electron” and “second-electron” reduction processes of MnO_2 respectively, each one contributing 308 mAh/g of theoretical specific capacity, and they occur by different mechanisms [15]. However, the second-electron process is typically nonexistent or greatly diminished in commercial Zn– MnO_2 batteries because it is preempted by the formation of inactive, resistive compounds (see Section 2.2.2.1).

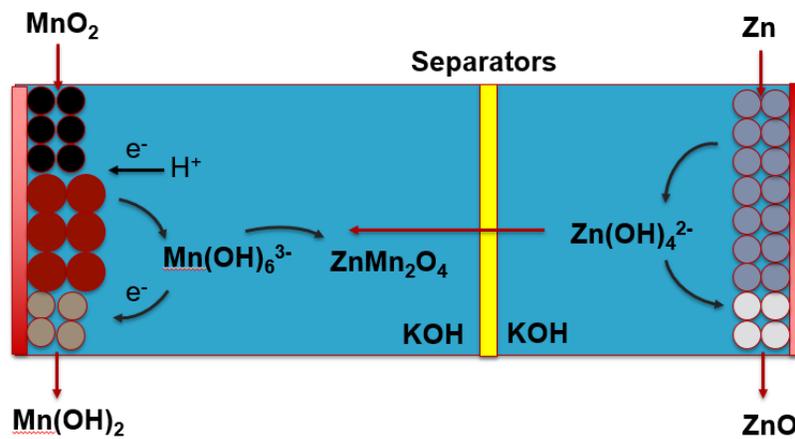
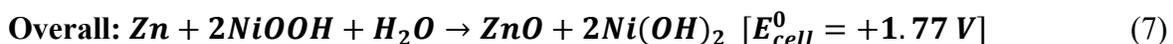
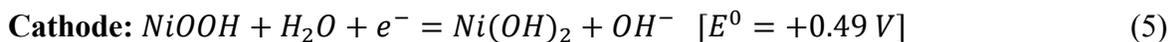


Figure 1. Schematic diagram showing operating principle of an alkaline Zn– MnO_2 battery during discharge [16]

1.2.2. Zn–Ni Batteries

Zn–Ni batteries were first developed in the 1920s and were investigated extensively in the 1970s and 1980s as a rechargeable system, emerging as a leading candidate for electric vehicle applications with hundreds of deep-discharge cycles demonstrated [17, 18]. The current technology has a practical energy density up to 140 Wh/kg or 300 Wh/L with lifetime up to ~500 charge-discharge cycles [19, 20].

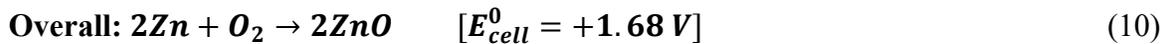
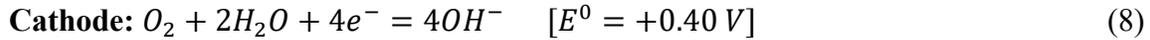
Like Zn– MnO_2 cells, Zn–Ni cells use an aqueous solution of KOH as the electrolyte and zinc as the anode material, with the same fundamental anode reaction during discharge (Eq. 2). However, the cathode in this case is nickel oxyhydroxide (NiOOH), which converts to nickel hydroxide [$\text{Ni}(\text{OH})_2$] during discharge:



The reverse reactions occur when the cell is recharged.

1.2.3. Zn–Air Batteries

Zn–air batteries were first patented in 1933 as a primary cell by G.W. Heise of the National Carbon Company [21]. As primary cells, they are still in widespread use as “button cells” in watches, hearing aids, and film cameras owing to their outstanding energy density (up to 440 Wh/kg or 1670 Wh/L), flat discharge profile, and long shelf life when sealed (up to 3 years) [10, 11]. Like Zn–MnO₂ and Zn–Ni batteries, commercial Zn–air batteries have a zinc paste anode and KOH electrolyte with the same underlying anode reaction (Eq. 2). However, in this case the reacting species at the cathode are atmospheric oxygen and water from the electrolyte to form hydroxyl ions that migrate into the paste:



This system is schematically illustrated in Figure 2a. Again, the reverse reactions occur during charge. The use of air as a reactant at the cathode contributes to the high energy density of Zn–air batteries, given that there is an essentially limitless supply of air from the atmosphere. The physical cathode is nonreacting and consists of a thin, porous gas diffusion layer (GDL) loaded with a catalyst material (Figure 2b). The GDL, which enables good transport of oxygen between the electrolyte and ambient air while preventing electrolyte leakage, is commonly made from carbon fiber-based paper or cloth. The catalyst accelerates the oxygen reduction reaction during discharge (Eq. 8) and, for a rechargeable system, it also accelerates the oxygen evolution reaction (the inverse of Eq. 8) during charge. These reactions are impractically slow in the absence of a catalyst. A wide variety of catalyst materials have been used, including precious metals (Pt, Ag, Ir), non-precious transition metal oxides, and doped carbon nanomaterials [22]. However, as discussed in Section 2.2.2.2 Air Cathodes, one particular challenge to making Zn–air systems highly rechargeable is to find a low-cost material that can effectively catalyze both the oxygen reduction and oxygen evolution reactions.

