A Stencil Printed, High Energy Density Silver Oxide Battery Using a Novel Photopolymerizable Poly(acrylic acid) Separator

Kyle Braam and Vivek Subramanian*

There has been tremendous work done toward the development of flexible and of low-cost, ubiquitous electronic systems for applications such as health monitoring and environmental sensing.[1,2] Such applications require an integrated power source, however; despite the significant progress in thin film electronics as a whole, associated high energy power sources are still poorly developed. A thin, cheap, high energy density battery is desired for many current flexible electronics applications such as displays, wireless sensors, and printed radio-frequency identification (RFID) tags[3–5] and has the potential to enable new fields such as wearable electronics and electronic skin.[6,7] The development of a low-cost, air-stable printed battery process that can be integrated with a printed electronics process is vital in this regard and would allow for the realization of lightweight, flexible, and fully powered electronic systems.[8]

There have been several demonstrations of partially printed batteries using various battery chemistries. We have previously reported on a planar, primary Ag2O–Zn battery with a capacity of 3.5 A h cm−2.[9] Additionally, planar MnO2, and Zn electrodes have been screen printed and have been used to demonstrate high utilization at current densities of 1 mA cm−2.[10] A partially printed alkaline-based MnO2–Zn battery using nylon mesh for support has realized capacities as high as 5.6 mA h cm−2.[11] A spray-painted lithium-ion battery has also been demonstrated, capable of going through at least 70 charge/discharge cycles and offering an energy density of 6 W h m−2.[12] All of these batteries are promising in their own right, but each suffer from several problems in need of addressing. Specifically, planar cells, while useful demonstration vehicles, suffer from significant internal resistance due to the large interelectrode gap, resulting in poor operating current capability and significant voltage drop under heavy load. Partial printing approaches attempt to address this by stacking the electrodes, but leave the battery unsuitable for integration in many process flows. Finally, cells that use lithium chemistries require inert processing and careful encapsulation, making them undesirable for use in low-cost process flows; indeed, once fully encapsulated, small lithium-based chemistries are at an overall capacity disadvantage versus less sensitive chemistries due to the added weight and volume of the encapsulation. In this paper, we demonstrate a battery technology that addresses all of these concerns. Specifically, we have developed a novel printable, photopolymerizable poly(acrylic acid) (PAA) separator that has a high ionic conductivity, and have used this to realize a high energy density, air-stable, and printed primary battery. This primary battery is designed for single use applications requiring a high energy density battery. The deposition of the layers on top of each other allows for a wide range of battery sizes and the ability to deposit on a variety of substrates. This is an improvement over partially printed systems that require assembly of the individual layers.

This key separator development has enabled the demonstration of a high energy density, stencil printed vertical silver oxide battery. There are many printing techniques that could be used to deposit battery layers, such as extrusion printing, inkjet, screen printing, and stencil printing.[13,14] The fabrication of high areal capacity batteries requires relative thick layers between 10 and 100 μm. We have chosen stencil printing to demonstrate a printed vertical battery structure using a low-cost process. An alkaline system was chosen over lithium-ion-based chemistries because an ideal low-cost, printed battery should have air-stable printing processes and not require an inert atmosphere, and furthermore, should allow for the use of low-complexity encapsulation rather than needing moisture- and oxygen-exclusive approaches. We use the silver oxide zinc chemistry because of the stable discharge potential, high open circuit voltage (1.8 V for AgO and 1.55 V for Ag2O), high specific density (300 W h kg−1), and energy density (750 W h dm−3).[15] To simplify our electrode design, we use monovalent silver oxide (Ag2O) in the cathode instead of divalent silver oxide (AgO); monovalent silver oxide has a higher electronic conductivity, even though it has a lower capacity than divalent silver oxide.

