Fabrication of a High-Performance Flexible Silver–Zinc Wire Battery

Alla M. Zamarayeva, Abhinav M. Gaikwad, Igal Deckman, Michael Wang, Brian Khau, Daniel A. Steingart,* and Ana Claudia Arias*

Conformable electronic wearable systems will enable improvements in human health monitoring. The development of a high energy density flexible wearable battery that maintains safe and stable operation under mechanical deformation is crucial for the autonomous operation of optimal wearable devices. The ideal wearable battery would not change the aesthetic features of the garment nor cause discomfort to the user. To date, most flexible batteries have been planar systems assembled by the consecutive stacking of electrodes and separators. This planar architecture can be flexed only in certain directions and could eventually fail due to delamination caused by shear forces imposed by flexing. This poses limitations of integration with wearable technologies. As an alternative architecture wire batteries offer omnidirectional flexibility; they can be folded into arbitrary shapes, wrapped around body parts like the neck or the wrist as well as weaved or sewn into fabrics.

In recent studies, new electrode composites were created in order to replace rigid components of conventional batteries with robust and compliant substitutes that enable such wire battery architectures. Lithium-ion (Li-ion) chemistries have received special attention due to their well-engineered stability and high energy density. However, simultaneously achieving high specific capacity and long cycle life of the wire batteries remains a challenge. Kwon et al. reported first Li-ion wire battery with linear capacity of 1 mAh cm$^{-1}$ at a discharge rate of 0.1C over eight cycles. Recently, Weng et al. reported an Li-ion battery based on carbon nanotube-lithium oxide composite yarns with improved cycle life of 100 cycles, but with a lower linear capacity of 0.22 mAh cm$^{-1}$. In addition, risk of migration of silver ions to the counter electrode and subsequent poisoning of the electrode is a major impediment to long cycle life in silver–zinc batteries, limiting battery life to 50–100 cycles depending on cycling parameters. Silver migration also causes growth of fine silver metal crystals inside the separator leading to short circuits. We mitigate this limitation and improve the lifetime of the battery by reducing the dissolution of silver ions with an optimized potassium hydroxide (KOH) concentration of 2 m in the electrolyte. In addition, 20 μm cellophane film was embedded between cathode and anode to form a sacrificial barrier. Cellophane mitigates the migration of silver ions to the separator and counter electrode by reducing them to insoluble silver metal and gets oxidized during this process. The optimum battery operation parameters were reached by studying the effect of cycling rate on the silver electrode morphology and electrochemical performance of zinc–silver battery. These modifications improved the performance...
to over 170 stable cycles. This high specific capacity and long cycle life silver–zinc wire battery create new possibilities in implementing wearable garments such as activewear with integrated performance trackers and continuous health monitoring systems, fashion wear, and jewelry with integrated electronics like LEDs or solar modules etc.

The schematic of the wire battery and the fabrication process are illustrated in Figure 1A,B, respectively. The anode is composed of electrodeposited Zn on tin-coated copper wire. Subsequently, the anode was dip-coated into the polyvinyl alcohol (PVA)-KOH polymer electrolyte, which served as a separator. A thin cellophane film was wrapped around the PVA separator to further reduce migration of silver ions toward the zinc electrode. The silver electrode was fabricated by dip coating a conductive stainless steel thread into a silver nanoparticle solution; subsequently, cathode was electrochemically oxidized to Ag$_2$O or AgO after the battery was fabricated. The electrode was then wrapped around the anode-electrolyte assembly resulting in a wire battery with a 2.5 mm diameter.

The mechanical flex stability of the wire battery anode depends critically on the morphology of electrodeposited Zn which can be controlled by adjusting the plating current.$^{[30,31]}$

Figure 2A,B shows the SEM images of the zinc deposit on the tin-coated copper wire after flexing, plated at 10 mA cm$^{-2}$ and 30 mA cm$^{-2}$ respectively. Figure 2A shows an anode with the compact boulder Zn morphology, obtained at lower current density. Figure 2B shows dendritic Zn deposit, plated at higher current density. The compact Zn fractured after flexing while dendritic Zn was able to maintain mechanical integrity. Void spaces in the dendritic Zn deposit make it more flexible than compact Zn. Subsequently, all Zn anodes were plated at the current density of 30 mA cm$^{-2}$ to achieve dendritic Zn morphology that withstands mechanical stresses. In addition, Chamoun et al.$^{[32]}$ showed that using dendritic and hyper dendritic zinc preforms can stabilize cycle life by altering ramification process.

