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McLean, VA

Water-Based Textile Batteries

Author: Nicholas S. Hudak, Ph.D.

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Abstract

Aqueous battery chemistries and materials are critical for water-compatible, smart textiles. Much of the previous research on textile batteries has focused on lithium-ion battery (LIB) chemistries, but these are extremely sensitive to air and water. There are several water-based battery chemistries, both non-rechargeable and rechargeable, that could be successfully used in textile batteries without concern for air or water exposure. These include aqueous lithium-ion batteries, zinc-carbon batteries, alkaline batteries, zinc-ion batteries, and aqueous metal-air batteries. Herein, these batteries are discussed in detail, and recent examples of flexible or textile-based prototypes are given.

Executive Summary

Aqueous battery chemistries and materials are critical for water-compatible, smart textiles. Much of the previous research on textile batteries has focused on lithium-ion battery (LIB) chemistries, but these are extremely sensitive to air and water. There are several water-based battery chemistries, both non-rechargeable and rechargeable, that could be successfully used in textile batteries without concern for air or water exposure. The use of water-based chemistries for textile batteries would enable smart fabrics with battery components that can be protected and preserved after repeated uses and washing.

Wearable electronic devices (AKA wearable “smart” devices) are a rapidly growing consumer market and are relevant for military and civilian applications. For example, wearable physiological sensors could improve situational awareness for dismounted warfighters and healthcare outcomes for patients that require continuous monitoring. Smart textiles are a subset of wearable electronic devices with the advantages of flexibility and potential for integration into clothing. This provides enhanced mobility for the wearer/user and the ability to conceal the electronic device in clothing. Further integration can be achieved by developing a power source that is also part of the fabric. The power source(s) could include an energy harvester, such as a photovoltaic or thermoelectric, and an energy storage device, such as a supercapacitor or battery.

The main challenges with integrating lithium-ion batteries into smart textiles and clothing are the sensitivity to air and water and the danger of flammable solvents required for their operation. Increased attention should be placed on battery chemistries that are compatible with air and water. Table 1 in the Conclusion section gives examples of flexible and textile battery prototypes with aqueous chemistries. Also given are the performance metrics in terms of area-specific capacity and energy and the main disadvantage of each type of battery.

Distinct from conventional lithium-ion batteries, aqueous lithium-ion batteries can operate effectively while being exposed to air and water. However, this approach has produced the lowest area-specific capacity amongst flexible battery types discussed here. Amongst zinc-based batteries, zinc-carbon batteries exhibit the lowest capacity and energy. This is not surprising given that commercial zinc-carbon batteries possess lower specific capacity and energy relative to other zinc batteries. The non-rechargeable, fabric-based alkaline Zn-MnO₂ battery (derived from commercial alkaline battery components) offers higher relative capacity and energy, but it contains caustic potassium hydroxide solution within its hydrogel electrolyte. Zinc-ion batteries, which operate with neutral-pH aqueous electrolytes, offer the advantages of rechargeability and safer electrolyte. Some recent examples of flexible and textile-based zinc-ion batteries show great potential for this battery chemistry to be applied effectively in textiles.

Aqueous metal-air battery chemistries may offer the highest capacity and energy per unit area, although there have been far fewer examples of flexible or textile prototypes. Further work should explore methods for fabricating such prototypes, including the optimization and incorporation of low-cost cathode catalysts. While aluminum-air textile batteries could offer the highest area-specific capacity, this battery chemistry has historically shown the most challenges with rechargeability. Nonetheless, it may be ideal for applications requiring only primary (non-rechargeable) energy storage. Zinc-air textile batteries may offer the greatest compromise for achieving high area-specific energy along with rechargeability.

Amongst the various battery chemistries that have been used for aqueous flexible and textile batteries, one commonality is the use of hydrogel-based electrolytes. The use of a gel makes the most sense for such batteries because it affords the dual benefits of a leak-free design with high

conductivity and reaction kinetics. Further studies of aqueous textile batteries should place the focus on the robustness of the hydrogel electrolyte and whether the battery can still operate after being soaked or vigorously washed in water and other solutions. Development and testing of the gel or polymer electrolyte should be a major focus of the next phase of research into textile batteries.

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1 Introduction

This report covers aqueous battery chemistries and materials that could be used for water-compatible, smart textiles. Much of the previous research on textile batteries has focused on lithium-ion battery (LIB) chemistries, but these are extremely sensitive to air and water. This introduces several challenges that are unique to textile-based applications, such as the appropriate barrier materials to be used and whether the battery components can be protected and preserved after repeated uses and washing. Despite the inclination to focus on high-capacity and high-energy lithium-based chemistries, there are several water-based battery chemistries that could be successfully used in textile batteries and for which proof-of-concept demonstrations have begun to emerge.

The intended audience for this report comprises developers of wearable electronics devices and smart textiles/fabrics. Such developers may benefit from in-depth knowledge of battery technologies, the challenges associated with integrating them into wearables or smart textiles, and potential solutions to these challenges. The goal of this introduction is to describe applications and state-of-the-art performance of textile energy storage devices, including supercapacitors and batteries. Section 1.3 describes the challenges unique to textile batteries, which may be solved by using water-compatible battery chemistries.

1.1 Textile Energy Storage Devices

Wearable electronic devices (AKA wearable “smart” devices) are a rapidly growing consumer market and are relevant for military and civilian applications. Smart eyewear and wristwatches have been the first types of wearables to emerge in the consumer market. Such devices are made of rigid components and can be designed by miniaturizing conventional electronic devices. Electronic devices based on textiles (known as smart fabrics, smart textiles, or e-textiles) are an emerging type of wearable device, largely still in the research and development stage. The advantages of smart textiles over other types of wearable devices are their flexibility and their ability to be integrated into clothing. This provides enhanced mobility for the wearer/user and the ability to conceal the electronic device in clothing. Further integration can be achieved by developing a power source that is also part of the fabric. The power source(s) could include an energy harvester, such as a photovoltaic or thermoelectric, and an energy storage device, such as a supercapacitor or battery [1].

The uniform of the dismounted warfighter is an example of a military application for textile-based electronic devices and power sources [2], [3]. Wearable sensors can enhance situational awareness by monitoring physiological status and environmental conditions. Integration of the power source into the warfighter’s uniform would reduce weight, increase maneuverability, and reduce sensor detectability. U.S. Army Natick Research, Development, and Engineering Center developed a screen-printed textile supercapacitor to power such sensors [3]. Wearable sensors for physiological conditions are also relevant for healthcare applications in general. Such sensors can be used to monitor body temperature, breathing patterns, cardiac activity, muscle activity, blood oxygen level, body movement, and chemical composition [4]. The transformation of such sensors into smart textiles is mostly in the research stage. However, as products enter the market, there will be increased demand for corresponding textile power sources.

As for the consumer market, Lenovo developed a “SmartVest” that contains an embedded electrocardiogram monitor consisting of 12 electrodes [5]. Levi’s and Google developed a smart

jacket with embedded wires that allows the user to interface with a smartphone via swiping on the sleeve [6]. There are also non-wearable applications for textile supercapacitors and batteries, for example tents, sails, and radiofrequency identification tags. Furthermore, organic electronics such as transistors [7] and non-volatile memory devices [8] have been embedded in banknotes for anti-counterfeiting purposes. These circuits and devices may require accompanying power sources on the banknote. Such a power source could be a non-rechargeable battery supplying low, intermittent power over a long time or a harvester-battery combination that can be recharged periodically.