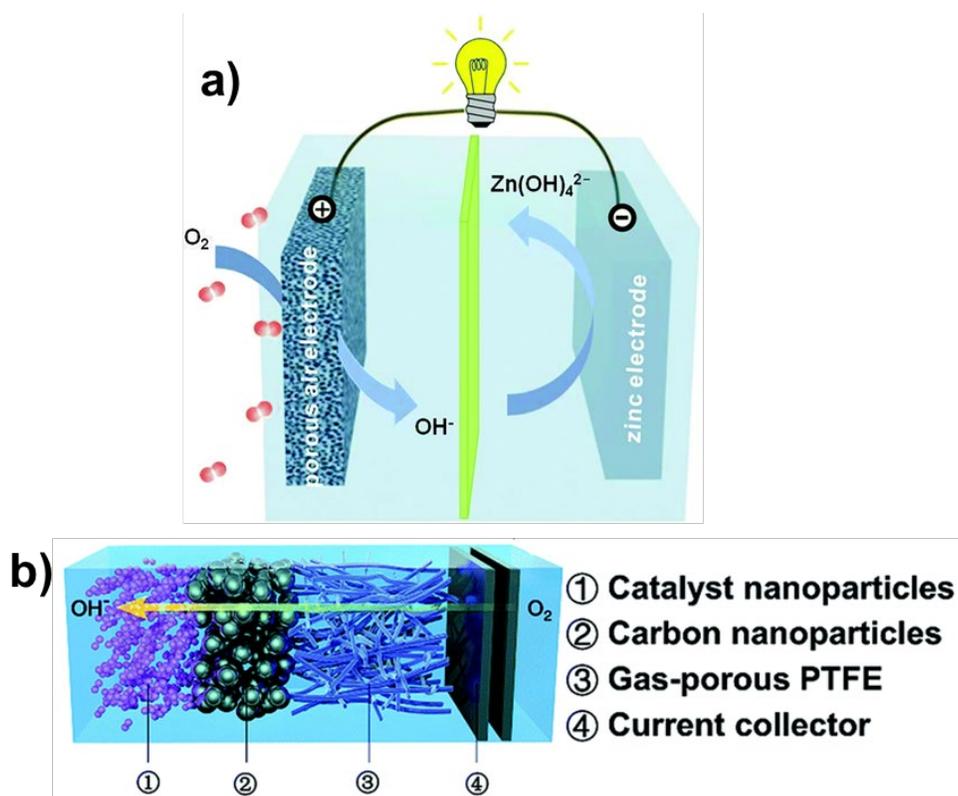


Figure 2. (a) Schematic diagram of a Zn–air battery during discharge [23]. (b) Exploded cross-sectional view of the air electrode [24]. (Both images are published by The Royal Society of Chemistry under a [CC BY-NC 3.0](https://creativecommons.org/licenses/by-nc/3.0/) License.)

2. State of Current Technology

2.1. Current Implementation

Numerous startup companies are developing alkaline zinc batteries for large-scale grid storage, microgrid, residential energy storage, and/or backup power applications. Although rechargeable zinc batteries have been widely scaled up and commercialized for backup power (particularly for data centers), the state of zinc batteries for the electric grid market is less mature. The following survey focuses on companies actively producing and/or deploying zinc battery systems for grid-tied applications.

Urban Electric Power (UEP), founded in 2012, led by Dr. Sanjoy Banerjee and based in Pearl River, New York, specializes in alkaline Zn–MnO₂ systems for power assurance (Figure 3), solar microgrids, and grid stabilization. UEP’s current battery technology features energy densities up to 100 Wh/L (accessing 20% of the first-electron capacity of MnO₂ and 9% of the total capacity of Zn) in cylindrical cells with total cell capacity between 200 and 350 Ah [16]. These cells are manufactured in a roll-to-roll process at scales of 200 MWh per year and costs of \$200/kWh [16]. As of June 2019, UEP had installed 210 kWh of residential systems, 488 kWh of small-scale commercial systems, and 2.8 MWh of large-scale commercial systems [25].