To simplify the fabrication process, the electrolyte/separator for the battery was constructed by dip-coating Zn anode into the PVA-KOH polymer gel. Using this approach, we benefit from chemical stability of PVA in alkaline media, its high ionic conductivity, and ability to sustain mechanical stress,$^{[33–35]}$ while utilizing simplicity of dip-coating technique. To inhibit undesired hydrogen evolution on the thermodynamically unstable Zn electrode KOH was saturated with zinc oxide (ZnO) and bismuth oxide (Bi$_2$O$_3$).$^{[36–38]}$ Conductivity of the PVA-KOH...
film used in the wire battery is $10^{-2}$ S cm$^{-1}$, as determined by impedance spectroscopy measurement (Figure S1, Supporting Information).

Silver–zinc batteries require additional separator-membrane on the positive side to protect the PVA separator and zinc anode from the oxidative attacks of silver ions. Ideal membrane should be permeable to hydroxyl species and impermeable to silver ions. However, designing ideal membrane remains a challenge due to synergic effect of several parameters that aid adsorption and migration of ionic species thought the polymeric matrix, such as pore size, electrostatic and steric factors. The cellophane membrane has been widely used as a barrier for silver migration in conjunction with different separators.[28,39] Cellulose—constituent component of cellophane—reduces silver ions to metallic silver, thus mitigating further migration of these species.[28,29] The major drawback of cellophane is its gradual destruction as a consequence of oxidative silver attacks. We utilized 20 μm cellophane film wrapped around PVA coating to serve as a sacrificial barrier for decelerating silver migration. To prolong the lifetime of the barrier we used the double layer of the film. Incorporation of the cellophane film results in the increase of the Ohmic and charge transfer resistances of the battery (Figure S2A, Supporting Information), as discussed in the Supporting Information. Nevertheless, its integration significantly prolongs the stable cycling of the battery, which otherwise loses 47% of its capacity after 30 electrochemical cycles (Figure S2B, Supporting Information).

To further decelerate silver ions migration and extend lifetime of the battery we adjusted the concentration of silver ions in the electrolyte by varying KOH concentration. The effect of KOH concentration in the electrolyte on the cycling performance of the silver–zinc wire battery operated at 0.25C charge and 0.5C discharge rates between 1 and 1.8 V is shown in Figure 3. Change in specific capacity with cycle number was investigated for 25 wt% (5.6 m), 20 wt% (4 m), and 10 wt% (2 m) KOH content in the electrolyte (Figure 3A,D, 3B,E, and 3C,F respectively). Initially, charge–discharge capacity is higher in the batteries containing more concentrated KOH solution, while the columbic efficiency is lower (2.7 mAh cm$^{-1}$ charge and 1.65 mAh cm$^{-1}$ discharge capacity for the battery with 25 wt% KOH content; 2.3 mAh cm$^{-1}$ charge and 1.55 mAh cm$^{-1}$ discharge capacity for the battery with 20 wt% KOH content; 1.3 mAh cm$^{-1}$ charge and 1.2 mAh cm$^{-1}$ discharge capacity for the battery with 10 wt% KOH content). As cycling progresses capacity of the batteries with 20 wt% and 25 wt% KOH content continuously decays and then abruptly falls below 20 wt% of its original value after 17 and 20 cycles respectively. In contrast, batteries with 10 wt% KOH demonstrate stable capacity throughout the cycle range. Both lower columbic efficiency and premature failure of the batteries with higher KOH content can be attributed to increased solubility of silver in more concentrated KOH solutions.[40,41] First, higher concentration of silver ions in the electrolyte of these batteries leads to accelerated silver migration, poisoning of Zn electrode and destruction of cellophane barrier, thus, expediting battery failure. Second, higher solubility of silver results in greater capacity losses on dissolution that do not recover in the consecutive cycles resulting in lower efficiencies. Additionally, Zn corrosion processes occurring on an anode are more thermodynamically favorable in higher concentrated KOH solutions. Therefore, part of the energy supplied on charge is consumed by Zn dissolution, further contributing to decrease in columbic efficiency.