1.2 Textile Energy Storage Prototypes and Performance

Most of the research on textile energy storage devices has focused on strategies for combining electrode materials, electrolytes, and fabric components into an operational, rechargeable cell. Hundreds of academic groups have followed this approach with a variety of materials, and six recent review articles provide a comprehensive description of all these efforts [1], [9]–[13]. The designs generally fall into two types of design approaches: (1) the two-dimensional (2D) “top-down” approach, in which off-the-shelf textiles are embedded with active materials and then layered to form the device, or (2) the one-dimensional (1D), “bottom-up” approach, in which all supercapacitor or battery materials are combined into a single yarn or cable [10]–[12]. Performance of the 2D prototypes can be quantified in terms of charge stored per unit area, with the best supercapacitors reaching 11.2 F/cm^2 [10], [14]. This is on par with the best-performing supercapacitors reported in the literature [15], [16] and corresponds to an area-specific energy density of 0.3 mWh/cm^2 . However, this performance was only achieved with the fabric immersed in a concentrated solution of potassium hydroxide, which is a caustic material. The highest reported charge capacity in a 2D textile battery is 3.9 mAh/cm^2 [11], [17], which was a non-rechargeable, alkaline zinc battery. This corresponds to 2.6 mWh/cm^2 energy density. The 9-fold higher energy density in the battery relative to the supercapacitor is typical amongst energy storage devices. For 1D energy storage yarns and cables, there is no standard metric for performance because of their unique and varied geometries. In most cases, they are comprised of distinct anode and cathode yarns, which are either coated or separated by an inactive material. The anode and cathode yarns are placed in parallel, twisted around each other to form a larger yarn, or synthesized together in a coaxial geometry [10], [11], [13]. Ultimately, the goal would be to weave or knit such yarns into a larger fabric, but there has been no significant demonstration or path forward for this approach. Furthermore, the large diameter of the prototypes demonstrated to date (as high as 2 mm) would make it difficult to weave or knit them into a larger fabric.

1.3 Challenges with Textile-Based Lithium-Ion Batteries

Despite the relatively high area-specific capacity demonstrated in an alkaline, Zn-based prototype [17], the focus of most research in textile batteries has been on LIB chemistries [1], [9]–[12]. This is presumably because lithium-based batteries provide the highest amount of charge and energy per unit weight compared to batteries based on other metals. Furthermore, LIBs are rechargeable, with a host of well-characterized materials that can potentially be incorporated into fibers, yarns, and textiles. However, LIBs are highly sensitive to air and water, exposure to which is detrimental to battery performance and safety [13], [18]. Commercial lithium-ion cells and batteries contain metallic packaging and hermetic seals as barriers to air and water. The metallic packaging takes the form of an aluminum pouch, as in prismatic batteries, or a hard-metallic case, as in coin cells or cylindrical batteries. It is unclear how such packaging

could be incorporated in a textile battery without compromising the mechanical properties and breathability of a fabric. In some reports of flexible LIBs, layers of polydimethylsiloxane (a silicone polymer) with thicknesses ranging from 10 μm [19], to 250 μm [20], to 1 mm [21] were coated onto a planar lithium-ion cell to provide a barrier. Although these cells were able to undergo charge-discharge cycling, it is unknown how the permeability of this barrier material, which is much higher than that of metallic barriers, would affect long-term performance. It would also be difficult to fabricate a breathable fabric with such a coating applied to protect all the battery materials.

An additional challenge with LIBs is that they typically contain flammable electrolyte solvents. These pose a safety hazard and thus would have limited utility in batteries that are fully integrated into wearable fabric. Both the packaging and flammability issues underscore a more fundamental challenge with the use of LIBs and textile-integrated power sources. There is no clear technical path forward for an integrated LIB, as one component in a smart textile, to be subjected to repeated washing and drying, even with modern dry-cleaning methods. This is already a challenge for smart textiles in general, evidenced by the Lenovo Smartvest and Levi's smart jacket. The former can only be washed at most 100 times [22] and the latter only 10 times [6] before performance degradation occurs. The "washability" issue is even more of a challenge for textile LIBs because they contain several heat- and water-sensitive chemicals. Indeed the battery that accompanies the Levi's smart jacket must be removed before the jacket can be laundered [6]. Of the six comprehensive review articles on textile energy storage, only Liao et al [13] addressed the issues of safety and washability. None of these reviews described efforts to waterproof textile LIBs or attempts at washing any type of textile battery.

As pointed out recently by Liao et al., the most obvious way to address the challenges of using nonaqueous LIBs as textile-integrated devices is to avoid their use altogether [13]. Increased attention should be placed on battery chemistries that are compatible with air and water. This report covers aqueous battery chemistries and materials that could be used for water-compatible, smart textiles. In each case, there are some examples of these battery chemistries already being demonstrated in flexible and textile-based devices.

2 Aqueous Lithium-Ion Batteries

One way to mitigate the air and water sensitivity and flammability of LIBs is to replace the flammable organic electrolyte solutions with aqueous electrolytes. Dahn and co-workers introduced the concept of an aqueous LIB in 1994 as a safe and cost-effective alternative to conventional lithium-based batteries [23]. They demonstrated that solutions of lithium nitrate and lithium hydroxide dissolved in water could be used effectively to form a rechargeable battery [23], [24]. Transition metal oxides like those in conventional LIBs were used as the active electrode materials. Lithium intercalation was the charge-transfer mechanism at both the positive and negative electrodes [24], so the battery operated in the same manner as conventional LIBs. However, the main disadvantage of these aqueous cells is that the average cell voltage was limited to ~ 1.5 V. Battery charging at voltages significantly higher than this would result in irreversible oxygen and hydrogen evolution at the positive and negative electrodes, respectively. Thus, the specific energy and energy density are one-third to one-half of the energy in conventional LIBs. Indeed, the main advantage of water-free, solvent-based electrolytes is that they withstand voltages greater than 4 V. The inherently lower energy density prevented aqueous LIBs from being heavily researched or commercialized in the years following these initial reports.

Recently, a collaboration between the Army Research Laboratory and the University of Maryland has created a resurgent interest in aqueous LIBs [25]. The researchers demonstrated that an unusually high concentration of lithium salt in water, called “water-in-salt” electrolyte, suppresses both hydrogen evolution and oxygen evolution, allowing the cell to be operated at significantly higher voltages than previously observed [25]. A diagram of the voltage window compared to that of pure water and conventional aqueous lithium-ion electrolytes is shown in Figure 1. In the initial demonstration, a solution of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in water with concentration of 21 moles per kilogram (compared to roughly 1 mole per kilogram in conventional electrolytes) exhibited conductivity of 9.0 mS/cm (comparable to conventional LIB electrolytes) and enabled a ~ 2.3 -volt battery [25]. A subsequent report produced a $\text{LiCoO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ aqueous cell with voltage up to 3.1 V and specific energy of 130 Wh/kg [26], which is roughly half that of state-of-the-art LIBs with non-aqueous electrolytes. He et al. developed non-fluorinated salts for these electrolytes to reduce cost and toxicity [27]. A performance comparison of these and other aqueous LIBs is shown in Figure 2. Lithium-metal [28] and lithium-ion/sulfur [29] versions of these “water-in-salt” batteries have also been demonstrated. Research into this type of battery continues to grow, making it increasingly likely to become a safer alternative to conventional LIBs.

