Highly flexible printed alkaline batteries based on mesh embedded electrodes

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Keywords: (Flexible Batteries, Polymer Electrolyte, Zn-MnO2, Mesh Architecture, Flexible Electronics)

Folding, conformable electronic devices cannot be realized until flexible batteries that match device form-factor and power requirements are developed. Existing flexible batteries exhibit a severe limitation due to internal short-circuits during flexing.[1] In our present work we demonstrate a printed alkaline battery fabricated with a polyacrylic acid (PAA) based polymer gel electrolyte (PGE). The electroactive materials were embedded into a mesh structure providing highly flexible electrodes. The flexible alkaline battery showed an open circuit potential of 1.52 V and discharge capacity of 5.6 mAh cm\(^{-2}\) when discharged at 0.5 mA. The discharge capacity of the printed battery was characterized in bend conditions ranging from 3.81 cm to 0.95 cm bending radii without any decrease in performance compared with the planar state. Two batteries connected in series and bent to a radius of 0.3 cm were able to power a green light emitting diode (LED).

Flexible electronics have been demonstrated for a wide range of functionality such as digital memory,[2] photovoltaic cells,[3] displays,[4] pressure sensors,[5] implantable medical...
Flexible batteries share several manufacturing challenges with flexible electronics due to the thermal budget imposed by plastic substrates, compatibility issues of different layers in the device and stability during bending. Bending mechanics of flexible electronic devices has been previously studied and various methods for strain management have been proposed, for example, by embedding the active device at a neutral strain position. While there has been much progress toward the development of flexible electronics, a similar level of maturity has not yet been achieved in flexible batteries. One approach to improve the mechanical stability of flexible electronics is to use very thin electrodes and a buckled structure architecture, thereby reducing the strain on these structures during bending. Similar principles are not as useful for flexible batteries because the cell capacity is directly related to the amount of electroactive material present. Hence a relatively large footprint is required for a thin battery in order to achieve the same capacity as of a typical battery with thick-film electrodes.

In printed batteries, the individual components (anode, cathode, current collector and the electrolyte) are deposited and patterned using printing techniques such as dispenser printing, screen printing, roll to roll printing and stencil printing. Here, we used stencil printing to deposit the electroactive material. Inks for anode and cathode are generally in the form of slurries of electroactive material mixed with a binder and a suitable solvent, where ink rheology can be tailored by adjusting the concentration of the binder. The overall flexibility of the battery depends on the mechanical properties of each individual component: anode, cathode, electrolyte, substrate and packaging.

The manganese dioxide (MnO₂) – Zinc (Zn) based primary alkaline battery leveraged in this work has long dominated the market for primary battery due to higher energy density, low internal resistance and relatively flat discharge. Other battery systems based on Zn-Silver Oxide and Lithium Ion provide high energy density and potential but are too
expensive for use in a large deployment of primary disposable batteries. This work also used a polymer gel electrolyte\cite{26} which have previously been used in batteries\cite{27} and capacitors\cite{28} due to their combination of mechanical stability, adjustable conductivity, and ease of packaging.\cite{24,29}

The innovation we report is a mesh embedded Zn-MnO\textsubscript{2} alkaline battery architecture that addresses the thickness and capacity limitations of thin film flexible batteries without compromising power performance of a traditional battery. The mesh structure acts as a support and reduces the stress on the electroactive material during mechanical flexing. Without a mesh support (using a non-porous substrate) it was observed that Zn and MnO\textsubscript{2} electrodes had an operating bend radius of 35-40 mm when the electrode thickness was 60-75 \textmu m and on repeated flexing, cracking and delamination of the electrode took place. To accommodate the mesh electrodes, polyacrylic acid (1,250,000 g mol\textsuperscript{-1}) based alkaline PGE was used as the electrolyte in the flexible battery, which was formed by dissolving PAA in aqueous potassium hydroxide (KOH) saturated with zinc oxide (ZnO).\cite{30} The current collector material should be highly flexible, have high conductivity and high crease resistance to ensure no ohmic loses during flexing. Here, we use silver composite ink as the current collector. In addition to materials such as carbon and silver\cite{15,18} researchers have also used carbon nanotubes as a current collector in flexible batteries due to their high flexibility and conductivity.\cite{1,17}