Figure 3D–F shows galvanostatic charge/discharge curves for the 4th, 10th, and 18th cycles of the batteries with 25 wt%, 20 wt%, and 10 wt% KOH content. As seen from the voltage values of charge–discharge curves, lowering KOH concentration from 25 to 10 wt% results in the potential drop of $\approx 0.05$ V. Decreasing of the electrolyte conductivity as the KOH content decreases.
is reduced from 25 to 10 wt% causes this drop. Consequently, energy efficiency of the batteries with lower KOH content is reduced. However, this compromise is compensated by the prolonged cycle life of the battery.

Current collector for the flexible electrode should provide mechanical support and conductive network to the electrode. Commonly, carbon-based current collectors such as carbon nanotube threads and carbon fibers have been used in the wire batteries due to electrochemical stability over the potential window of the battery.\[^{[10,11,13,14,22]}\] However, the low electronic conductivity of carbon-based materials leads to high Ohmic potential drops when the battery is operated at high C-rates. In order to reduce potential drops we chose stainless steel (SS) threads as the current collector for silver electrodes. SS threads are highly conductive and have porous architecture. The cyclic voltammetry (CV) shows that threads oxidize during the first charge cycle (Figure S3, Supporting Information) and remain stable over subsequent cycles. As a result, their resistance increases from 7 to 15 Ohms. Even with initial increase in resistance, the conductivity of the SS threads is an order of magnitude higher than that of the carbon-based fibers, making SS threads a reasonable choice for the current collector.

To reduce fabrication costs and improve shelf life of the battery, we constructed cathode by dip-coating stainless steel thread in the silver nanoparticle ink. The deposition results in uniform silver coating, as shown in the Figure S4 (Supporting Information). The assembled silver electrode can be oxidized to Ag$_2$O or AgO and the battery can be formed when needed.\[^{[42]}\] Thus, battery components are subjected to the oxidative attack of silver oxide for a shorter period of time. Therefore, by using silver nanoparticle ink, we achieved good printability and simple fabrication of the cathode as well as extended shelf life of the battery.

The percent utilization of electrodes is one of the factors determining cycle life of silver zinc batteries. Utilization of silver on the order of 57% of the theoretical capacity has been used to design long-life cells.\[^{[28]}\] The utilization of silver electrode in the wire battery ranged between 47% and 60.5% of the theoretical capacity of Ag$_2$O, at 0.5C rate of discharge, resulting in the 109–140 mA h g\(^{-1}\) designed capacity based on silver cathode, which was a limiting electrode in the battery. Variations in the capacity utilization of silver are caused by differences in morphology of thread-embedded electrodes originated from random distribution of thread fibers and manual dip-coating process. Automating dip-coating process can minimize the range of silver utilization fraction. The capacity ratio of anode to cathode in the wire battery is 2.75 to 1. Therefore, cycling of Zn was limited to a range of 17%–22% of anode theoretical capacity at 0.5C discharge rate. The utilization of Zn to the fraction of its theoretical capacity is crucial for preventing failure of the battery through occlusion of mass transport of Zn electrode. Mass transport is hindered by formation of ZnO during discharge, which commences at the separator and moves toward the current collector;\[^{[41–43]}\] It has been shown that cycling of pre-formed dendritic zinc to a fraction of its total capacity mitigates the aforementioned failure mechanism for many cycles.\[^{[32]}\]

Based on the cycling performance of our batteries compared with the known mechanisms mentioned above, the Ag/Ag$_2$O cathode is both the capacity limiting electrode as well as the cycling critical electrode. CV data for the silver electrode and discussion of the processes occurring during electro-oxidation of silver in alkaline solutions are presented in the Supporting Information (Figure S5A). Particle-size maintenance during AgO/Ag$_2$O to Ag conversion on discharge is critical to maintain cyclability. The particle size is determined by the rate at which battery is discharged with smaller particles formed at faster discharge rates.\[^{[66,47]}\] Smaller particles are desirable as they can be fully oxidized on the consequent charge, while oxidation in the larger particles will stop at the thickness determined by ionic transport limitations (Figure S5B, Supporting Information). In order to determine the optimum discharge rate, silver–zinc batteries were discharged at slow (0.05C and 0.1C) and fast (0.5C and 0.25C) rates between 1.8 and 1 V (Figure S4C,D, Supporting Information). The corresponding cycling profiles show that optimum discharge rate is >0.5C. Therefore, in order to maintain stable capacity, batteries presented in this work were discharged at the rates 0.5C and above.