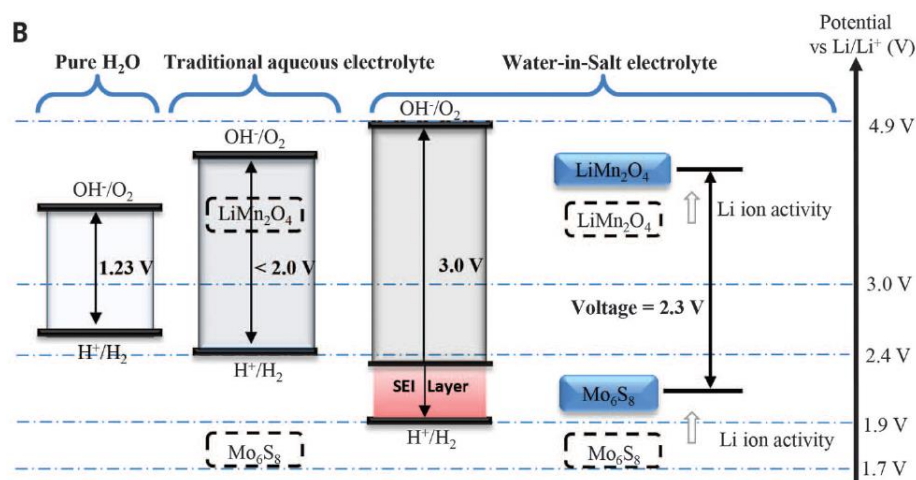


Figure 1. Electrochemical stability window for water-in-salt electrolytes with the modulated redox couples of LiMn_2O_4 cathode and Mo_6S_8 anode resulting from high salt concentration [25].

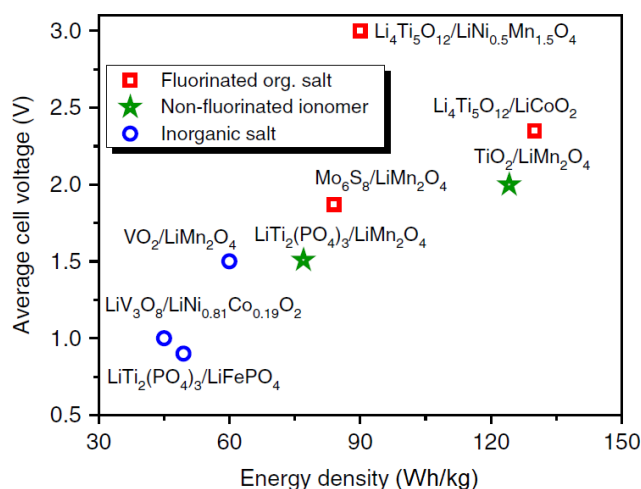


Figure 2. Performance data (cell voltage and specific energy) of aqueous LIBs with various electrochemical couples and electrolyte salts [27]. These values can be compared to 3.7 V and 200-400 Wh/kg for state-of-the-art, non-aqueous LIBs.

Collaborators from the University of Maryland, the Army Research Laboratory, Johns Hopkins University, and the Huazhong University of Science and Technology used the “water-in-salt” electrolyte approach to develop a flexible, gel-based battery with a lithium vanadium fluorophosphate compound as the active material at both electrodes [30]. The gel polymer electrolyte was fabricated by mixing poly(vinyl alcohol) (PVA) with a 25 mol/kg mixture of LiTFSI in water. The use of an aqueous, gel polymer provides a path forward to creating a flexible LIB without the need for the more rigid packaging required by flammable, air-sensitive battery chemistries. The area-specific capacity of the cell was 0.58 mAh/cm^2 (compared to 3.9 mAh/cm^2 , the highest reported value in a textile battery described in Section 1), and it retained 87% of its initial capacity after being charged and discharged for 4,000 cycles. It was also able to maintain good performance following mechanical stresses such as bending and cutting. This contrasts with a conventional, flammable LIB, which experiences catastrophic failure and often

fire or explosion when ruptured. This prototype was intended for flexible electronics applications, but there has been no published approach or strategy to make it into a textile-based device or to incorporate the materials onto fabric.

Recent advances to the gel-based, flexible, aqueous LIB have demonstrated that it can maintain its charged voltage and some of its power output even after being cut, immersed in salt water, and subjected to ballistic impact (Gerasopoulous, Materials Research Society Spring 2019 Meeting). However, both the published article [30] and recent conference presentation appear to have used metallic pouch packaging, as in a conventional LIB cell, which suggests that some type of protective barrier or packaging would be required in a final product. Furthermore, the immersion of the unpackaged cell in saltwater would, over time, result in a dilution of the concentrated lithium salt, thus limiting the effectiveness and very nature of the water-in-salt electrolyte. Thus, it is unclear whether this battery chemistry, even with the electrolyte in gel form, could be effective in textile form and whether the authors intend to make it into a textile. Some type of waterproofing strategy may prevent dilution of the concentrated water-in-salt mixture, but it may also limit the flexibility and breathability of a textile. These complications and the lack of a technical path toward textile integration make it unlikely that aqueous lithium-ion is the best battery chemistry for textiles.

3 Zinc Batteries

Among aqueous batteries, zinc-based battery chemistries are the most common. For example, the ubiquitous “alkaline battery” is based on a zinc anode reaction. Other aqueous zinc battery chemistries are zinc-carbon, zinc-ion, and zinc-air. Although some new non-aqueous zinc chemistries have emerged, commercial zinc batteries are all based on aqueous electrolytes. This is mainly because the zinc metal deposition/stripping reaction is well within the voltage stability window of water.

3.1 Zinc-Carbon Batteries

One of the earliest types of primary (i.e. non-rechargeable) batteries is the zinc-carbon battery, which utilizes zinc metal as the anode and manganese dioxide (MnO_2) as the active cathode material. The chemistry uses an acidic electrolyte solution consisting of ammonium chloride (NH_4Cl), zinc chloride (ZnCl_2), or a combination of both dissolved in water. The “carbon” in the name refers to acetylene black or graphite, which is mixed with the MnO_2 to improve conductivity and retain moisture [18]. Depending on the exact cell composition, the irreversible discharge reaction produces some mixture of MnOOH , ammonia, ZnO , Mn_3O_4 , and other compounds containing Zn and Cl. These batteries are still commercially relevant for some applications requiring low-rate or intermittent heavy-rate discharge. High demand for zinc-carbon batteries still exists in developing countries because of the low cost compared to alkaline Zn- MnO_2 batteries, but they are less common in the developed world [18]. Like their alkaline counterparts, zinc-carbon batteries are often sealed in metallic cans and are commercially available in a variety of cylindrical form factors.

Perhaps because of the lack of rechargeability and inferior energy density (relative to other primary batteries and even some rechargeable batteries), the zinc-carbon chemistry has rarely been considered for flexible and textile batteries. Hiralal et al. demonstrated a flexible zinc-carbon battery that utilized a complex of ZnCl_2 , NH_4Cl , and poly(ethylene oxide) (PEO) as the electrolyte [31]. Several nanomaterials were incorporated to improve performance, and the battery discharge produced an area-specific capacity of 2.6 mAh/cm^2 over a 5-hour discharge with average voltage around 1.2 V. This is a remarkably high capacity compared to most textile batteries and is especially impressive because a solid electrolyte was used without being soaked in water. Yu et al. demonstrated an alternative approach using carbon fibers as the basis for a flexible zinc-carbon battery [32]. To fabricate this cell, carbon fibers were dip-coated with anode or cathode paste and heated to evaporate the solvent. An illustration of the cell configuration is shown in Figure 3. An insulating separator wire was wrapped around the Zn anode wire; anode and cathode wires were placed next to each other in a plastic tube filled with liquid electrolyte. The area-specific capacity of this construct was as high as 1.85 mAh/cm^2 with a discharge voltage around 1.1 V. The diameter of this cable-type battery was not explicitly given, but it is roughly 1 mm, considering that the MnO_2 /carbon diameter is 0.5 mm. Thus, it would be difficult to weave or knit a textile from such a large-diameter battery, but it is possible that further advances could scale this diameter down to a workable fiber. This would result in an advanced approach to fabricating a flexible, aqueous zinc battery.