The battery was fabricated by stencil printing the individual layers from a slurry solution (Figure 1A). After stencil printing the silver current collector and zinc electrode, the acrylic acid solution electrolyte was polymerized on top of the battery. A novel hydrogel based on a crosslinked acrylic acid is used as the separator layer. Separator systems based on PAA have been reported previously,[8,11,16,17] however, none have been incorporated into a fully printed battery. Here we demonstrate the development and characterization of a photopolymerized PAA separator for alkaline batteries. This novel separator allows us to deliver excellent internal resistance, robust mechanical characteristics, and easy printing-based integration; as we will show below, this allows for achievement of robust operation even under mechanical flexion.

The separator layer consists of a crosslinked acrylic acid with poly(ethylene glycol) divinyl ether (PEGDE) (Mn = 250 g mol−1)
as a crosslinker. (Figure 2A) and a poly(ethylene oxide) filler. The polyacrylic gel electrolyte was synthesized by a free-radical method using the water soluble photo initiator, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, also known as IGRA-cure 2959 (Figure 2B). Unlike other alkaline separators based on poly(vinyl alcohol) or cellulose, separators based on PAA are not susceptible to oxidation by silver oxide. However, separators based on poly(acrylic acid)s act as hydrogels, and are thus excellent water absorbers. This can cause expansion problems, especially since the PAA gel is polymerized in situ on top of the printed zinc electrode. To address this, we developed a robust crosslinking and mechanical stabilization strategy. The crosslinking is optimized to produce a mechanically robust gel network. The polymerization conditions, such as pH, filler material, and monomer and crosslinker concentration, have an important effect on the resulting gel network. To achieve a strong gel network, PEGDE ($M_n \approx 250$ g mol$^{-1}$) was used as a crosslinker. A cross linking concentration of 1 wt% was used in the PAA gel as this was found to give optimal performance. Lower concentrations resulted in incomplete gel formation with insufficient mechanical strength. Higher concentrations (4–5 wt%) had poor solubility, degrading ink properties during printing.

A high molecular weight poly(ethylene oxide) (PEO) ($M_v \approx 600\,000$ g mol$^{-1}$) was added as a filler material to the gel solution to improve the mechanical stability of the polymerized separator. The addition of PEO filler results in an increase in the Young’s modulus of the resulting gel (Figure 3A). The increased stability is proposed to be a result of the polymer strands ionic crosslinking with each other. However, a consequence of the high molecular weight PEO is that the viscosity rapidly increases with increasing PEO filler percentage (Figure 3B). For the use of the PAA separator in a battery, PEO is added at a concentration of 2.5 wt%. At higher polymer concentrations, the viscosity of the solution increases too much. The increased viscosity traps nitrogen bubbles during degassing, which remain in the prepolymerized solution and introduce holes in the final polymerized film. These holes allow for shorting during the silver oxide electrode deposition. By using the concentration herein, we are able to achieve good mechanical stability without bubble inclusion.

The swelling of the PAA gel depends on the monomer and crosslinker ratio and the pH of the solution. The ratio of acrylic acid and PEGDE was chosen to minimize swelling of the gel separator, yet still allow for gel formation. Higher acrylic acid content leads to greater swelling of the gel separator. For high pH, the swelling of the PAA gel is reduced due to the reduction of free water available, because water molecules are largely solvated by the potassium hydroxide salt. With increasing molarity of the saturating solution, we see a decrease in the swelling ratio (Figure 3B), where the swelling ratio, Q is:
The fabricated batteries, upon saturation with 8.4 M KOH, demonstrate an open-circuit potential of ≈1.54–1.55 V. The batteries were discharged at 2C, C, and C/2 rates with respect to the silver oxide capacity. The printed silver oxide battery exhibits high discharge capacity even at high rates of discharge (2C rates) (Figure 4A). At higher discharge rates, we see a decrease in potential likely due to an increase in the concentration overpotential, the surface overpotential at the electrode/electrolyte interface, and a voltage drop due to the ohmic resistance of the battery. Further studies with electrochemical impedance spectroscopy are required in the future to examine the reactions at the electrode interface and quantify the discharge phenomena. The batteries achieve high silver oxide utilization with reductions between 90% and 100% of the deposited silver oxide. Note that we obtain good battery-to-battery reproducibility (≈10% variation in observed capacity). Complete silver oxide reduction is unlikely for two reasons: first, there is some reduction of the silver oxide by poly(vinyl alcohol) binder in basic solutions and second during deep discharge, there is likely a loss of electrical contact to some of the particles of silver oxide due to the shape change of the electrode during discharge.