In general a silver–zinc battery can be charged to 1.8 V or 2 V to form monovalent zinc–silver oxide (Zn-Ag$_2$O) or divalent zinc–silver oxide (Zn-AgO), respectively.

The full cell reaction between zinc with AgO proceeds via two-step mechanism

\[
\text{Zn} + 2\text{AgO} \Leftrightarrow \text{Ag}_2\text{O} + \text{ZnO} \quad (1.86 \text{ V})
\]

\[
\text{Zn} + \text{Ag}_2\text{O} \Leftrightarrow 2\text{Ag} + \text{ZnO} \quad (1.59 \text{ V})
\]

While the Ag$_2$O versus Zn proceeds with reaction 2 alone.

By utilizing the full valence range of silver the Zn-AgO system delivers higher energy density than Zn-Ag$_2$O. However, other parameters such as efficiency and cycle stability of the battery are important. We investigated the performance of both systems by operating the batteries between 1 and 1.8 V (to form Ag$_2$O) as well as between 1 and 2 V (to form AgO) at 0.5C discharge and 0.25C charge rates. Figure 4A shows the cycling performance of the battery charged to 1.8V. Figure 4B shows charge–discharge curves for 2nd, 50th, 100th, and 150th cycles of the battery. The capacity of the battery gradually increases up to 131st electrochemical cycle (from 1.22 to 1.41 mAh cm\(^{-2}\)) and then decreases to 1.22 mAh cm\(^{-2}\) by 170th cycle. The increase in capacity can be attributed to higher silver electrode utilization as cycling proceeds. Since morphology of silver electrode changes with each electrochemical cycle, minor variations in capacity are expected. The higher electrode utilization could be caused by increase in porosity of the electrode as a result of cycling and, thus, higher electro-active surface area exposed to electrolyte. The increase in electrode porosity is confirmed by the SEM characterization of morphology of the silver electrode that had undergone 180 electrochemical cycles (Figure S5, Supporting Information) versus as prepared silver electrode (Figure S4C,D, Supporting Information). The decrease in capacity after 131st cycle could occur due to multiple factors associated with battery aging, such as deterioration of cellulose barrier and PVA separator, corrosion of current collectors and loss of electrolyte due to its migration through plastic seals. The aging process is also accompanied by increase in
internal resistance of the battery. It is represented by the potential drop of 0.1 V observed from the plateau of the discharge curve for 150th electrochemical cycle in Figure 4B. The battery was charged at 0.1C, 0.25C, and 0.5C, and discharged at 0.2C, 0.5C, and 1C rates, respectively (the discharge to charge rate ratio was kept as two to one for consistency) (Figure 4C,D). Specific discharge capacity decreased from 1.85 mAh cm⁻² at 0.2C to 1.45 mAh cm⁻² at 1C, resulting in ≈20% capacity loss. Decrease in capacity is related to higher ohmic potential drop when the cell is cycled at higher rates. Efficiency increased from ≈93% at 0.2C to ≈95% at 0.5C and ≈97% at 1C, due to variation in silver morphology, as discussed previously. Thus, operating the wire battery at higher rates resulted in better stability and higher columbic efficiencies. To investigate the performance of AgO-Zn system, the wire battery was cycled between 1 and 2 V. The discharge capacity increased by ≈15% as compared to the battery charged to 1.8 V (Figure 5, Supporting Information). However, the cell cycled with only 80% efficiency. Using AgO the capacity started to decrease after 60 cycles, leading to ≈40% capacity loss after 100 cycles. Thus without control of the formation of AgO from Ag₂O, batteries charged to 2 V exhibit lower efficiencies and shorter cycle life than batteries cycle limited to 1.8 V. Therefore, despite higher capacities achieved by cycling battery 2 V, it is advantageous to operate the battery between 1 and 1.8 V as documented well.[28]

Stable electrochemical performance under mechanical deformation is another key requirement for a wearable battery. Figure 5A,B shows the cycling performance and galvanostatic charge–discharge curves of Ag-Zn wire battery cycled at 0.25C charge and 0.5C discharge rates between 1 and 2 V while being subjected to 100 flexing cycles to a specified bending radius under quasi-static (i.e., slow) conditions. To control flexing diameter, the battery was wrapped around a cylinder of 2.54, 1.60, 1.27, and 1 cm diameters as shown in Figure 5C. The diameter of the control cylinder was decreased after each set of 100 bending cycles. Figure 5A shows that the capacity remains stable even after repeated flexing up to a bending radius of 5 mm. As seen from Figure 5B, resistive overpotential does not seem to be a function of flex to different diameters, indicating that no delamination or significant cracking of active layers occurs. These results confirm that the wire battery can successfully withstand mechanical perturbations that are expected to occur during wearing.