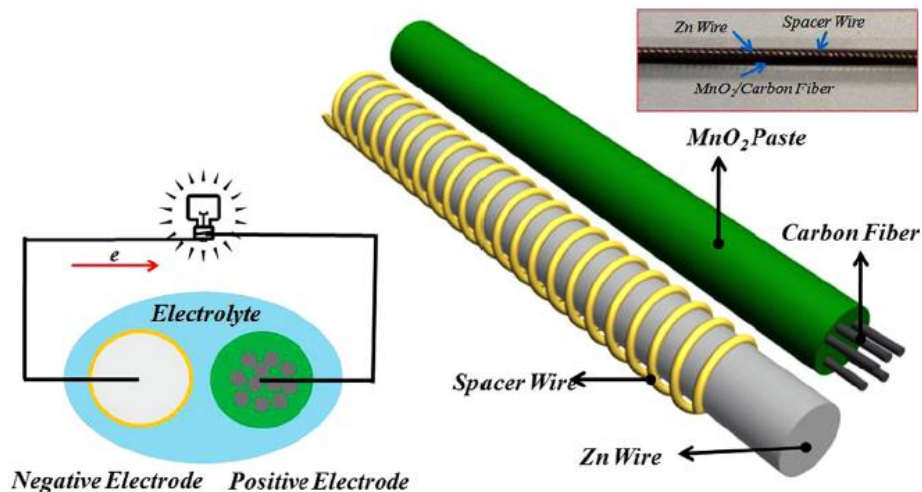


Figure 3. Illustration and photograph of the fiber battery based on Zn wire and MnO₂/carbon fiber [32].

3.2 Alkaline Batteries

The alkaline battery is the predominant primary battery for commercial products in the U.S. and most other developed nations [18]. The common term “alkaline battery” refers to a specific battery chemistry with a zinc metal anode, MnO₂ cathode, and potassium hydroxide (KOH) solution as electrolyte. Although it is slightly more expensive than the zinc-carbon batteries discussed in Section 3.1, its gravimetric and volumetric energy densities are two and three times higher, respectively. These cells produce several discharge products, namely MnOOH and Mn₃O₄ at the cathode and Zn(OH)₂ and ZnO at the anode. Despite the ubiquity and commercial relevance of alkaline batteries, they have not been widely considered for flexible and textile-based applications. This is probably because they are non-rechargeable and have several complicating factors, especially the corrosive nature of the electrolyte and the evolution of hydrogen gas at the anode. The lack of rechargeability of alkaline Zn-MnO₂ is mainly due to the formation of zinc “dendrites” at the anode during plating. During battery charging, zinc metal should ideally form on the anode in a flat, planar geometry. In reality, it deposits with a rough texture. In alkaline electrolyte, it forms spikes, or dendrites, that can propagate through the cell, causing electrical shorts and cell failure.

Despite the apparent reluctance to pursue the alkaline chemistry for textile-based devices, one of the most highly cited and best-performing examples of any type of textile battery is an alkaline cell with conductive fabric as substrate [17]. Gaikwad et al. used dip coating to deposit “MnO₂ ink” and “Zn ink” onto silver-coated nylon fabrics. These fabric electrodes were then combined with a viscous, gel polymer electrolyte composed of poly(acrylic acid) (PAA) and KOH solution. Thus, the battery consisted of all the major components of an alkaline cell in the form of a stretchable fabric. The use of the gel electrolyte is novel in that the liquid is somewhat contained. The authors did not apparently use a crosslinking strategy, which could be used in future versions to confine the liquid electrolyte even more effectively. Diagrams and photographs of the stretchable alkaline battery, including after being stretched to 100% tensile strain, are shown in Figure 4. It produced a capacity of 3.875 mAh/cm² (the highest area-specific capacity observed in a textile, to our knowledge) with a discharge voltage of about 1.3

V. Similar materials and approaches were used to fabricate a flexible alkaline battery [33] and “sponge” alkaline battery [34], both of which exhibited comparable performance to the fabric-based example. Despite the relatively high capacity of these batteries, very little follow-up work has occurred. The corrosive, highly alkaline nature of the electrolyte probably precludes it from being useful in a textile application. It would not be safe to use against human skin and would lose its alkalinity upon washing.

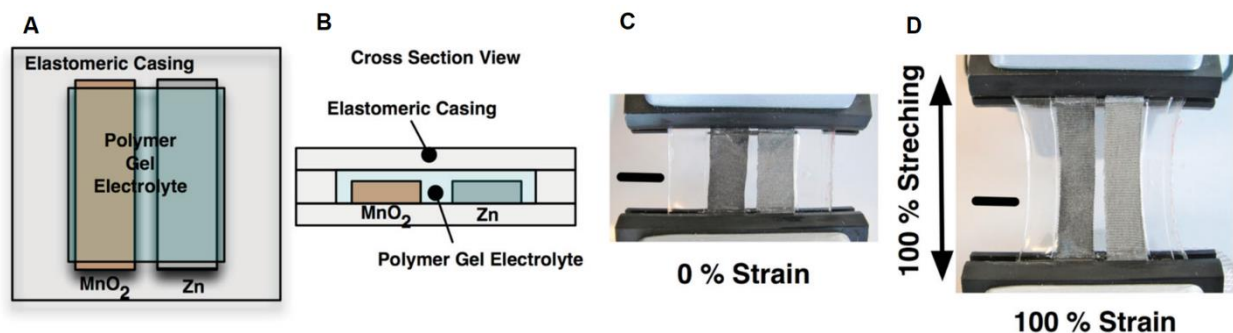


Figure 4. Stretchable alkaline battery on fabric. (a) top-view diagram; (b) cross-section diagram; (c) photograph of battery under no strain and (d) under 100% strain [17].

3.3 Zinc-Ion Batteries

The rechargeable zinc-ion battery (ZIB) evolved from the zinc-carbon and alkaline batteries discussed in Sections 3.1 and 3.2, respectively. This battery has been the subject of intense research efforts over the last decade but has not been commercialized in any form. At least three review articles have covered the high volume of work published in this area [35]–[37]. The ZIB is seen as a safer and lower-cost alternative to the LIB because it is based on an aqueous electrolyte and metallic elements that are more abundant. The main feature of the ZIB is the use of a neutral or near-neutral electrolyte instead of the alkaline electrolyte or the $\text{NH}_4\text{Cl}/\text{ZnCl}_2$ electrolyte of the zinc-carbon battery. Neutral electrolytes not only limit corrosion but also suppress the formation of zinc dendrites, thus enabling rechargeability [35], [38]. The neutral electrolyte is usually an aqueous solution with a zinc salt such as zinc sulfate (ZnSO_4). Thus, another distinguishing factor of this battery chemistry is that the Zn^{2+} ions can shuttle back and forth between anode and cathode during charge and discharge (though this has not been proven to be the charge-discharge mechanism for all ZIB compositions). A diagram of the ZIB chemistry with an $\alpha\text{-MnO}_2$ cathode is shown in Figure 5. In this version of the zinc-ion chemistry, Zn^{2+} ions and water molecules intercalate into the tunnels of the $\alpha\text{-MnO}_2$ structure during battery discharge, and they are removed from the cathode during charge [39].