A flow diagram illustrating the fabrication steps for a mesh embedded flexible electrode is shown in Figure 1A. The choice of the mesh size depends upon the thickness of electrode required and the particle size of the electroactive material. A 50-mesh size (defined as the number of holes in a linear inch) nylon mesh was used as a support for the electroactive inks. A polyester [polyethylene terephthalate (PET)] sheet was attached to one side of the nylon mesh to support the electroactive slurry during printing and curing steps. The electroactive slurry of Zn and MnO\textsubscript{2} was stencil printed on individual nylon-mesh substrates.
The mesh was then cured in an oven at 70 °C for 3 hours to remove any residual solvent. After the curing process the PET support was removed, as illustrated in Figure 1A. The optical images of the highly flexible sheets of Zn and MnO\textsubscript{2} are shown respectively in Figures 1B and 1C. A thin layer of silver ink is stencil printed onto the underside of the mesh to form the current collector. The silver current collector is cured in an oven at 100 °C for 30 minutes giving a surface resistivity of \( \sim 0.015 \, \Omega \, \text{sq}^{-1} \). The flexible embedded mesh is cut into appropriate sizes that are used to assemble a flexible printed battery with sandwich-type architecture, as illustrated in Figure 1D. The individual components (anode, cathode, electrolyte and separator) are placed on top of each other, which contributes to a reduced overall footprint of the battery. An optical image of the assembled printed flexible Zn-MnO\textsubscript{2} alkaline battery is shown in Figure 1E. A typical battery, as shown in Figure 1E, has an active surface area of \( 1.0 \times 0.5 \, \text{inch} \) \( (3.2 \, \text{cm}^{2}) \).

The top surface of the mesh embedded Zn and MnO\textsubscript{2} electrodes and silver current collector were characterized by scanning electron microscopy (SEM). The topographic micrographs of the nylon substrate, embedded electrodes and printed silver current collector are shown in Figure 2 A-D while the cross-section micrographs are shown in Figure 2 E-H. Both topography and cross-section SEM analysis clearly show that Zn and MnO\textsubscript{2} inks occupy the void spaces in the mesh substrate after the printing process is complete. Figures 2F and 2H demonstrate that good electrical contact of Zn and MnO\textsubscript{2} with the silver current collector has been achieved.

Electrochemical impedance spectroscopy (EIS) was carried out to measure the effect of potassium hydroxide (KOH) and PAA concentration on the conductivity of the electrolyte gel. EIS experiments were carried out using a custom-made conductivity cell with stainless steel (SS) electrodes and a fluctuation voltage of 50 mV at frequency ranging from 10 Hz to 1 MHz. The intercept on x-axis of the imaginary resistance \( (Z_{\text{img}}) \) versus real resistance \( (Z_{\text{real}}) \) plot was taken as the resistance \( (R_{\text{elec}}) \) of the electrolyte and was converted to conductivity (S
by the formula (conductivity = thickness / (R_{elec} \times area)). As shown in Figure 3A the conductivity of the electrolyte gel rose steeply until 2 M KOH concentration and then increased more slowly at higher concentration. Figure 3B shows the effect of varying PAA concentration in the gel. Contrary to general observation, the conductivity of the PAA based PGE increased with increasing PAA concentration. This is due to high molecular weight (1,250,000 g mol⁻¹) of PAA, which lead to a large increase in the aqueous electrolyte absorbed by the PAA based gel without a significant increase in the concentration of the non-conductive PAA.