We further arranged multiple batteries in series to form modules with high output voltage. Figure 6 shows three batteries connected in series and sealed within heat shrinkage plastic tube. The battery module was able to continuously power a red LED display while being deformed.

In conclusion, we demonstrated a new design and fabrication approach of the wire battery, with linear capacities between 1.2 and 1.8 mAh cm⁻² at 0.5C discharge rate, by utilizing low-cost fabrication processes and the silver–zinc battery chemistry. The volumetric and gravimetric energy densities of the wire battery reach 53.4 Wh L⁻¹ and 18.35 Wh kg⁻¹ respectively at 0.5C discharge rate. We show that the lifetime of the battery can be improved to over 170 stable cycles by optimizing potassium hydroxide (KOH) concentration in the electrolyte to reduce the dissolution of silver ions and by embedding a cel-lulophane membrane between the anode and cathode to inhibit migration of silver ions toward the zinc electrode. The wire battery can withstand multiple bending cycles without change in electrochemical performance. It has versatile form factor that can be tuned toward specific applications.

Several milestones have to be overcome to further improve compliant technologies based on silver–zinc chemistry and alkaline systems in general. One of the unresolved issues is a lack of binders that are stable in alkaline media, provide good adhesion of an active material to the substrates and at the same time have a rheology suitable to printing. Another drawback of silver–zinc technology is relatively short cycle life. Development of a
A separator/electrolyte that inhibits silver migration can prolong cycle life of silver–zinc batteries. Polymer electrolyte for primary printed silver zinc battery was recently reported,[24] however similar electrolyte for rechargeable system is still to be developed. For wire or fiber shaped devices, electrochemically stable current collector with high conductivity is another important constituent required to scale such battery to arbitrary length.

**Experimental Section**

**Zinc Electrodeposition:** Corresponding amounts of KOH (Sigma-Aldrich 85% anhydrous pellet) and ZnO (Sigma-Aldrich 99.9%) were dissolved in deionized (DI) water to produce 5.6 \( \text{m} \) KOH 0.37 \( \text{m} \) ZnO solution. 0.1 g of Bi₂O₃ (Sigma-Aldrich 99.999%) was added to the solution and mixed overnight. Solution was decanted to remove bismuth oxide that remained as a solid precipitate. Zn was electrodeposited on a tin-coated copper wire (Belden) from prepared electrolyte in the galvanostatic mode at the current density of 30 mA cm\(^{-2}\) for 5000 s using a Gamry Potentiostat.

**Silver Electrode Preparation:** Stainless steel coated conductive thread (Sparkfun, conductive thread #60) was dipped into silver nanoparticle ink (DuPont 5064H). The composition of the ink is as follows: Dimethyl Glutarate (5%–10%); Dimethyl Succinate (1%–5%); Vinyl Polymer (5%–10%); Silver (Metallic) (60%–100%); Ketone Solvent (10%–30%). Silver nanoparticles are in the shape of flakes with the size distribution varying from nanometer range to \( \approx 5 \) μm (Figure S4B, Supporting Information). Excess ink was thoroughly removed. Silver-coated thread was sintered for 30 min at 140 °C in the vacuum oven. Resulting silver electrode was \( \approx 250 \) μm thick. The electrode was calendared to 20% of its original thickness using a calendar press.

**Polymer Electrolyte Preparation and Characterization:** PVA (Sigma-Aldrich, MW 85 000–124 000, 99% hydrolyzed) was mixed with DI water in the 1:10 ratio and left to dissolve overnight in the oven at 80 °C. The liquid electrolyte was added to the mixture drop by drop to achieve 1:1.3 PVA:KOH ratio (by dry weight). The mixture was stirred for at least 2 h. The resulting gel electrolyte was used for dip coating of Zn electrode or casted in the petri dish to obtain polymer film that was used in electrochemical impedance spectroscopy (EIS) measurements. To perform EIS measurements, the film of 1 in.\(^2\) area and approximate thickness of 0.5 mm was sandwiched between two stainless steel electrodes. The measurement was done using Gamry Potentiostat at frequencies ranging from 106 to 0.1 Hz at amplitude of 10 mV.