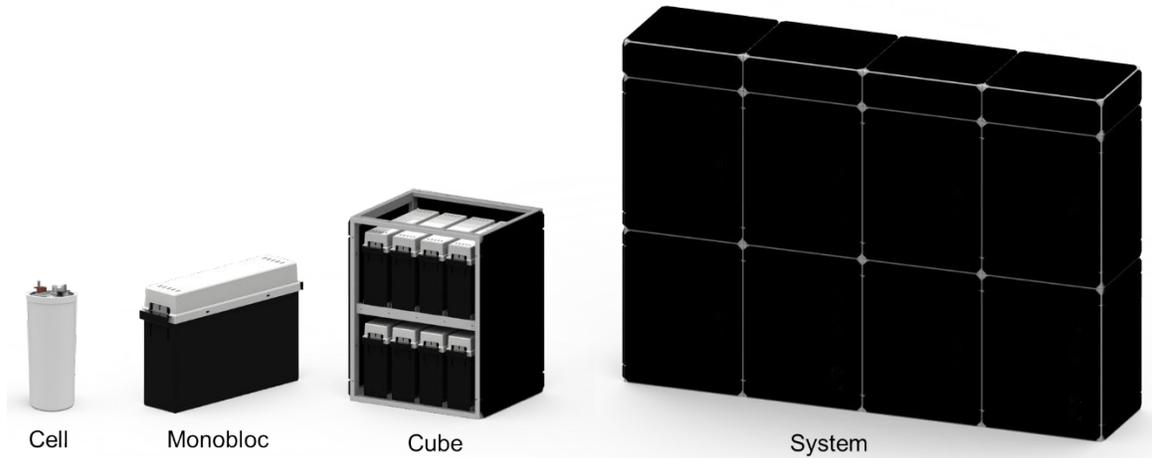


Figure 3. Illustration of configuration of UEP cells for its power assurance system. Each monobloc consists of four cells totaling up to 2 kWh, each cube consists of 10 monoblocs, and each system consists of a variable number of cubes with up to 16 kWh of usable energy [16].

In backup power, UEP’s initial target market, UEP notably supplied a new UPS system for the San Diego Supercomputer Center [16]. This is a 1 MW installation providing 4-hour backup (compared to 15 minutes for the previous lead-acid system), with over 12,000 200-Ah prismatic cells. UEP also has several smaller installations in the grid and microgrid arena. It built a solar/grid-tied system in India with 6 kW delivery that is compatible with existing inverter and battery management system (BMS) technology used for lithium-ion systems [16]. In partnership with New Mexico State University and Sandia National Laboratories (Sandia), UEP has implemented prototype outdoor systems that feature direct DC pairing of batteries and solar panels using low-cost (<\$50) electronics, and that can withstand the large temperature variations characteristic of the New Mexico climate (-20°C to 40°C) [16].



Figure 4. UEP Zn–MnO₂ battery system tied to 400 W wind generator and 1770 W photovoltaic array, to be deployed in the Navajo Nation [26, 27]

As another demonstration project, UEP is collaborating with Sandia and the Navajo Tribal Utility Authority to deploy three Zn–MnO₂ battery banks at remote off-grid houses on the Navajo Nation in the Southwestern United States, intended to replace traditional lead-acid technology [26]. Each system will be 2.5 kWh with 10-hour runtime, tied to a 400 W wind generator and 1770 W photovoltaic array (Figure 4). Finally, UEP has a 200 kW/800 kWh grid-tied demonstration system in the basement of Steinman Hall on the City College of New York (CCNY) campus [28]. This system was built in 2013 and supports peak load management and demand response for the building.

NantEnergy (formerly Fluidic Energy) is currently the only company selling rechargeable Zn–air systems for the electric grid market, in addition to supplying backup power for businesses and telecom networks. Founded in 2007 and based in Scottsdale, Arizona, NantEnergy’s technology was still fairly limited in energy density as of February 2017 at 35 Wh/kg [29], but the company announced in September 2018 that it had reached the manufacturing cost threshold of \$100/kWh [30]. As of December 2019, NantEnergy had deployed over 120 microgrids in remote communities in Indonesia (Figure 5), Madagascar, various countries in Central America, and the United States that are powered solely by solar panels coupled with its Zn–air or hybrid Zn–air/Li–ion energy storage system [31]. NantEnergy’s current Generation 8 technology has a system voltage of 48 V_{DC}, four modules per system with 10 Zn–air cells per module, nameplate capacity of 30 kWh with no depth of discharge (DoD) limitations, and peak power of 2.6 kW. It is rated to withstand environmental temperatures of -20°C to 50°C with a service life of 3 years before intervention [32].



Figure 5. One of NantEnergy’s remote microgrid installations in Indonesia [33]

NantEnergy’s notable installations in the United States include a solar microgrid for a communications tower in Great Smoky Mountains National Park, installed in Spring 2017 in collaboration with Duke Energy, an electric power holding company based in Charlotte, North Carolina. The 10 kW solar array is coupled with a 95 kWh Zn–air battery system and enabled removal of a transmission line through the forest [34]. A larger, more recent microgrid installation at eight California car dealerships was unveiled in September 2019 in collaboration with MBL Energy, a commercial solar energy installer based in San Jose, California. In total, it consists of 1.555 MW of photovoltaics paired with 567 kWh of NantEnergy’s behind-the-meter battery storage [35].