The printed batteries also demonstrate good performance under flexing, attesting to their viability for use in flexible electronics applications (Figure 4B). The percentage of silver oxide utilized is greater than 90% and the variability is within the experimental uncertainty of the measurement. Noticeably, the discharge potential remains constant with increasing bend radius, indicating the tested bend radius do not disturb battery performance. We also do not observe any significant increase in contact resistance, suggesting that the contacts and associated interfaces are mechanically stable within the regimes studied herein. Previously, it has been shown that printed batteries under flexion demonstrate increased performance due to interfacial contact.11 The high performance of our printed batteries demonstrates good interfacial contact.

The capacity of the demonstrated printed silver oxide battery is ≈5.4 mA h cm−2 at a C/2 discharge rate of 2.75 mA cm−2. This value is comparable or better than the reported areal capacities of other printed batteries in the literature19 (Figure 4C). Another important figure of merit to take into consideration is the energy density. For example, the areal capacity specifications of a printed battery could be increased arbitrarily by depositing thicker layers, though this will obviously detract from flexibility and deployability in real thin-film system applications. This will result in a greatly increased areal capacity, while volumetric energy density will stay largely unchanged. For the developed printed silver oxide battery, we report a volumetric capacity of 7.1 mA h cm−3 and volumetric energy density of 10 mW h cm−3 while maintaining an overall thin battery stack and good mechanical flexibility; note that volumetric energy densities are not reported for many of the aforementioned literature cells, so a direct comparison is not possible. The gravimetric energy density for this printed silver oxide battery is 18.9 mA h g−1. These values are important to quantify and compare across different chemistries and battery geometries.

Even higher densities are certainly achievable in the future. The active material consisting of the silver oxide and zinc...
electrodes contribute a small fraction (28 wt%) of the material components of the printed battery (Figure 4D). Optimizing the cell design, for example, by decreasing the separator thickness and reducing the zinc to silver oxide ratio could further increase the energy density. The electrode composition could also be modified by utilizing divalent silver oxide (AgO), which has a theoretical capacity of 432 mA h g\(^{-1}\) instead of monovalent silver oxide (Ag\(_2\)O) which has a capacity of 231 mA h g\(^{-1}\). This will not only increase the capacity, but also increase the open-circuit voltage to 1.8 V due to the higher reduction potential of AgO, resulting in a further increase in energy density.

We have demonstrated the development of a high ionic conductivity, photopolymerizable alkaline separator based on poly(acrylic acid). This separator demonstrates good mechanical stability and ionic conductivities on the order of 0.4 S cm\(^{-1}\). The PAA separator may be used with other alkaline chemistries beyond that demonstrated herein, and indeed, may also be useful in any application requiring hydrogels, such as tissue engineering. Using the synthesized PAA separator, we have demonstrated a stencil printed silver oxide battery with areal capacities of 5.4 mA h cm\(^{-2}\) and volumetric capacities of 7.1 mA h cm\(^{-3}\). The batteries show no difference in discharge upon flexing at a bend radius of 1.0 cm, indicating their potential in flexible applications. The processes developed are scalable to large scale manufacturing and allow for customization to the application. The demonstrated flexible, high energy density, stencil printed battery has the potential to useful in many flexible and printed devices and applications.