**Silver–Zinc Wire Battery Assembly:** Zn electrode was dip-coated with PVA polymer electrolyte. The procedure was repeated five times letting the gel coating to dry in between in order to prevent short circuits. The cellophane film (McMaster Carr) was cut into stripes and then wrapped around anode–electrolyte assembly followed by wrapping silver electrode. To perform electrochemical characterization, the device was calendared to 20% of its original thickness using a calendar press.

**Figure 5.** A) Capacity per unit length (mAh cm\(^{-1}\)) and columbic efficiency (%), B) galvanostatic charge discharge curves of silver–zinc wire battery cycled at 0.25C charge and 0.5C discharge rates between 1 and 2 V. Battery was periodically subjected to 100 flexing cycles by being wrapped around a cylinder of 2.54, 1.60, 1.27, and 1 cm diameters, as shown in panel C). Radius of the cylinder was decreased after each set of 100 bending cycles.

**Figure 6.** Three batteries in series sealed in chemically resistive tubing powering LED screen while A) being wrapped around the cylinder of 0.85 cm radius and B) tied in a nod.
sealed within transparent elastomeric adhesive pouch (3M 4910). The schematic of the encapsulation is presented in Figure S7 (Supporting Information). It consists of three adhesive elastomeric sheets, with a well cut in the middle sheet. The bottom and the middle sheets were first adhered together; the battery was then placed into the well and covered with the top sheet, leaving the current collectors exposed. Liquid electrolyte containing 2 m KOH 0.2 m ZnO saturated with Bi2O3 was added before sealing the battery in the amount of 50 μL cm−2 under Grant No. DGE-1106400. The authors would like to thank National Science Foundation Graduate Research Fellowships Program for granting access to his laboratory and Prof. Paul Wright for granting access to his laboratory and composition mentioned above) before sealing the ends of the tube to avoid the undesirable effects of heat exposure, such as damage of polymer electrolyte or cellophane barrier.

Device and Electrode Characterization: Cyclic voltammetry measurements were carried out using Gamry Potentiostat. Full cells were tested using MTI battery analyzer. SEM microscopy was carried out on TM-1000 (Hitachi).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Figure S1. High frequency region of the Nyquist plot of the PVA-KOH polymer electrolyte.

Impedance measurement was performed at frequencies ranging from $10^6$ to 0.1 Hz at amplitude of 10 mV. The ionic conductivity, $\sigma$, of the polymer electrolyte was calculated according to the formula $\sigma = \frac{l}{RA}$, where $l$ is the film thickness, $R$ is the bulk resistance and $A$ is the area of the film. The bulk resistance was determined from the high-frequency intercept of the impedance curve with the real axis.
Figure S2. A) Nyquist plots and B) cycling performance of the wire batteries with and without embedded cellophane film. Charge-discharge curves for the C) 2nd and D) 50th electrochemical cycles of the battery in B).

To investigate the effect of embedding cellophane film on the impedance of the wire battery we performed EIS measurements of the batteries with and without cellophane membrane and correlated them with electrochemical data. EIS measurements were performed at frequencies ranging from $10^6$ to 0.1 Hz at amplitude of 10 mV at open circuit condition. The battery was tested after assembly and equilibration for 2 hours. The resulting Nyquist plots are shown in the Figure S2 A. They consist of depressed semicircle in high to medium frequency range (in the lower range of abscissa axes) and sloping tale in the low frequency range (in the higher range of abscissa axes). Inductive data obtained at high frequencies do not influence the rest of the spectra\textsuperscript{11} and do not bear interest to the discussion, therefore, they were excluded from the plot. The high frequency intercept with abscissa corresponds to
the Ohmic resistance of the battery and is dominated by the electrolyte resistance. The depressed semicircle can be attributed to the kinetic impedance due to charge transfer interfaces within the battery, such as particle to particle interface, current collector to particle interface and particle to electrolyte interface. The depressed shape results from the variations in capacitance and resistance throughout the electrodes caused by non-uniform morphology. Kinetic response combines contribution from both electrodes but is dominated by the impedance of limiting silver electrode. The low frequency range is attributed to the solution diffusion Warburg process at the cathode.