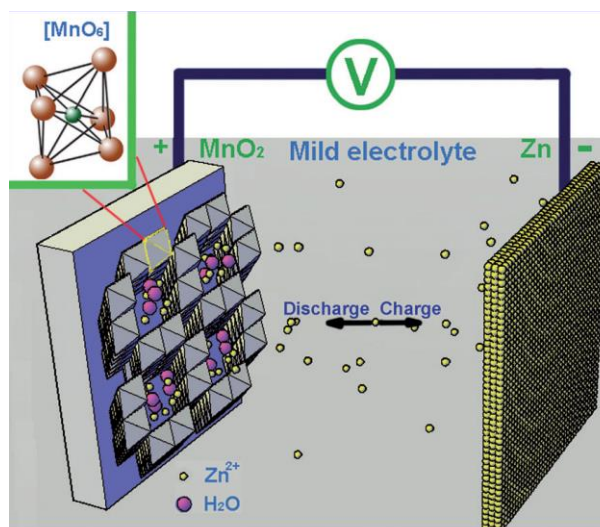


Figure 5. The chemistry of a zinc-ion battery with Zn^{2+} ions migrating between tunnels of an $\alpha\text{-MnO}_2$ cathode and a Zn anode. The inset shows the structural unit of the MnO_6 octahedron in $\alpha\text{-MnO}_2$ [39].

While ZIBs always utilize zinc metal as the anode, the materials used for the cathode vary widely. Active cathode materials can be divided into three general categories: manganese oxides, vanadium compounds, and Prussian blue analogs (hexacyanoferrates) [35]–[37]. The wide array of such materials and their key electrochemical properties (discharge potential and specific capacity) are shown in Figure 6. Manganese oxides have a plethora of polymorphs with similar structures, and they form various compounds during electrochemical reduction and oxidation. This has led to varying observations and explanations of the cathode reaction mechanisms in ZIBs [40]. Experimental reports have shown that the MnO_2 capacity results from reversible Zn^{2+} insertion/extraction, reversible H^+ insertion/extraction, conversion to MnOOH , or a combination of these mechanisms [36]. Regardless of the mechanism, polymorphs such as $\alpha\text{-MnO}_2$ nanoparticles [39], $\alpha\text{-MnO}_2$ nanofibers [41] and nanorods [42], [43], mesoporous $\gamma\text{-MnO}_2$ [44], and highly crystalline ramsdellite [40] have all been used to form cathodes that can undergo reversible charge-discharge cycling in ZIBs. As shown in Figure 6, specific capacities for these compounds range from 100-400 mAh/g, which is 1-4x that of LIB cathode materials. The discharge potential of ZIBs made with these cathodes are 1.2-1.4 volts, which is common for aqueous batteries.

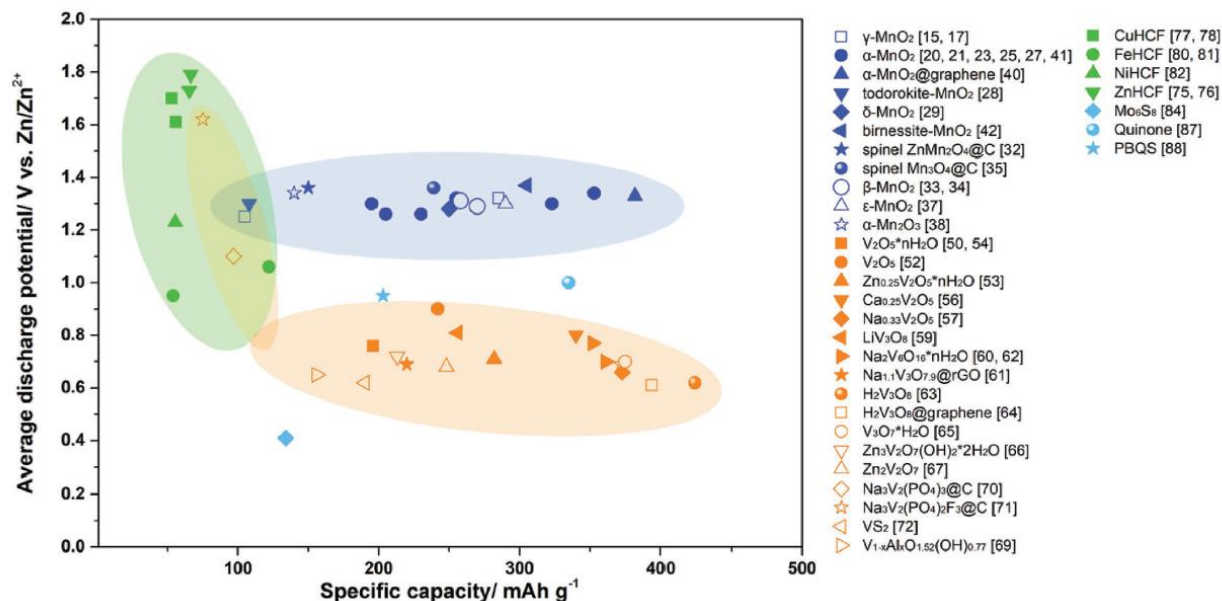


Figure 6. Average discharge potentials and specific capacities of active cathode materials for ZIBs [35].

Vanadium oxides, phosphates, and sulfides have also been widely researched for ZIB cathodes. With these materials, the electrode reaction mechanisms are simpler because Zn^{2+} insertion usually does not take place. Thus, they have longer cycle lives and higher rate performances than Mn-based cathodes [35], [36]. Contrary to previous results, Wan et al. recently demonstrated dual Zn-ion and proton insertion in a sodium vanadium oxide hydrate ($\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$) [45]. This unique cathode chemistry resulted in high specific capacity of 380 mAh/g with 82% capacity retention after 1000 cycles. The main disadvantage of V-based cathodes, as shown in Figure 6, is lower discharge potential, which ranges from 0.6-0.9 V. Conversely, Prussian blue analogues (AKA hexacyanoferrates) exhibit discharge potentials as high as 1.8 V but suffer from low specific capacity and poor cycling performance [35], [37]. Prussian blue analogues were originally explored as enabling cathode materials for novel sodium-ion and potassium-ion batteries, but their structural limitations have prevented any major breakthroughs for ZIBs.

Along with the impressive amount of research on ZIB materials in more conventional prototypes, the chemistry has also been widely used to create flexible batteries, which was comprehensively reviewed by Yu et al. [46]. This includes printed batteries and textile-, fabric-, or fiber-based batteries. Most of the prototypes were based on aqueous gel (AKA hydrogel) electrolytes, which can enable a leakage-free design and eliminate the need for protective packaging or a barrier layer. This contrasts greatly with LIBs, which require “highly reliable protective packaging to avoid the electrolyte leakage and reconcile with the washing need of wearable devices” as pointed out by the review article on flexible ZIBs [46].

One common approach for flexible ZIBs is to form a layer of gel electrolyte and then press a flexible cathode and anode film on either side. For example, Li et al. used $\alpha\text{-MnO}_2$ as the cathode, a combination of gelatin and polyacrylamide swelled with ZnSO_4 solution as the electrolyte, and flexible carbon nanotube paper as current collectors [47]. The prototype achieved an area-specific current and energy of 4.6 mAh/cm² and 6.2 mWh/cm², respectively, and it retained 97% of its initial discharge capacity after 1000 charge-discharge cycles. It was

operable after or while being subjected to abusive tests such as bending, cutting, and soaking in water and aqueous solutions. This performance is on par with the best textile batteries, but the prototype does not contain any fabric components and could not be used in textile applications. A two-dimensional fabric-based approach by Qiu et al. involved the electrodeposition of MnO₂ nanorods (cathode) and zinc nanoparticles (anode) separately on nitrogen-doped carbon cloth electrodes [48]. An illustration of the battery fabrication and chemistry is shown in Figure 7. The electrolyte was a polyvinyl alcohol gel containing LiCl-ZnCl₂-MnSO₄ solution. The prototype achieved an area-specific current and energy of 1.7 mAh/cm² and 2.2 mWh/cm², respectively (calculated from data given), and it retained 93.6% of its initial discharge capacity after 1000 charge-discharge cycles.