Rheology experiments were carried out to study the effect of printing and flexing on the PGE. While the PGE is a highly viscous gel under no external stress, its viscosity decreases with shear rate (shear thinning), showing pseudoplastic behavior as seen in Figure 3C. The high viscosity of the gel simplifies packaging and prevents leakages in cases when the cell is ruptured. In case of large scale manufacturing of the printed batteries the PGE could be printed using a dispenser based setup where the PGE is forced through tubes of decreasing internal diameter. The shear thinning behavior of the PGE can be used advantageously to allow printing at a lower pressure head. The behavior of the PGE in the flexible battery during flexing to different bend radii was simulated by a strain sweep experiment, as shown in Figure 3D. A strain sweep from 0.0001 to 0.02 was carried in logarithmic scale with strain rate ranging from $1.06 \times 10^{-6}$ to $2.55 \times 10^{-4}$ on 1.7% PAA in 8 M KOH. The strain sweep experiment was carried out at frequency of 1 Hz to simulate flexing the battery from its neutral position once every second. $G'$ [elastic (storage) modulus] is indicative of gel like behavior and $G''$ [viscous (elastic) modulus] is indicative of liquid like behavior. The $G'$ and $G''$ values are almost constant in the strain sweep; indicating that mechanical integrity of the PGE in maintained in the strain range that the PGE will experience during flexing. One can expect a decrease in the $G'/G''$ value when the gel breaks down and starts behaving like a liquid. In our study the PGE was drop-cast on the electrode surface and a 200-mesh size
nylon mesh was sandwiched between the two electrodes, which acts as the separator, giving an overall thickness of separator and PGE of 80 µm.

The discharge characteristics of the flexible battery are shown in Figure 4A. The battery had a discharge capacity of 4.5 mAh cm\(^{-2}\) at discharge rate of 1.0 and 2.0 mA, increasing to 5.6 mAh cm\(^{-2}\) at a lower discharge rate of 0.5 mA. The performance of the battery during flexing was then characterized by bending the battery around various diameter cylinders (0.95 – 3.81 cm) during the discharge experiment, as shown in Figure 4B. It is clear from this data that the battery showed no degradation in performance when flexed. In fact, the discharge performance of the battery was seen to improve after bending, due to compression of the battery, which leads better interfacial contact between the PGE and electrodes. These devices perform well in comparison to currently commercially available Zn-MnO\(_2\) based flexible batteries which typically have a maximum discharge capacity in range of 2.0 – 2.7 mAh cm\(^{-2}\) and a minimum bend radius of 2.5 – 4 cm.\(^{[31]}\) Figure 4C shows the polarization of the battery from open circuit potential (OCP) to 0.5 V at 50 mV s\(^{-1}\). A high current density of 51 and 53 mA cm\(^{-2}\) was observed in a flat and a battery flexed to 2.54 cm bend radius respectively when polarized to 0.8 V. The high discharge current is useful for applications requiring large current for short time period. EIS experiments carried out on an unstrained battery show low impedance (Fig. 4D), thereby reducing ohmic losses during discharge. Power requirements for flexible electronic devices can range from high voltage, low amperage (eg. organic TFTs\(^{[9]}\)) to relatively low voltage and high amperage (eg. organic LEDs\(^{[7]}\)). As such it is important that the flexible battery design can be easily customized to provide the necessary power and energy requirements within the desired footprint. The ability to use customize these batteries to operate devices was illustrated (Fig. 4E) by connecting two cells in series to power a green LED (operating voltage of 1.9 - 2.4 V and current consumption from 4 - 32 mA). This battery is still able to power the LED even when folded over to a bend radius of 0.3 cm (Fig. 4F).
We have demonstrated a flexible printed battery with a mesh support, which shows a significant improvement with respect to operating bend radius when compared to currently available flexible batteries. The mesh support enables these flexible batteries to also exhibit a high capacity due to increased thickness of the electrode. This battery design can be customized to power devices with various power and energy requirements, and the process can be readily integrated with the current large scale manufacturing techniques. The mesh architecture is not limited to alkaline battery system and could be used with other battery chemistries. Readily customized flexible batteries such as those described here will help to realize the potential of flexible mobile electronic devices.