**Experimental Section**

The bottom current collector was prepared by stencil printing Creative Materials conductive ink 120–07 on to a poly(ethylene terephthalate) (PET) plastic substrate from DuPont. The stencil height was 300 µm. Zinc slurries were prepared and deposited on the silver current collector by stencil printing. The 5 wt% binder solution was prepared by dissolving low-viscosity methylcellulose (Fluka, 300–560 cPs for a 2% aqueous solution at 20 °C) in deionized water for at least 12 h. Zinc powder (99.999%) 40 mesh (Strem Chemicals) was added to the slurry solution to give a ratio of 98:2 zinc to methylcellulose. The zinc slurry was stencil printed using a stencil height of 300 µm, area of 5 mm \(\times\) 10 mm. The zinc and silver oxide slurries thickness were deposited to give a Zn to Ag\(_2\)O capacity ratio of 4. This value was chosen to form silver oxide-limited capacity batteries; since silver is the most expensive component of the battery, this is typically the desired optimization strategy. No additives were added to minimize corrosion of the zinc electrode. The printed electrode was dried on a hotplate for 20 min at 40 °C. Mass values were taken after drying to calculate the capacity of the electrode. The printed electrode mass values are \(~14.6\, mg\).

The gel solution was prepared by mixing 0.5 mL of acrylic acid with 6.25 mL of H\(_2\)O that contained 1 M equivalent of KOH (0.4092 g). The KOH is added to produce a solution with a pH of 7. The appropriate
amount of PEO (Sigma–Aldrich, \( M_v \approx 600000 \text{ g mol}^{-1} \)) was dissolved into the solution by stirring at 300 RPM at room temperature until dissolved. For a 2.5 wt% PEO concentration 0.1930 g of PEO was added to the solution. After the PEO dissolved, the water soluble photoinitiator 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone 0.5 wt% (0.0354 g) and crosslinker poly(ethylene glycol) divinyl ether (PEGDE (\( M_n \approx 250 \text{ g mol}^{-1} \)) 1.0 wt% (0.0723 g) were added to the solution. Once dissolved, nitrogen gas was lightly bubbled through the solution for 10 min to remove oxygen in the solution.

The gel solution was then stencil printed inside a 300 µm thick stencil to give a polymerized thickness of \( \approx 200 \mu \text{m} \) above the Zn electrode after polymerization. A PET plastic sheet was placed on top of the Sylgard 184 polydimethylsiloxane (PDMS) stencil to remove excess amount of solution from the mold, set the thickness, and impede exposure of oxygen to the gel solution during polymerization. The substrate was placed under a Spectroline UV lamp for 10 min. Next, the stencil and PET layer were removed and the silver oxide slurry was stencil printed (300 µm stencil) upon the electrode followed by the silver flake/PEO slurry (400 µm stencil). The silver oxide slurry was made by dissolving 0.025 g of 99% hydrolyzed, \( M_w \approx 89000–98000 \text{ g mol}^{-1} \) PVA (Sigma–Aldrich) in 1 g of DI H\(_2\)O. Then, the silver oxide was added to make 98:2 weight ratio Ag\(_2\)O (99.99% silver (I) oxide, Strem Chemicals) to the PVA slurry. The silver flake slurry was prepared by dissolving 0.2631 g of high molecular weight PEO (Sigma–Aldrich, \( M_w \approx 600000 \)) in 5 mL of deionized H\(_2\)O. Silver flake was added to make an 80:20 weight ratio of silver flake solution to PEO. Mass calculations for the silver electrode are taken by measuring the mass of the deposited slurry and calculating the active material from the mass loading of the ink. A typical deposition will give an electrode mass of \( \approx 24 \text{ mg} \). After printing the silver flake conductor, the entire stack battery was dehydrated for 30 min at 40 °C. The battery was rehydrated by placing the battery in zinc oxide saturated 8.4 M KOH for 25 min. The batteries were then encapsulated by lamination in polyethylene pouches to prevent dehydration.

**Figure 4.** A) Battery discharge at different C-rates. B) Discharge performance under flexing. C) Comparison of areal capacities of different printed battery chemistries. D) Distribution of battery components by weight.
Acknowledgements

Portions of this work were funded by Intel Corporation through custom funding via the Semiconductor Research Corporation. Additional portions of this work were funded by the National Science Foundation.

Received: September 8, 2014
Revised: October 17, 2014
Published online: December 5, 2014