Figure S2 A shows the Nyquist plots of the batteries with and without cellophane film (double layer 20 µm each). The intercept with abscissa increased by 62 Ohms and the radius of the semicircle increased by 17 Ohms as a result of embedding the cellophane barrier. Increase in the abscissa intercept indicates that the film hindered ionic transport of electrolyte ions and resulted in the increased PVA-KOH-cellophane composite resistance if compared to PVA-KOH and, thus, increased Ohmic resistance of the battery. Increase in the radius of the semicircle must be due to changes in particle-to- electrolyte interface, since current collector-to-particle and particle-to-particle interface remain unchanged. Since silver electrode is in direct contact with the cellophane film, such response could be an indicator of poorer wetting of the film, if compared to PVA electrolyte.

Cycling performance and charge-discharge curves of the 2nd and 50th electrochemical cycles of the batteries with and without cellophane film are shown in Figure S2 B-D. Battery with cellophane maintains stable performance, while battery without cellophane looses 47% of its capacity after 30 cycles (Figure 2S B). Discharge potential of the battery decreases by 0.09 V after embedding the cellophane film (Figure 2S C), however, this difference reduces to 0.06 V by the 50th electrochemical cycle (Figure 2S D). Lowering of the battery discharge potential is a reflection of increase in the Ohmic resistance of the battery with embedding of
the cellophane film. As cycling progresses, the polymer electrolyte in the battery without cellophane deteriorates, resulting in the increase of the Ohmic resistance of this battery. As a result, the difference between discharge potentials of two devices reduces, making the Ohmic contributions from the cellophane less profound.

Therefore, cellophane film contributed to increase in Ohmic and charge transfer resistances of the battery. Nevertheless, second separator is a necessary component to achieve long cycle life of the battery. The battery without this modification looses capacity as a result of gradual poisoning of the PVA electrolyte and zinc electrode. Even after integration of the cellophane film, the total resistance of the device was in the same range or smaller than have been previously reported for the wire batteries.\textsuperscript{[5,6]} It is important to note that structural and transport parameters of cellophane strongly depend on the film fabrication process.\textsuperscript{[7]} Therefore, for higher rate applications, where resistance losses should be further minimized, different film alternatives can be considered.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Cyclic voltammogram for the silver electrode current collector (stainless steel thread) in 2M KOH 0.2M ZnO saturated with Bi2O3 vs. Hg/HgO at 0.1 mV s\textsuperscript{-1}. The oxidation peak is seen only in the fist cycle, indicating that the thread is oxidized during the fist cycle and remains electrochemically inert during the consecutive cycles.}
\end{figure}
Figure S4 SEM micrograph of the A) – D) top view and E) – F) cross section of the silver electrode constructed by dip coating of the stainless steel thread into the silver nanoparticle ink A) – B) before and E) – F) after calendaring. Silver ink coating has good uniformity throughout the thread.

Figure S5 SEM micrograph of cycled 180 times (in a charged state) silver electrode constructed by dip coating of stainless steel thread in the silver nanoparticle ink. Silver ink remains adhered to the thread after cycling.
Electro-oxidation of silver

Electro-oxidation of silver in alkaline solutions is a two-step process and can be represented in the simplified form by the following equations:

\[
2Ag + 2OH^- \leftrightarrow Ag_2O + H_2O + 2e^- \quad (1)
\]

\[
Ag_2O + 2OH^- \leftrightarrow Ag_2O_2 + H_2O + 2e^- \quad (2)
\]