2.2. Challenges

2.2.1. Anode Issues

Despite their safer nature and potentially competitive energy density and cost, rechargeable alkaline zinc systems have not penetrated deeply into the grid storage market. This largely stems from the inherently poor reversibility of the zinc anode in alkaline electrolytes. The performance-limiting issues of zinc are illustrated in Figure 6 and are summarized in the following sections. For more in-depth coverage of these phenomena and mitigatory strategies, see to the many review papers on alkaline zinc electrodes in scientific journals [10, 17, 23, 36-40]

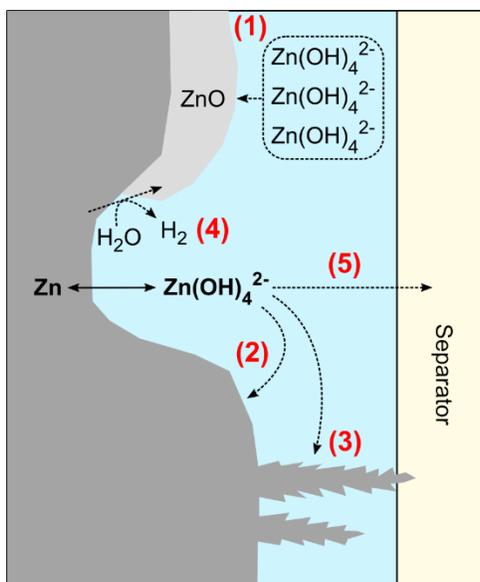


Figure 6. Schematic diagram illustrating fundamental performance-limiting issues with the zinc electrode in alkaline electrolytes: (1) passivation, (2) shape change or redistribution of active material, (3) dendrite formation, (4) hydrogen evolution or corrosion, and (5) crossover of zincate to the cathode.

Passivation. During discharge, the zinc electrode undergoes oxidation. However, when metallic zinc is oxidized in a strongly alkaline solution, it does not directly turn into zinc oxide (ZnO), but dissolves in the solution as the zincate ion $[\text{Zn}(\text{OH})_4]^{2-}$. This means that if more than a small fraction of the zinc electrode's theoretical capacity is accessed during discharge, enough material can dissolve to locally supersaturate the electrolyte with zincate. As a result, ZnO precipitates out of solution and forms a layer on the electrode surface that is insulating and hinders movement of ions to the underlying Zn metal, which in turn lowers the achievable power and discharge capacity of the system. This passivation phenomenon is exacerbated in commercially relevant systems that use very limited amounts of electrolyte (≤ 2 mL per mL of anode volume) due to the more rapid saturation and depletion of hydroxide ions [39].

Shape Change. Shape change refers to the spatial redistribution of zinc material over repeated cycling. This occurs due to the mobility of zincate ions in the electrolyte combined with uneven current distribution over the electrode. Over time, this leads to accumulation of zinc in certain regions of the electrode, causing irreversible reduction in active material surface area and achievable capacity. In addition, during discharge, the electrolyte near the anode surface can become more concentrated with zincate than the bulk electrolyte. This makes shape change worse

in batteries with vertically arranged electrodes, because the higher zincate concentration near the electrode increases the local density of the electrolyte, resulting in a net downward flow and gradual movement of zinc material toward the bottom of the electrode [41, 42].

Dendrite Formation. During charge, zincate is electrochemically reduced back to metallic zinc, which deposits on the electrode surface. The deposited zinc crystals can have many different shapes with different feature sizes and surface areas, depending on factors such as the applied current, voltage, current collector, temperature, and electrolyte concentration. As in lithium-ion batteries, dendrites (branched tree-like structures with sharp tips) are one possible shape of deposited zinc, and are of concern because their growth, if unimpeded, can result in penetration of the battery separator and short-circuit failure of the battery. While there is no single system parameter that triggers dendrite growth, the risk is greater at high, prolonged current densities and higher concentrations of KOH.

Hydrogen Evolution. Zinc metal corrodes spontaneously in strong base, consuming water and generating ZnO and hydrogen gas (H₂). This results in self-discharge of the cell at rest. In addition, H₂ generation competes with Zn deposition during charge, reducing cycle efficiency, increasing internal pressure, and depleting water. Depleting water, in turn, creates local concentration gradients of hydroxide ions and increases cell resistance. Indium, bismuth, and, historically, lead are common additives to battery-grade zinc, typically in sub-1% amounts, that can help to mitigate hydrogen generation [43].

2.2.2. Cathode Issues

2.2.2.1. MnO₂ Cathodes

In addition to the problems of Zn anodes in alkaline environments, the use of MnO₂ as the cathode material poses its own challenges to rechargeability. In a complete discharge, MnO₂ is electrochemically reduced in a two-step process, each step involving one electron per unit of MnO₂ for a theoretical delivered capacity of 308 mAh per gram of MnO₂. In the first-electron process, a proton inserts into the characteristic tunneled crystal structure of EMD, which formally transforms to manganese(III) oxyhydroxide, MnOOH, as Mn is reduced from the +4 to the +3 oxidation state. This process generates significant volume expansion of the crystal lattice that can lead to structural degradation (EMD crystal fracture) and release of soluble Mn³⁺ before complete first-electron reduction.