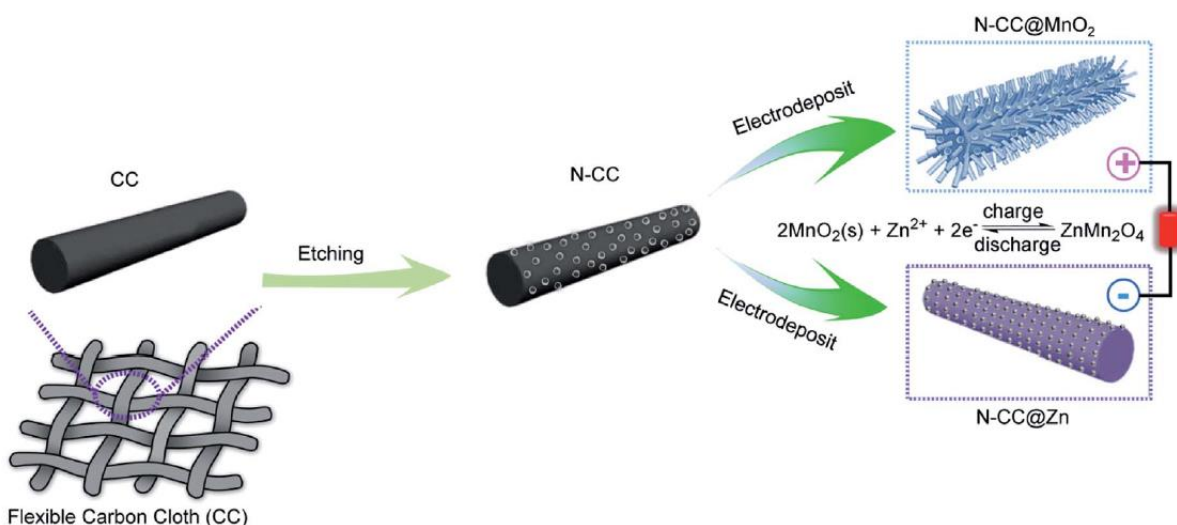


Figure 7. Schematic illustration of a flexible battery based on nitrogen-doped carbon cloth and Zn-MnO₂ chemistry [48].

Researchers at the City University of Hong Kong recently developed novel, aqueous, zinc-ion textile batteries using both the one-dimensional yarn approach [49] and the two-dimensional fabric approach [50]. In the case of the yarn prototype, several innovations were combined to achieve a device that was “quasi-solid-state”, washable, and elastic. The cathode was fabricated by roll-dip-coating carbon nanotube yarn in a paste containing MnO₂ paste (with acetylene black and polytetrafluoroethylene binder). The anode was fabricated by electrodepositing zinc metal onto carbon nanotube yarn. The electrolyte was an aqueous gel (AKA a “hydrogel”) made of crosslinked polyacrylamide (a mechanically tougher alternative to polyvinyl alcohol) soaked in ZnSO₄ solution for up to 72 hours. The yarn battery was assembled by winding the cathode yarn and anode yarn in parallel around an inert elastic fiber and then coating with the gel electrolyte. This assembly was then coated with Eco-flex silicone as a waterproofing strategy. The battery capacity was 302.1 mAh/g relative to the mass of MnO₂. Although this performance metric does not reflect the mass of the entire device, it is a competitive cathode capacity compared to conventional lithium-ion and zinc batteries. In terms of cycling stability 98.5% of this capacity was retained after 500 charge-discharge cycles. Various types of deformation were tested, including bending, knotting, and twisting, and the capacity retention after all of them was greater than 90%. Additionally, the waterproofing was tested by soaking the device in water for 12 hours, after which 96.5% of the capacity was recovered. This is one of few examples of waterproofing performed on any type of textile battery [49].

Zhi and co-workers from City University of Hong Kong also reported an innovative two-dimensional, multifunctional, flexible fabric containing both a triboelectric nanogenerator (a type of energy harvester) and a ZIB [50]. A diagram of the fabrication process and the full, integrated device is shown in Figure 8. The core of the device was an inactive, support fabric onto which active materials were coated, “fixed”, or injected. Fabrication of the battery electrodes was similar to that of the one-dimensional yarns described above except that carbon cloth was used as the substrate instead of the nanotube yarn. The carbon cloths with MnO₂ and Zn were then “fixed” onto the support fabric, and a gel electrolyte made of gelatin and ZnSO₄ solution was injected between the electrodes. From the information given in the publication, the area-specific capacity and energy are estimated to be as high as 0.8 mAh/cm² and 1 mWh/cm², respectively. Upon charge-discharge cycling at a rate of roughly two cycles per hour, the capacity retention was 82.3% of the initial capacity after 500 cycles. This is a promising battery chemistry and fabrication process for a textile-based device, but there are some notable challenges. First, the thickness of the support fabric is 7.5 mm, which is far too large for any practical textile application; it is unclear why the authors did not use a thinner substrate. Second, the gel electrolyte was composed of ZnSO₄, a common component for ZIBs, and a gelatin component about which no details were given. Because the gel electrolyte is critical to the electrochemical and mechanical performance of this type of battery, there must be a more detailed and strategic analysis of the electrolyte fabrication, components, and properties. This should also be combined with a waterproofing strategy and associated testing under exposure to water and aqueous solutions.

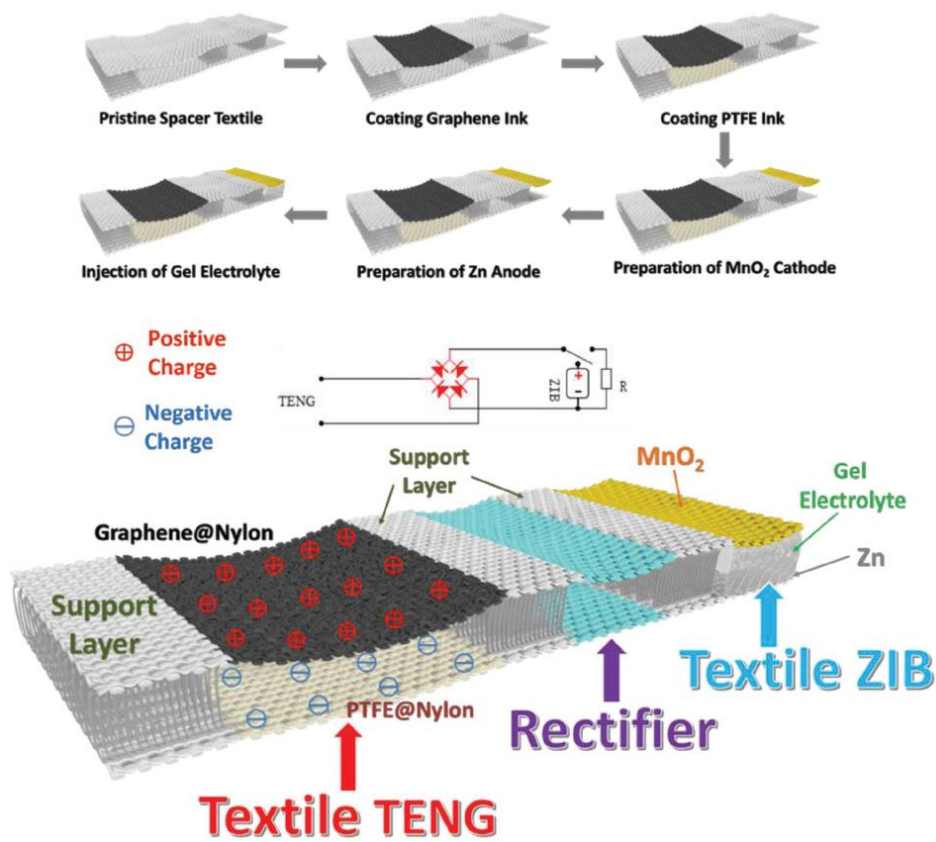


Figure 8. Fabrication and completed structure of a fabric-based, multifunctional energy harvester and zinc-ion battery (ZIB) [50].