However, other processes such as nucleation overvoltages, solid-state diffusion, and dissolution of silver complicate this scheme. \(Ag_2O\) formation proceeds through dissolution precipitation mechanism.\(^{[1]}\) This process starts with dissolution of silver species in KOH forming \(Ag(OH)^-\). When saturation of the KOH solution with \(Ag(OH)^-\) approaches two times the solubility limit, \(Ag_2O\) precipitates out on the electrode forming an oxide film on the Ag surface. While \(Ag_2O\) film grows, ionic transport though the oxide layer is gradually hindered until it reaches the value of dissolution rate. In the sintered silver electrodes, the \(Ag_2O\) layer can grow up to 2 micron in thickness before the formation of \(AgO\) begins.\(^{[2,3]}\) The growth of \(AgO\) phase takes place throughout the \(Ag_2O\) layer. The potential of the electrode further increases to oxygen generation regime when growth of \(AgO\) stops.
Figure S6 A) Cyclic voltammogram for the silver electrode in 2M KOH 0.2M ZnO saturated with Bi$_2$O$_3$ vs. Hg/HgO at 0.1 mV s$^{-1}$. CV measurement was conducted from 0 to 0.6 V against Hg/HgO reference electrode at rate of 0.1 mV s$^{-1}$. Anodic peaks are associated with formation of Ag$_2$O and AgO, as well as possible formation of higher level oxides$^{[4-6]}$ and dissolution of silver to form Ag(OH)$^-$. Cathodic peaks represent their counterparts. Peaks for the oxidation and reduction reactions are fused together - indication of incomplete conversion of Ag to Ag$_2$O before the reaction of Ag$_2$O to AgO starts, and the same is true for the reduction reactions. It can be attributed to the size of silver particles. The height of the peaks increases with scan number indicating increasing oxidation of the silver electrode. Beyond 0.6 V oxygen is generated at the electrode. B) Diagram illustrating morphological changes in silver electrode operated at slow vs. fast charge/discharge rate.

Comparison of the cycling performance of silver-zinc batteries charged at the same rate to 1.8 V and discharged at different rates to 1 V. Specific capacity (mAh cm$^{-1}$) and columbic...
efficiency (%) of two batteries C) charged at rate 0.05C, discharged at rates 0.1C and 0.05C
D) charged at rate 0.25C, discharged at rates 0.25C and 0.5C. Capacity gradually fades with
cycle number when the batteries are discharged at 0.05C and 0.1C rates. The decline is more
pronounced in the cells discharged at rate 0.05C than in those discharged at 0.1C. Capacity
fluctuates when the battery is discharged at 0.25C and is stable when the battery is discharged
at the 0.5C rate. Cycling performance of Ag-Zn battery depends on cycling rate due to the
changes in morphology of silver electrode that occur with each charge-discharge cycle.
Silver particles that are formed on discharge at fast rates are of a smaller size and therefore
are oxidized more readily on consecutive charge.
Figure S7 A) Capacity per unit length (mAh cm\(^{-1}\)) and columbic efficiency (%) of silver-zinc wire battery cycled at 0.25C charge and 0.5C discharge rates between 1V and 2V. B) Galvanostatic charge-discharge curves for 2\(^{nd}\), 50\(^{th}\) and 100\(^{th}\) cycles of the battery. Potential drop of the battery operated to 2V is observed after 50\(^{th}\) cycle (verses 150\(^{th}\) cycle in the battery operated to 1.8 V). Accelerated failure of the battery operated to 2 V occurs due to increased concentration of silver ions in the electrolyte and thus faster silver diffusion through cellophane barrier, as well as undesired oxygen evolution. Both phenomena are caused by spontaneous AgO to Ag\(_2\)O decomposition via reaction 2AgO → Ag\(_2\)O + \(\frac{1}{2}\) O\(_2\), which is thermodynamically favorable in the basic environment.\(^1\) From the galvanostatic discharge curve in Figure S5 B we observe only one discharge plateau, instead of expected two plateaus. Potential values of the observed plateau correspond to those of Ag\(_2\)O-Ag couple, while plateau corresponding to AgO-Ag\(_2\)O couple is absent. Single plateau indicates that Ag\(_2\)O to AgO transition that occurs in a bulk of the electrode\(^3\) does not proceed to an end leaving the Ag\(_2\)O-Ag film on the surface. This film insulates AgO layer from being in contact with current collector. Since the potential of an electrode is determined only by the compounds that are in contact with the current collector,\(^4,7\) the higher voltage step is given up, while additional capacity is gained. The single discharge plateau is a favorable phenomenon, since such discharge profile is highly desirable for practical applications. Thus, cycling of the wire batteries to 2 V results in \(~15\%\) capacity gain, while retaining practical advantages of single plateau discharge.
Figure S8 Schematic of the battery encapsulation components used for sealing the battery before performing electrochemical characterization.