In the second-electron reaction, where Mn is reduced from the +3 to the +2 oxidation state, Mn³⁺ ions from the MnOOH dissolve into the electrolyte, where they are reduced and re-deposited back onto the electrode as manganese(II) hydroxide, Mn(OH)₂. However, this process simultaneously generates compounds such as hausmannite (Mn₃O₄) and hetaerolite (ZnMn₂O₄), which are electrochemically inactive and insulating, resulting in permanent loss of capacity and conductivity. Hetaerolite forms due to the presence of zincate ions, which are originally generated at the anode but can pass unimpeded through most commercial battery separator materials. The effect of these electrochemically inactive Mn₃O₄ and ZnMn₂O₄ compounds is severe enough that commercial disposable alkaline batteries, which have high active material loadings, cannot even access the second-electron capacity, and are effectively limited to the first electron capacity [15]. A less significant source of capacity loss in the second-electron process is that Mn³⁺ can dissolve and migrate from the electrode where it can no longer participate in electrochemical reactions.

These issues of crystal fracture and Mn^{3+} dissolution can be avoided by restricting the battery cycling protocol to 20% of the first-electron capacity of MnO_2 , which allows it to last 1,000 cycles or more, but this limits the energy density to levels that are not competitive in the long run for grid storage [44].

2.2.2.2. Air Cathodes

For Zn–air batteries, while the air electrode may be simple in principle, it is difficult, in practice, to design for long-term rechargeability. Perhaps the biggest engineering challenge is to find an oxygen reaction catalyst that is stable over repeated charge/discharge in the strong alkaline environment, as well as bifunctional—able to promote both the oxygen reduction reaction (ORR, Eq. 8, which occurs on discharge) and the oxygen evolution reaction (OER, the reverse of Eq. 8, which occurs on charge) effectively. Furthermore, the catalyst must be selective in the sense of maximizing yield of the desired reaction products and minimizing or mitigating the effects of undesirable byproducts such as peroxide radicals and carbonates. Traditionally, precious metals such as platinum and iridium, or their oxides have worked well toward these ends, but their high price and low abundance make them undesirable for large-scale application. One possible strategy is to introduce separate electrodes for the ORR and OER, but this requires a more complex cell design with increased weight and volume [36]. As a result, there is ongoing research into earth-abundant transition metal (cobalt, nickel, manganese) oxides or sulfides, doped porous carbon materials, and semiconducting polymers as alternatives [45].

Another challenge is to engineer the GDL and its interfacial properties with both the catalyst and electrolyte to maximize performance. The GDL must be thin, porous, and hydrophobic to facilitate air transport and to suppress electrolyte evaporation and flooding. It also must be robust enough to provide long-term support to the catalyst in the alkaline environment and highly conductive to provide a pathway for current. At the same time, the catalyst must be relatively hydrophilic—enough to maximize catalytic activity, but not so much that the active sites are flooded—while maintaining good adhesion and a conductive pathway to the GDL.

2.2.3. Electrolyte Issues

In general, alkaline zinc batteries use an electrolyte of 20–45% KOH by weight, although the exact electrolyte formulation is a balance of several competing factors. The conductivity of KOH solutions reaches a maximum between 25 and 30 wt. %, while the kinetics of zinc oxidation and reduction are maximized between ~25 and 35 wt. % KOH. At the same time, with higher KOH concentrations, electrodes are reported to deliver higher specific capacities, but the solubility of ZnO also increases, exacerbating shape change. Thus, researchers have sought numerous additives for KOH solutions that provide good conductivity, limit zinc dissolution, and promote formation of more compact zinc deposits (as opposed to dendrites).

A more general shortcoming of batteries with water-based electrolytes is that while they are more attractive from safety and cost standpoints, they tend to have limited voltage range compared to lithium-ion batteries with organic electrolytes. This, in turn, can limit the energy density of zinc batteries despite the higher specific capacity of their electrode materials. For example, the nominal voltage of a lithium cobalt oxide (LCO) battery is 3.6 V, compared to 1.65 V for a Zn–Ni or Zn–air battery, and 1.5 V for a Zn– MnO_2 battery. This means that even if a zinc battery can cycle at its full capacity, the areal capacity of each electrode must be at least 20–30 mAh/cm² (compared to 1–5 mA/cm² for an LCO battery) to be competitive with lithium-ion on a specific energy basis.

This requires high loadings of active material in the electrodes that exacerbate the performance-limiting phenomena described earlier.

2.2.4. Safety Concerns

Alkaline zinc batteries are generally described as safe and non-hazardous. The materials are non-flammable without the risk of thermal runaway. In addition, they are relatively benign from an environmental standpoint, being recyclable and posing little health hazard from exposure other than the corrosive nature of the electrolyte. However, there are few safety or abuse studies of large-format zinc batteries published.

One obvious concern is the buildup of potentially explosive hydrogen gas, owing to the spontaneous corrosion of zinc but exacerbated by overcharge. This requires pressure relief devices in each cell, adequate ventilation of the room containing the battery system, and gas monitoring apparatus. Also, metallic zinc with small particle size and high surface area can oxidize rapidly and ignite upon exposure to air when damp, possibly posing a hazard in the event of overcharge.