Experimental

The starting point for the mesh embedded electrode was a non-conductive 50-mesh size nylon mesh (McMaster-Carr). The aqueous inks for anode and cathode were prepared by mixing the electroactive material, additive and binder. These anode and cathode inks were prepared using standard battery compositions.[23] The anode ink was a mixture of (in weight percent) 73% Zn, 6% ZnO, 3% Bi₂O₃ and 18% polyethylene oxide (PEO, 100,000 g mol⁻¹) in water. ZnO and Bi₂O₃ were used as an additive to prevent hydrogen formation by zinc dissolution. The cathode ink was a mixture of 68% battery grade MnO₂ (Tronox), 6% synthetic graphite powder (20-25 micron), 6% KOH and 20% PEO in water. Silver ink (AG-800, Conductive Compounds, Inc.) was used as a current collector on the mesh embedded with Zn and MnO₂. Different concentrations (1-10 M) of KOH were prepared by dissolving KOH pellets in DI water. The solution was then stirred with ZnO until saturation, with excess ZnO removed by filtration. The PGE was prepared by dissolving polyacrylic acid (PAA, 1,250,000 g mol⁻¹) in the aqueous electrolyte. The mixture was stirred until a homogenous gel was formed. 200-mesh size nylon mesh was used as a separator and the assembled battery was heat sealed inside a polyethylene pouch.
The EIS experiments were carried out using a 4192A LF impedance analyzer (HP) and a custom-made conductivity cell with SS electrodes. The area of the electrode was 3.95 cm² and the distance between the electrodes was 0.28 cm. SEM images of the battery components was taken using a JEOL 7400 SEM. The battery characterization experiments were carried out on PAR 263 potentiostat/galvanostat (Princeton Applied Research). Rheology of the PGE was studied using an AR 2000Ex rheometer (TA instruments) and electrical conductivity measurements were carried out using a four-point probe (M-700, Magne-Tron Instruments).

Acknowledgements
A.M. Gaikwad would like to acknowledge the PARC summer internship program for financial support.

Received: March 8, 2011
Revised: 
Published online: June 10, 2011
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**Figure 1.** A) Flow diagram for making the mesh embedded printed MnO$_2$ cathode and Zn anode with printed silver current collector. B) Optical images of Zn electrode. C) Optical image of MnO$_2$ electrode. D) Schematic diagram of the cross-section of assembled Zn-MnO$_2$ alkaline battery with sandwich type architecture. E) Optical image of flexible Zn-MnO$_2$ battery laminated inside a polyethylene pouch.
Figure 2. A) SEM image of the 50-mesh size nylon mesh used as a support for the electrodes. B) Top surface of the mesh embedded Zn electrode. C) Top surface of the mesh embedded MnO$_2$ electrode. D) Top surface of the silver current collector. E) Cross-section SEM image of the Zn electrode. F) Magnified SEM image of the Zn-Silver interface. G) Cross-section SEM image of the MnO$_2$ electrode. H) Magnified SEM image of the MnO$_2$-Silver interface.
Figure 3. Characterization of polyacrylic acid (PAA) based alkaline polymer gel electrolyte (PGE). A) Conductivity (S cm$^{-1}$) of 1.7% PAA (1,250,000 g mol$^{-1}$) dissolved in KOH versus Molarity (M) of KOH plot. B) Conductivity (S cm$^{-1}$) versus concentration (%) of PAA. C) Viscosity (Pa.s) versus Shear Rate (s$^{-1}$) at various concentrations (%) of PAA. D) Response from the strain sweep of 0 – 0.02 on 1.7% PAA in 8M KOH at 1 Hz to emulate the behavior of the PGE during flexing.
Figure 4. Characterization of the flexible printed battery (Active foot-print area of 3.2 cm²).

A) Discharge profile of the flexible battery when discharged at 0.5, 1 and 2 mA when flat. B) Discharge profile of the flexible battery when flexed to different radii of curvature while discharging. Discharge experiments were carried out at 1 mA. C) Polarization curves at 50 mV s⁻¹ of a flat battery and a flexed battery with a radius of curvature of 2.54 cm. D) EIS of the battery under no strain. E) Demonstration of two flexible cells connected in series to power a green LED. F) The flexible batteries connected in series were able to power the green LED when flexed to a bend radius of 0.3 cm.
Highly flexible printed alkaline batteries based on a mesh embedded architecture are demonstrated. The mesh acts as a support for the electroactive material during flexing. Two cells connected in series and bent to a radius of 0.3 cm are able to power a green light emitting diode (LED).

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