4 Metal-Air Batteries

Metal-air batteries are those in which oxygen from the ambient air is reduced, with the help of a catalyst, at the cathode during discharge. Concomitantly, the metallic anode is oxidized, and both electrode reactions can be reversible, forming a rechargeable battery. Rechargeable metal-air batteries can be composed of many different metal-electrolyte-catalyst compositions, aqueous or non-aqueous, and they are seen as a promising technology because of the high theoretical energy density [18], [51]. Aqueous metal-air batteries may be an attractive option for textile batteries because they are meant to be exposed to air and are insensitive to moisture. Among the aqueous metal-air battery chemistries, zinc-air and aluminum-air have been the most widely examined [18]. Non-rechargeable zinc-air batteries have been widely commercialized for medical, military, and industrial applications. They are considered the ideal power source for hearing aids because of their high volumetric energy, low cost, and environmental friendliness [18]. Aluminum-air batteries have been widely researched because of their high theoretical capacity and energy. They have mainly been considered for military and niche applications [52]. However, there have been limited applications because of many technical challenges, including anode corrosion, inability to reach theoretical voltages, consumption of water during discharge, and lack of rechargeability [18], [52].

Similar to the alkaline batteries discussed in Section 3.2, the electrolyte in conventional zinc-air batteries is a highly alkaline solution, usually potassium hydroxide (KOH) because of its good conductivity and electrode kinetics. There have recently been efforts to develop neutral and near-neutral electrolytes for zinc-air batteries because they have the potential to improve calendar life and enable rechargeability [53]–[57]. Prior to the emergence of textile electronics and textile batteries, Zhu et al introduced the concept of an alkaline gel electrolyte for zinc-air batteries as a “solid” electrolyte with flexibility [58]. This aqueous gel (or “hydrogel”) was composed of poly(acrylic acid) and KOH and was offered as an improved alternative to the more common poly(ethylene oxide)-based electrolytes used for LIB. It offers better control over the molecular weight and crosslink density so that the desired mechanical properties can be achieved. The non-rechargeable zinc-air battery made with this electrolyte produced a stable discharge curve around 1.1-1.3 volts. The authors also examined the conductivity of the gel electrolyte with varying concentrations of KOH, as shown in Figure 9. Interestingly, the conductivity of the gel electrolyte in the absence of KOH was 0.15 S/cm, which is a non-negligible value and possibly sufficient for battery operation. However, the battery performance in such an electrolyte was not reported. Following on this work, Wu et al. incorporated PVA with PAA to increase water swelling in a gel electrolyte and demonstrated both zinc-air batteries and aluminum-air batteries with the electrolyte [59]. Zhang et al. demonstrated aluminum-air batteries with similar KOH/PAA gel electrolytes [60]. The authors reported high area-specific capacity and energy of 29.2 mAh/cm² and 30.8 mWh/cm², respectively, but the cells were not flexible or textile-based in any way.

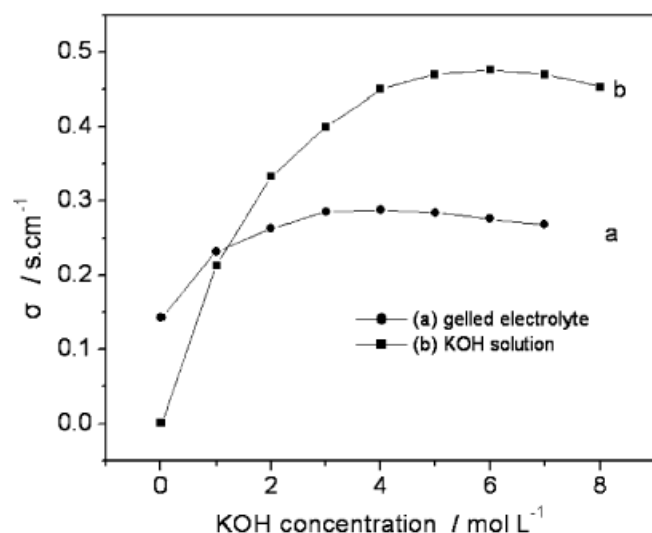


Figure 9. Conductivity of the KOH polymer gel electrolyte and KOH solution as a function of KOH concentration [58].

Recently, hydrogel electrolytes have been used to fabricate stretchable [61] and flexible [62], [63] metal-air batteries based on zinc or aluminum. Tan et al. showed that polyacrylamide could be used in place of PAA, PEO, and PVA for improved mechanical integrity and cycle life [62]. The area-specific capacity of the aluminum-air battery with neutral-pH polyacrylamide electrolyte was estimated to be 20 mAh/cm², but the conditions under which this was measured were not given. A flexible zinc-air battery containing poly(vinyl alcohol)-KOH gel electrolyte produced over 14 mAh/cm² with ~15 mWh/cm² energy [63]. The amount of capacity was proportional to the thickness of the zinc anode, showing that the design was not cathode-limited, i.e. was able to make full use of the unlimited amount of oxygen in ambient air. This is depicted in the voltage-upon-discharge curve shown in Figure 10.

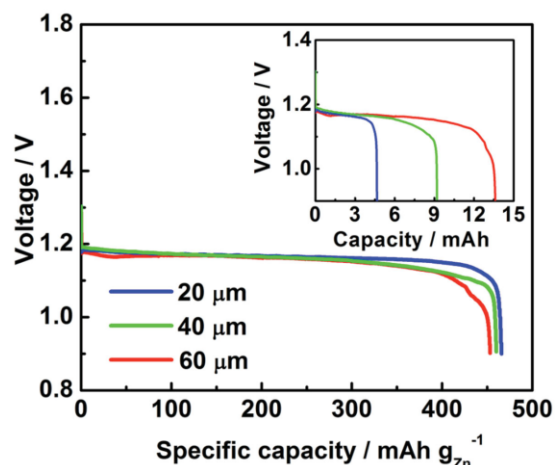


Figure 10. Voltage during discharge as a function of specific capacity at three varying zinc anode thicknesses. The inset shows the raw capacity values for the three thicknesses of zinc [63].

Several one-dimensional zinc-air battery designs have recently been reported in the form of a cable [64], a fiber [65], and a knittable wire [66]. The latter reference is the only known example

of a textile zinc-air battery being fully realized. A collaboration between Tianjin University (China) and Argonne National Laboratory fabricated the battery by coating a zinc wire with “chiffon” band and a PVA-KOH gel electrolyte. The wire was then coated with a cathode catalyst made of hybrid nanosheets of Co_3O_4 and nitrogen-doped reduced graphene oxide. The capacity of this catalyst was proportional to the length of the wire. It was knitted into a fabric sleeve and used to power an LED watch [66]. Washing or soaking tests on this fabric were not attempted but would be very useful to determine whether this type of prototype could be practical for textile-based applications.