Additionally, despite being well-established, there are currently few safety standards specific to zinc battery systems [46]. However, Underwriters Laboratories (UL), a global safety certification company, and the National Fire Protection Association (NFPA) have several standards that could apply to zinc systems. UL 2054 (Household and Commercial Batteries) covers batteries powering household products, including small-format alkaline cells. UL 1989 (Standby Batteries) references some lead-acid replacement technologies such as Zn–Ni and provides testing protocols for pressure relief, flammability, over-charge/discharge, and physical shock. UL 1973 (Batteries for Use in Stationary, Vehicle Auxiliary Power and Light Electric Rail [LER] Applications) does not specifically mention zinc chemistries but suggests ways to introduce and investigate failures at the single-cell level in non-lithium-ion systems. Other standards relevant to grid-level energy storage systems are: UL 9540 (Energy Storage Systems and Equipment), UL 9540A (Test Method for Evaluating Thermal Runaway Fire Propagation in Battery Energy Storage Systems), and NFPA 855 (Standard for the Installation of Stationary Energy Storage Systems), although none of these specifically discuss zinc. Thus, the general advice is to use whatever codes and standards apply to the final product or application for the zinc battery rather than the specific chemistry.

2.3. Opportunities/Emerging Technologies

This section is limited to performance-improving strategies for zinc batteries that are being pursued by companies involved in the grid storage market, along with their collaborators. For a more comprehensive treatment of approaches to mitigate problems in zinc batteries, refer to the review papers previously mentioned [10, 17, 23, 36-40]

Urban Electric Power's current technology is based on a limited-DoD strategy to achieve long cycle life (>300) in its commercial alkaline Zn–MnO₂ batteries [25]. In this approach, the electrodes are “over-built” such that only a small fraction of the theoretical capacity of each electrode ($\leq 20\%$ of the first-electron capacity of MnO₂ and $\leq 9\%$ of the total Zn capacity) is accessed in each half-cycle. These levels of utilization are low enough to prevent or minimize crystalline fracture and subsequent detrimental Mn³⁺ solubilization at the cathode, and to minimize or slow down shape change and passivation at the anode, thereby extending electrode and battery lifetime [44]. Thanks to the low cost of the raw materials, this has enabled pilot scale manufacturing of systems with delivered cell energy densities of ~100 Wh/L at \$300/kWh, again with estimated costs of \$200/kWh when manufactured at larger scales of 200 MWh per year.

However, to lower costs and increase energy density further to be competitive with Li-ion, the DoD must be improved without sacrificing cycle life. Also, as previously mentioned, because of the low operating voltage of Zn–MnO₂ compared to Li-ion chemistries, active material loading must be high for Zn–MnO₂ to be competitive (on the order of 15–30 mAh/cm² of electrode).

Toward this end, several breakthroughs in Zn–MnO₂ battery technology have been reported in the academic literature in the past three years, as follows. In 2017, Yadav *et al.* demonstrated a MnO₂ cathode featuring metallic copper and bismuth oxide (Bi₂O₃) additives, which enabled reversible cycling at or near the full capacity of MnO₂ (617 mAh/g) versus a NiOOH anode for 1,000–3,000 cycles, with a high areal capacity of 21–29 mAh/cm² [47]. The authors reported that, at least in the first five cycles, the MnO₂ was stabilized by conversion of the original EMD material after the first cycle into a layered structure where copper ions could insert reversibly. The authors also tested the modified cathode with a standard Zn anode in a large-format prismatic cell, and while this resulted in modest energy losses relative to using the NiOOH anode, the cell still delivered ~120 Wh/L for 90 cycles [47]. By introducing a thin membrane (~250 μm thick) of calcium hydroxide [Ca(OH)₂] between the electrodes, cells delivered >80% of the full MnO₂ capacity for 900 cycles, although at a slight cost of energy density due to lowering the zinc utilization from 15% to 8% [48]. UEP is currently seeking to scale up and commercialize this improved cathode formulation with cell energy densities of ~175 Wh/L and full scale production targets of \$50/kWh, which would enable competition with lead-acid systems [27].

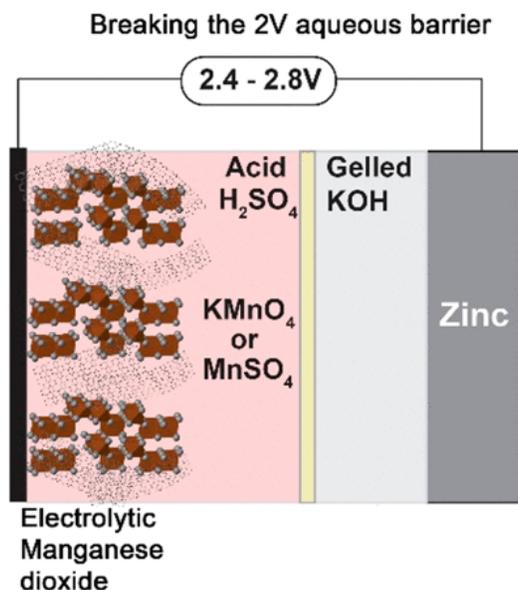


Figure 7. Schematic diagram illustrating high-voltage Zn–MnO₂ battery with dual electrolyte [15]

In late 2019, Yadav *et al.* introduced a strategy for aqueous Zn–MnO₂ batteries to reach voltages as high as 2.8 V while cycling reversibly at the theoretical first-electron capacity of MnO₂ (308 mAh per gram of MnO₂ in the cathode) [15]. This is twice the voltage of conventional alkaline batteries and could enable Zn–MnO₂ to compete more effectively on a specific energy basis with lithium-ion batteries, which have lower specific capacity but operating voltages of 3–4.5 V. These results were achieved using a special cell with individual cathode and anode compartments, where the cathode compartment is filled with an acidic electrolyte (based on sulfuric acid with potassium permanganate or manganese sulfate) and the anode compartment is filled with KOH electrolyte in a gelled form (Figure 8). No other unconventional separator materials or electrode additives are

required. UEP is evaluating this system as its long-term product goal with projected cost of \$20/kWh at scale and allowing entry into the e-mobility market [16].