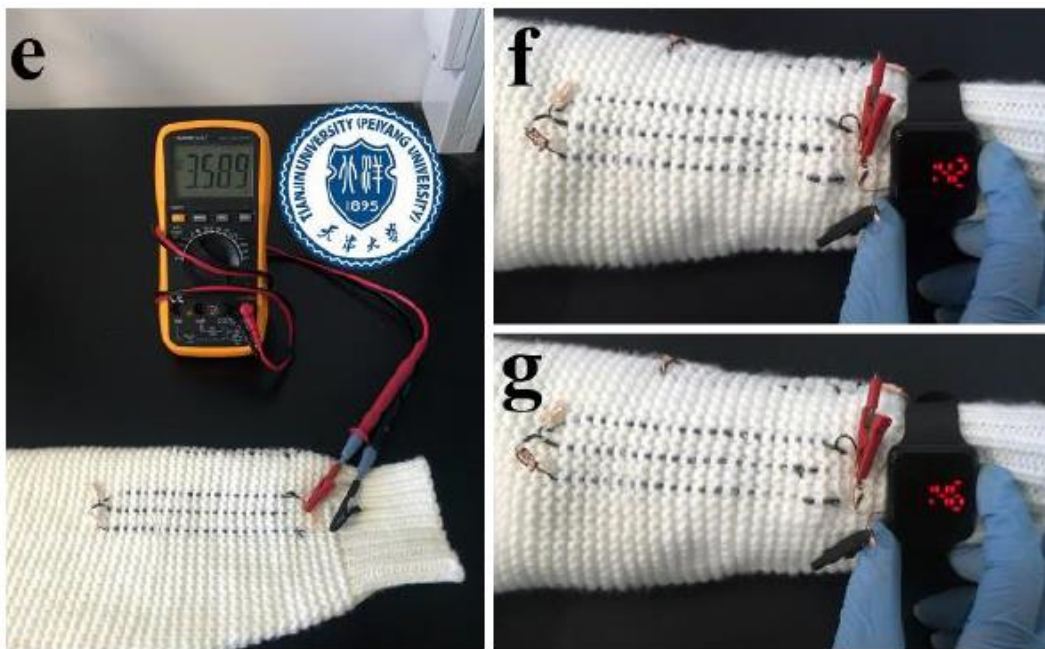


Figure 11. (e) Open-circuit potential demonstration of a cloth knitted with three one-dimensional zinc-air batteries wired in series. (f) and (g) Photographs of an LED watch powered by the same cloth [66].

5 Conclusion

For each battery chemistry discussed in this report, flexible or textile-based prototypes have been demonstrated with the performance expressed in capacity and energy per unit area. The best-performing prototype for each battery chemistry is given in Table 1 for an overall comparison. Despite the potential for high-energy performance in LIBs, the aqueous version of this battery chemistry produces the lowest area-specific capacity amongst flexible battery types. Although aqueous LIBs have been greatly improved in recent years, they are still hindered by several key performance limitations; in particular, voltages are usually limited to less than 3 volts, and electrode materials have complex compositions that may be cost-prohibitive.

Amongst the zinc-based batteries, the lower performance observed in flexible zinc-carbon batteries is not surprising given that commercial zinc-carbon batteries possess lower specific capacity and energy, relatively. The non-rechargeable, fabric-based alkaline battery offers higher relative capacity and energy, but it contains caustic KOH solution within the hydrogel electrolyte. Zinc-ion batteries offer the advantages of rechargeability and safer electrolyte, and this explains why research into this battery chemistry has increased greatly in recent years. Some recent examples of flexible and textile-based ZIBs are promising and show great potential for this battery chemistry. The combination of zinc anode, MnO_2 cathode, and gel-based electrolyte on fabric or fiber substrates is perhaps the simplest and most approachable way to fabricate a rechargeable, aqueous, textile battery. However, as shown in Table 1, this battery chemistry still has some challenges to overcome such as low area-specific energy and complex electrolyte composition.

Finally, the metal-air battery chemistries may offer the highest capacity and energy per unit area, although there have been far fewer examples of flexible or textile prototypes. Further work should explore methods for fabricating such prototypes, including the optimization and incorporation of low-cost cathode catalysts. While aluminum-air textile batteries could offer the highest area-specific capacity, this battery chemistry has historically shown the most challenges with rechargeability. Nonetheless, it may be ideal for applications requiring only primary (non-rechargeable) energy storage. Zinc-air textile batteries may offer the greatest compromise for achieving high area-specific energy along with rechargeability.

Table 1. Comparison of prototype batteries (flexible, textile, and other) in terms of area-specific performance

prototype description	capacity (mAh/cm ²)	energy (mWh/cm ²)	main disadvantage	ref.
rechargeable, flexible, aqueous, lithium-ion battery with PVA gel	0.58	1.4	high concentration of lithium salt can leach out	[30]
non-rechargeable, flexible zinc-carbon battery with PEO electrolyte	2.6	3.1	acidic electrolyte	[31]
non-rechargeable, stretchable alkaline fabric battery with PAA-KOH gel	3.9	5.0	caustic, alkaline electrolyte	[17]
rechargeable, flexible zinc-ion battery with hydrogel-ZnSO ₄ electrolyte	4.6	6.2	no textile components	[47]
rechargeable zinc-ion battery (carbon cloth) with PVA gel electrolyte	1.7	2.2	complex electrolyte composition	[48]
rechargeable zinc-ion battery (three-layer fabric) with gelatin-ZnSO ₄	0.8	1	low relative energy and thick textile substrate	[50]
non-rechargeable aluminum-air battery with PAA-KOH gel	29.2	30.8	not flexible and no textile components	[60]
rechargeable, flexible zinc-air battery with PVA-KOH gel	14	15	no textile components	[63]

Amongst the various battery chemistries that have been used for aqueous flexible and textile batteries, one commonality is the use of hydrogel-based electrolytes. The use of a gel makes the most sense for such batteries because it affords the dual benefits of a leak-free design with high conductivity and reaction kinetics. This type of electrolyte has been demonstrated with various polymers including PEO, PVA, PAA, polyacrylamide, and combinations thereof. Various salts, most commonly KOH and ZnSO₄, have been tested for zinc and aluminum batteries. The use of such hydrogels in flexible energy storage devices has been comprehensively reviewed [67] and shown to be very effective for various battery chemistries. However, aside from leak-free design and good electrochemical properties, textile batteries have additional performance requirements, mainly the ability to be washed and worn safely. Further studies of aqueous textile batteries should place the focus on the robustness of the hydrogel electrolyte and whether the battery can still operate after being soaked or vigorously washed in water and other solutions. The salts used in hydrogel electrolytes will undoubtedly be diluted or replaced with repeated usage, and this will affect the electrochemical performance of this battery. This complication may require the use of a polyelectrolyte, or “ionomer”, which is a polymer with ionic species covalently attached to the backbone. PAA is such a polyelectrolyte and thus deserves further consideration. Development and testing of the gel or polymer electrolyte should be a major focus of the next phase of research into textile batteries.

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Appendix A Abbreviations and Acronyms

1D	one-dimensional
2D	two-dimensional
cm	centimeter
F	Farads
kg	kilogram
LIB	lithium-ion batteries
LiTFSI	lithium bis(trifluoromethane sulfonyl)imide
mm	millimeter
mAh	milliampere hours
mol	moles
mWh	milliwatt hours
PAA	poly(acrylic acid)
PEO	poly(ethylene oxide)
PVA	poly(vinyl alcohol)
V	volt
ZIB	zinc-ion battery