Besides UEP, several other companies are investigating next-generation zinc battery technologies toward grid storage applications but have not yet brought products to the market. These companies (not including those developing zinc flow battery technologies, which are highlighted in Chapter 6, Redox Flow Batteries) and their innovations are profiled next.

e-Zn, a Canadian company founded in 2012, is built around a “zinc reactor” cell with KOH electrolyte and separate sections for charging and discharging (Figure 9) [49]. When the system is charged, zinc metal deposits on the electrodes in the charging section at the top of the cell and is then mechanically wiped off to fall into the discharge section at the bottom. During discharge, the zinc is dissolved at electrodes in the discharge section and pumped back to the top of the charging section. Despite the relatively high cost of the power components (\$1,000–\$1,500/kW), e-Zn claims that its technology can operate at \$30/kWh due to its scalable runtime, low-cost active materials, high energy density, and lack of capacity fade [49].

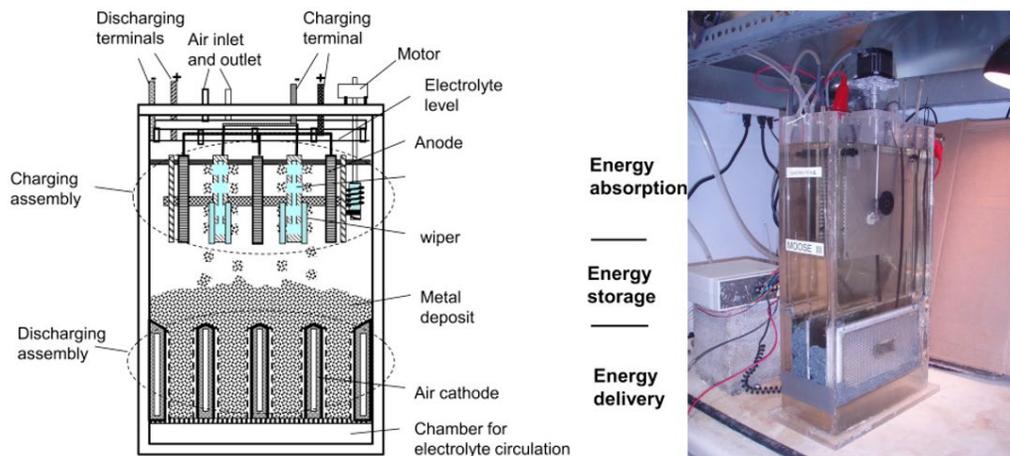


Figure 8. Schematic diagram (left) and photograph of a prototype (right) of the “zinc reactor” electrochemical cell introduced by e-Zn [49]

EnZinc is an American company founded in 2009, developing three-dimensional porous “zinc sponge” materials for anodes in Zn–Ni batteries (Figure 9). This technology was pioneered at the US Naval Research Laboratory and is based on the principles that an interconnected, continuous network of zinc can enable more uniform current distribution over the electrode, suppressing formation of dendrites upon charge; and that confining zinc oxidation to small pores upon discharge can suppress long-term redistribution or loss of active material [19, 20, 50, 51]. While the company is currently targeting the e-mobility market, it is also exploring stationary applications, having been granted an exclusive license to commercialize this technology for microgrids in addition to electric vehicles [52]. Proof-of-concept studies showed that the zinc sponge material could achieve over 100 high-rate cycles (1.5 hour discharge) at nominally 40% DoD as a coin cell, putting its specific energy on par with lithium-ion, but no larger-format systems have yet been reported publicly [19].

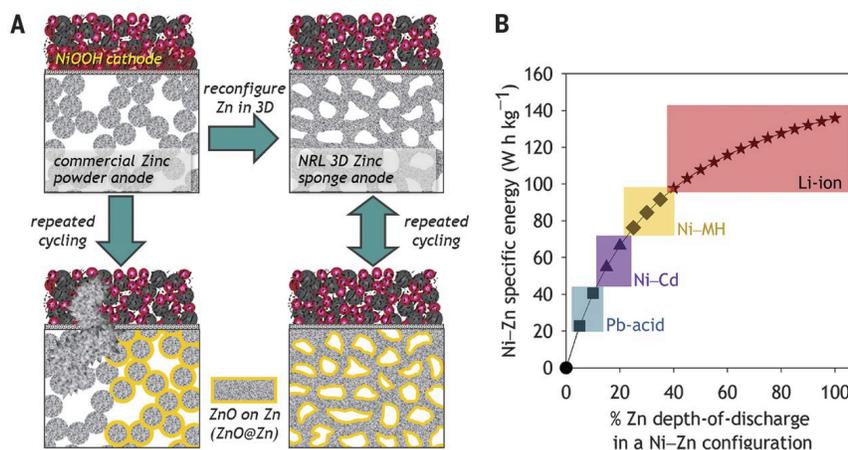


Figure 9. (a) Schematic diagram illustrating 3D zinc sponge electrode technology originally developed at US Naval Research Laboratory and being commercialized by EnZinc. (b) Plot showing energy density capability of the 3D zinc–nickel system, as determined by Zn DoD, compared to various common battery chemistries [19].

Cumulus Energy, a British company established in 2012, has reported a copper/zinc battery technology that can achieve a levelized cost of energy of £120/MWh—the equivalent of pumped hydro. The key characteristic of Cumulus’s system is the addition of a semipermeable membrane between the copper and zinc electrodes preventing the respective ions from migrating to the opposite electrode, enabling rechargeability [53]. Cumulus reports that its technology has a 30-year lifetime with 80% round-trip efficiency and 98% recyclability at end-of-life, but has not yet announced any completed systems other than a 20 kWh prototype [54].

Ionic Materials, an American company founded in 2011, has developed a non-flammable solid-state polymeric electrolyte with high ionic conductivity at room temperature comparable to conventional liquid electrolytes [55]. Initially seeking to replace conventional flammable organic electrolytes for lithium-ion batteries, Ionic Materials has more recently been investing in solid electrolytes for alkaline zinc batteries, which could improve rechargeability and performance at different temperatures [56]. While the company has target markets in grid storage in addition to electric vehicles and consumer electronics, its strategy is to license out its engineering to existing battery companies rather than manufacture its own battery systems [57].

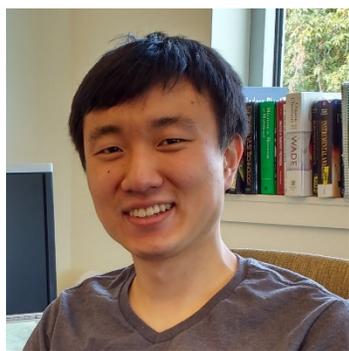
3. Concluding Remarks

To be successful for grid storage, batteries must not only have high energy density and cycle life, but also be safe and inexpensive. Alkaline zinc batteries have theoretical energy densities on par or higher than commercial Li-ion technology, along with safer, more environmentally friendly and low-cost components with a well-established supply chain, which should enable scalable production well under \$100/kWh. Unfortunately, achieving such high energy densities and low costs requires using a large fraction of each electrode’s capacity during operation, which severely limits rechargeability and currently limits zinc’s competitiveness. Anodes degrade due to the solubility and mobility of zinc in the strongly alkaline electrolyte. On the cathode side, MnO₂ exhibits structural breakdown and formation of inactive compounds on discharge, while air cathodes present their own difficulties of bifunctional catalysts and interfacial engineering to optimize performance.

Mitigating or avoiding these problems is a major challenge. A variety of possible solutions—using modified electrode architectures, electrode or electrolyte additives, special separator materials, or nontraditional cycling protocols—are already in the academic literature but have not been realized commercially. Currently, the industry for large-format rechargeable zinc batteries is still quite small, with most players limited to the backup power market and only two companies (Urban Electric Power and NantEnergy) that have developed and deployed marketable products for the electric grid. However, these companies have yet to gain a foothold over the better-established lithium-ion, sodium-ion, and lead-acid technologies.

Future research should focus on improvements to existing zinc technology that are cost-effective and scalable. Most reports so far have been on lab-scale cells with a few ampere hours (Ah) of capacity or less and lack critical analysis of system cost. In addition, many of these reports also use impractical cell designs (such as cells with huge excesses of electrolyte relative to electrode size, often loaded with soluble active species, such as zincate, that go unaccounted for when determining the DoD or specific capacity metrics) and/or very slow charge/discharge rates that are unrealistic for grid storage. These proposed improvements should be re-validated under more commercially relevant conditions. As previously mentioned, limiting the amount of electrolyte can introduce additional problems, such as more severe passivation of the anode, which must be considered as well.

Finally, further studies are needed concerning the safety of large-scale zinc battery systems. The general perception (and common selling point) of aqueous batteries is that they pose no risk of flammability and thermal runaway, but this must be verified at scale. Zinc corrosion occurs spontaneously in alkaline electrolytes and produces potentially explosive hydrogen gas, requiring adequate venting and monitoring mechanisms. Furthermore, metallic zinc particles can oxidize rapidly and ignite upon exposure to air when damp. While there are few to no safety standards specific to zinc batteries, researchers should apply existing safety test protocols from the various UL and NFPA standards for stationary systems, outlined in Section 2.2.4. That said, the use of water-based electrolytes and less toxic materials gives zinc batteries an inherent advantage over lithium-ion systems.



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